INORGANIC COORDINATION CHEMISTRY

Kai Landskron
Lehigh University

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Book: Inorganic Coordination Chemistry (Landskron)

Kai Landskron

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CHAPTER OVERVIEW

1: Atomic Structure

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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1.1: Historical Development of Atomic Theory

Development of Atomic Theory

Since the ancient times, humans thought of explaining the material world in all of its complexity. The basic idea behind all element theories is that the matter that surrounds us is composed of more simple matter. This matter may be composed of even simpler matter. The most simple matter would be called an element.

The first element theories were one element theories: The greek philosopher Thales thought water was the only element, and everything was a form of water. Anaximenes thought air was the only element, and Heraclitus believed fire was the only element (Figure 1.1.1).

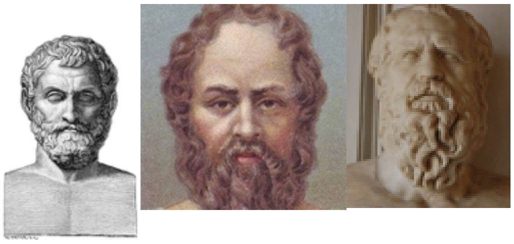


Figure **1.1.1** Thales (640-545 BC) (Attribution: Ernst Wallis et al [Public domain] https://commons.wikimedia.org/wiki/File:Illustrerad_Verldshistoria_band_I_Ill_107.jpg), Anaximenes (585-525 BC) (Attribution: https://commons.wikimedia.org/wiki/File:Anaximenes_of_Miletus_Painting.jpg) and Heraclitus (544 – 483 BC) (Attribution: RoyFokker [CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)]), respectively.

However, with only one element assumed it was difficult to explain the material world in all its complexity satisfactorily. This could be done more satisfactorily by a multi-element theory. The first philosopher who introduced a multi-element theory was Empedocles. He suggested a four-element theory with fire, air, water, and soil as the elements (Figure 1.1.2).

Figure 1.1.2 Empedocles (495 – 435 BC) (Attribution: Thomas Stanley, The history of philosophy, 1655 [Public domain] https://commons.wikimedia.org/wiki/F...Philosophy.jpg)

First atomistic ideas

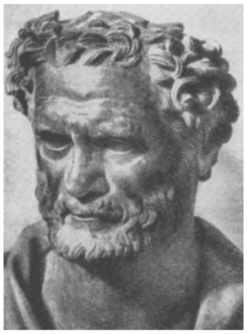


Figure 1.1.3 Democrites (460 – 370 BC) (Attribution: Strannik 92 [CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)] https://commons.wikimedia.org/wiki/File:Demokrit.jpg)

The element theories of Thales, Anaximenes, Heraklitus, and Empedocles were all non-atomistic. This means that they did not include the idea that elements were made of small particles that were indivisible. The first greek philosophers that introduced atomistic element theory were Leukippes, and Democrites (Figure 1.1.3). They assumed that particles cannot be divided into smaller particles infinitely often. Ultimately, after many divisions, one would arrive at particles that could not be further divided, and these particles would be called atoms. Atomistic element theory allows for many different elements which helps to explain the complexity of the material world satisfactorily. However, Leukippes and Democrites did not know how many different elements there were, and how different atoms of different elements were actually distinguished. This question would not be answered until about 2000 years later.

Modern Atomic Theories

Figure 1.1.4 Antoine Lavoisier, the father of modern chemistry, discovered the law of conservation of mass in 1774. (Attribution: Louis Jean Désiré Delaistre (1800–1871); drawing by Julien Léopold Boilly (1796–1874). [Public domain], https://commons.wikimedia.org/wiki/F...sier_color.jpg)

Although the atomistic idea was already known in the antique, it became forgotten for a long time and was only reintroduced about 2000 years later with Dalton’s atom hypothesis. What lead to Dalton’s atom hypothesis? The first discovery that was important to the development of modern atomic theory was the law of the conservation of mass by Antoine Lavoisier (Fig. 1.1.4). Historically, the conservation of mass and weight was kept obscure for millennia by the buoyant effect of the Earth's atmosphere on the weight of gases, an effect not understood until the vacuum pump first allowed the effective weighing of gases using scales. Until then, in many instances mass seemed to appear or disappear. For example, the mass of wood seems to disappear when it is burned. However, the mass of the wood actually does not disappear it is just converted into the mass of gases, mainly carbon dioxide. When scientists realized that mass never disappeared they could for the first time embark on quantitative studies of the transformations of substances. This in turn led to the idea of chemical elements, as well as the idea that all chemical processes and transformations are simple reactions between these elements. The **law of conservation of mass** states that the mass of a closed system of substances will remain constant, regardless of the processes acting inside the system. An equivalent statement is that matter cannot be created or destroyed, although it may change form. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

Law of Constant Composition

The discovery of the law of the conservation of mass led to the discovery of the law of the constant composition (also called law of definitive proportions) by Joseph Proust (Fig. 1.1.5). This law was the result of chemical analysis that determined the mass ratio of elements in pure substances. It was found that a pure substance always contains exactly the same proportion of elements by mass. For example the element analysis of pure substances containing the elements carbon and oxygen would be either 42.9% carbon and 57.1% oxygen or 27.3% carbon and 72.7% oxygen.

Figure 1.1.5 Joseph Proust (1754-1826) (Attribution: The original uploader was HappyApple at English Wikipedia. [Public domain] https://commons.wikimedia.org/wiki/F...ust_joseph.jpg)

The law was questioned by Proust's fellow Frenchman Claude Louis Berthollet, who argued that the elements could combine in any proportion. The very existence of this debate was because at the time the distinction between pure chemical compounds and mixtures had not yet been fully developed. When two pure compounds of two different elements are mixed, then the mixture can have a continuous mass ratio between the two elements because compounds can be mixed at any ratio. So, for the example in the two compounds between carbon and oxygen, in mixtures of the two there could be carbon to oxygen ratios varying continuously between 27.7 % to 42.9% carbon, and 42.9% to 72.7% oxygen. It was an accomplishment of Proust that he was able to correctly distinguish between pure compounds and mixtures.

The Law of Multiple Proportions

Figure 1.1.6 John Dalton 1766-1844 (Attribution: Charles Turner [Public domain] https://commons.wikimedia.org/wiki/F...les_Turner.jpg)

John Dalton (Fig. 1.1.6) discovered the law of multiple proportions by close analysis of Proust’s law of constant composition. He noticed that if two elements form more than one compound between them, then the ratios of the masses of the second element which combines with a fixed mass of the first element will be the ratios of small whole numbers, also called integer numbers. Let us see what is the meaning of the law of the multiple proportions by an example:

Example 1.1.1

The first compound contains 42.9% by mass carbon and 57.1% by mass oxygen.

The second compound contains 27.3% by mass carbon and 72.7% by mass oxygen.

Show that the data are consistent with the Law of Multiple Proportions!

Solution

In 100 g of the first compound (100 is chosen to make calculations easier) there are 57.1 g O and 42.9 g C.

The mass of O per gram C is:

57.1 g O / 42.9 g C = 1.33 g O per g C

In 100 g of the second compound, there are 72.7 g O and 27.3 g C.

The mass of oxygen per gram of carbon is:

72.7 g O / 27.3 g C = 2.66 g O per g C

Dividing the mass O per g C of the second (larger value) compound by the mass O per g C of the first compound gives:

2.66 : 1.33 = 2 : 1

2 and 1 are both integer numbers.

Dalton's Atom Hypothesis

Dalton argued that atoms could explain the law of the multiple proportions. If one assumed that elements were made of the same type of indivisible particles, that are identical in mass and all properties then, because these particles can only come in integer numbers, different atoms can be combined to form compounds also only in integer numbers. Thus, in a pure compound atoms of unlike elements would be combined in small whole number ratios. Consequently a given compound always has the same relative number and types of atoms. Chemical reactions would involve reorganization of atoms, but the atoms would retain their identity. Atoms could be rearranged in a chemical reaction but not created or destroyed.

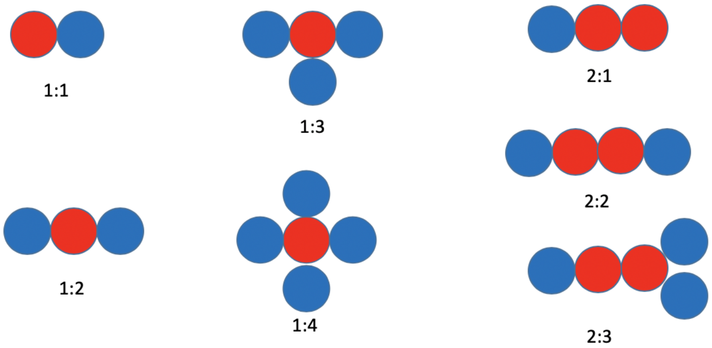


Figure 1.1.7 Illustration of the law of the multiple proportions for two generic, different atoms (red and blue balls).

Figure 1.1.7 is a simple illustration how atoms can explain the law of multiple proportions. The blue and red balls symbolize different atoms of different elements. It is possible to combine a red atom with one, two, three, or four blue atoms to make four different compounds. It is for example also possible to combine two red atoms with one, two or three blue atoms. In all of these compounds as well as in all other thinkable ones, the blue and red atoms can only be combined in integer numbers.

Dalton's Atom Symbols

Dalton also thought of symbols for the atoms of the different elements. The symbols are different from the element symbols that are used today, but the concept is the same. You can see some of them in Figure 1.1.8. For example oxygen is represented by a white ball, while carbon is symbolized by a black ball. You can also see that Dalton already combined atom symbols of different elements to illustrate compounds. For example he combined one white ball with one black ball to indicate carbon monoxide, while he combined two white balls with one black ball to indicate carbon dioxide. In this case he correctly identified the ratios of atoms in the two compounds. However, you can see that this is not always the case. For example, he combined one hydrogen atom (white ball with a dot in the middle) with one oxygen atom to indicate the composition of water. However, as we know today, a water molecule has two hydrogen atoms and one oxygen atom. Why has he been right with the carbon-oxygen compounds, but wrong about the water? The answer is that at the time he could determine the atom ratios only from the law of the multiple proportions. At the time there was only one compound known that was made of hydrogen and oxygen, water, so he assumed the simplest atom ratio of 1:1. If he had known hydrogen peroxide, which has the composition H_2O_2, and thus half as much hydrogen per oxygen, he would have probably correctly assigned the correct hydrogen to oxygen ratio to water. In the case of the carbon oxides, he assigned the compositions correctly because both carbon monoxide and carbon dioxide were known at the time.

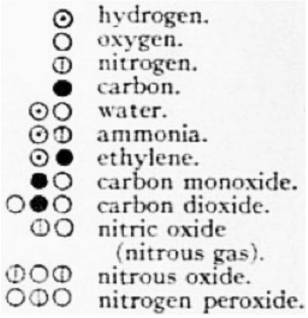

⊙ hydrogen.
○ oxygen.
⦶ nitrogen.
● carbon.
⊙○ water.
⊙⦶ ammonia.
⊙● ethylene.
●○ carbon monoxide.
○●○ carbon dioxide.
⦶○ nitric oxide (nitrous gas).
⦶○⦶ nitrous oxide.
○⦶○ nitrogen peroxide.

Figure 1.1.8 Dalton's atom symbols (Attribution: Encyclopædia Britannica, 1911 [Public domain] https://commons.wikimedia.org/wiki/F...an_symbols.png)

Subatomic Particles

Dalton’s atomic theory stated that different elements were made of different atoms, but did not explain what made the atoms different. The answer is that atoms are composed of subatomic particles, protons, neutron, and electrons, and the number of the protons and electrons in an atom defines the element it represents. So after all, atoms are not so indivisible. However, an atom can still be seen as the smallest particle that represents the full properties of an element. If an atoms gets divided further into subatomic particles then these properties are being lost. To understand atoms further, we must therefore understand the subatomic particles they are made of. The first subatomic particle that was discovered was the electron. It was found through the investigation of so-called cathode rays which were a mysterious phenomenon at the time. Cathode rays occur when a high voltage of about 10-20 kV is applied to an evacuated tube (0.0001 mm Hg). You can see such a tube with a cathode ray going through in Figure 1.1.9. The big question was: What causes these rays?

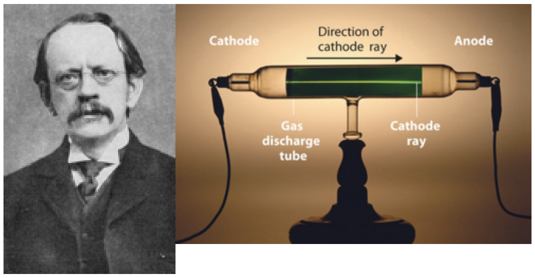


Figure 1.1.9 Joseph John Thomson (1856-1940) (Attribution: https://commons.wikimedia.org/wiki/F....J_Thomson.jpg, PD-US-expired)
and his experimental apparatus (Attribution: Chemlibetexts https://chem.libretexts.org/@api/dek...338&height=228, creativecommons.org/licenses/by-nc-sa/3.0/us/).

The answer was found by John Joseph Thomson. He applied electric and magnetic fields to these rays and found them deflected. When an electric field was applied the beam was deflected toward the positive pole. When an equally strong electric and magnetic field was applied, and the magnetic field was perpendicular to the electric field then these fields canceled out, and the rays were no longer deflected. Thomson concluded that these rays must consist of negatively charged particles emitted by the negatively charged electrode because they were attracted by the positive pole of the electric field: Electrons. Knowing the forces associated with the electrical and magnetic fields, he was able to calculate a mass to charge ratio of the electrons which is 5.6857 x 10E-9 g/C. After Thomson, Robert Millikan performed another experiment, the so-called oil drop experiment, that allowed to determine the charge and the mass of the electron. The charge of an electron is -1.6 x 10E-19 C, and its mass is 9.1 x 10E-28 g.

Thomson’s plum pudding atomic model

The discovery of the electron led Thomson to the development of a first atomic model that would include a subatomic particle. It is named plum pudding model (Fig. 1.1.10). In the Thomson atom model electrons are embedded as little particles in a positively charged mass like raisins are embedded in a cake. This atom model is still far from the atom model that we accept today, but it represented an important step forward, because it introduced for the first time the idea that atoms are not indivisible, but contain subatomic particles.

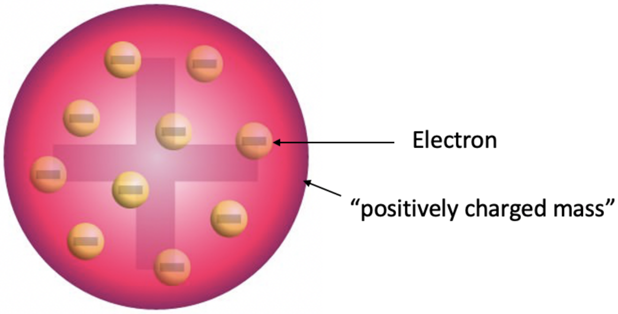


Figure 1.1.10 Thomson’s plum pudding atomic model (Attribution: Fatfission (public domain) https://commons.wikimedia.org/wiki/File:Plum_pudding_atom.svg)

Rutherford's Atom Model

Ernest Rutherford (Fig. 1.1.11) wanted to test Thomson's plum pudding atom model by experiment. To do so, he placed a photographic film around a gold foil (Figure 1.1.12). In the following he bombarded the gold foil with alpha radiation. Alpha radiation is a form of radioactivity and consists of helium nuclei, also called alpha-particles. It was known at this time the alpha-particles were positively charged and had a large mass compared to an electron. Rutherford's hypothesis was that if Thomson's atom model was true, then the alpha particles should all go straight through the gold foil like a bullet going through a plum pudding. Therefore, a blackening of the photographic film, which served as the alpha radiation detector, should only occur directly behind the gold film.

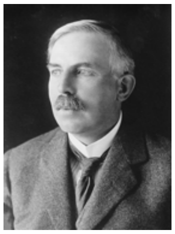


Figure 1.1.11 Sir Ernest Rutherford (1871-1931) who earned the Nobel prize for chemistry 1908. (Attribution: George Grantham Bain Collection (Library of Congress) [Public domain], commons.wikimedia.org/wiki/F...erford_LOC.jpg)

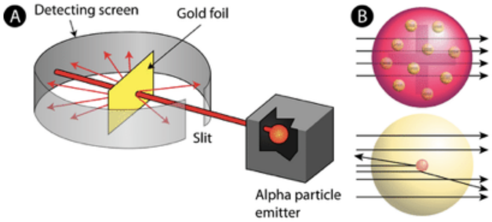


Figure 1.1.12 Rutherford's Gold Foil Experiment

However, what Rutherford observed was that while most of the alpha-particles went straight through the gold foil, some of them were deflected, and a few of them were even reflected. Rutherford concluded that Thomson's plum pudding model must be wrong. A bullet shot at a plum pudding would just never be reflected by the plum pudding and come back at you.

He suggested that the atom would be made of a positively charged nucleus where almost the entire mass of the atom would be concentrated. In the event of a collision between the alpha particle and that nucleus, the alpha particle would be reflected. In the event of an alpha particle passing by the nucleus close, the alpha particle would be deflected. In the event of an alpha particle passing the nucleus in larger distance, the alpha particle would pass the atom practically non-deflected. The observation that most of the alpha particles were not deflected led Rutherford to the conclusion that the overall atom must be much larger than the nucleus, in fact, the data allowed him to calculate that the radius of the atom would be about 10,000 times larger than the radius of the nucleus. This implies that the atoms would be mostly empty space. To explain the empty space, Rutherford assumed that the electrons would move in orbits around the nucleus like planets around the sun. This would be called the planetary model of the atom (Fig. 1.1.13).

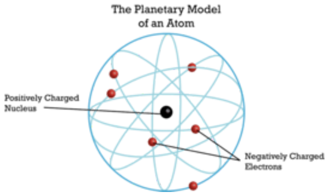


Figure 1.1.13 Rutherford's Atom Model

Bohr's Atom Model

Rutherford's atom model was another big step forward in the development of atomic theory, however there were inherent problems with it as it violated fundamental principles of physics. An electron in an orbit is a self-accelerating electrically charged particle, and according to the laws of physics such particles must emit electromagnetic radiation. However, under normal circumstances atoms do not emit electromagnetic radiation. Secondly, even if the electron emitted electromagnetic radiation, then this would mean that the electron would lose energy because electromagnetic radiation is a form of energy. However, an electron constantly losing energy would make it unstable in its orbit around the nucleus, and it should spiral downward closer to the nucleus until the atom was eventually collapsed. It is however, experimentally not observed that atoms collapse, they are quite stable species. These difficulties of the Rutherford atom model meant that it could not be the final answer to atomic structure. Niels Bohr (Fig. 1.1.14) was aware of the problems of the Rutherford model, and two new developments in physics, namely the concept of the quantization of energy and atomic spectra helped him to develop an improved atom model, known as Bohr model. To understand this model let us look first at the quantization of energy and atomic spectra.

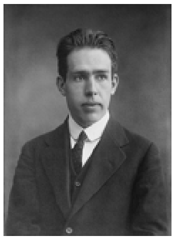


Figure 1.1.14 Niels Bohr (1885 - 1962) (Attribution: Bain News Service, publisher Restored by: Bammesk [Public domain], commons.wikimedia.org/wiki/F...in_-_35303.jpg)

Blackbody Radiation

The quantization of energy was discovered in the context of the physical phenomenon called “blackbody radiation”. Blackbody radiation is the electromagnetic radiation any object sends out due to its temperature (Fig. 1.1.15).

Figure 1.1.15 An example of blackbody radiation emitted by hot, volcanic lava. (Attribution: Hawaii Volcano Observatory (DAS) [Public domain], commons.wikimedia.org/wiki/F...hoehoe_toe.jpg)

It’s distribution of wavelengths follows curves that depend on the temperature and are shown in Figure 1.1.16. You can see that for each temperature the intensity first increases with increasing wavelength, then goes through a maximum, and finally decreases again. You can also see that the overall intensity of the blackbody radiation increases with temperature and that the maximum of the curve shifts to smaller wavelengths with increasing temperature. Objects at room temperature do not emit much blackbody radiation and the wavelengths are far longer than visible for the human eye. However, when an object is heated high enough, intensity increases and wavelength decreases, and the object starts to glow. For instance, lava (Figure 1.1.15) has a temperature high enough so that its blackbody radiation is visible for the human eye. With increasing temperature objects first glow red, then orange, then yellow, and eventually white. This is because red is the color associated with the largest wavelength, and as temperature increases other colors mix into red, until the object glows white. At extremely high temperatures the blackbody radiation also has a significant intensity in the UV region. Such temperatures occur in welding processes, for example, and for this reason welders need to wear glasses that block the UV radiation. The wavelength and intensity of blackbody radiation can be easily measured, but at the beginning of the 20th century there was no good explanation for its behavior. Classical theory predicted that intensity would continuously increase with decreasing wavelength at any temperature which was not in accordance with experimental observation.

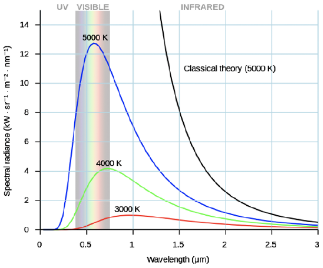


Figure 1.1.16 Experimentally measured intensity of blackbody radiation as a function of wavelength for 3000, 4000, and 5000 K vs. intensity predicted by classical theory (5000 K). (Attribution: Darth Kule commons.wikimedia.org/wiki/F...Black_body.svg)

To bring experiment and theory in accordance, Max Planck made the radical assumption that the energy associated with radiation of a given wavelength or a given frequency was quantized. It would be an integer multiple n of that frequency ν, multiplied with proportionality constant h, know today as the Planck constant.

$$E = n\,h\,\nu$$

Equation 1.1.1 The Planck-Einstein equation.

Using this assumption he was able to derive the Planck equation (Equation 1.1.2) which correctly describes the intensity and wavelength distribution of the blackbody radiation for any temperature. The correct description of blackbody radiation strongly supported Planck’s assumption that energy was quantized, but it did not prove it or explain it. The proof and the explanation was found only later. Initially Planck assumed it merely to fit the data.

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} * \frac{1}{e^{\left(\frac{hc}{\lambda kT}\right)} - 1}$$

$\mathrm{h} = \text{Planck's constant} = 6.626 * 10^{-34}\, J * s$
$\mathrm{c} = \text{speed of light} = 2.997925 * 10^{8}\, m\,/\,sec$
$\lambda = \text{wavelength (m)}$
$\mathrm{k} = \text{Boltzmann's constant} = 1.381 * 10^{-23}\, J/K$
$\mathrm{T} = \text{temperature (K)}$

Equation 1.1.2 Planck's equation

Bohr's Atom Model

The second development that contributed to Bohr’s atom model was the absorption and emission spectra of atoms. It was experimentally observed that under certain circumstances atoms would send out or absorb electromagnetic radiation of discreet wavelengths that were characteristic for an atom. For example, H atoms would absorb or emit at four discreet wavelengths in the visible region of the electromagnetic spectrum (Fig. 1.1.17).

Figure 1.1.17 The hydrogen emission spectrum in the visible region (Balmer series). (Attribution: Merikanto, Adrignola [CC0], commons.wikimedia.org/wiki/F...spectrum-H.svg)

This is known as the Balmer series named after its discoverer Johann Balmer. Friedrich Paschen and Chester Lyman later found that H also absorbs and emits at discreet wavelengths in the IR and UV region respectively. These wavelengths are known as the Paschen and Lyman series, respectively (Fig. 1.1.18).

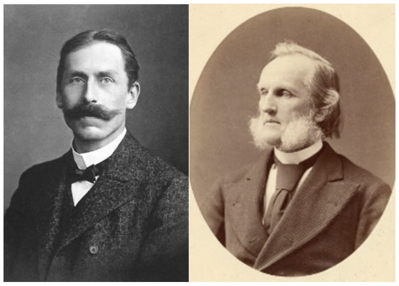


Figure 1.1.18 Friedrich Paschen (1865 – 1947) (Attribution: www.maerkischeallgemeine.de [Public domain], commons.wikimedia.org/wiki/F...n_Physiker.jpg) and Chester Lyman (1814-1988) (Attribution: commons.wikimedia.org/wiki/F...mith_Lyman.jpg), respectively.

For the absorption and emission spectra of H a simple mathematical relationship between the energies associated with the wavelengths can be found. The energy is proportional to a constant, today known as the Rydberg constant, times one over an integer number square minus one over another integer number square, whereby the second integer number would be larger than the first one (Eq. 1.1.3). The observation of integer numbers showed that also the energy and the wavelengths of the atomic absorption and emission spectra are quantized. The question was what the quantization of the absorption spectra meant for atomic structure.

$$\Delta E = R_H\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

Equation 1.1.3 Rydberg formula for the emission of light with particular energies.

Bohr answered the question the following way. He argued, that like in the Rutherford model the electrons would move in orbits around the nucleus. A balance of opposite centrifugal forces and Coulomb attractions would hold the electron stable in the orbit. However, because energy is quantized, also the angular momentum of the electron would be quantized, and thus, only discreet radii would be allowed. The most inner orbit would have the quantum number n=1, the next higher orbit the quantum number n=2, and so forth (Fig. 1.1.19).

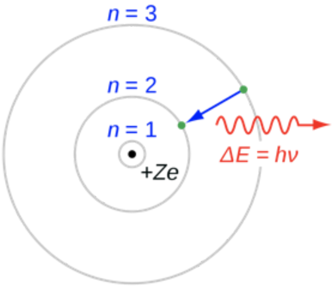


Figure 1.1.19 Bohr atom model (Attribution: JabberWok [CC BY-SA (http://creativecommons.org/licenses/by-sa/3.0/)], commons.wikimedia.org/wiki/F...atom_model.svg)

The quantization of the electron energies and the radii would be the explanation why electrons, despite self-accelerating, do not continuously emit electromagnetic radiation. Electromagnetic radiation is only emitted when an electron jumps from an outer orbit of higher energy to an inner orbit of lower energy. This radiation must have a discreet wavelength because the energy difference between two orbits is discreet. Vice versa, an atom can adsorb electromagnetic radiation of specific wavelength and energy that is suitable to make the electron jump from an inner to an outer orbit. In sum, the quantization of the energy and the radii would explain the quantization of the absorption and emission spectra. The question is: Can the radii be calculated, and what are the associated energies of the electrons in the orbits?

Definition: Bohr's Postulates (1913)

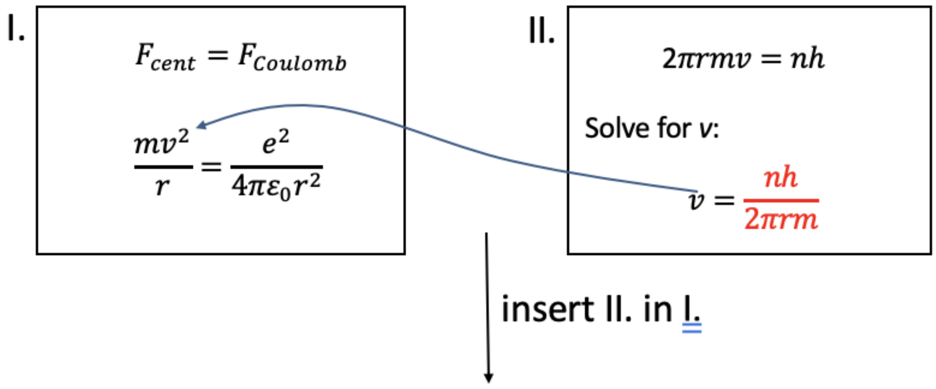
1. An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.

2. Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is an integral multiple of h/2π.

3. Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy E remains constant.

4. Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy, discontinuously changes its motion so that it moves in an other orbit of total energy. The frequency of the emitted radiation is equal to the quantity divided by h.

To calculate the radii and energies of the electron in the H atom Bohr made two assumptions: Firstly, the centrifugal force associated with the electron moving in the orbit would be assumed equal to the Coulomb force between the electron and the proton so that the electron would be stable in the orbit. Secondly, the angular momentum of the electron would be quantized and an integer multiple of the Planck constant h. The factor 2π is because E = h/2π x angular frequency. The angular frequency (also called angular speed) is the angular displacement (in degree or rad) per time unit. Angular frequency is frequency x 2π. We can rearrange this equation by solving it for v and then insert the equation into equation I giving the result as shown in Fig. 1.1.20.



$$\frac{mn^2h^2}{4\pi^2 r^3 m^2} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

v = velocity of the electron
e = elementary charge = 1.602176 53(14) × 10^{-19} C
e_0 = dielectric constant of the vacuum
m = mass of the electron

Figure 1.1.20 Derivation of the radii of the electron orbits (part 1).

We can then multiply this equation by $4\pi\varepsilon_0 r^2$, divide by e^2, and multiply it by r. This gives us the term $r=(n^2h^2\varepsilon_0)/(\pi me^2)$. Analyzing the term shows us that r is only a function of the quantum number n, specifically the radius is proportional to n^2 (Fig. 1.1.21). All other terms are constants, namely the Planck constant h, the dielectric constant of the vacuum, π, the mass of the electron, and the elementary charge. By inserting the quantum numbers into the equation we can calculate the actual values for the radii. For example, when we insert 1 for the quantum number n, we get the radius for the most inner orbit of the electron in the H atom. It is 5.29 x 10^{-11} m. If we inserted 2 for n, we would get the second radius, if we inserted 3, we would get the third radius and so on.

$$\frac{mn^2h^2}{4\pi^2 r^3 m^2} = \frac{e^2}{4\pi\varepsilon_0 r^2} \qquad |\times 4\pi\varepsilon_0 r^2$$

$$\frac{n^2h^2\varepsilon_0}{\pi rm} = e^2 \qquad | \div e^2 \quad |\times r$$

$$r = \frac{n^2h^2\varepsilon_0}{\pi me^2}$$

For the first radius (n=1): $r = \frac{1^2h^2\varepsilon_0}{\pi me^2} = 5.29\times10^{-11}m$

Figure 1.1.21 Continuation of the derivation of the radii of the electron orbits.

Now let us calculate the energies of the electron on these radii. Generally, the overall energy of the electron is the sum of the kinetic and potential energies. The kinetic energy of a moving object is given by $E_{kin}=1⁄2\ mv^2$. We know that m must be the mass of the electron, but what is the velocity of the electron? We can derive it from equation I we previously used by solving it for v^2 (Fig. 1.1.20). We can then insert the term for v^2 into the equation $E_{kin}=1⁄2\ mv^2$, which gives $E_{kin}=e^2/(8\pi\varepsilon_0 r)$, Fig. 1.1.23.

Now let us consider the potential energy. The potential energy is the Coulomb energy between the proton and the electron in the H atom. The formula for the Coulomb energy of two particles having two opposite elementary charges is $E_{pot}=-e^2/(4\pi\varepsilon_0 r)$. Note that this energy has a negative algebraic sign because the forces between the proton and the electron are attractive (Fig. 1.1.23).

$$E = E_{kin} + E_{pot}$$

Equation I:

$$E_{kin} = {}^{1}\!/_{2}\, mv^2 \qquad E_{pot} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$v^2 = \frac{e^2}{4\pi\varepsilon_0 rm}$$

$$E_{kin} = \frac{e^2}{8\pi\varepsilon_0 r}$$

Figure 1.1.23 Derivation of kinetic, potential, and overall energies of the H electron (part 1).

We can now add up the kinetic and the potential energy to give the overall energy which is E = E_{kin}+E_{pot}= [e^2/(8πε$_0$r)] - [e^2/(4πε$_0$r)] = e^2/(πε$_0$r) (1/8-1/4) = -e^2/(8πε$_0$r). We can then use the term we previously calculated for r (Fig. 1.1.21) and insert it into the term for the overall energy. As a result the overall energy becomes E=-(e^4m)/(8$\varepsilon_0^2$$n^2$$h^2$), Fig. 1.1.24. As we can see, the energies for the electrons in the different orbits are also only a function of the quantum number n, specifically, they are a function of 1/n^2. Note also that the overall energy is negative. This is because the energy is a binding energy. Because of the negative algebraic sign, a higher quantum number n means a higher, because less negative energy. At very high quantum numbers n the value for E would approach zero, meaning that the binding energy for the electron would approach zero. The higher the orbit of the electron the more energy it has and the less strongly it is bound to the atom.

$$E = E_{kin} + E_{pot} = \frac{e^2}{8\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r} = \frac{e^2}{\pi\varepsilon_0 r}\left(\frac{1}{8} - \frac{1}{4}\right) = -\frac{e^2}{8\pi\varepsilon_0 r}$$

B/c we had calculated before: $r = \frac{n^2h^2\varepsilon_0}{\pi m e^2} \longrightarrow E = -\frac{e^4 m}{8\varepsilon_0^2 n^2 h^2}$

Figure 1.1.24 Continued derivation for the energies of the H electron.

Formula for energy of electron in a specific orbit:

$$E = -\frac{e^4 m}{8\varepsilon_0^2 n^2 h^2}$$

Formula for energy difference between two orbits:

$$\Delta E = -\frac{e^4 m}{8\varepsilon_0^2 n_{high}^2 h^2} - -\frac{e^4 m}{8\varepsilon_0^2 n_{low}^2 h^2} = \frac{e^4 m}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

Empirically Rydberg found the H spectrum:

$$\Delta E = R_H\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

Because ΔE (theory) = ΔE (empirical):

$$R_H = \frac{e^4 m}{8\varepsilon_0^2 h^2}$$

Figure 1.1.25 Comparing derived energies of the H electron with those experimentally found in the H spectrum.

Finally let us calculate energy differences between electrons in different orbits. Subtraction of the terms for the energies of two electrons in two different orbits gives ΔE=(e^4m)/(8$\varepsilon_0^2$$h^2$) (1/($n_{low}^2$) - 1/(n_{high}^2)), Fig. 1.1.25. The calculated and empirically found ΔE match excellently, the empirically found Rydberg constant matches the theoretically derived constant (e^4m)/(8$\varepsilon_0^2$$h^2$). Thus experiment and theory are in accordance. Bohr’s theory is able to explain the H spectra very well, and can predict both radii of electron orbits and energies. The Bohr model for the first time introduced the quantization of electron states in atoms, and in this regard in was a big step forward. However, there were still problems with Bohr’s theory. It could only explain the H spectra well, but failed to explain the spectra of all other atoms. Secondly, Bohr’s postulates seemed ad hoc and lacked an explanation. There was no good explanation why an electron in a quantized orbit would not emit electromagnetic radiation continuously. Thus, the Bohr model could still not be the final answer to atomic theory. In fact, it lacks to take an important property of the electron into account: The wave-particle dualism of the electron.

Definition: Problems with Bohr's Theory

1. It can explain only the H spectrum and fails to explain all the spectra of all other atoms.
2. Bohr’s postulates are ad hoc. They lack an explanation.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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1.2: The quantum-mechanical model of the atom

Wave Particle Dualism

The phenomenon of the wave-particle dualism was first discovered for electromagnetic radiation, and the extended to all other particles including the electron. It began with the investigation of the photoelectric effect by Albert Einstein (Fig. 1.2.1 and Fig. 1.2.2).

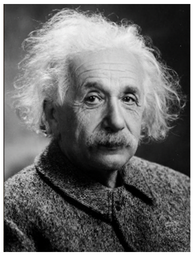


Figure 1.2.1 Albert Einstein, Nobel Prize 1921. (Attribution: Photograph by Orren Jack Turner, Princeton, N.J. Modified with Photoshop by PM_Poon and later by Dantadd. [Public domain], commons.wikimedia.org/wiki/F...lanck_1933.jpg)

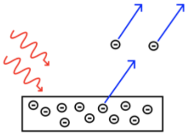


Figure 1.2.2 The photoelectric effect (Attribution: Wolfmankurd [CC BY-SA (http://creativecommons.org/licenses/by-sa/3.0/)]. commons.wikimedia.org/wiki/F...ric_effect.svg)

The photoelectric effect occur when a metal surface is irradiated by light. Above a certain frequency, or below a certain wavelength, light is able to eject electrons from the metal surface. The threshold frequency depends on the metal. Below the threshold frequency no electrons get ejected. Einstein investigated the maximum kinetic energy of the ejected electrons as a function of the frequency of the light. He found that there was a linear relationship. He analyzed the slope of this line and found that the slope was the Planck constant h. This would mean that electrons had an energy $E=h\nu$ minus an energy E_B that would be needed to overcome the binding energy, also called the work function, of the electron in the metal (Figure 1.2.3, left).

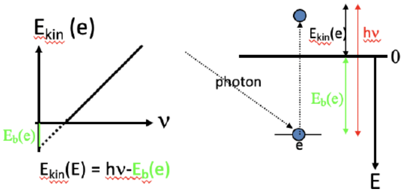


Figure 1.2.3 Maximum kinetic energy of the ejected electron as a function of the frequency of light (left), and mechanistic interpretation of the photoelectric effect (right).

The equation $E=h\nu$ was previously derived by Planck (Fig. 1.2.4) based on the assumption that energy was quantized, and now Einstein had experimentally found it again in the quest to explain the photoelectric effect. This would mean that light was quantized. The quantization would be explained by the fact that light would not only have wave but also particle properties, and these particles would be called photons. Assuming photons the photoelectric effect could be easily explained (Figure 1.2.3, right). When light hits the metal surface the photon collides with the electron. Only when the photon had an energy larger than the work function of the metal, the electron would be ejected and would have a kinetic energy equal to the difference between the energy of the photon and the binding energy. The wave-particle dualism of light, and electromagnetic radiation in general can also be mathematically derived. Because mass can be converted into electromagnetic radiation according to the equation $E = mc^2$, and the energy of electromagnetic radiation is $E=h\nu$, $mc^2=h\nu$. We can solve the equation for ν, and then it is $\nu=mc^2/h$. With $\nu=c/\lambda$, and solved for λ, the equation becomes $\lambda=h/mc$. This equation shows the wave particle-dualism of electromagnetic radiation because it relates a wavelength to a mass. In fact, the mass of the particle associated with electromagnetic radiation, the photon, is inverse proportional to the wavelength of the electromagnetic radiation. The discovery of the wave-particle dualism of electromagnetic radiation was a radically new concept that is difficult to grasp intellectually up to this date because the human mind tends to see waves and particles to be mutually exclusive. However, it is one of the most fundamental principles of nature. As we will see later, not only electromagnetic radiation shows the wave particle dualism, but all particles including electrons.

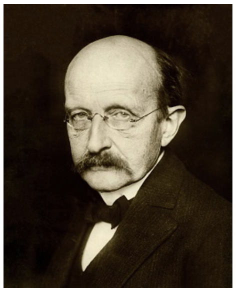


Figure 1.2.4 Max Planck, Nobel Prize 1918 (Attribution: commons.wikimedia.org/wiki/F...lanck_1933.jpg)

Wave Particle Dualism of Massive Particles

The wave-particle dualism was originally thought to be valid for the photon only. A young French physics PhD student, Louis De Broglie had the radical idea that not only the photon, but all particles would exhibit the wave particle dualism, including the electron. Einstein's formula $\lambda = h/mc$ would just need to be slightly rearranged into $\lambda = h/mv$, whereby m would be the mass of the particle, and v would be the velocity of the particle. This idea was much disputed at the time, and Louis De Broglie's PhD thesis was almost not accepted. However, eventually the wave-particle dualism of the electron was proven by electron diffraction experiments, and Louis De Broglie was awarded the Nobel prize in 1929. Today, we believe that all particles show the wave-particle dualism, and no experiment up to this date indicates an exception.

Figure 1.2.5 Louis de Broglie 1892-1987, Nobel Prize 1929 (Attribution: Unknown commons.wikimedia.org/wiki/F...roglie_Big.jpg, PD-US expired)

Standing Waves

With the discovery of the wave-particle dualism of the electron, and the observation of the quantization of electronic states in atoms led physicists focus on a field in physics in which waves are quantized. The field of standing waves (Fig. 1.2.6).

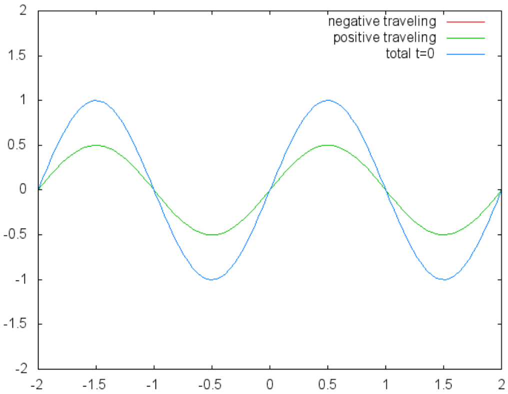


Figure 1.2.6 Two confined traveling waves (red and green) producing a standing wave (blue) due to their interference. (Attribution: Govindabalan [CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)], commons.wikimedia.org/wiki/F..._animation.gif)

Standing waves are a quite common phenomenon. You can for example trigger a standing waves by plucking a guitar string. This causes the guitar string to vibrate in standing waves with discreet, quantized wavelengths. The vibration with the longest wavelength is the so-called ground vibration. Its wavelength is two times the length of the guitar string. In addition, so-called higher harmonics are possible. The first harmonic has a wavelength equal to the length of the guitar string, the second one, has a wavelength equal to two-thirds of the length of the string, the third one has a wavelength equal to half of the length of the string, the fourth one has a wavelength equal to one third of the length of the guitar string, and so fourth (Fig. 1.2.7).

Figure 1.2.7 Standing waves (Attribution: Adjwilley [CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)], commons.wikimedia.org/wiki/F...n_a_string.gif)

It can be easily seen that the possible wavelengths at which the string can vibrate follow the equation $\lambda=2L/n$, whereby n is an integer, or a quantum number, and L is the length of the guitar string. Thus, we can say that the waves associated with the guitar string vibrations are quantized. Why are these waves called standing waves? This is because the positions of the crests and the troughs and the nodes do not move. They remain at the same position on the guitar string at any point in time. It should be said here that the standing nature of the waves is actually an illusion. There are actually two waves traveling in opposite direction on the guitar string, and these waves interfere with each other so that a standing wave is produced (this is illustrated in Fig. 1.2.6). When the guitar string is plucked two waves are sent into opposite direction on the guitar string toward the two opposite ends on the guitar string. Once they have reached these ends they get reflected and sent into the opposite direction until they again reach the ends of the guitar string where they get reflected again. During this process, which happens over and over again, the two waves interfere and produce the standing wave. In sum, the fact that the wave is confined within the guitar string, leads to the quantized standing waves.

Electron in a One-Dimensional Box

Let us know go from a vibrating guitar string to an electron in a one-dimensional box of length *a* having infinitely high walls. Inside the box the potential energy of the electron is zero, in the walls the potential energy is infinite (Figure 1.2.8).

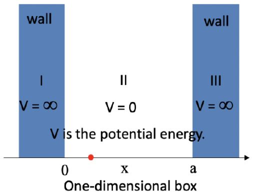


Figure 1.2.8 Electron (red dot) in a one-dimensional box with a potential energy V=0 within the box and infinite potential energy within the walls (the walls may be thought infinitely high).

Due to its kinetic energy the electron can travel on a line within the box until it hits the wall (Fig. 1.2.9, A). At the wall it is getting reflected and forced to travel into the opposite direction until it again hits the wall where it reverses direction again, and so forth. Consider now that the electron does not only have particle, but also wave properties. Because of that also a wave travels along the line, gets reflected at the wall, travels into opposite direction, gets reflected again and so on. These waves can interfere with it other just like the waves traveling on the guitar string to produce a standing wave. Thus, the electron in the one-dimensional box should behave like a standing wave, and this wave should be quantized (Fig. 1.2.9, B-F).

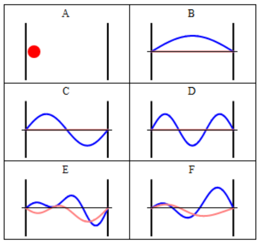


Figure 1.2.9 Electron traveling in a one-dimensional box acting as a standing wave (Attribution: Sbyrnes321 [CC0], commons.wikimedia.org/wiki/F...lAnimation.gif)

How can we mathematically describe the electron in the box as a standing wave? Generally, you can describe a standing wave by a wave function. A wave function tells the amplitude of the standing wave at a particular position in the one-dimensional box. How can we find the wave function? We can start out from a differential equation that is generally valid for standing waves (Eq. 1.2.1).

$$\frac{d^2\Psi(x)}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \Psi(x)$$

Equation 1.2.1 Standing wave differential equation.

It says that the second derivative of the amplitude of the wave function at the position x is equal to $-(2\pi/\lambda)^2$ multiplied with the amplitude of the wave function at the position x. Let us now consider that the kinetic energy of the electron is $E = 1/2mv^2$ and expand the equation by m.

$$\begin{tikzcd}
E = \frac{1}{2} mv^2 & & & \\
E = (mv)^2/2m \arrow[r] & (mv)^2 = 2mE \arrow[r] & mv=[2mE]^{1/2} \arrow[r] & \lambda = h/[2mE]^{1/2} \\
\lambda = h/mv \arrow[r] & mv=h/\lambda \arrow[ur] & &
\end{tikzcd}$$

Equation 1.2.2 Solving for λ from kinetic energy equation and De Broglie equation.

Let us then solve the equation for (mv) . Now let us solve the De Broglie equation for mv and insert mv by h/λ in the previous equation. Finally, let us solve the equation by λ and we will get $\lambda = h/[2mE]^{1/2}$, Eq. 1.2.2. We can now substitute λ by $h/[2mE]^{1/2}$ in the differential equation. Slightly rearranged this equation becomes the Schrödinger equation for the electron in the one-dimensional box (Equation 1.2.3).

$$\left[\frac{d^2}{dx^2}\,\frac{-h^2}{8\pi^2 m}\right]\Psi(x) = E_{kin}\Psi(x)$$

Equation 1.2.3 Schrödinger Equation for the electron in a 1-D box.

The Schrödinger equation is a differential equation. To get the wave function that describes the electron in the box we need to solve the differential equation. One possibility solve a differential equation is to guess its solution, and after that show that the solution is right. This is the approach we want to pursue here. A very general wave function is one that is a sum of a sinus term and a cosinus term of the coordinate x whereby we shall assume two general coefficients r and s in front of x, and two other general coefficients A and B in front of the sinus and the cosinus term, respectively.

$$\Psi = A \sin rx + B \cos sx$$

Equation 1.2.4 Generic solution to the differential equation.

We can now think of so-called boundary conditions for the wave function which will make the wave function more specific. A boundary condition is a property the wave function must have to be a sensible solution to the differential equation. We can assume a first boundary condition which assumes that at the position x=0 the amplitude of the wave function must be 0. This can be assumed because at these positions the "electron wave" gets reflected at the wall. That means that the wave function cannot have a cosinus term and thus B must be 0. If the wave function had a cosinus term it would not be 0 at x = 0 because the cosinus of 0 is not 0.

$$B = 0 \qquad \Psi = A \sin rx$$

Equation 1.2.5 Boundary condition 1 for the wave function

The second boundary condition is that the amplitude of the wave function is zero at x = a. Again, this is because the electron hits the wall at x = a and reverses its direction. The sinus function is only zero at x = a when ra is an integer number n times π: ra=nπ. This means that r must be nπ/a.

$$ra = n\pi \quad \text{or} \quad r = n\pi/a$$

Equation 1.2.6 Boundary condition 2 for the wave function

Thus, the wave function must be A=sin(nπx/a). We can see that the wave function that describes the electron as a standing wave in the one-dimensional box is quantized because the quantum number n appears.

$$\Psi = A \sin(n\pi x/a)$$

Equation 1.2.7 The wave function considering boundary conditions 1 and 2.

Inserting the quantum numbers n into the wave functions produces all the standing waves the electron can adopt (Fig. 1.2.10). You can see that the number of nodes and the wavelengths of the waves depend on the quantum number n. For n = 0 there is no node and the wavelength is twice the length of the box, for n = 2 there is one node and the wavelength is equal to the length of the box, for n =3 there are three nodes and the wavelength of the wave is 2/3 of the lengths of the box and so forth. We can illustrate that the wave function describes the waves depicted in Figure 1.2.10 by an example. The amplitude for the wave for n=2 is zero in the middle of the box where x = a/2. If we insert a/2 into the equation for Ψ then Ψ = A sin(nπ2a/a)= A sin(nπ) = 0 because it is the property of a sinus function to be 0 at an integer number multiple of π. We could also insert other values for x and n into the wave function, and would get the expected amplitude. This shows that the wave function correctly represents the standing waves the electron can adopt.

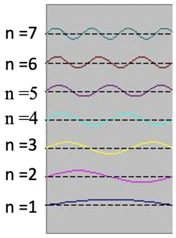


Figure 1.2.10 Standing waves corresponding to the wave function for different quantum numbers n.

We are still not quite finished with the wave function because we have not determined the parameter A in front of the sinus term. To obtain it we need to consider a third boundary condition (Eq. 1.2.8).

$$\int_0^a \Psi^2 dx = 1$$

Equation 1.2.8 Boundary condition 3.

It says that the integral of the square of the wave function over the length of the box must be equal to one. We can understand this boundary condition when we consider that the square of the wave function represents the probability to find the electron at a particular position in the box. The value the square of Ψ adopts at a position x within the box represents the probability to find the electron at this position when we consider the electron as a particle. This is called the Born interpretation of the wave function, named after the German physicist Max Born.

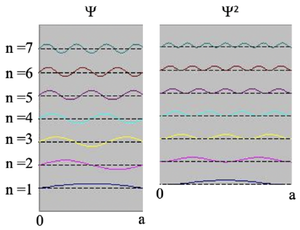


Figure 1.2.11 Standing waves corresponding to the wave function and its square.

Because the probability to find the electron anywhere in the box must be 100%, the integral of the square of the wave function over the entire box must be 100% or 1. One can show, and we omit the necessary mathematical steps for clarity here, that the boundary condition is only fulfilled when A is equal to the square root of 2/a. The final wave function is then psi is equal to 2/a sin(nπx/a). The factor square root of 2/a is called the normalization constant of the wave function because it adjusts the amplitude of the wave function so that the probability to find the electron anywhere in the box is 100%.

The Schrödinger Equation for the H Atom

Let us now go from an electron in a 1-dimensional box to the electron in the hydrogen atom. What is similar and what is different between these two cases. A similarity is that the electron is confined in an atom just like the electron is confined in the 1D box. Thus, like in the 1-dimensional box the electron should behave like a standing wave. While in the one-dimensional box there is only one coordinate to consider, there are three coordinates to consider for the electron in the atom. This is because an atom is spherical and thus three coordinates x, y, and z are necessary to describe a position within the atom. A second major difference is that the potential energy of the electron is zero at any position within the box, while it is not zero in the hydrogen atom. This is because in an atom there are attractive Coulomb forces between the nucleus and the electron. The further away the electron is from the nucleus the higher its potential energy. This is because it takes energy to pull the electron away from the nucleus.

Figure 1.2.12 Erwin Schrödinger (1887-1961), Nobel Prize 1933 (Attribution: Nobel foundation [Public domain] commons.wikimedia.org/wiki/F...ger_(1933).jpg)

We therefore need to modify the Schrödinger equation that we used previously for the one-dimensional box the following way. Firstly, we need to expand the operator for the kinetic energy from one to three dimensions and introduce the coordinates y and z in addition to x. Secondly, we have to add an operator for the potential energy to the equation. The potential energy is the Coulomb energy between the proton and the electron. It is similar to the term we previously used for the calculation of the potential energy of the electron in the Bohr model. Instead of the radius r we use now the square root of the sum of the square of the three coordinates x, y, and z, to indicate the Coulomb energy of the electron at any position within the atom. Our wave function will now be a function of three coordinates x, y, and z. This means our wave function will now be three-dimensional and represent three-dimensional standing waves. Three-dimensional waves are harder to imagine compared to 1-dimensional ones, but have the same properties, which are that the position of the crests, troughs, and nodes does not move.

$$\left[\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)\frac{-h^2}{8\pi^2 m}+\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right]\Psi(x,y,z)=E\ \Psi(x,y,z)$$

Operator for kinetic energy + Operator for potential energy
(Coulomb energy)

Equation 1.2.9 Schrödinger equation for the H atom.

In order to get the wave functions for the electron we need to solve the Schrödinger equation for the hydrogen atom. To do so, we need to think about the boundary conditions for the wave function. One condition is that the square of the wave function approaches zero when we go very far from the nucleus, and r, the distance from the nucleus approaches infinite. Secondly, like in the one-dimensional box, the integral over the square of the wave function must be one. This is because the probability to find the electron somewhere in the atom must be 100%. Thirdly, it would be sensible to assume that the wave function must be continuously differentiable and single valued (Fig. 1.2.13).

Boundary conditions for y:
$\Psi^2 = 0$ for $r \rightarrow \infty$
$\int \Psi^2 dr = 1$
-continuously differentiable and single valued

Figure 1.2.13 Boundary conditions for the wave function of the electron in the hydrogen atom.

The Spherical Polar Coordinate System

The mathematical process to solve the Schrödinger equation is beyond the scope of this course and you are referred to Physical Chemistry classes and textbooks for the details. We shall only provide an brief outline of the process here. It is mathematically simpler to solve the Schrödinger equation in spherical polar coordinates instead of cartesian coordinates. Therefore, we obtain the solutions of the Schrödinger equation, the wavefunctions, in polar coordinates. The position of a point is specified by three numbers: the *radial distance* of that point from a fixed origin, its *polar angle* measured from a fixed zenith direction, and the *azimuthal angle* of its orthogonal projection on a reference plane that passes through the origin and is orthogonal to the zenith, measured from a fixed reference direction on that plane (Fig. 1.2.14).

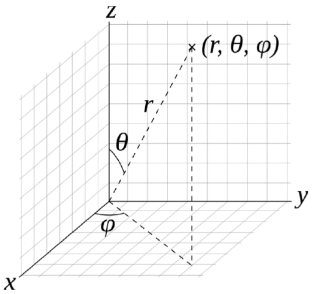


Figure 1.2.14 Illustration of the spherical polar coordinate system.

Solutions of the Schrödinger Equation

The wavefunction is then a function of r, θ and φ, in particular it is a product of a radial wave function which is function of r, a colatitude wave function, which is a function of θ, and an azimuthal wave function which is a function of φ (Eq. 1.2.10). You can see the explicit forms of the radial, colatitude, and azimuthal functions in Fig. 1.2.15.

$$\Psi(r,\theta,\phi) = R(r)\times\Theta(\theta)\times\Phi(\phi)$$

Equation 1.2.10 The wave function for the electron in the H atom as a function of r, θ and φ

Radial wave function ⟶ $R_{n,l} = r^l L_{n,l} e^{-r/na_0}$

Colatitude wave function ⟶ $\Theta(\theta) = (-1)^m\sqrt{\frac{2l+1}{2\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta).$

Azimuthal equation ⟶ $\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}.$

Figure 1.2.15 Explicit forms of the radial, colatitude and azimuthal functions

We do not need to understand all details here, but need to realize that these wavefunctions are functions of quantum numbers. In contrast to the electron in the one-dimensional box not only one, but three quantum numbers need to be considered. Beyond the quantum number n, which is the called the principal quantum number, there is also a so-called orbital quantum number l, and a magnetic quantum number m. The quantum number n only occurs in the radial wave function, the quantum number l only occurs in the radial and colatitude function, and the quantum number m only occurs in the colatitude and the azimuthal part of the wave function. The values the orbital quantum number l can adopt depends on n, it can be between 0 and n-1 for a given quantum number n. The magnetic quantum number m depends on the quantum number l, and can run from –l to +l. So, for example when n is equal to 2, l can vary between 0 and 1, and for l equal to 2, m can adopt any value between -2 and 2, namely -2,-1, 0, +1, and +2 (Fig. 1.2.16).

Principal quantum number: n
Orbital quantum number: l (l = 0.....n-1)
Magnetic quantum number m (m = -l......+l)

Figure 1.2.16 The quantum numbers of the wave function of the H atom.

These wave functions have a particular name in chemistry. They are called orbitals. One can understand an orbital as the three-dimensional wave function that describes the electron in an atom as a standing wave. Thus, an orbital is a state the electron can adopt, and when we say that an electron is in a particular orbital we mean that the electron is in a particular state.

The spin quantum number s

Within an orbital an electron can adopt two different spins described by the spin quantum number s. This quantum number is not a result of the Schrödinger equation, but was found experimentally. The spin quantum number s can adopt two values: +1/2 and -1/2. We say an electron is spin up when s = +1/2, and spin down when s = -1/2.

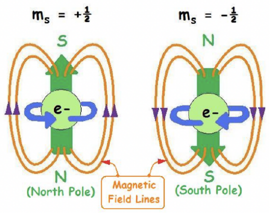


Figure 1.2.17 Electron spin (Attribution: Chemlibretexts.org chem.libretexts.org/@api/dek...jpg?revision=1, CC BY-NC-SA 3.0)

The spin quantum number is understood most easily when you view the electron as a particle rotating around its own axis. A counter-clockwise rotation would be associated with s=+1/2, a clockwise rotation would be associated with s=-1/2. The rotation produces a magnetic field with the direction of the field lines depending on the direction of rotation.

The 1s Orbital

Let us now insert the quantum numbers into the general form of the wave function for the electron in the hydrogen atom, and calculate their explicit mathematical forms. Let us start with the smallest possible numbers. When we insert n=1, l=0, and m=0 we get the wave function for the 1s orbital (Eq. 1.2.11).

$$\Psi_{1s} = \overset{\Phi(\phi)}{\frac{1}{\sqrt{2\pi}}} \overset{\times}{\times} \overset{\Theta(\theta)}{\frac{1}{\sqrt{2}}} \overset{\times}{\times} \overset{R(r)}{\frac{2}{a_0^{3/2}} e^{-r/a_0}}$$

Equation 1.2.11 Wave function for the 1s orbital

You can see that the colatitude and azimuthal parts of the wave functions, together also called the angular part of the wave function, are simple numbers, namely one over the square root of two pi, and one over the square root of two respectively. The angles theta and phi do not appear and that means that the wave function is angle-independent. This implies that the orbital has a spherical shape.

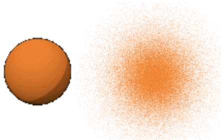
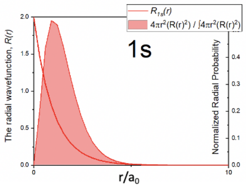


Figure 1.2.18 Common depictions of the 1s orbital

The radial part of the wave function has an exponential term e to the power of –r over a_0. The number ***e*** is the Euler number, that is the base of the natural logarithm. It is approximately equal to 2.71828. a_0 is the Bohr radius, which is the distance of the electron from the proton for the electron on its first orbit according to the Bohr atom model. We calculated it previously, and it was 5.29 x 10^{-11}m. r is the distance from the nucleus. This exponential term has a constant in front of it which is 1 over the Bohr radius to the power of three over two. Because the radial part of the wave function is e to the power of –r, the amplitude of the radial part of the wave function declines exponentially with increasing distance r from the nucleus. This is true for the entire wave function because the angular parts of the wave function are just simple numbers. You can see the exponential decline of the amplitude of the wave function as a function of the radius r in units of the Bohr radius a_0 in the graph below (Fig. 1.2.19).



-maximum at r=a_0

Figure 1.2.19 Amplitude of the radial wave function R of the 1s orbital as a function of the radius r in units of the Bohr radius a_0, and radial probability function (Attribution: Chemlibretexts chem.libretexts.org/@api/deki/files/205599/clipboard_e63775e352caeb1d434fe16aa3fa22d21.png?revision=1, http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

This means that the 1s orbital must be a spherical orbital with its amplitude exponentially declining with increasing distance from the nucleus. This can be graphically depicted via a density of points around the nucleus (Fig. 1.2.18). A higher density of points means higher amplitude and a lower density of points means smaller amplitude. The fact that the amplitude is the highest closest to the nucleus means that the probability to find the electron in a particular point in space is the highest closest to the nucleus. This is because the square of the wave function for the 1s orbital represents the probability to find the electron at a particular point in space. However, the probability to find the electron at a certain distance from the nucleus is not the highest closest to the nucleus. This is because the probability to find the electron at a certain distance from the nucleus is the probability to find the electron at a particular point in space times the number of points in space that have that particular distance. The number of points in space that have a particular distance r from the nucleus is related to the surface of a sphere with the a radius r. The surface of a sphere A is given by the formula $A=4\pi r^2$. Thus, the probability to find the electron at a particular distance r from the nucleus is equal to the surface of a sphere with the radius r times the radial wave function square. This defines the radial probability function $R_P=4\pi r^2R^2$.

The graph for the radial probability function is depicted in Figure 1.2.19. You can see that it is zero when r=0 which is due to the r^2 term which becomes zero at r = 0. At small r values the $4\pi r^2$ term dominates the overall function and the probability to find the electron increases with r. However, because the exponential term of the radial function becomes more and more significant at larger r values, the radial probability function goes through a maximum and then declines. At distances r approaching infinite the function approaches zero. The maximum of the curve represents the distance at which it is most likely to find the electron. Interestingly, it is equal to the Bohr radius r. That means that Bohr was not so wrong after all. However, he was wrong in the sense that he viewed the electron as a classical particle being only at that radius. Instead, the electron, due to its wave properties, it is not only at the Bohr radius $r_{0,}$ but most likely we can find it there.

The result that the probability to find the electron at a specific point in space is the greatest at the nucleus does away with the question of why the H atom does not collapse. Because the amplitude of the wave function is the greatest closest to the nucleus we can actually say in a way that the atom is collapsed. Nonetheless, the atom is mostly empty space because of the delocalization of the wave function that describes the state of the electron. The delocalization of the electron due to its wave properties also makes the question of the size of an orbital non-trivial. The wave function approaches zero only for r approaching infinite, but never becomes zero. This means that to account for all electron density the orbital would be infinitely large. This however would not be a sensible definition. The commonly accepted definition is that the size of an orbital is defined by the space that contains 90% of its electron density. We can depict orbitals according to this definition. For the case of the 1s orbital the radius of the sphere that represents the 1s orbital is chosen so that the probability to find the electron within a sphere of that radius is 90%.

The 2s Orbital

Inserting n=2, l=0, and m=0 into the general wave function gives us the wave function for the 2s orbital (Eq. 1.2.12).

$$\Psi_{2s} = \overset{\Phi(\phi)}{\frac{1}{\sqrt{2\pi}}} \times \overset{\Theta(\theta)}{\frac{1}{\sqrt{2}}} \times \overset{R(r)}{\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left[2-\frac{r}{a_0}\right] e^{-r/2a_0}}$$

Equation 1.2.12 Wave function for the 2s orbital

Like in the case of the 1s orbital, the angular parts of the wave function are only simple numbers. Thus, the 2s orbital is also a spherical orbital. Like in the 1s orbital, the radial part of the wave function has an exponential term of the type e^{-r} and a simple coefficient. However, there is an additional term $2-r/a_0$. Due to the exponential term, the amplitude of the wave function declines exponentially with r. However, because of the term $2-r/a_0$ the wave function becomes negative, and then approaches 0. The radius at which the wave function changes its algebraic sign is called a spherical node. The node is spherical because it describes the surface is a sphere. On the surface of this sphere the amplitude of the wave function is zero. The radius at which the wave function changes its algebraic sign is $2a_0$. This becomes clear when we consider that the term $2-r/a_0$ becomes zero when $r=2a_0$ because $2-2a_0/a_0=0$. When this term is zero then the entire wave function becomes zero. We can illustrate the change of the algebraic sign in the 2s orbital using colors as shown below (Fig. 1.2.20).

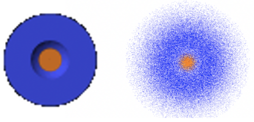


Figure 1.2.20 Common depictions of the 2s orbital.

The orange sphere indicates the space in which the amplitude of the 2s orbital is positive, and the blue area indicates where it is negative. The interface area where the color changes represents the node. By multiplying the square of the radial wave function R with $4\pi r^2$ we obtain the radial probability function for the 2s orbital (Fig. 1.2.21).

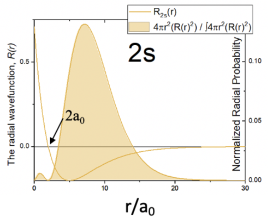


Figure 1.2.21 Amplitude of the wave function of the 2s orbital as a function of the radius r in units of the Bohr radius a_0 a well as the radial probability function (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...png?revision=1, http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

You can see that similar to the 1s orbital, the probability to find the electron on a radius closest to the nucleus is 0. However, unlike the 1s orbital there are now two maxima instead of only one. This second maximum is imposed by the spherical node of the 2s orbital. The second maximum is larger than the first one. Generally, the probability to find the electron further away from the nucleus is greater compared to the 1s orbital. That means that the 2s orbital is larger than the 1s orbital. This reflects the general trend that orbitals with a higher quantum number n tend to be larger and the probability to find the electron further away from the nucleus is greater.

The 3s Orbital

Let us look at one more s orbital, the 3s orbital (Eq. 1.2.13).

$$\Psi_{3s} = \overset{\Phi(\phi)}{\frac{1}{\sqrt{2\pi}}} \times \overset{\Theta(\theta)}{\frac{1}{\sqrt{2}}} \times \overset{R(r)}{\frac{2}{81\sqrt{3}\,a_0^{3/2}}\left[27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right] e^{-r/3a_0}}$$

Equation 1.2.13 Wave function for the 3s orbital.

The angular parts of the wave function for the 3s orbital are again simple numbers, which implies that the orbital is again spherical. Generally all s orbitals are spherical.

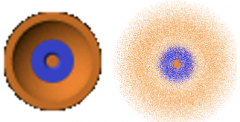


Figure 1.2.22 Common depictions of the 3s orbital

The radial part of the wave function can be divided into the parts. The first part is a simple number, then there is the term $27-18r/a_0+2r^2/a_0^2$, and the exponential term $e^{-r/3a_0}$. Because of the exponential part the amplitude of the wave function declines exponentially with increasing r. However, then the wave function becomes negative, goes through a minimum, then becomes positive again, goes through a small maximum, and finally approaches zero. The fact that the wave function changes its algebraic sign two times means that the 3s orbital has two spherical nodes. These spherical nodes are due to the second term which is a square function of the type $ax^2 + bx + c$, whereby in this case $a = 2/a_0^2$, $b =-18/a_0$ and $c=27$. When this term becomes zero the entire wave function becomes zero. Square functions have two solutions according the formula $x=(-b\pm\sqrt{(b^2-4ac)})/2a$. The solutions give the radii for the two spherical nodes of the 3s orbital. We omit the exact calculation of the radii for briefness and clarity reasons here. You may calculate them as a homework.

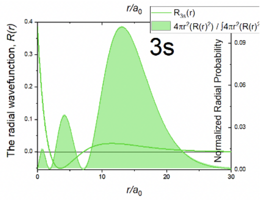


Figure 1.2.23 Amplitude of the wave function of the 3s orbital as a function of the radius r in units of the Bohr radius a_0 as well as radial probability function. (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...png?revision=1, http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

Because of the two spherical nodes, the radial probability function R_p has three maxima. A very small one close to the nucleus, are larger one further away from the nucleus, and the largest one at even greater distance from the nucleus. Overall, the 3s orbital is larger than the 2s orbital confirming the general trend that s orbitals increase in size with increasing quantum number n.

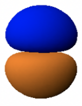
The $2p_z$ Orbital

Now let us look at orbitals in which the orbital quantum number l is larger than 0. When l is equal to 1, then n must be at least 2. An orbital with n=2 and l=1 is a 2p orbital. Overall, three 2p orbitals must exist because for l=1, the magnetic quantum number m can adopt three values: -1, 0, and +1. The orbital with m=0 is called the $2p_z$ orbital. Let us look at the mathematical form of this wave function (Eq. 1.2.14).

$$\begin{array}{cccccc} & \Phi(\phi) & \times & \Theta(\theta) & \times & R(r) \\ \Psi_{2p_z} = & \frac{1}{\sqrt{2\pi}} & \times & \frac{\sqrt{6}}{2}\cos\theta & \times & \frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}\,e^{-r/2a_0} \end{array}$$

Equation 1.2.14 Wave function for the $2p_z$ orbital

Analyzing the angular parts of the wave function shows that while the azimuthal part is still a simple number, the colatitude part is not, it is a function of θ. This means that the amplitude of the wave function is now angle dependent, which implies that the orbital cannot be spherical. Instead the 2p orbital has the shape of a dumbbell which is oriented along the z-axis. One lobe is above the xy plane, and the other lobe is below the xy plane. These two different lobes have a different algebraic sign, indicated by different colors (Fig. 1.2.24).



$2p_z$ (l=1, m=0)

planar node (xy plane)

Figure 1.2.24 Common depiction for the $2p_z$ orbital

Within the xy plane the amplitude of the wave function is zero. The xy plane represents a so-called planar node. A planar node is a type of an angular node. The name angular node is because it is due to the fact that the angular part of the wave function is not a simple number, but a function of an angle, in this case θ. We can show that the angular part of the wave function produces the planar node in the xy plane when we convert it from spherical into Cartesian coordinates (Eq. 1.2.15).

$$\Theta\Phi(x,y,z) = \frac{1}{2}\sqrt{\frac{3z}{\pi r}} \quad \text{is 0 for } z = 0$$

Equation 1.2.15 Angular part of the wave function of $2p_z$ in cartesian coordinates. The function becomes zero when z=0.

We can see that the angular part of the wave function is only a function of z. We can also see, that the angular part of the wave function becomes zero when z=0. When the angular part of the wave function becomes zero, then the wave function of the entire orbital becomes zero. Z is zero only in the xy plane, and this explains why the xy plane is a planar node.

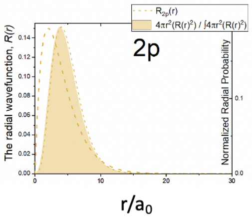


Figure 1.2.25 Amplitude of the wave function of the $2p_z$ orbital as a function of the radius r in units of the Bohr radius a_0 as well as radial probability function. (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...png?revision=1, http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

Now let us look at the radial part of the wave function. It is made of three terms: a simple constant, the term r/a_0, and the exponential term $e^{-r/2a_0}$. Because of the term r/a_0 the radial part of the wave function is zero at r=0. This means that it is very unlikely to find the electron at a point in space directly at the nucleus. This behavior is opposite to s orbitals. Because the r/a_0 term dominates the behavior of the wave function at small r value, the amplitude first increases. However, at larger r values the exponential term becomes more an more important which forces the amplitude of the radial function through a maximum, after which it declines and approaches zero. The radial wave function never changes algebraic sign. Therefore, the $2p_z$ orbital does not have a spherical node. The radial probability function has a similar shape compared to the radial function. It is zero at r=0 and goes through a maximum before it declines again and approaches zero (Figure 1.2.25).

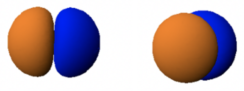
The $2p_x$ and $2p_y$ Orbital

The $2p_x$ and the $2p_y$ orbitals are obtained when the quantum numbers m are 1, and -1, respectively.

$$\begin{array}{cccccc} & \Phi(\phi) & \times & \Theta(\theta) & \times & R(r) \\ \Psi_{2p_{x/y}} = & \frac{1}{\sqrt{2\pi}}e^{\pm i\phi} & \times & \frac{\sqrt{3}}{2}\sin\theta & \times & \frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}\,e^{-r/2a_0} \end{array}$$

Equation 1.2.16 Wave function for the $2p_x$ and $2p_y$ orbital

They have the same shape as the $2p_z$ orbital, but their orientation is different. The dumbbell of the $2p_x$ orbital is oriented along the x-axis, and that of the $2p_y$ orbital is oriented along the y-axis.



(l=1, m=1) (l=1, m=-1)

planar node = yz plane planar node = xz plane

Figure 1.2.26 Common depictions for the $2p_x$ and $2p_y$ orbitals, respectively

This is because the $2p_x$ orbital has a planar node in the yz plane, and the $2p_y$ orbital has a planar node in the xz plane. The planar nodes are due to the angular part of the wave functions of these orbitals.

$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{3x}{\pi r}}\ \text{ is 0 for x = 0}$$

$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{3y}{\pi r}}\ \text{ is 0 for y = 0}$$

Equation 1.2.17 Angular part of the wave function of $2p_x$ and $2p_y$, respectively. The wave functions become 0 for x=0 and y=0, respectively.

As one can see, the angular parts of the wave function contain both the angles θ and Φ. When converted into Cartesian coordinates (Eq. 1.2.17) one can see that the angular function of the $2p_x$ orbital is only a function of x, and the angular function of the $2p_y$ orbital is only a function of y. The functions become zero for x=0 and y=0, respectively. X is zero only in the yz plane, and y is zero only in the xz plane, hence these nodes are planar nodes. The radial wave function is exactly the same as for the $2p_z$ orbital.

The 3p Orbitals

Now let us look at the 3p orbitals. In a 3p orbital the quantum number n=2 and l=1. Like for the case of the 2p orbitals there are three p orbitals because the magnetic quantum number m can adopt the values -1, 0, and +1. The wave function of the $3p_z$ orbital is shown below (Eq. 1.2.18).

$$\Psi\ 3p_z = \overset{\Phi(\phi)}{\frac{1}{\sqrt{2\pi}}}\quad \overset{\Theta(\theta)}{\frac{\sqrt{6}}{2}\cos\theta}\quad \overset{R(\,r\,)}{\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left[6-\frac{r}{a_0}\right]\frac{r}{a_0}e^{-r/3a_0}}$$

Equation 1.2.18 Wave function for the $3p_z$ orbital

One can see that the angular part of the wave function is exactly the same as for the $2p_z$ orbital. This means that like in the $2p_z$ orbital there must be a planar node in the xy plane. When you look at the radial part of the wave function you can see that it is composed of four terms, a simple constant, a term $6-r/a_0$, the term r/a_0, and the exponential term $e^{-r/3a_0}$. Because of the term r/a_0 the wave function becomes zero at r=0. Because of the term $6-r/a_0$ the wave function has a spherical node. This is because when $6-r/a_0=0$ the entire wave function becomes 0. We can determine the radius at which the wave function becomes zero by solving the equation $6-r/a_0=0$ for r, which gives $r=6a_0$. Overall, the radial function is zero at r=0, goes through a maximum, changes its algebraic sign at the spherical node at $r=6a_0$, has a minimum, and then approaches zero for very large distances r (Fig. 1.2.28).

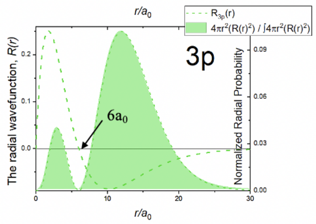


Figure 1.2.28 Amplitude of the wave function of the $3p_z$ orbital as a function of the radius r in units of the Bohr radius a_0 as well as radial probability function

The radial probability function has two maxima, a small one close to the nucleus, and a larger one further away from the nucleus. Overall the radial probability function is further away from the nucleus compared to the 2p orbitals, which implies that the 3p orbital is larger.

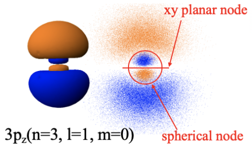


Figure 1.2.29 Common depiction for the $3p_z$ orbital

The overall shape of the $3p_z$ orbital is determined by the both the spherical and the planar node (Fig.1.2.29). Due to the planar node in the xy plane it has a dumbbell shape and is oriented in z direction. However, because of the spherical node the algebraic sign of the wave function changes within the two lobes of the dumbbell. Finally let us consider the $3p_x$ and the $3p_y$ orbitals. They would have the same shape as the $3p_z$ orbital, but they would be oriented in the x and the y direction respectively. We could also think about what would happen to the p orbitals if we increased the quantum number n further. In this case the dumbbell shape would remain, but additional spherical nodes would be introduced. A 4p orbital would have two spherical nodes, a 5p orbital three spherical nodes, and so on. The size of these p orbitals would also increase with the quantum number n.

The $3d_{z^2}$ Orbital

Now let us consider the orbitals with the orbital quantum number l=2. These orbitals are so-called d-orbitals. Because the principal quantum number n always has to be at least one integer number larger than the quantum l, the d orbitals with the smallest quantum number n are the 3d orbitals. For each quantum number n there must be five d orbitals because for l=2 the magnetic quantum number m can adopt the values -2, -1, 0, -1, +1, and +2. Let us first look at the 3d orbital with m=0. This orbital is called the $3d_{z^2}$ orbital. Its wave function is shown below (Eq. 1.2.19).

$$\Psi_{3d_{z^2}} = \overset{\Phi(\phi)\ \Theta(\theta)}{\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1)}\qquad \overset{R(\,r\,)}{\frac{1}{81\sqrt{15}}\left[\frac{2}{a_0}\right]^{3/2}\frac{r^2}{a_0^{\,2}}e^{\frac{-r}{3a_0}}}$$

Equation 1.2.19 Wave function for the $3d_{z^2}$ orbital

You can see that the radial function is a product of three terms: a constant, a term r^2/a_0^2, and the exponential term $e^{-r/3a_0}$. The exponential term is the same as for the 3p orbitals. Because of the term r^2/a_0^2 the amplitude of the wave function is 0 at r=0. The amplitude then increases with r, goes through a maximum, and then approaches zero. This means that the wave function never changes its algebraic sign, and therefore it does not have spherical nodes. The radial probability function has a similar shape compared to the radial function (Figure 1.2.30). The electron probability is somewhat further away from the nucleus compared to the 3p orbitals, meaning that the 3d orbital is somewhat larger than the 3p orbital.

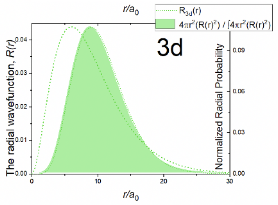


Figure 1.2.30 Amplitude of the wave function of the $3d_{z^2}$ orbital as a function of the radius r in units of the Bohr radius a_0 as well as radial probability function

You can see that the angular part of the wave function is a function of θ which means that the orbital will be non-spherical and there will be at least one angular node. In this case the angular nodes are two conical nodes. These nodes describe two cones that give the orbital its characteristic shape. It is a doughnut ring in the xy plane around a dumbbell pointing into z direction. The dumbbell and the doughnut have different algebraic signs indicated by different colors (Figure 1.2.31). Note that in contrast to the p orbitals the two lobes of the dumbbell have the same algebraic sign.

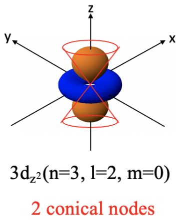


Figure 1.2.31 Common depiction for the $3d_{z^2}$ orbital with conical nodes (red).

We can understand that the $3d_{z^2}$ orbital has two conical nodes when we convert the angular part of the wave function into Cartesian coordinates (Eq. 1.2.20).

$$\Theta\Phi(x,y,z)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2-x^2-y^2)}{r^2}$$

Equation 1.2.20 Angular part of the wave function of the $3d_{z^2}$ orbital in cartesian coordinates.

You can see that it is a function of $2z^2-x^2-y^2$. This is the mathematical form of cones. The angular part of the wave function becomes 0 when $2z^2=x^2-y^2$ which is true on the surface of two cones, one above the xy plane and one below the xy plane. The name of the $3d_{z^2}$ orbital is because it is a function of z^2.

The $3d_{x^2-y^2}$ Orbital

Let us next look at the $3d_{x^2-y^2}$ orbital (Eq. 1.2.21).

$$\begin{array}{ccc} & \Phi(\phi)\,\Theta(\theta) & R(r) \\ \Psi_{3d_{x^2-y^2}}= & \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos^2 2\phi & \frac{1}{81\sqrt{15}}[\frac{2}{a_0}]^{3/2}\frac{r^2}{a_0{}^2}e^{\frac{-r}{3a_0}} \end{array}$$

Equation 1.2.21 Wave function for the $3d_{x^2-y^2}$ orbital

The radial part of the wave function is the same as the one for the $3d_{z^2}$ orbital. The angular part of the wave function is both a function of θ and Φ and thus there are angular nodes to expect. We can find them again when we convert the angular part of the wave function from spherical to Cartesian coordinates.

$$\Theta\Phi(x,y,z)=\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2-y^2)}{r^2}$$

Equation 1.2.22 Angular part of the wave function of the $3d_{x^2-y^2}$ orbital in cartesian coordinates.

You can see that the angular function is a function of x^2-y^2. The function becomes zero when $x^2-y^2=0$. This is the case when x=y or x=-y. X is equal to y on two lines that bisect the 90 degree angle between the x and the y axis. The coordinate z is completely variable. Thus, overall, the wave function becomes zero on two planes that stand perpendicular to the xy plane and bisect the 90 degree angle between the x and the y axis. These two planes are therefore the two planar nodes of the orbital.

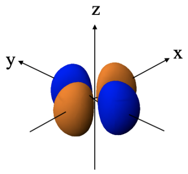
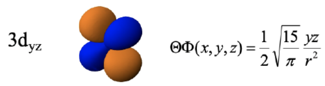


Figure 1.2.32 Common depiction of the $3d_{x^2-y^2}$ orbital

Because of the two planar nodes the orbital has four lobes lying on the x and the y axis, respectively. Lobes lying on the x-axis have the opposite algebraic sign compared to those lying on the y-axis. The name of the dx^2-y^2 orbital is because it is a function of x^2-y^2.

The $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals

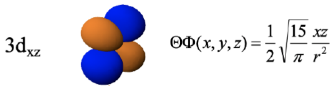
The remaining d orbitals are the $3d_{yz}$, the $3d_{xz}$, and the $3d_{xy}$. The radial function of these orbitals is just like the ones we previously discussed. The angular part of the wave functions is shown here directly in Cartesian coordinates. The d_{yz} orbital is a function of yz. The function becomes zero when either y=0 or z=0. y is zero in the xz plane, and z is zero in the xy plane. Therefore these planes are planar nodes of the orbital. Because of these nodes, the orbital has four lobes which lie in the yz plane whereby the lobes are in between the y and the z axes. Note that adjacent lobes have opposite algebraic sign, and opposite lobes have the same algebraic sign.



$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$$

Figure 1.2.33 Angular wave function for the 3d$_{yz}$ orbital, and the common depiction for this orbital

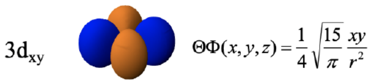
The 3d$_{xz}$ orbital is a function of xz, and thus the function becomes zero with x=0 or z=0. This defines that yz and the xy planes as the two planar nodes. The orbital has the same shape as the 3d$_{yz}$, except that the four lobes lie within the xz plane instead the yz plane.



$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$$

Figure 1.2.34 Angular Wave function for the 3d$_{xz}$ orbital, and the common depiction for this orbital

The 3d$_{xy}$-orbital is a function of xy, and thus its wave function becomes zero at x=0 or y=0. Therefore, the xz and the yz planes are the planar nodes and the orbital has four lobes in the xy plane in between the x and the y axis. Note that the 3d$_{xy}$ and the 3d$_{x^2-y^2}$ look very similar but are different. The difference is that the 3d$_{x^2-y^2}$ orbital has its lobes on the x and the y axis, while the 3d$_{xy}$ orbital has the lobes in between the x and the y axis. One can also say that the 3d$_{x^2-y^2}$ orbital is rotated by 45 degree around z with respect to the 3d$_{xy}$ orbital.

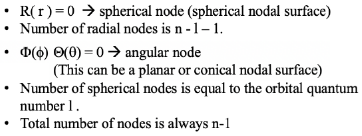


$$\Theta\Phi(x,y,z)=\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$$

Figure 1.2.35 Angular wave function for the 3d$_{xy}$ orbital, and the common depiction for this orbital

Rules for Angular and Spherical Nodes

Of course, we could now discuss the size and shape of many other orbitals such a the 4d orbitals or the 4f orbitals, but this will be beyond scope. Instead, let us think about if there are general rules that allow the prediction of the number of spherical and angular nodes in an orbital. The number of radial nodes is always equal to n-l-1, the number of angular nodes is equal to l, and the total number of nodes is always n-1. This means that the number of nodes increases with the quantum number n. If we increase the quantum number l for a given quantum number n, then we replace spherical nodes by angular nodes. This is summarized in Figure 1.2.36.



- $R(r) = 0$ → spherical node (spherical nodal surface)
- Number of radial nodes is n - l – 1.
- $\Phi(\phi)\ \Theta(\theta) = 0$ → angular node
  (This can be a planar or conical nodal surface)
- Number of spherical nodes is equal to the orbital quantum number l .
- Total number of nodes is always n-1

Figure 1.2.36 Rules for angular and spherical nodes

The Orbital Energies for the H Atom

The Schrödinger equation does not only allow to calculate the orbitals of the hydrogen atom, but also their energies. The energies of Bohr and Schrödinger model match: E = constant/n^2 : This means that orbitals with the same quantum number n have the same energies. The energies are **not** a function of the quantum numbers l and m. The energies are negative because they are binding energies. In other words: Adding an electron to a proton is an exothermic process. The binding energy for the energy increases as the orbital energy decreases (Fig. 1.2.37).

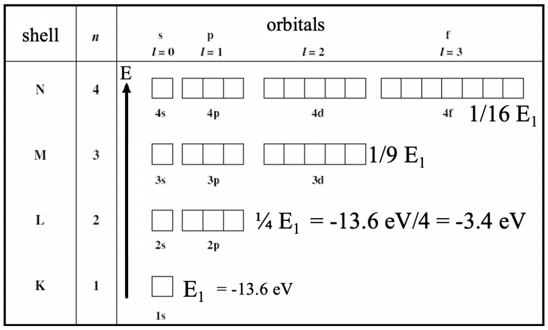


Figure 1.2.37 Orbital energies from the 1s orbital to 4f orbital. K, L, M, N indicate the shells associated with a quantum number n.

For the 1s orbital of H the energy is -13.6 eV, the energy of the 2s and the 2p orbitals are ¼ of that, the energy of the 3s, 3p, and 3d orbitals are 1/9 of the energy of the 1s orbital and so forth. Note at ¼ and 1/9th of -13.6 eV is more than -13.6 eV due to the negative algebraic sign. The electron volt is a unit of energy. It is the amount of kinetic energy gained by a single unbound electron when it passes through an electrostatic potential difference of one volt, in vacuum.

$$1\ \text{eV} = 1.602176\ 53(14)\times10^{-19}\ \text{J}.$$

Equation 1.2.23 The electron volt to joule unit conversion.

In other words, it is equal to one volt (1 volt = 1 joule per coulomb) times the charge of a single electron (in coulombs). It is a very small unit of energy which is practical for orbital energy calculations because the orbital energies are very small (Eq. 1.2.23).

Multi-electron Atoms

Thus far we have only considered the orbitals for the hydrogen atom which contains only one electron. Can we also solve the Schrödinger equation for atoms that have more than one electron and get the exact energies of the orbitals? The answer is no, this mathematically not possible. The process is just already too complex even for only two electrons. The Schrödinger equation can only be solved for one electron systems. Therefore, the description of the atomic structure of all other atoms must work with approximations. Let us first consider the He atom. It has only one more electron than hydrogen. It is a useful approach to approximate multi-electron atoms as one-electron systems first, and then approximate the electron-electron interactions. Electron energies in an atom with more than one proton should follow the equation $E_n=-Z^2x13.6\ eV/n^2$, whereby Z is the number of protons.

$$E_n = -\frac{Z^2\ 13.6\ \text{eV}}{n^2}$$

Equation 1.2.24 The orbital energies for atoms with more than one proton

The binding energy of the electron increases proportionally to the square of the number of protons because the attractive Coulomb forces that act on the negatively charged electrons increases with the number of positively charged protons in the nucleus. One can experimentally measure the orbital energies via ionization energies. The energy required to remove an electron in a particular orbital from the atom is equal to the binding energy for the electron in that orbital. Therefore the ionization energy IE = $-E_n$ (E_n = orbital energy). According to the Schrödinger model the orbital energy for a helium electron in a 1s orbital should be E_{1s}=$-(2^2\times13.6\text{ eV})/1^1$ =-54.4 eV (Eq. 1.2.25).

$$E_{1s} = -\frac{2^2 \times 13.6\ eV}{1^1} = -54.4\ eV$$

Equation 1.2.25 Energy for a helium electron in a 1s orbital.

However, the experimentally measured ionization energy of the electron is +24.6 eV, which means that the real orbital energy is -24.6 eV, and not -54.4 eV. On the other hand, the ionization of a He^+ ion is +54.4 eV which is exactly what we would expect. We can explain this phenomenon by the fact that the Schrödinger model works for a single electron only and must neglect electron interactions. In a He^+ ion there is only one electron, therefore the Schrödinger model correctly predicts the energy of the electron. However, in a helium atom there are two electrons, and the Schrödinger model cannot account for the electron-electron interactions. Therefore, it does not give the correct energy for the electrons in a Helium atom. The electron-electron interactions can be viewed as shielding effects. This means that the first electron shields part of the nuclear charge from the second electron. Therefore, the second electron experiences a reduced Coulomb force from the nucleus. Because of the reduced Coulomb force, the binding energy is smaller. It is reduced from -54.4 eV to -24.6 eV. It should be pointed out that the two electrons in the 1s orbital of the He atom are indistinguishable, that means they both have the reduced binding energy. The binding energy only increases to -54.4 eV after one of the two electrons has been removed.

The net positive charge from the nucleus after accounting for shielding effects is called the effective nuclear charge. For the helium atom the effective nuclear charge is 1.34. We can calculate the effective nuclear charge from the experimentally measured first ionization energy. Solving the equation for Z_{eff} gives Z_{eff}=1.34 (Eq. 1.2.26).

$$E = -\frac{Z_{eff}^2}{n^2} \times 13.6\ eV = -24.6\ eV \quad \text{b/c } IE(He) = 24.6\ eV$$

$$Z_{eff} = \sqrt{n^2 \times \frac{24.6\ eV}{13.6\ eV}} = \sqrt{1^2 \times \frac{24.6\ eV}{13.6\ eV}} = 1.34$$

Equation 1.2.26 Calculation of Z_{eff} in the Helium atom from first ionization energies.

The Lithium Atom

Now let us go to the atom with three electrons, the lithium atom. Following the so-called Aufbau principle we would fill the first two electrons into the 1s orbital, because the 1s orbital is the orbital with the the lowest energy. However, the third electron does not fit into the 1s orbital because of the Pauli principle.

Figure 1.2.38 Wolfgang Pauli (1900-1958), Nobel prize 1945 (Attribution: Nobel foundation [Public domain], commons.wikimedia.org/wiki/File:Pauli.jpg, PD-US-expired)

The Pauli principle states that no two electrons in an atom can have the same four quantum numbers. For that reason an orbital cannot accommodate more than two electrons. Within an orbital two electrons must have different spin quantum numbers s. We can indicate this by writing the electrons as arrows pointing up and down into a square box which represents the orbital. The third electron of the lithium would need to go to the orbital with the next higher energy.

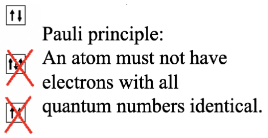
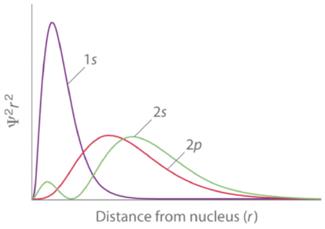


Figure 1.2.39 Illustration of the Pauli Principle

According to the Schrödinger model, the energy of an orbital is only a function of the quantum number n, and we would have two choices: The 2s and the 2p orbitals. Both of them would have the same energy. However, in the lithium atom the 2s orbital has a somewhat lower energy than the 2p orbital. This can again be explained by shielding effects. The 2s orbital penetrates the 1s orbital slightly better than the 2p orbitals. Because of that, the 1s orbital shields the nuclear charge from the nucleus less for the 2s orbital compared to the 2p orbitals. The ground state electron configuration, which is the atom electron configuration having the lowest energy, must therefore be $1s^2\ 2s^1$. We can see that the 2s orbital penetrates the 1s orbital slightly better than the 2p orbital from the graph for the radial probability functions of the orbitals shown in Figure 1.2.40.



Graph of radial probability functions of the 1s, 2s, and 2p orbitals (Attribut
es/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Miessler%2C_Fischer%2C_Tarr)/2%3A_Atomic_Structure/2.2%3A_The_Schr%C3%B6dinger_equation%2C_particle_in_a_box%2C_and_atomic_wave
censes/by-nc-sa/4.0/)

The second large maximum of the function of the 2s orbital is actually further away from the nucleus compared to the maximum associated with the 2p orbital. However, because the 2s orbital has a small second maximum very close to the nucleus, the 2s orbital overall penetrates the 1s orbital better, and therefore the shielding effect of the 1s orbital on the 2s orbital is smaller compared to the 2p orbitals.

Generally we can say, the smaller the quantum number l for a given quantum number n, the better the penetration ability of this orbital. Due to the better penetration ability, the shielding is less and thus the effective nuclear charge that acts on the electron in the orbital is higher. The higher effective nuclear charge leads to a lower energy of this orbital. For that reason the energy sequence of orbitals with the same quantum number n increases from s to p to d to f.

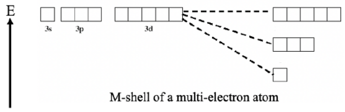


Figure 1.2.41 The energy sequence of orbitals with the quantum number n=3 in a multi-electron atom.

For example, a 3s orbital has a lower energy then a 3p orbital which has a lower energy than a 3d orbital (Fig. 1.2.41).

Slater's Rules

Because an orbital energy can be calculated from the effective nuclear charge, it would be useful if the effective nuclear charge could be somehow estimated by simple approximations.

Figure 1.2.42 John C. Slater (1900-1976) (Attribution: Biographical Memoirs, National Academy of Sciences, vol. 53. 1982., http://scarc.library.oregonstate.edu/coll/pauling/bond/pictures/portrait-slater.html)

The so-called Slater rules, named after their developer John C. Slater (Fig. 1.2.42), are a simple tool that give a good estimate for the effective nuclear charge of orbitals in multi-electron atoms. The Slater rules estimate a shielding constant σ that allows to calculate the effective nuclear charge Z_{eff} from the nuclear charge according to Z_{eff}=Z-σ.

The rules for the estimation of σ are the following. Firstly, we need to recognize that the rules for s and p electrons are slightly different than those for d and f electrons. This is because s and p electrons of the same quantum number n have somewhat higher penetration abilities compared to d and f electrons. For both groups the first step is the same. We write out the electron configuration of the atom according to their quantum numbers n and l as shown below (Fig. 1.2.43).

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)….

Figure 1.2.43 First step to calculate the shielding constant σ

Note that this order does not exactly reflect the order of energy. Electrons that have similar shielding effects are grouped together in parentheses. You can see that s and p orbitals of the same quantum number n build a group, all other orbitals are their own group.

To estimate the shielding constant for an s or a p orbital we can now apply the following rules:

a) Electrons to the right of the (ns, np) group contribute nothing to σ. This is because these electrons are further away from the nucleus than the electron of consideration.

b) Each of the other electrons in the same (ns, np) group contribute 0.35 to σ. These electrons are in the same shell as the electron of consideration, and thus have similar distance to the nucleus. For this reason their shielding is modest only and can be estimated to be about 35% of a full elementary charge, or 0.35.

c) Each electron in the n-1 shell contributes 0.85 to σ. Those electrons are significantly closer to the nucleus compared to the electron of consideration. For that reason they shield significantly better, approximately 85% of an elementary charge, or 0.85.

d) Each electron in the n-2 shell or below contributes 1.00 to σ. Those electrons are much closer to the nucleus than the electron of consideration and can fully shield an elementary charge. Its contribution to the shielding constant is therefore approximated to be 1.

Now let us look at the Slater rules for d and f electrons.

a) Electrons to the right of the (nd) or (nf) group contribute nothing to σ. This is again because the electron is further away from the nucleus than the electron of consideration, and thus cannot contribute to shielding.

b) Each of the other electrons in the same (nd) or (nf) group contribute 0.35 to σ. This is again because these electrons have similar distance compared to the electron for which we calculate the shielding constant, and thus the shielding is modest.

c) Each electron to the left of the (nd) or (nf) group contributes 1 to σ. Those electrons are considered much closer to the nucleus, and thus they shield a full elementary charge.

Note that the values 0.35, 0.85, and 1 have been chosen so that the results from the Slater rules are in the best possible accordance with experimental measurements of orbital energies. Remember, when we discussed the helium atom we said that the measurement of ionization energies can provide experimental orbital energies.

Slater's Rules Applied to Multi-Electron Atoms

Let us practice the Slater rules by a few examples. We can, for instance, calculate the effective nuclear charge that acts on a 2p electron in an oxygen atom. To answer this question we need to first write out the electron configuration according to the quantum numbers n and l and group the orbitals correctly (Fig. 1.2.44).

Electron configuration $(1s^2)(2s^2\ 2p^4)$

Figure 1.2.44 Slater electron configuration of oxygen

Next, we need to consider that the effective nuclear charge Z_{eff} is the nuclear charge Z minus the shielding constant σ. Then, because oxygen has eight protons, the nuclear charge is 8. From that we need to subtract the shielding constant. Firstly, we need to realize that there are 5 electrons in the same group as the 2p electron of consideration. These are the two 2s electrons and the three other 2p electrons. These five electrons shield with a factor of 0.35 because they are in the same group as the 2p electron for which we want to calculate the shielding constant. Note that this fourth 2p electron does not get a factor because it is the electron for which we calculate the shielding constant. In addition, we need to consider the two 1s electrons. They are in an n-1 shell, therefore they contribute with a factor of 0.85. Overall, the effective nuclear charge on the 2p electron is 8-(2 x 0.85)-(5 x 0.35)= 4.55 (Fig. 1.2.45).

$$\begin{aligned} Z^* &= Z - \sigma \\ &= 8 - \underbrace{[5 \times (0.35)]}_{(2s,\ 2p)} - \underbrace{[2 \times (0.85)]}_{(1s)} = 4.55 \end{aligned}$$

Figure 1.2.45 Effective nuclear charge on the 2p electron of an oxygen atom

We can also ask what is the effective nuclear charge on a 1s electron in the oxygen atom. It is 8-0.35=7.65 (Fig. 1.2.46).

$$Z_{eff} = \underset{(1s)}{8-0.35} = 7.65$$

Figure 1.2.46 Effective nuclear charge on the 1s electron of an oxygen atom

This is because we only need to consider the second electron in the 1s orbital to calculate the shielding constant σ. It contributes with a factor of 0.35 because it is in the same group as the 1s electron of consideration. The 2s and the 2p electrons are in a group right to the 1s orbital, therefore they do not contribute to the shielding.

Slater's Rules and the Aufbau Principle

The Slater rules are of great help to understand the so-called Aufbau principle, which says that for an atom in the ground state the electrons are in the orbitals of the lowest energy. To some extent the orbitals energies follow the quantum number n, but this is not always the case. For example, the element potassium has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^0\ 4s^1$ and not $1s^22s^22p^6\ 3s^23p^6\ 3d^1$. This means that the energy of the 3d orbital must be higher than the energy of the 4s orbital. Can the Slater rules predict that? Let us therefore calculate the energy of the 3d and 4s orbital using the Slater rules, and see if the energy of the 3d orbital comes out higher than the electron of the 4s orbital.

For the 3d orbital, the shielding constant is 18x1=18 because there are 18 electrons besides the 3d electron of consideration, and all the 18 electrons are in a lower shell. Therefore, they all contribute with a factor of 1. The nuclear charge Z of the potassium is 19. Therefore, the effective nuclear charge Z_{eff}= 19-18=1 (Fig. 1.2.47).

$$\sigma = 18 \times 1 \rightarrow Z_{eff} = 19\text{-}18 = 1$$

Figure 1.2.47 Calculation of effective nuclear charge for the 3d electron of potassium

Now let us do the analogous calculation for the 4s electron. For the 4s electron the Slater rules for s electrons apply. According to that, the two 3s and the six 3p electrons contribute 0.85 to the shielding constant because they are in an n-1 shell. The remaining two 1s, two 2s, and six 2p electrons are in an n-2 or lower shell and therefore contribute with the factor of 1. Therefore, the overall shielding constant is 8 x 0.85 + 10 x 1 = 16.8. The effective nuclear charge Z_{eff} is therefore 19-16.8=2.2 (Fig. 1.2.48).

$$\sigma = 8 \times 0.85 + 10 \times 1 = 16.8 \rightarrow Z_{eff} = 2.2$$

Figure 1.2.48 Calculation of the effective nuclear charge for the 4s electron of potassium

We can see that a higher effective nuclear charge acts on a 4s electron compared to a 3d electron, which indicates that the orbital energy for the 4s electron will be lower compared to the 3d electron. We can calculate the orbital energies by using the formula $E=(Z_{eff}^2)/n^2$ ×13.6 eV (Eq. 1.2.27).

$$E = -\frac{Z_{eff}^2}{n^2} \times 13.6\ eV$$

Equation 1.2.27 Equation for orbital energies

For the 3d electron we insert Z_{eff}=1 and n=3 which gives -1.51 eV, Eq. 1.2.28.

$$E(3d) = \frac{-\ 1^2\ 13.6\ \text{eV}}{3^2} = -\ 1.51\ \text{eV}$$

Equation 1.2.28 Equation for orbital energy of the 3d electron of potassium

For the 4s electron insert Z_{eff}=2.2 and n=4 which gives -4.14 eV.

$$E(4s) = \frac{-\ 2.2^2\ 13.6\ \text{eV}}{4^2} = -\ 4.14\ \text{eV}$$

Equation 1.2.29 Equation for orbital energy of the 4s electron of potassium

As expected, the energy of the 4s electron is lower than the energy of the 3d electron. This explains why the electron configuration with the 4s electron as the valence electron is preferred over that with the 3d electron as the valence electron. Overall, we can see that the Slater rules can correctly predict electron configurations of atoms and the Aufbau principle.

Let us do another, more complex example: There are two conceivable electron configurations for Fe. One in which the 4s subshell is filled before the 3d subshell, and one in which the 3d subshell is filled before the 4s subshell. For the first case the electron configuration is $1s^22s^22p^63s^2\ 3p^6\ 4s^2\ 3d^6$. For the second case, the second electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^0$. We can see that the two electron configurations are the same for the 1s, 2s, 2p, 3s, and 3p electrons. We therefore focus on the remaining eight electrons, denoted in red, and calculate their energies.

In this case, we need to compare the sum of the electron energies for both electron configurations to be able to decide which electron configuration is favored. We calculate the sum of the energies of the eight electrons for the first electron configuration the following way: In the first step we need to rewrite the electron configuration in Slater form: $(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^6)(3d^6)(4s^2)$.

Next, we can calculate the shielding constant for a 3d electron. We can ignore the two 4s electrons because they are to the right of the d electron of consideration, and do not contribute to the shielding. However, we do need to consider the five other 3d electrons that are in the same group as the 3d electron of consideration. They contribute with the factor of 0.35. The other 18 electrons contribute 1.00 because they are in a lower shell. Because the effective nuclear charge of Fe is 26, the effective nuclear charge Z_{eff} is Z_{eff}=26-19.75=6.25 (Eq. 1.2.30).

$$\sigma_{3d} = 5(0.35)+18(1.00)=19.75 \qquad Z_{eff}(3d)=26-19.75=6.25$$

Equation 1.2.30 Equation for the shielding constant and effective nuclear charge of the 3d electron of an iron atom

For a 4s electron, there is one other 4s electron in the same group which contributes with a factor of 0.35. In addition, there are 14 electrons in an n-1 shell, namely the 3s, the 3p, and the 3d electrons. They contribute 0.85 to the shielding constant. The remaining 10 electrons are in an n-2 shell or lower, therefore they contribute with the factor 1.00. This gives an overall shielding constant of 22.25. From that we can calculate the effective nuclear charge for a 4s electron which is 26-22.25=3.75.

$$\sigma_{4s}=1(0.35)+14(0.85)+10(1.00)=22.25 \qquad Z_{eff}(4s)=26-22.25=3.75$$

Equation 1.2.31 Equation for shielding constant and effective nuclear charge of the 4s electron of an Fe atom

We can now calculate the electron energies. It is the sum of the energies for the 3d and 4s electrons. The electron energy for a single electron is $E=-(Z_{eff}^2)/n^2$ ×13.6 eV= $-(6.25^2)/3^2$×13.6 eV=-59.03 eV. Because we have six 3d electrons, the overall energy for the six electrons is 6 x -59.03 eV = -354.17 eV (Eq. 1.2.32).

$$E(3d) = -\frac{Z_{eff}^2}{n^2} \times 13.6\ eV = -\frac{6.25^2}{3^2} \times 13.6\ eV = \text{-59.03 eV.}$$

$$\text{For six 3d electrons:}\quad E(3d) = 6 \times -59.03 eV = -354.17 eV$$

Equation 1.2.32 Equation for the electron energies of the six 3d electrons in an iron atom

The energy of a single 4s electron is $E=-(3.75^2)/4^2$ ×13.6 eV=-11.95 eV. For two 4s electrons the energy is 2 x -11.95 eV= -23.90 eV.

$$E(4s) = -\frac{3.75^2}{4^2} \times 13.6\ eV = -11.95\ eV$$

$$\text{For two 4s electrons:}\quad E(4s) = 2 \times -11.95 eV = -23.90 eV$$

Equation 1.2.33 Equation for the electron energies of the 4s electron in iron

The sum of all electrons is then -354.17 eV + (-23.90 eV) = -378.1 eV (Eq. 1.2.34).

$$E(4s + 3d) = -354.17eV - 23.90eV = -378.1eV$$

Equation 1.2.34 Equation for the sum of all electrons

Now let us calculate the energy for the second electron configuration. First we need this electron configuration in Slater configuration. Next, we can calculate the shielding constant for the d electrons. It is σ_{3d} = 7(0.35) + 18(1.00) = 20.45 because there are seven other 3d electrons in the same group and 18 electrons in lower shells. The effective nuclear charge is then Z_{eff} (3d) = 26- 20.45 = 5.55.

$$\sigma_{3d} = 7(0.35) + 18(1.00) = 20.45$$
$$Z_{eff}\,(3d) = 26 - 20.45 = 5.55$$

Equation 1.2.35 Equation for the shielding constant and effective nuclear charge of the 3d electrons of iron (second configuration)

The sum of the electron energies for the eight d electrons is then E(Σ 3d)=-8($5.55^2/3^2$) eV=-372.3 eV, Eq. 1.2.36.

$$E(\Sigma\, 3d\,) = -8\frac{5.55^2}{3^2}\,eV = -372.3\ eV$$

Equation 1.2.36 Equation for the sum of the electron energies for the eight d electrons of iron

We can can see the energy of the second electron configuration is somewhat higher, and thus less preferred. This is in accordance with the experimentally observed ground state electron configuration of the Fe atom. Again, we see that the Slater rules can correctly predict the ground state electron configuration of atoms.

The Aufbau Principle and the Spin Pairing Energy

The Slater rules are suitable to account for shielding effects in multi-electron atoms which are of electrostatic nature. However, not only electrostatic effects influence the orbital energies, there are also magnetic effects. This is because each electron has a spin with a magnetic field associated with it. The electrons behave like little magnets that can interact with each other. These interactions can be either attractive or repulsive, which influences the electron energies. The electron energies are usually minimized when the number of electrons with the same spin is maximized. This is known as Hund's (Fig. 1.2.49) rule of maximum spin multiplicity.

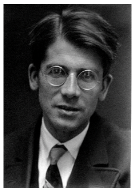


Figure 1.2.49 Friedrich Hund (1898-1997) (Attribution: GFHund [CC BY (https://creativecommons.org/licenses/by/3.0)], commons.wikimedia.org/wiki/F...%B6ttingen.jpg)

In the previously example we have seen that the electron configuration $4s^2$ $3d^6$ is favored in Fe because of electrostatic shielding effects. In addition, it also favored by magnetic effects. In this electron configuration there are four unpaired electrons, while in the electron configuration $3d^8$ there are only two unpaired electrons.

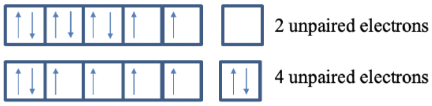


Figure 1.2.50 Electron configuration of Fe depicted regarding spin pairing

We can now understand the Aufbau principle for multi-electron atoms (Figure 1.2.51).

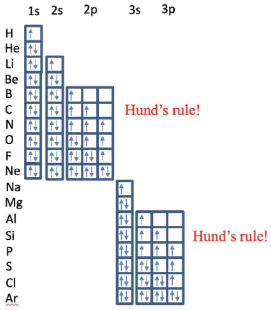


Figure 1.2.51 Electron configuration of atoms following the Aufbau principle

For H and He the 1s orbital gets filled. From lithium to beryllium the 2s subshell gets filled, and from boron to neon the 2p subshell gets filled under consideration of Hund's rule. You can see that for carbon the two 2p electrons are both spin up in different 2p orbitals. For nitrogen there are three unpaired electrons in the 2p orbitals. From the element oxygen on, we have to start pairing spins until all spins are paired in neon. From Na to Ar the 3s and the 3p orbitals get filled according to the same principles.

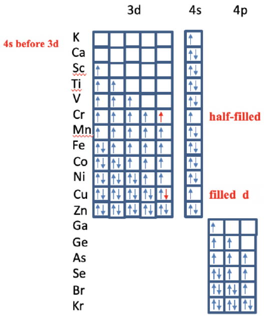


Figure 1.2.52 Continuation of electron configuration of atoms following the Aufbau principle

After that, the 4s orbitals of K and Ca get filled, and then the 3d orbitals of the elements from Sc to Zn (Fig. 1.2.52). We have seen previously that the Slater rules nicely show why. You can see that there are two anomalies though. For the chromium, the electron configuration is $4s^1$ $3d^5$ and not $4s^2$ $3d^4$. This is because there are more unpaired spins in this electron configuration, and a half-filled 3d subshell with unpaired spins only represents a particularly stable electron configuration. The second anomaly occurs for the element Cu which has an electron configuration $4s^13d^{10}$ and not $4s^23d^9$. This is because a d^{10} electron configuration is a particular stable electron configuration. After the 3d subshell is filled, the 4p subshell is filled for the elements from Ga to Kr. Again, the electrons are filled into the orbitals according to Hund's rule. We could extend our consideration to even heavier elements, but will be beyond scope.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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1.3: Periodic Properties of Atoms

The Periodic Table of Elements

Having understood the Aufbau principle we can now understand the periodic table of the elements. The periodic table was actually invented a long time before the quantum-mechanical atom model was developed. It was first introduced by Mendeleev and Meyer who ordered the elements according to their masses in a row. Whenever an element had a property similar to an element that already was previously considered a new row was begun. This gave a table with rows and columns. Within a row the mass of the elements would increase, within a column one would find the elements that had similar properties. The rows would be called periods, and the columns would be called groups, hence the name periodic table of the elements. At the time Mendeleev and Meyer invented the periodic table, there were still many elements undiscovered visible as “holes” within the periodic table. However, over time the periodic table became complete (Fig. 1.3.1).

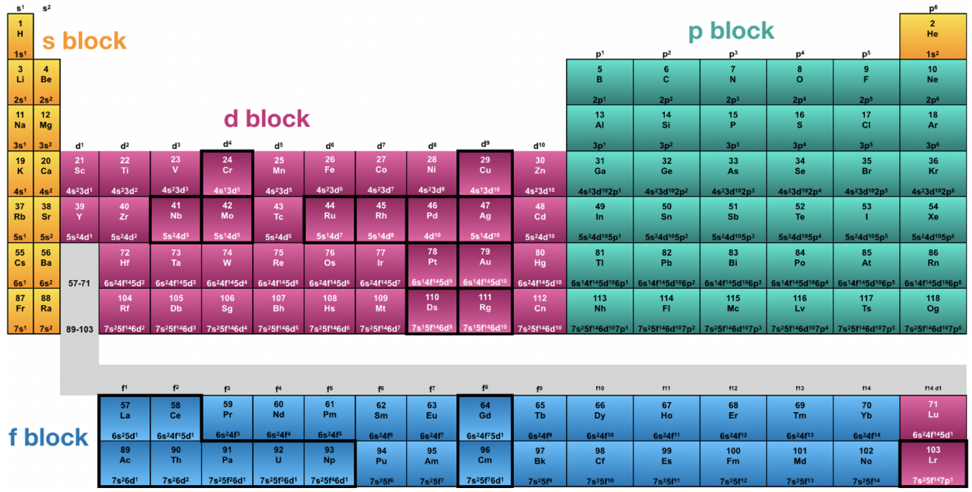


Figure 1.3.1 The periodic table of elements (Attribution: Kathryn Haas https://chem.libretexts.org/Bookshel...bau_Principle#)

Today we know 118 elements completing seven periods and 18 groups. Today, the elements are not ordered by mass, but by the atomic number (number of protons), however this did not change the original periodic table much because except for a very few elements the mass of the elements follows the atomic number. Before the quantum-mechanical model was developed, it was not understood why elements within the same group had similar properties. When you analyze the electron configuration of the atoms you can see that all atoms in the same group have the same type of outmost electrons, also called valence electrons. These electrons are the electrons that have the greatest distance from the nucleus and have the highest energies. Because they have the highest energies, they are also the electrons that are most reactive, and determine the chemical and physical properties of the element. For example, in the first group all elements have one s electron as the valence electron. Because these electrons have the highest energy and are most reactive, they determine the properties of the atom, and thus the elements in the first group have similar properties.

When you look into group 2, all the electrons have two s electrons as the valence electrons. An exception is the element helium which is placed into group 18 which is called the group of the noble gases. The other group 18 elements have two s and six p electrons of the same quantum number n as valence electrons. The behavior of He is much more similar to that of the other group 18 elements, namely it is a gas with extremely low reactivity. This property is due to the fact that like the other noble gases He has a full shell. Elements with a full shell are particularly unreactive because full shells represent particularly stable electron configurations, also called noble gas configurations.

Group 1, group 2 and He are called the s-block of the periodic table because they are the elements that only have s electrons as valence electrons. From group 3 to group 12 there are elements with s and d electrons as valence electrons. These elements are the d-block of the periodic table. The d-block begins with group 3 where there is only one d electron together with two s electrons, and ends with group 12 where there are ten d and two s electrons. In group 12 the d subshell is completely filled with electrons. From group 13 to group 18 we find electrons that have p electrons as valence electrons. There are six groups because p orbitals can accommodate up to six p electrons. In group 13 there is only one p valence electron, in group 14 there are two, in group 15 there are three, in group 16 four, in group 17 five, and in group 18 there a six except the Helium which we previously discussed already. Group 13 to 18 is called the p block of the periodic table. The s-block and the p block elements together are also called the main group elements, the elements of the d-block are called the transition metals. The elements of the main groups have specific names. Group 1 elements except hydrogen are called the alkali metals, group 2 elements the earth alkaline metals, group 13 elements the triels, group 14 elements the tetrels, group 15 elements the pnictides, group 16 elements are the chalcogens, group 17 elements the halogens, and group 18 elements the noble gases.

Finally, there is the f block of the periodic table. The f-block contains the elements with f-valence electrons. Because there are seven f-orbitals for a given quantum number n, the f orbitals can accommodate up to 14 electrons, and thus there are 14 groups. The f block is actually located in between the s block and the d block of the periodic table, but is typically written underneath the rest of the periodic table. This is done because the periodic table would become too wide if it was placed between the s and the d block. Note that the f-block elements do not have a group number. Note also that the elements on the left end of the f-block, lanthanum and actinium, actually do not have f-valence electrons. They are actually group 3 elements located underneath the elements scandium and yttrium. The first row of the f-block is are called the lanthanides, which is the greek meaning the elements following the lanthanum. Only the elements following the lanthanum have f-valence electrons. Analogously, the actinium is not an actual f-block element, only the elements that follow the actinium. They are called the actinides.

The quantum mechanical model of the atoms also explains why the periodic table has periods. Each period is associated with a quantum number n, the first period with n=1, second period with n=2 and so forth. Within a period the available s and p valence orbitals of a specific quantum number n are getting filled. Subshells of a lower quantum number may also be filled within the period. For example, the 3d subshell gets filled within the fourth period, and the 4f subshell gets filled in the 6th period.

Elements with electron configurations that deviate from the expected electron configuration are highlighted in bold (Figure 1.3.1). There are only exceptions for the d-block and f-block elements. We discussed some of them already, for example the Cr and the Cu. In addition, for instance, Pd has the electron configuration $4d^{10}$ instead of $5s^24d^8$, and Pt has the electron configuration $6s^15d^9$ instead of $6s^25d^8$. We can explain these exceptions when considering the complex electrostatic and magnetic interactions of electrons in multi-electron atoms. Not everything can be explained by the simple concepts of Slater rules and Hund’s rule.

As chemists we should always know our periodic table. Learning is easier with music, and there is a fabulous song by Tom Lehrer that can help you to learn the periodic table. The link to a respective YouTube video is provided below.

https://www.youtube.com/watch?v=DYW50F42ss8

Atomic Radii

Let us now look at what is called the periodic properties of atoms. These are properties which change due to the position of the element within the periodic table. Let us first consider how the atomic radii of the atoms depend on the position of the atom in the periodic table, Fig. 1.3.2.

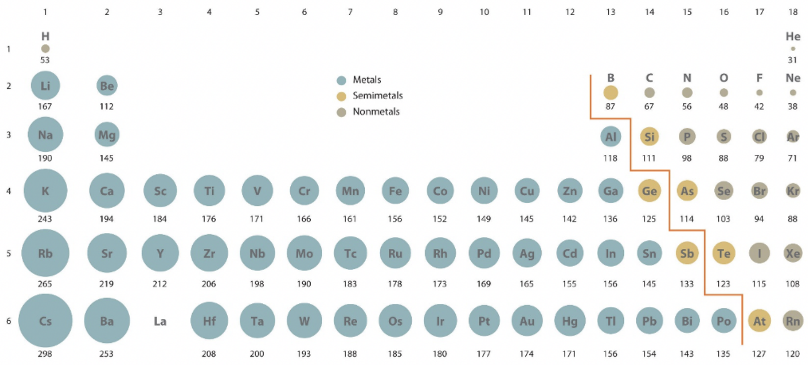


Figure 1.3.2 Calculated atomic radii of the elements in the periodic table (Attribution: Webelements.com, https://chem.libretexts.org/@api/deki/files/27875/bd05f43d0392ab934fc21044ccca1cfd.jpg?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

When you look at how the atomic radii change within a period you can easily see that they decrease from the left to the right in the periodic table. The decrease is more significant for the s and p block elements compared to the d block elements. We can explain this effect using the concept of effective nuclear charge. As we go from the left to the right in the periodic table we add electrons to the same shell. Because also a proton is added to the nucleus with each electron added, the electron experiences a greater attractive force from the nucleus. This effect tends to increase the effective nuclear charge. However, there is also an opposite effect. Because there is one more electron, there are more electron-electron repulsion and shielding effects, and this tends to decrease the effective nuclear charge. Because the new electron is added to the same shell, the shielding effects do not fully compensate for the additional Coulomb force coming from the additional proton in the nucleus, and thus the effective nuclear charge increases. This higher effective nuclear charge pulls the electrons closer to the nucleus, and thus the atom size decreases. For the d-block elements new d electrons get added to a more inner subshell, for example for the d-block elements of the 4th period the d electrons get added to the 3d subshell. Because of that, these 3d electrons can more effectively shield nuclear charge from the outmost two 4s electrons, and thus the decrease of the atomic radius is less pronounced. In summary:

Trend 1: Atomic radius decreases continuously within a period.

A second trend is that each time a new period is begun the atomic radius jumps dramatically. For example it jumps from 31 pm to 167 pm as we go from the helium to the lithium, and from 38 pm to 190 pm as you go from the neon to the sodium. This trend is because the electrons get filled into a new, more outer shell when a new period is begun. This outer shell is located much farther away from the nucleus, and thus the radius of the atom increases. In addition, the electrons in the inner shells can very effectively shield the nuclear charge from the electron added to the new shell which tends to increase atom radius. In summary:

Trend 2: Atomic radius jumps when a new period is begun.

As a third trend you can see that the atomic radii increase as you go down a group. This is because within a group there are the same number and type of valence electrons, but the valence electrons are in a more outer shell associated with a higher quantum number n. In a somewhat different view we can also argue that the first two trends add up to give the third trend. The effect of jump of atomic radius when a new period is begun is greater than the effect of decline of the radius within a period. As a result, the radius tends to increase as you go down a group. In summary:

Trend 3: Atomic radius increases continuously within a group.

The determination of an atomic radius is not as trivial at it may seem. You can obtain it either from quantum mechanical calculations, or determine it experimentally. If you calculate it, then the radius is defined as the radius that defines the volume in which the electron can be observed with 90% probability. The radii that you see in Figure 1.3.2 are actually calculated radii. If you determine the radius experimentally, then there are again different subtypes of radii. The so-called metallic, or crystal radii, the vanderWaals radii, and the covalent radii. The covalent radius is the half of the distance between two, same atoms in a molecule held together in a single covalent bond.

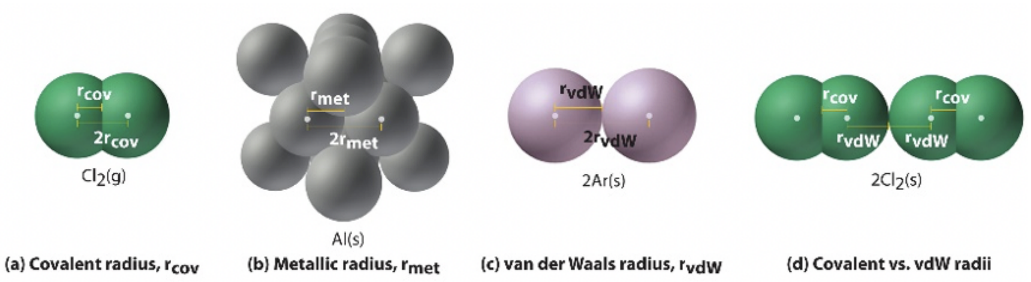


Figure 1.3.3 Atomic radii for a) covalent radius b) metallic radius c) van der Waals radius d) covalent vs vdW radii (Attribution: Chemlibretexts. https://chem.libretexts.org/@api/dek...jpg?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

This is unambiguous for molecules such as Cl_2, the other halogens, and for other cases such as hydrogen, carbon (as diamond), sulfur, and a few other cases. However for oxygen, O_2, the situation is less clear as the order of the oxygen-oxygen bond is 2. In this case, it is necessary to infer the covalent radius from molecules containing O-O single bonds or from molecules containing an E-X single bond (E=element) in which the covalent radius of X is known. The van der Waals radius is half the distance between two same atoms in a crystal when there is no actual bonding between the atom except weak van der Waals forces. For example, in solid argon, there are only van der Waals forces between the atoms, and half the distance between the atoms in solid argon is the Van der Waals radius. For chlorine, for example, the van der Waals radius is half the distance between two chlorine atoms of two different Cl_2 molecules in solid Cl_2. Note that the van der Waals radius of chlorine is different than the covalent radius of chlorine. This again shows that there is a certain ambiguity when determining an atomic radius, and therefore it is always important to say what definition of atomic radius you use. Lastly, there is also the metallic radius that applies to solid metals in which metal atoms are held together by metallic bonding. The metallic radius is the defined as half the distance between the centers of two metal atoms within a metal.

First Ionization Energy

The first ionization energy is another important periodic property of the elements. It is defined as the energy required to remove an electron from a neutral atom in the gas phase. It is important to understand that we refer to an atom in the gas phase here, because only in the gas phase atoms do not significantly interact with each other. Therefore, only when looking at an atom in the gas phase we can truly determine the properties of single, isolated atoms. Let us look at the two images (Figure 1.3.4) to determine periodic trends.

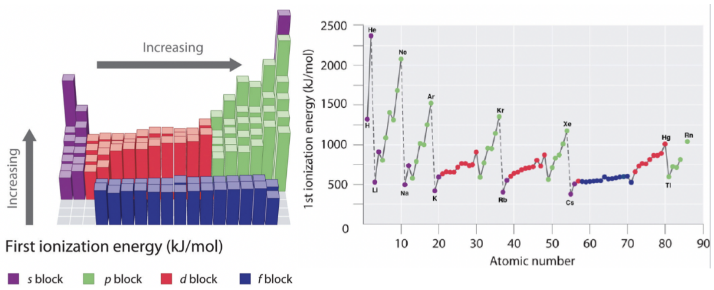


Figure 1.3.4 First ionization energies as a third dimension in the periodic table (left) and as function of atomic number (right) (Attribution: ChemlibreTexts https://chem.libretexts.org/@api/dek...png?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

First of all we need to realize that all 1st ionization energies are positive. This means that it always requires energy to remove an electron from a neutral atom. You can understand this when you consider that all electrons in an atom are bound to the nucleus via a binding energy. If an ionization energy was negative then this would mean that the atom would spontaneously lose an electron, and spontaneously ionize. This would be unreasonable.

Now let us see how the first ionization energy changes within a period. We can see that it increases as we go from the left to the right within a period. This trend can be explained by the fact that the effective nuclear charge increases from the left to the right within a period. As the effective nuclear charge increases, the pull of the nucleus on the outmost electron increases, and thus the harder it is to remove this electron from the atom. You can see, however, that within the main group elements the trend is two times broken. The group 13 elements have a lower ionization energy than the group 2 elements, and the group 16 elements have a lower ionization energy than the group 15 elements. This phenomenon can be explained by the fact that the filled and half-filled subshells in group 2 and group 15 represent particularly stable electron configurations, and thus the electrons within these subshells have unusually low energy. For that reason these electrons are harder to remove from the atoms. The group 2 elements have filled s subshells, and the group 15 elements have half-filled p subshells. You can also notice that the increase in ionization energy is less pronounced within the d-block, and even less pronounced with in the f-block. This is because the effective nuclear charge on the outmost electrons does not increase as much because inner d and f orbitals are getting filled. You can also see that the group 13 elements have a lower ionization energy than the group 12 elements. This is because in group 13 a new p subshell is begun and the new electrons get added to the outmost shell where shielding effects are smaller.

As a second trend you can see that whenever a new period is begun, the ionization energy drastically drops. This is because the new electron is added to a new, more outer shell where the effective nuclear charge acting on the new electron is much smaller. The third trend is that the ionization energy becomes smaller as we go down a group. This is because the effective nuclear charge on the valence electrons decreases because the quantum number n of the valence electrons increases. There is one peculiarity that needs additional explanation. The drop of ionization energy from hydrogen to lithium in the first group is unusually large. This is because hydrogen is the only element for which there are no shielding effects, simply because the hydrogen has only one electron. For that reason the valence 1s electron of the hydrogen is far harder to remove than the valence s electrons of the other group 1 elements.

Electron Affinity

Now let us consider the first electron affinity (Figure 1.3.5). It is defined as the energy required or released when you add an electron to a neutral atom in the gas phase. Again, we look at an atom in the gas phase, because we want to consider an isolated atom that does not make significant interactions with other atoms.

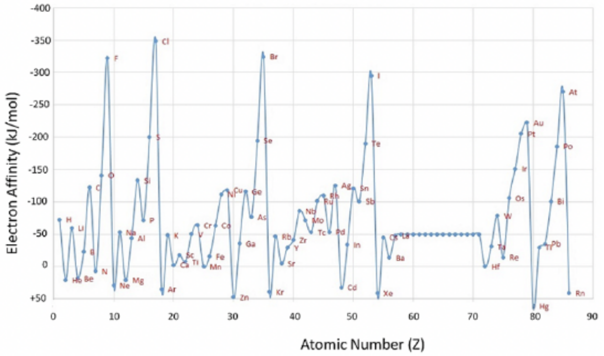


Figure 1.3.5 Electron affinity vs Atomic Number (Attribution: Chemlibretexts. https://chem.libretexts.org/@api/dek...780&height=456 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

We can see from the graph that most elements have negative electron affinities, meaning that the addition of a free electron to a neutral atom is exothermic, and releases energy, however, this is not always the case. Some elements have negative electron affinities, in particular the noble gases, but also Be, N, Mg, Zn, Cd, and Hg. Zn, Cd, and Hg, are group 12 elements with a full d subshell which is particularly stable. An additional electron would need to be added to a p orbital of a higher shell which is energetically quite unfavorable. Similarly, Be and Mg have filled s subshells which are also fairly stable. Adding an additional electron would need to start an new subshell, which is energetically not favorable. You can see that Ca and Sr have electron affinities of about 0, and that of Ba is only slightly negative showing that higher periods make the addition of an electron to a new p shell slightly more favorable. Nitrogen has a half-filled p subshell, which is also a quite stable electron configuration, and therefore adding an electron is not favorable. The addition of an electron is slightly more favorable for the other group 15 elements, however, these also tend to have rather low electron affinities.

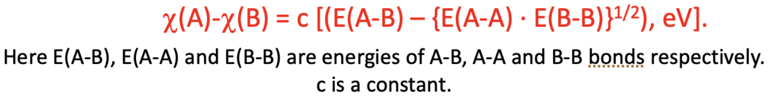
Generally, for the main group elements the electron affinity tends to increase from the group 1 to group 17. However, the trend is broken for group 2 and group 15 elements because these elements have full and half-filled subshells, respectively. In addition, it is noteworthy that group 1 elements have higher electron affinities than group 3 elements. This is because adding an electron to a group 1 element produces a full s subshell which is fairly stable. For the d-block elements, the electron affinity tends to increase from group 3 to group 11, but the trend is broken multiple times showing that each element would need to be investigated individually which is beyond the scope here. There is a big drop in electron affinity from group 17 to group 18 which is easily explained by the fact that the addition of an electron to a group 17 element produces a filled shell, while a group 18 element already has a full shell, and the addition of an electron would start a new shell. Similarly, there is a sharp drop in electron affinity from group 11 to group 12, as an addition of an electron to a group 11 atom produces a full subshell, while the addition of an electron to a group 12 element would require the start of new, more outer subshell. For the p block elements the electron affinity tends to first increase from period 2 to 3, and then decrease. For the s-block there is a steady decrease down a group. For d block elements there is no clear trend for the electron affinity.

Electronegativity

Lastly, let us study the electronegativity as a periodic property. The electronegativity is the measure of the ability of an atom to attract electrons within a chemical bond. It is related to the electron affinity in the sense that both period properties measure the force by which an electron is attracted to a neutral atom. However, the electron affinity is associated with isolated atoms, that do not make bonds to neighbored atoms, while the electronegativity refers to atoms that are bonded to neighbored atoms. The importance of the electronegativity stems largely from its ability to predict and understand the nature of the bonding between atoms, in particular, covalent, ionic, and metallic bonding.

Electronegativity Scales

Electronegativity was a concept first developed by Linus Pauling to describe the relative polarity of bonds and molecules. He argued that the electronegativity of an atom could be derived from bond energy differences between homoleptic and heteroleptic bonds (Eq. 1.3.1).



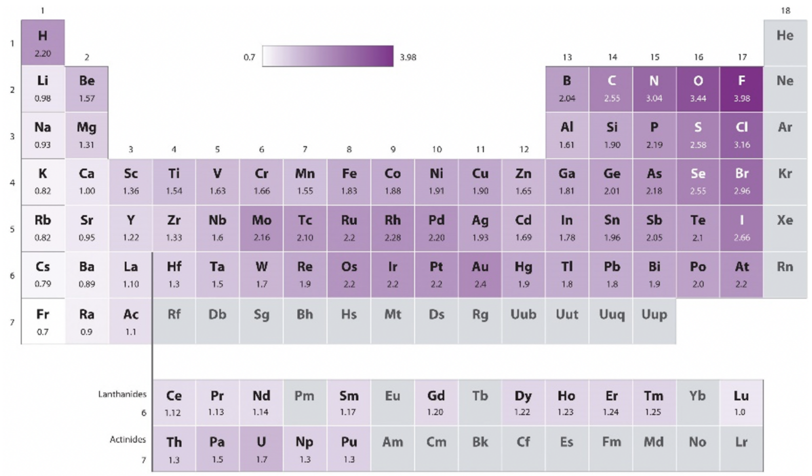
$$\chi(A)-\chi(B) = c\,[(E(A\text{-}B) - \{E(A\text{-}A)\cdot E(B\text{-}B)\}^{1/2}), \text{eV}].$$

Here E(A-B), E(A-A) and E(B-B) are energies of A-B, A-A and B-B bonds respectively.
c is a constant.

Equation 1.3.1 Electronegativity according to Pauling, eV = electron volts.

For example, the energy required to break the bond in H_2 is 432 kJ mol^{-1}, and for F_2 it is 159 kJ mol^{-1}. However the energy required to break a bond in HF is 565 kJ mol^{-1}, which is much higher than expected just by averaging the energy of the two homonuclear bonds (296 kJ mol^{-1}). Pauling argued that the difference could be assigned to electrostatic attractions between the F and H "ends" of the molecule whereby the F end has more electron density and the H end has less electron density. The greater the difference between the average energy of the homoleptic bonds and the heteroleptic bonds, the greater the electronegativity difference between the atoms, and the greater the polarity of the heteroleptic bond.

First, Pauling used the arithmetic means of the heteroleptic bond energies, later he used the geometric means, because he found empirically that it worked better (Equation 1.3.1). The geometric mean of the homoleptic bond energies is the square root of the product of the homoleptic bond energies. This method only provided electronegativity differences. He therefore needed to define a reference atom with an arbitrarily defined electronegativity value, and then determine the electronegativity values of all other atoms relative to that value. He chose the most electronegative atom, the fluorine atom, as the standard and assigned a value of 4.0. The values of all other atoms vary between 0.7 (Fr) and 3.44 (O), and are shown in the periodic table on the below (Fig. 1.3.6).



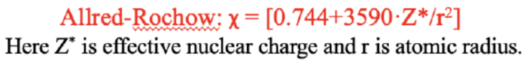
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.3.6 Periodic trends of electronegativity (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

What are the periodic trends? One can see that within a period the electronegativity values of the main group elements strictly increase with the group number. Note though that the noble gases do not have a Pauling electronegativity because, with few exceptions, noble gases do not make compounds and thus no bond energies are available for them. We can also see that for main group elements the electronegativity strictly decreases down a group. This makes the fluorine the most electronegative atom, and the cesium the least electronegative atom. Cesium has an electronegativity value of 0.7. We ignore the radioactive francium here. For the d-block, the trends are less strict, but there is a tendency of electronegativity increase from group 3 to group 11. All group 12 elements have smaller electronegativities compared to their neighbored group 11 elements. What about trends within a group? In group 3 to group 5 there is a small decrease in electronegativity down a group. For group 6 and 9, the period 5 elements have higher values than their neighbored elements in period 4 and 6. For group 10 to 12 the electronegativity increases down a group. The d-block element with the highest electronegativity is the gold, it has a value of 2.4. Note that this is similar to the electronegativity of non-metals such as I, S, and P. For these reasons, sometimes gold can behave like a non-metal in compounds with very low electronegativity. For example, there is the compound cesium auride (CsAu) which is a transparent, ionic crystalline compound due to the high electronegativity difference between cesium and gold. The f-block elements generally have low electronegativity.

The Pauling electronegativity scale is derived from empirical data on bond energies. It works very well in practice and it is up to date the most used electronegativity scale. However, it does not to relate electronegativity to other periodic properties, and the quantum-mechanical model of the atoms. One electronegativity scale that addresses this short-coming the Allred-Rochow scale. It relates the electronegativity to the Coulomb force that acts on an electron on the surface of an atom. The Coulomb force is proportional to the effective nuclear charge Z* and inverse proportional to the atomic radius square. Z^*/r^2 is multiplied with a factor of 3590 and a value of 0.744 is added to this term. These numbers are empirically chosen so that the values of the Allred-Rochow scale become comparable to the Pauling scale.

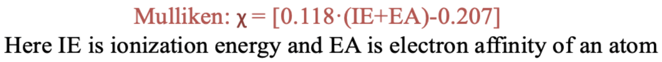


Allred-Rochow: $\chi = [0.744+3590 \cdot Z^*/r^2]$

Here Z^* is effective nuclear charge and r is atomic radius.

Equation 1.3.2 Allred-Rochow definition of electronegativity

Another frequently used scale is the Mulliken electronegativity scale. The Mulliken scale relates the electronegativity to the sum of the first ionization energy IE and the first electron affinity EA. We would intuitively agree that the ability of an atom to attract electrons within a chemical bond is the higher, the harder it is to remove an electron from an isolated atom, and the easier it is to add an electron to an isolated atom. The numbers 0.118 and -0.207 are empirically chosen to make comparisons to the Pauling scale possible. The Mulliken scale is related to the Allred-Rochow scale in the sense that you can explain ionization energies and electron affinities of atoms with the concept of the effective nuclear charge.

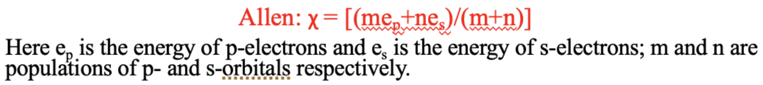


Mulliken: $\chi = [0.118 \cdot (IE+EA)-0.207]$

Here IE is ionization energy and EA is electron affinity of an atom

Equation 1.3.3 Mulliken definition of electronegativity

Another electronegativity scale has been developed by Leland C. Allen. It designed for main group elements in particular. It argues that the electronegativity is proportional to the average energy of the s and p valence electrons in the atom. This electronegativity concept also has a relationship to that of Allred-Rochow, because orbital energies can be calculated from the effective nuclear charge.



Allen: $\chi = [(me_p+ne_s)/(m+n)]$

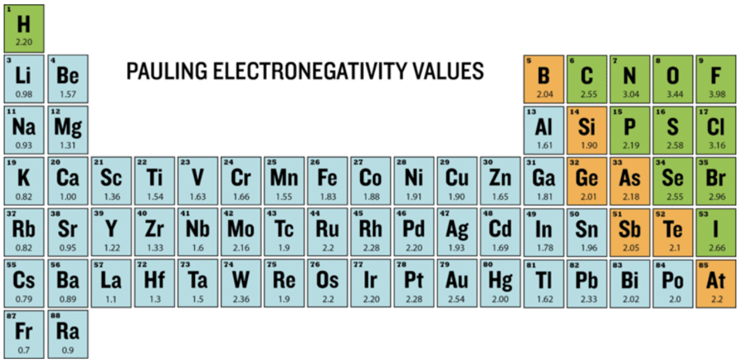
Here e_p is the energy of p-electrons and e_s is the energy of s-electrons; m and n are populations of p- and s-orbitals respectively.

Equation 1.3.4 Leland C. Allen definition of electronegativity

Overall, you can see that the electronegativity scales are inter-related, they say essentially the same, but present electronegativity from a somewhat different perspective.

Electronegativity of the Elements and Chemical Bonding

One of the most powerful attributes of electronegativity is that it can predict what type of chemical bond is to expect in elements and compounds. Let us first look at the bonding between elements.



PAULING ELECTRONEGATIVITY VALUES

1 H 2.20																	
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16	
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96	
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66	
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2	
87 Fr 0.7	88 Ra 0.9																

Figure 1.3.7 Pauling electronegativity values for the elements (Attribution: Ck12.org https://www.ck12.org/flx/show/default/image/user%3Ack12editor/201411241416847232690011_ab8840393ea93a2a7c9fc01e395da3b2-201411241416847569430107.png https://creativecommons.org/licenses/by-nc/3.0/legalcode)

In the depicted periodic table (Figure 1.3.7) you can see the type of chemical bonding between atoms indicated by different colors. There is metallic bonding in metals, indicated by the color blue. In metallic bonds the electrons are shared between atoms but are delocalized over many atoms in the metal. The green color indicates covalent bonding seen in non-metals. In covalent bonding the electrons are shared, but localized in between typically two atoms. Metalloids have chemical bonding with a mix of covalent and metallic character shown in orange. There is electron-sharing with a moderate degree of delocalization. The Pauling electronegativity values of the elements are written underneath the element symbols.

Can we relate the electronegativity values to the chemical bonding in the elements? We can clearly see that elements with high electronegativity values significantly above 2.0, the non-metals, tend to make covalent bonds in between them. All metalloids with a hybrid covalent-metallic character, have intermediate electronegativity around 2.0. Most metals have low electronegativity values below 2.0 except noble metals like Pt and Au. Overall, we can say that there is a clear relationship between the bonding type in an element and its electronegativity. Now let us see if electronegativity can also predict chemical bonding in compounds.

Ketelaar's Triangle

The ability of electronegativity to predict the bonding type in compounds can be understood by Ketelaar's triangle, named after J.A.A. Ketelaar.

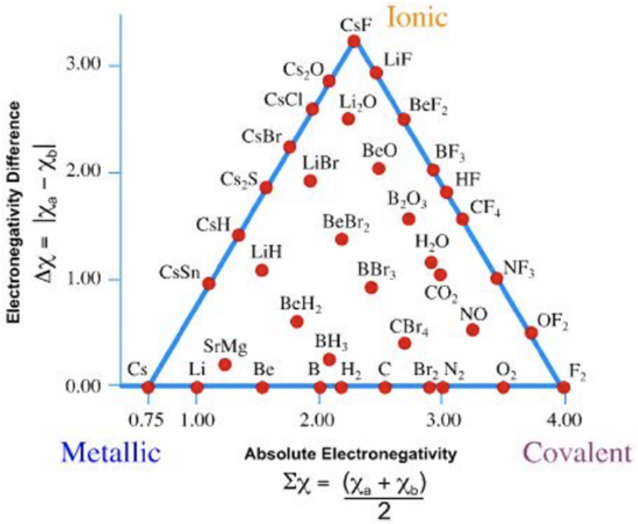


Figure 1.3.8 Ketelaar's Triangle (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=2 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

You can see that Ketelaar's triangle has three corners (Figure 1.3.8). Two of the corners are occupied by the elements F and Cs, and the third corner is occupied by CsF. All elements are located on the horizontal edge of the triangle, and there many compound indicated by dots either on the two other edges or within the triangle. There are no compounds or elements outside of the triangle. How can we understand this triangle and what does it say about the relationship between bonding character and electronegativity? To understand this, look at the two axes. The horizontal x-axis represents the average electronegativity of the atoms in an element or a compound. The vertical y-axis represents the electronegativity difference between the atoms in the elements or the compound. For elements the electronegativity difference between the atoms is zero, because in an element all atoms are of the same type. Therefore, all the elements lie on the horizontally oriented edge of the triangle. Because Cs is the element with the lowest electronegativity, it lies furthest to the left on this edge. Fluorine is the element with the highest electronegativity, and thus lies the furthest on the right side. The other elements are in located in between the cesium and the fluorine on the edge. The higher the electronegativity of the elements, the further right their position on this edge of the triangle.

For compounds, the electronegativity difference between atoms is never exactly zero, therefore all compounds are located above the horizontal edge of the triangle. The compound with the highest electronegativity difference is the CsF. Its average electronegativity is the sum the electronegativity of Cs and F divided by 2: Therefore, CsF defines the third corner of the triangle. All other compounds must lie on the edges or within the triangle. All cesium compounds are located on the edge between the Cs and CsF, and all the fluorine compounds are located on the edge between CsF and F2. The compounds of all other elements are inside the triangle. The position of the compound on or in the triangle defines its bonding character. The closer the position of the compound toward the Cs corner, the more metallic, the closer the position is to the F2 corner, the more covalent, and the closer it is to the CsF corner, the more ionic. For example Li_2O is located close to CsF, and the bonding would be predominantly ionic, although there is also a small degree of covalent and metallic bonding. In contrast to that, SrMg has mostly metallic bonding, a little bit of covalent bonding, and even less ionic bonding. The bonding situation in LiH is in between metallic and ionic, with a little bit of covalent bonding character mixed in. Note that a 100% ionic bond is not possible because the electronegativity difference is finite, and thus there must always be a certain degree of electron sharing. In contrast to that, a 100% covalent bond is possible because electrons can be equally shared between two atoms when the electronegativity difference is zero.

The take home message is that in compounds and elements there is usually a mix of bonding types, and not a single bonding type, even through one bonding type may strongly dominate. The concept of electronegativity, and Ketelaar's triangle in particular, is extremely helpful to predict to which degree the three bonding types are present in a substance.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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Concept Review Questions Chapter 1

Concept Review Questions

Section 1

1. Which were the elements in the antique non-atomistic element theories?

2. Explain the definition of the term “atom” as introduced by Leukippes and Demokrites.

3. What does the law of the conservation of mass state?

4. Who discovered the law of the conservation of mass?

5. What obscured the discovery of the law of the conservation of mass for a long time?

6. Explain why the discovery of the law of the conservation of mass was important for the development of atomic theory.

7. What does the law of the constant compositions state?

8. Who discovered the law of the constant compositions?

9. What does the law of the multiple proportions state?

10. Who discovered the law of the multiple proportions?

11. Explain why the law of the multiple proportions can be explained by Dalton’s hypothesis.

12. Explain what cathode rays are and how they are being produced.

13. Explain how Thomson identified electrons in cathode rays.

14. Explain why Rutherford’s gold foil experiment disproves Thomson’s atom model.

15. Describe Rutherford’s atom model and explain why it is in agreement with his gold foil experiment.

16. Which two opposing forces keep electrons stable in the orbit around the nucleus according to Rutherford’s atom model?

17. What are the two basic problems with Rutherford’s atom model?

18. What is blackbody radiation?

19. What assumption did Max Planck make to explain the spectra of blackbody radiation?

20. Objects first start to glow red, then, orange, and finally white with increasing temperature. Explain why.

21. What is meant by the “Balmer series”, the “Paschen series” and the “Lyman series”?

22. Explain why the atomic absorption and emission spectra inspired the Bohr atom model?

23. What is the meaning of an angular momentum in physics?

24. Name the four postulates of Niels Bohr that lead to his atom model.

25. Mathematically derive the terms for the allowed radii and the allowed energies for the electron in an H atom according to Bohr.

26. Explain why the results of the above calculations explain the atomic spectra of the H atom.

27. What are the two major problems of the Bohr atom model?

Section 2

1. What is the photoelectric effect?

2. Explain how Einstein verified Planck’s law by investigating the photoelectric effect.

3. Explain why the wave-particle dualism can explain the photoelectric effect.

4. What is the name of the particle associated with electromagnetic radiation?

5. Derive the formula for the wave-particle dualism of electromagnetic radiation.

6. Give a definition for standing matter waves.

7. Explain why standing matter waves are quantized.

8. Derive the Schroedinger equation for the electron in the one-dimensional box.

9. What are the boundary conditions for the wavefunctions describing the electron in a one-dimensional box.

10. Derive the wavefunction for the electron in the one-dimensional box.

11. Explain qualitatively what are the major similarities and differences for an electron in a one-dimensional box compared to an electron in a hydrogen atom.

12. What are the quantum numbers in the solution of the Schroedinger equation for the hydrogen atom?

13. The radial probability function is the product of the formula for the surface of a sphere multiplied with the square of the radial function. Explain why this product gives the probability to find the electron at a certain distance (radius) from the nucleus.

14. At which radius r has the radial probability function of the 1s orbital its maximum?

15. What is a spherical node in an orbital?

16. What is an angular node in an orbital?

17. What types of angular nodes do we know?

18. Can an s orbitals have angular nodes?

19. Can p and d orbitals have spherical nodes?

20. Name an orbital that has a conical node.

21. What are the formulas for the number of radial, angular, and total number of nodes in an atom?

22. On which quantum number do the orbital energies in the H atom depend on according to the wavemechanical model of the H atom?

23. The energy of an electron in the ground state of the hydrogen is -13.6 eV. Explain why this energy is negative.

24. What are the energies of the electron in the hydrogen atom when the electron is in a 2p and 4f orbital respectively?

25. Explain the concept of shielding in multi-electron atoms.

26. Explain why the energy of a 2s orbital in Li is smaller than that of a 2p orbital.

27. What are the Slater rules for s,p,d, and f electrons respectively?

28. What is special about the electron configurations of Cr and Cu?

29. Explain the concept of the spin-pairing energy.

30. What does Hund’s rule state?

Section 3

1. Write down the periodic table of the elements for the elements with the atomic numbers 1 to 86. Include element symbols only.

2. Listen to Tom Lehrer’s “The Elements” song. Relax.

3. Which are the three periodic trends for the atomic radii of the elements of the periodic table? Explain these trends.

4. What is the definition of the ionization energy, the electron affinity, and the electronegativity?

5. Which are the three periodic trends for the first ionization energies of the elements of the periodic table? Explain these trends INCLUDING their exceptions.

6. The electron affinities of the group 2, 12, and 18 elements as well as the electron affinity of N are negative. Explain.

7. Alkali metals have a relatively high electron affinity. Explain.

8. Explain how Pauling derived his electronegativity scale.

9. What the periodic trends for the electronegativity of the elements of the periodic table?

10. Explain why CsAu is an ionic crystal.

11. Explain why electronegativity differences are related to the dissociation energy differences of homonuclear and heteronuclear bonds.

12. Explain the concepts of the Allred-Rochow, Mulliken, and Allen electronegativity scale.

13. Which of the four electronegativity scales we talked about in class cannot make statements about the electronegativity of noble gases like Ne or He. Why?

14. We combine two elements of low electronegativity to form a compound. Which bonding type would you expect for this compound?

15. If two elements with high electronegativity are combined, which bonding results then?

16. If two elements of very different electronegativities are combined, what is the bonding in the compound?

17. Explain the concept of Ketalaar’s triangle.

18. Can there be any compounds outside Ketelaar’s triangle?

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Homework Problems Chapter 1

Homework Problems

Section 1

Exercise 1

Cobalt forms two sulfides, CoS and Co_2 S_3. Predict the ratio of the masses of sulfur that combine with a fixed mass of cobalt to form CoS and Co_2S_3

Answer

In Co_2S_3 there are 1.5 S atoms per Co atom

In CoS there is 1 S atom per Co atom

Mass ratio of S in the two compounds is 1:1.5 = **2:3**

Exercise 2

What is true about the Rutherford atom model?

a. It explains why atoms do not send out electromagnetic radiation permanently
b. It explains why alpha particles get scattered by atoms
c. It explains the atomic spectrum of the hydrogen atom
d. It explains the wave-particle dualism

Answer

b) It explains why alpha particles get scattered by atoms

Exercise 3

The Bohr radius (the radius of the electron orbit for the H atom in its ground state) is 5.29×10^{-11} m. Calculate the radius of an electron in the third shell of the H atom according to the Bohr atom model.

Answer

$r_3 = 3^2 \times 5.29 \times 10^{-11}$ m $= 47.61 \times 10^{-11}$ m.

Section 2

Exercise 1

The electron in an H atom undergoes an electronic transition from the 3rd to the 2nd shell. What frequency does the light that is emitted have? The energy of the electron in the first shell is -2.18×10^{-18} J.

Answer

Energy of electron in the 3rd shell: $E_3 = -2.18 \times 10^{-18}$ J / $3^2 = -0.24 \times 10^{-18}$ J

Energy of electron in the 2nd shell: $E_2 = -2.18 \times 10^{-18}$ J / $2^2 = -0.545 \times 10^{-18}$ J

Energy difference between the two electrons: $E_3 - E_2 = 0.305 \times 10^{-18}$ J

Frequency of emitted light: $n=(E_3-E_2)/h = 0.305 \times 10^{-18}$ J/ 6.63×10^{-34} Js $= 4.60 \times 10^{14}$ s^{-}

Exercise 2

What is the mass of a photon with a wavelength of 400 nm that travels though space?

Answer

$\lambda = h/mc \rightarrow m = h/\lambda c = 6.63 \times 10^{-34}\,\text{Js} / (400 \times 10^{-9}\text{ m} \times 3.00 \times 10^{8}\text{ m/s}) = 5.525 \times 10^{-36}$ kg.

Exercise 3

Two objects are moving at the same speed. Which (if any) of the following statements are true?

a. The DeBroglie wavelength of the heavier object is longer than that of the lighter one.
b. If one object has twice as much mass as the other, its wavelength is one-half of the other
c. Doubling the speed of one of the objects will have the same effect on its wavelength as doubling its mass.

Answer

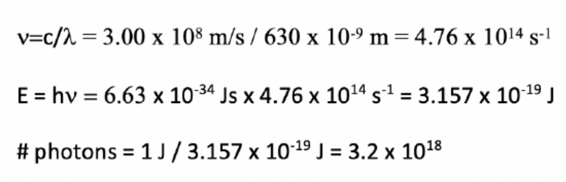
a) If one object has twice as much mass as the other, its wavelength is one-half of the other

b) Doubling the speed of one of the objects will have the same effect on its wavelength as doubling its mass

Exercise 4

The power of a red laser with a wavelength of 630 nm) is 1.00 Watt (1.00 Js). How many photons per second does the laser emit?

Answer



$\nu = c/\lambda = 3.00 \times 10^{8}\text{ m/s} / 630 \times 10^{-9}\text{ m} = 4.76 \times 10^{14}\text{ s}^{-1}$

$E = h\nu = 6.63 \times 10^{-34}\text{ Js} \times 4.76 \times 10^{14}\text{ s}^{-1} = 3.157 \times 10^{-19}\text{ J}$

photons = $1\text{ J} / 3.157 \times 10^{-19}\text{ J} = 3.2 \times 10^{18}$

Exercise 5

Which of the following waves would you consider to be standing matter wave?

a. The vibration of a drum.
b. Sound traveling through open air.
c. A tsunami.
d. None of the above.

Answer

a) The vibration of a drum.

Exercise 6

Assume an electron travels in a one-dimensional box (as discussed in class) of the length of 1 m. Look up relevant constants in the internet or a suitable textbook.

a. What is the wavelength of the associated standing matter wave in the ground state?
b. What is the velocity of the electron in the ground state?
c. What is the energy of the electron in the ground state?

Answer

a) λ=2L = 2m

b) $$v = \frac{h}{m\lambda} = \frac{6.63\times10^{-34}\,m^2kg}{9.1\times10^{-31}\,kgs\times2m} = 3.6\times10^{-4}\,m/s$$

c) $$E = \frac{1}{2}mv^2 = \frac{1}{2}\times9.1\times10^{-31}\,kg\times(3.6\times10^{-4})^2\,\frac{m^2}{s^2} = 5.9\times10^{-38}\,J$$

Alternatively the energy can also be calculated the following way giving the same result (within rounding errors):

$$E = \frac{n^2h^2}{8ma} = \frac{1^2\times(6.63\times10^{-34}\,m^2kg/s)^2}{8\times9.1\times10^{-34}\,kg\times1m} = 6.0\times10^{-38}\,J$$

Exercise 7

An electron in the first excited state travels with a velocity of 15 m/s within a one-dimensional box. What is the length of the box?

Answer

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\,m^2kg/s}{9.1\times10^{-31}\,kg\times15m/s} = 4.9\times10^{-5}\,m$$

In the first excited state n =2. For n = the length of the box is equal to the wavelength. Therefore the length of the box is 4.9 x 10^{-5} m.

Exercise 8

What are orbitals (more than one answer can be correct)?

a. Wave functions that describe the electrons as three-dimensional standing matter waves in an atom.
b. Spaces inside an atom in which the electron travels as a classical particle.
c. Solutions of the Schrödinger equation for the hydrogen atom.

Answer

a) Wave functions that describe the electrons as three-dimensional standing matter waves in an atom.

c) Solutions of the Schrödinger equation for the hydrogen atom.

Exercise 9

Which quantum numbers l are allowed when the quantum number n is 4?

Answer

l can be 3,2,1,0

Exercise 10

Which quantum numbers m are allowed when the quantum number l is 3?

Answer

-3,-2,-1,0,+1,+2,+3

Exercise 11

What is true about the following wave function?

$$\Psi = \frac{1}{\sqrt{2\pi}} \quad \frac{\sqrt{6}}{2}\cos\theta \quad \frac{4}{81\sqrt{6}a_0 3/2}\left[6 - \frac{r}{a_0}\right]\frac{r}{a_0}e^{-r/3a_0}$$

a. Its does not have angular nodes
b. Its does not have spherical nodes
c. Its amplitude is 0 at the nucleus
d. The wave function represents an s orbital

Answer

c) Its amplitude is 0 at the nucleus

Exercise 12

The angular part of the wavefunction of an orbital has the following form:

$$\Theta\Phi(x,y,z) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2-y^2)}{r^2}$$

Which planes are the planar nodes in this orbital?

Answer

The wavefunction is 0 for x=y and x=-y. So it is two planes that bisect the x and the y axis.

Exercise 13

Order the following orbitals with respect to their penetration abilities:

4s, 4p, 4d, 4f

Answer

4s > 4p > 4d > 4f

Exercise 14

What is the effective nuclear charge on an electron in an He^+ ion?

Answer

$$\sigma = 0 \rightarrow Z_{eff} = Z = 2$$

Exercise 15

Calculate the orbital energy of a 3p electron in a sulfur atom using the Slater rules.

Answer

$(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^4)$

$$\sigma = 5\times 0.35 + 8\times 0.85 + 2\times 1 = 10.55$$
$$Z_{eff} = Z - \sigma = 16 - 10.55 = 5.45$$
$$E = -\frac{Z_{eff}^{2}\times 13.6eV}{n^{2}} = -\frac{5.45^{2}\times 13.6eV}{3^{2}} = -44.9eV$$

Exercise 16

Calculate the orbital energy of a 3d electron in a palladium atom using the Slater rules.

Answer

$(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^6)(3d^{10})(4s^2 4p^6)(4d^8)(5s^2)$

$$\sigma = 9\times 0.35 + 18 = 21.15$$
$$Z_{eff} = Z - \sigma = 46 - 21.15 = 24.85$$
$$E = -\frac{Z_{eff}^{2}\times 13.6eV}{n^{2}} = -\frac{24.85^{2}\times 13.6eV}{3^{2}} = -933eV$$

Exercise 17

Calculate how much higher the first ionization energy of an oxygen atom is compared to a fluorine atom. Use the Slater rules to answer the question.

Answer

O: $(1s^2\ )$ $(2s^2\ 2p^4)$

$$\sigma(2p_{oxygen}) = 5\times 0.35 + 2\times 0.85 = 3.45$$
$$Z_{eff}(2p_{oxygen}) = Z(2p_{oxygen}) - \sigma(2p_{oxygen}) = 8 - 3.45 = 4.55$$
$$E(2p_{oxygen}) = -\frac{Z_{eff}^{2}\times 13.6eV}{n^{2}} = -\frac{4.55^{2}\times 13.6eV}{2^{2}} = -70.4eV$$

$$\sigma(2p_{fluorine}) = 6\times 0.35 + 2\times 0.85 = 3.8$$
$$Z_{eff}(2p_{fluorine}) = Z(2p_{fluorine}) - \sigma(2p_{fluorine}) = 9 - 3.8 = 5.2$$
$$E(2p_{fluorine}) = -\frac{Z_{eff}^{2}\times 13.6eV}{n^{2}} = -\frac{5.2^{2}\times 13.6eV}{2^{2}} = -91.9eV$$

$$E(2p_{fluorine}) - E(2p_{oxygen}) = -91.9eV - (-70.4eV) = -21.5eV$$
$$\rightarrow \Delta IE = IE_{fluorine} - IE_{oxygen} = 21.5eV$$

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CHAPTER OVERVIEW

2: Symmetry and Group Theory

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2.1: Symmetry Elements and Operations

Symmetry in Chemistry

Symmetry is actually a concept of mathematics and not of chemistry. However, symmetry, and the underlying mathematical theory for symmetry, group theory, are of tremendous importance in chemistry because they can be applied to many chemistry problems. For example it helps us to classify the structures of molecules and crystals, understand chemical bonding, predict vibrational spectra, and determine the optical activity of compounds. We will therefore first discuss the general foundations of symmetry and group theory, and then apply them to chemical problems, in particular chemical bonding.

Let us first find a definition for symmetry. Symmetry is very familiar to us as we associate symmetry with beauty, but very familiar things are not necessarily easy to define scientifically. One common definition is that symmetry is the self-similarity of an object. The more similar parts it has the more symmetric it appears. For example, we would argue that the two wings of the butterfly depicted look similar. If the left wing was very different from the right wing the butterfly would look less symmetric.

Figure 2.1.1 Symmetry depicted through an image of a butterfly (Attribution: Chemlibretexts https://chem.libretexts.org/@api/dek...jpg?revision=2 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

How can we measure the self-similarity, or symmetry of an object quantitatively? We can do this using the concept of the symmetry operation. It is defined as a movement of an object into an equivalent indistinguishable orientation. The number and kind of symmetry operations that can be carried out defines the symmetry of the object.

Definition: Symmetry Operation

Movement of an object into an equivalent indistinguishable orientation

Symmetry operations are carried out around so-called symmetry elements. A symmetry element is a point, line, or plane about which a symmetry operation is carried out. Let us understand know what symmetry elements and operations exist.

Definition: Symmetry Element

A point, line or plane about which a symmetry operation is carried out

The Identity Operation (*E*)

The most simple operation is the identity operation. It can be denoted by the Schoenflies symbol *E*. Schoenflies symbols are the most common symbols to denote a symmetry operation. The identity operation says that each object is self-similar to itself when you do not move it in any way. This is a trivial statement, but as we will see later, the identity operation is necessary to make the mathematical framework of symmetry, group theory, complete. The identity operation is present in any object. In the example of the depicted snail shell it is the only operation (Fig. 2.1.2).

Figure 2.1.2 Snail shell (Attribution: Petr Kratochvil http://res.publicdomainfiles.com/pdf...8045418010.jpg)

The Proper Rotation Operation

The proper rotation operation is a counter-clockwise rotation about a proper rotational axis by an angle of 360° over an integer number n. After that rotation the object must be indistinguishable from its original form. That means that the object after the rotation must superimpose the original object before the rotation. For example, when n=4, then we rotate around 90°, and after that the object must superimpose its original form. The proper rotational axis is the symmetry element associated with the proper rotation operation. It’s Schoenflies symbol is C_n, whereby n is called the order of the rotational axis. A proper rotational operation has the symbol C_n^m, whereby m counts the number of times the operation is carried out. Overall we rotate by and angle of 360°× m/n when we carry out an operation C_n^m. This means that when m=n, then we have rotated around 360° (Fig. 2.1.3). Then all points in the object are at their original position. It is as though we had done nothing with the object. We can also say we have reached the identity *E*. In mathematical form we can say that $C_n^n=E$. If we rotated one more time, $C_n^{(n+1)}$, then this would be equal to rotating only one time, and thus $C_n^{(n+1)}=C_n^1$. For example if n=4, then rotating four times around 90° will produce the identity. We have rotated around 4 x 90°=360° which is the same a though we had not rotated at all, because all points in the object are in their original position after a 360° rotation. If we rotated 5 times around 90°, it would the same as rotating only one time.

$$C_n^m = 360° \times \frac{m}{n}$$

$$C_n^n = E$$

$$C_n^{n+1} = C_n^1$$

Figure 2.1.3 Properties of the proper rotation operation

If an object has several axes with different order n, then the one with the highest order is called the *principal axis*. If there is more than one axis of the same order, then they get distinguished by primes if they are not conjugate. We will learn about the exact definition of conjugation somewhat later, we can however often see by inspection if two axes are conjugate. This is usually the case when they pass through the object in a equivalent way, and rotate the object in an equivalent way. Axes that pass through less many bonds, get less many primes. This is just a convention, but you have to follow it. An additional rule is that an axis which is in the same position as the principal axis gets the least number of primes. For example, a square planar molecule such as $PtCl_4^{2-}$ has a C_4 principal axis standing perpendicular to the square plane of the molecule. There is an additional C_2 axis where the C_4 axis runs. It is present because one can also rotate around 180°, and not only around 90°. This C_2 axis does not get any prime. You an see that there are four additional C_2 axes, two of them are denoted C_2’, and two others are denoted C_2’’. You can see that the two axes which only have one prime pass through two Pt-Cl bonds, while the ones that have two primes, do not pass through any bonds. The two C_2’ axes are conjugate, meaning that they transform the object in an equivalent way. The two C_2’’ axes are also conjugate.

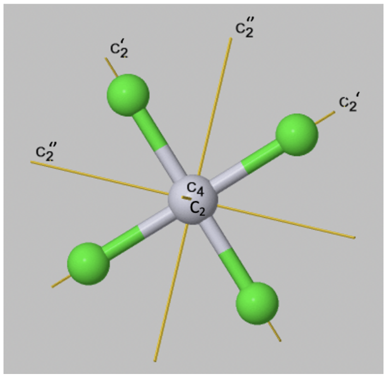

Figure 2.1.4 Proper rotational axes in the $PtCl_4^{2-}$ molecular anion. (Attribution: symotter.org/gallery)

We can now think about how we can write out the axes and their associated proper rotational operations in a systematic way. Let us first look at the symmetry elements, the proper axes: We conventionally write the principal axis first, and then all other axes from their highest to their lowest order. When there are axes of the same order, those with the least number of primes get denoted first, and those with the highest number of primes last. If there are conjugate axes then their number is placed in front of their Schoenflies symbol. For the proper axes of the $PtCl_4^{2-}$ the notation would therefore be: C_4, C_2, $2C_2'$, $2C_2''$. Now let us see how to denote the rotation operations that are associated with these symmetry elements. The notation follows the same rules as for the symmetry elements. In addition, we have to consider that we must not count identical operations twice, we also do not denote the operations that are the same as the identity. For the C_4 axis there are four operations until we reach the identity. C_4^1, C_4^2, C_4^3, and C_4^4. For each of the C_2, C_2', and C_2'' elements there are two operations until the identity is reached. C_2^1, C_2^2, $C_2^{1'}$, $C_2^{2'}$, $C_2^{1''}$, $C_2^{2''}$. The C_4^4, the C_2^2, the $C_2^{2'}$, and the $C_2^{2''}$are the same as the identity and therefore we do not consider them. In addition we can see that the C_4^2 is the same as the C_2^1. This is because the C_4 and the C_2 axes are in the same location, and rotating two times around 90° is the same as rotating one time around 180°. By convention we eliminate the operation associated with the higher order, thus the C_4^2. The overall notation would then be: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$ (Fig. 2.1.5).

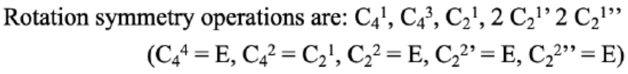
Rotation symmetry operations are: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$
($C_4^4 = E$, $C_4^2 = C_2^1$, $C_2^2 = E$, $C_2^{2'} = E$, $C_2^{2''} = E$)

Figure 2.1.5 Proper rotation operations in $PtCl_4^{2-}$

The Reflection Operations (σ)

Let us look at reflection operations which are carried out around reflection planes, or mirror planes. Mirror planes have the Schoenflies symbol σ. When we carry out a reflection operation, then we move any point of the object to the other side of the mirror plane. There are two types of mirror planes, so-called horizontal mirror planes and vertical mirror planes. A horizontal mirror plane always stands perpendicular to the principal axis. For example in the depicted BH_3 molecule there is a horizontal mirror plane that stands perpendicular to a C_3 principal axis (Fig. 2.1.6). A horizontal mirror plane has the Schoenflies symbol σ_h.

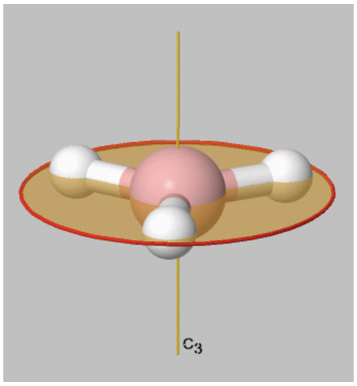

Figure 2.1.6 Visual depiction of the horizontal mirror plane of BH_3, σ_h (Attribution: symotter.org/gallery)

A vertical mirror plane has the property that it contains the principal axis, this means that it is part of the principal axis. It is denoted σ_v. The BH_3 molecule has three vertical axes that pass through the three B-H bonds. You can see that each of them contain the principal C_3 axis (Fig. 2.1.7). The three vertical mirror planes are conjugate, and therefore they are not distinguished by primes. We can write a coefficient 3 in front of the symbol σ_v to indicate that there are three conjugate vertical mirror planes.

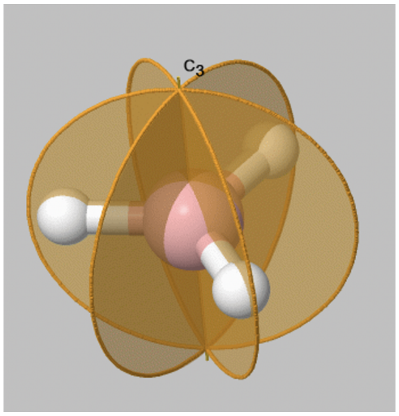

Figure 2.1.7 Visual depiction of the vertical mirror planes of $BH_{3,}$ 3 σ_v (Attribution: symotter.org/gallery)

Now let us look at how many symmetry operations are associated with a particular mirror plane. Fortunately, things are simple here: There is only one reflection operation associated with one mirror plane. This because reflecting two times at a mirror plane produces the identity E: σ_v^2=E. More generally, when we reflect n times, and n is an even number then this is the same as the identity or, σ_v^n=E (n is even). When n is odd the reflecting n times is the same a reflecting only one time or, $\sigma_v^n=\sigma_v^1$ (n=odd).

The horizontal mirror plane of the BH_3 molecule deserves an additional comment. Carrying out the horizontal reflection does not change the position of any atom. It is important to understand why the operation does exist despite the fact it does not change the position of any atom. The criterion is not whether the position of an atom is changed, but whether the position of the points in the object changes. In the case of the BH_3 molecule the part of the molecule that is located above the mirror plane will be located below the mirror plane after the reflection operation has been carried out. Vice versa any part of the molecule that was formerly below the mirror plane will be located above the mirror plane after the reflection operation has been carried out. For example the lower half of the B atom with be above the mirror plane, and the half above the plane will be below the plane after the execution of the reflection operation.

Like non-conjugate proper rotations are distinguished by primes, also non-conjugate vertical mirror planes must be distinguished by primes. The smaller the number of bonds the vertical mirror plane contains, the larger the number of primes.

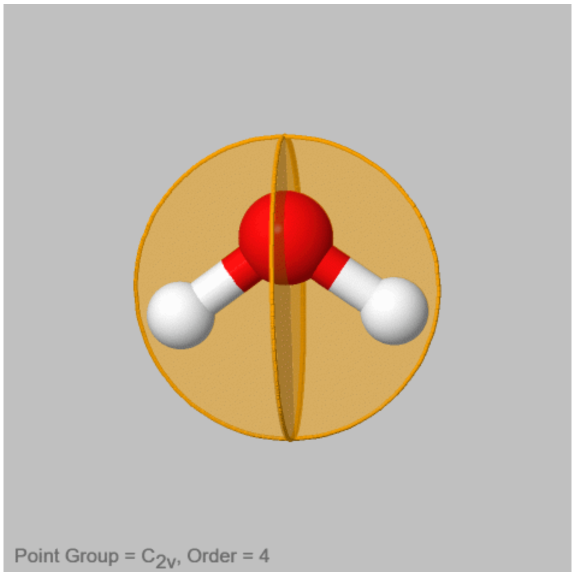

Figure 2.1.8 Non-conjugate vertical mirror planes of H_2O (Attribution: symotter.org/gallery)

For example in the water molecule (Fig. 2.1.8) there are two non-conjugate vertical mirror planes. One contains the two O-H bonds, the other stands perpendicular to the first mirror plane. It is easy to see that these two mirror planes will not move the points in the atom in an equivalent way, and therefore they are not conjugate. The first mirror plane does not change the position of any atom, while the second one swaps the positions of the two hydrogen atoms. Therefore, the second mirror plane not containing any O-H bonds gets one prime the one that contains the O-H bonds doe not get a prime.

Dihedral Reflection Planes (σ_d)

A special case of a vertical mirror plane is a dihedral mirror plane, denoted σ_d. A dihedral mirror plane bisects the angle between two conjugate C_2 axes.

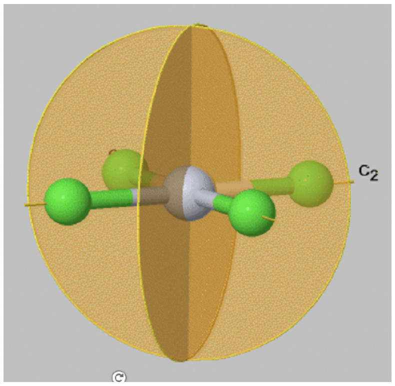

Figure 2.1.9 Dihedral mirror planes of $PtCl_4^{2-}$ (Attribution: symotter.org/gallery)

For example, in the $PtCl_4^{2-}$ anion (FIg. 2.1.9) there are two vertical mirror planes that bisect the angle between the two conjugate C_2 axes that pass through the Pt-Cl bonds. Therefore, these mirror planes are vertical mirror planes σ_d.

The Inversion Operation (*i*)

Let us look next at the inversion operation which is symbolized by a Schoenflies symbol *i*. The symmetry element associated with an inversion, is the inversion center, also called center of symmetry. It is a single point. When an inversion operation is performed, then each point of the object is moved through the inversion center to the other side. Each coordinate in the object (x,y,z) is inverted into the coordinates (-x,-y,-z).

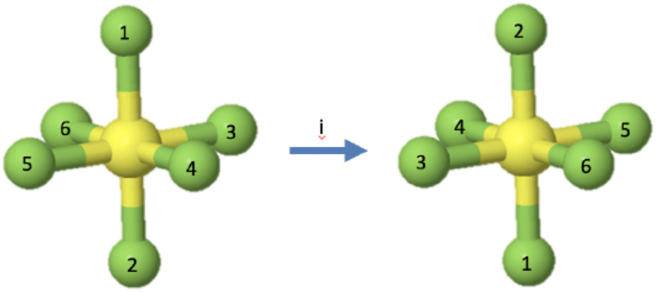

Figure 2.1.10 The inversion operation for SF_6 (Attribution: symotter.org/gallery)

For example, the octahedral molecule SF_6 has an inversion center in the center of the molecule (Fig. 2.1.10). When the inversion operation is carried out, then each fluorine atom is moved through the inversion center to the other side. This means that the fluorine atoms 1 and 2 swap up their positions, the fluorine atoms 3 and 5 swap up their positions, and so do the fluorine atoms 4 and 6. The sulfur atom does not change its position. There is only one inversion operation associated with each inversion center. Inverting two times, or more generally, an integer number of two times produces the identity. Inverting an odd number of times is the same as inverting one time.

The Rotation-Reflection Operation (S_n)

The rotation-reflection operation S_n is the most complex symmetry operation. It is carried out in two steps. First, a rotation around an improper axis is carried out. The angle is determined by the order n of the improper axis, and is 360°/n. This axis is called improper, because the object does not need to superimpose the original object after the rotation. Achieving superposition requires the second step which is the reflection at a mirror plane that stands perpendicular to the improper axis. Only after the second step the operation is complete. The presence of the rotation-reflection does not require a proper rotational axis or a regular mirror plane σ to exist, however it also do not preclude their existence.

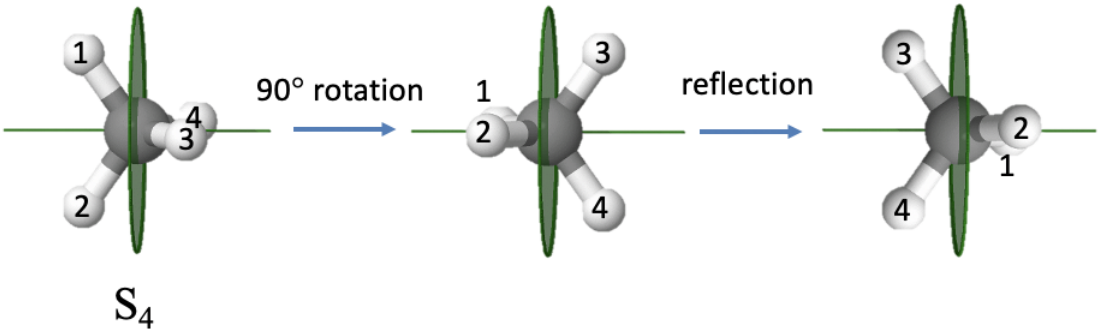

Figure 2.1.11 The improper S_4 rotation for CH_4 (Attribution: symotter.org/gallery)

An example of a molecule with an improper axis is the methane molecule (Fig. 2.1.11). It has an S_4 improper axis. The axis bisects the H-C-H tetrahedral bond angle. The order of the axis is four which requires that we rotate by 90° around this axis. You can see that after we carry out the rotation, the molecule does not superimpose the original molecule. Only after we reflect the rotated molecule at a mirror plane standing perpendicular to the improper axis the molecule superimposes the original molecule.

Properties of the Rotation-Reflection Operation (S_n)

The rotation-reflection has a number of interesting properties. One of the them is that an S_1 operation is the same as a reflection. This is because the order 1 implies a rotation around 360° which produces the identity, and all points within the object are in their original position. This is the same as though we had not rotated at all. This means actually we only did the second step, the reflection, and therefore the S_1 is identical to a “regular” reflection. The second property is that an S_2 operation is the same as an inversion. When you rotate around 180° and then reflect perpendicular to the improper axis of rotation, the positions of the points in the object change exactly the same way as they do when you invert through an inversion center.

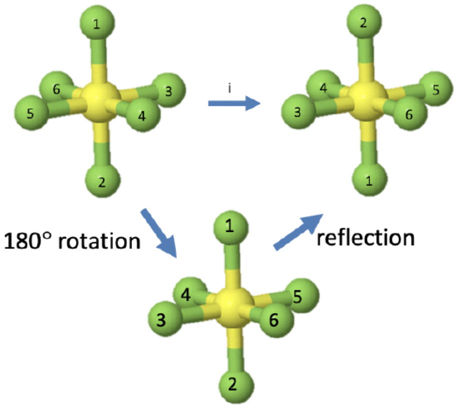

Figure 2.1.12 Rotation-Reflection operations for SF_6 (Attribution: symotter.org/gallery)

Look for example at the SF_6 molecule again (Fig. 2.1.12) which has an inversion center in the center of the atom. We previously saw that when we carry out the inversion, the atoms 1 and 2 swap their position, and so do the atoms 3 and 5, as well as the atoms 4 and 6. Let us carry out the rotation-reflection, and see if the atoms change the same way. Firstly we rotate 180° around an axis that goes through the atoms 1 and 2. This leaves the positions of the atoms 1 and 2 unchanged, but swaps up the positions of the atoms 3 and 5, as well as the atoms 4 and 6. Next we must do a reflection at a plane that stands perpendicular to the improper axis. It is the plane defined by the atoms 3, 4, 5, and 6. Reflection at this plane does not change the positions of the atoms 3, 4, 5, and 6, but it swaps up the positions of the atoms 1 and 2, which lie above and below the plane, respectively. We can see that the positions of the atoms are the same as after the inversion.

The fact that we can express a reflection by an S_1 rotation-reflection, and an inversion by a S_2 rotation-reflection means that the reflection and the inversion are not independent symmetry operations, and we would not need them. The symmetry of an object could be fully described by the identity, proper rotations, and rotation-reflections. However, by convention, we use reflections and inversions instead of S_1 and S_2, simply because it is easier for the human mind to perform 1-step operations, rather than 2-step operations.

Improper rotations have different properties depending on whether the order of the axis is even or odd. For even orders, the presence of an S_n improper rotational axis implies that there must also be a proper rotational axis with an order n/2. For improper axes of even orders n the identity is produced after n rotation-reflections (Fig. 2.1.13).

S_n with n even → molecule contains $C_{n/2}$

$$S_n^n = E$$

Figure 2.1.13 Properties of improper rotations with even order *n*

For improper axes of odd order n, carrying out the rotation-reflection n times is the same as carrying out a reflection at a horizontal mirror plane. We need to do the rotation-reflection 2n times to reach the identity (Fig. 2.1.4).

S_n with n odd → molecule contains C_n and σ_h

$$S_n^n = \sigma_h$$

$$S_n^{2n} = E$$

Figure 2.1.14 Properties of improper axes of odd order *n*

Rotation-Reflections of PF_5 (an example with odd order)

Let us show these properties using two examples. Let us first look at an example with an improper rotation of odd order. The PF_5 molecule has trigonal pyramidal shape with three F atoms in the equatorial plane, and two additional F atoms above and below the plane. The F atoms have been numbered from 1 to 5 as indicated by the subscripts that follow the element symbol (Fig. 2.1.15). The PF_5 has an improper rotational axis S_3 that stands perpendicular to the equatorial plane going through the P-F_1 and P-F_2 bonds. Let us carry out the S_3 symmetry operations step by step and see how the atoms move.

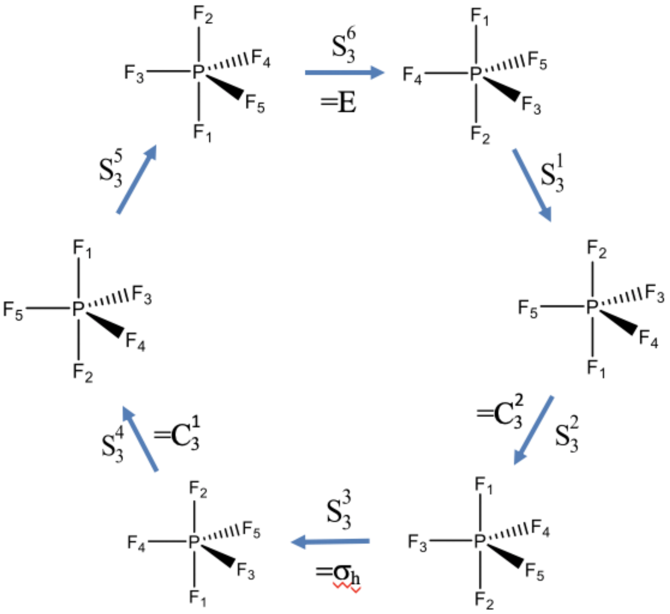

Figure 2.1.15 S_3 symmetry operations for PF_5

We would expect that after we carry out the operation six times the identity will be produced. After three rotation-reflections we would expect that the object has been moved the same way a horizontal mirror plane would do. After the first rotation-reflection the atoms F_1 and F_2 have swapped their positions, and the three F atoms in the equatorial plane have been rotated by 120 degrees counter-clockwise. The F_5 atom now occupies the position of the F_4, the F_4 has been rotated into the position of the F_3, and the F_3 has been moved into the position of the F_5. The second S_3 operation again swaps up the F_2 and F_1 atoms, and rotates the remaining F atoms by 120°. Now the F_5 atoms points toward us, the F_4 atom points away from us, and the F_3 atoms is in the paper plane. Carrying out the operation a third time again swaps the F_1 and F_2 and rotates F_3, F_4, and F_5 counter-clockwise by 120°. Now let us compare the position of the atoms with the atom positions of the molecule we started with. We see that the position of the equatorial F atoms are same as in the beginning, but the position of the axial F_1 and F_2 atoms have been swapped up. This is equivalent to a reflection at a horizontal mirror plane located within the equatorial plane. This horizontal mirror plane would only swap up the axial F atoms, but would not move the equatorial ones. The S_3^4 operation again swaps up the position of the F_1 and the F_2 atoms, and rotates the equatorial F atoms by 120° counter-clockwise. Now, F_4 points toward us, F_3 points away, and F_5 is in the paper plane. After the fifth rotation-reflection F_1 and F_2 are again swapped so that F_1 is below and F_2 is above the equatorial plane.

The atoms F_3, F_4 and F_5 are rotated so that F_3 is in the paper plane, F_5 points toward us, and F_4 points away from us. The sixth rotation-reflection again swaps up F_1 and F_2, and rotates the other F atoms around 120° counter-clockwise. We can now see that the produced molecule is the same as the one we started with, and the identity has been produced.

It is also noteworthy that the S_3^2 and the S_3^4 operation can be expressed by simpler operations, namely C_3^2 and C_3^1 proper rotation operations. We can understand this considering that an S_3^2 operation requires that we reflect two times, and reflecting two times is just like not reflecting at all. So effectively, we only have two rotations around 120° which is equivalent to C_3^2. Similarly, the S_3^4 operation requires to reflect four times, which is the same as not reflecting at all. Thus, effectively, we only rotate four times around 120°. This is the same as rotating only one time around this angle, which is equivalent to a C_3^1 operation.

Using similar considerations, we can also understand why the S_3^3 operation is equivalent to a σ_h. In this case, we rotate 3 x 120° = 360°, and rotating around 360° is the same as not rotating at all. In addition, we carry out a reflection three times. Reflecting an odd number of times is the same as reflecting only one time. Thus overall, we effectively carry out a single reflection only.

Overall, only the S_3^1 and the S_3^5 operations are unique, all others can be expressed by other, simpler operations.

Rotation-Reflections of CH_4 (an example with even order)

Let us illustrate the properties of an improper rotational axis with even order using the example methane (Fig. 2.1.16).

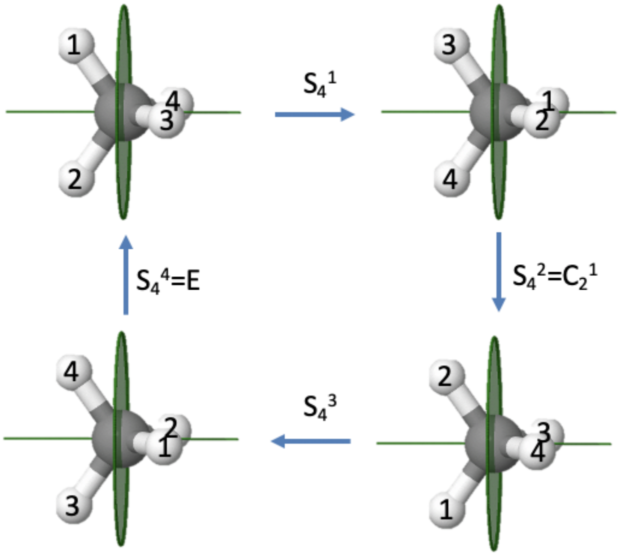

Figure 2.1.16 S_4 symmetry operations for CH_4 (Attribution: symotter.org/gallery)

We previously saw that the methane molecule has an S_4 improper axis. Executing the symmetry operation once moves the H atoms 1 and 2 to the right, whereby atom 1 points to the back and atom 2 points to the front. After the second rotation-reflection the atoms 1 and 2 are reflected back to the left side, but because we have rotated two times by 90° atom 2 points up, and atom 1 points down. Similarly, atoms 3 and 4 are reflected back to the right side, but atom four points toward us and atom 3 points to the back. After three rotation-reflections, the atoms 1 and 2 are again on the right side with atom 2 pointing to the back and atom 1 pointing to the front. Atoms 3 and 4 are on the left with atom 4 pointing up, and atom 3 pointing downward. After the operation is carried out four times, all atoms are back in their original position, meaning the identity has been produced. This is what we expected for an improper rotation of even order. We can see in addition that the S_4^2 operation is the same as an C_2 operation. Rotating two times about 90° is the same as rotating about 180°. Reflecting two times is the same as not reflecting at all. Therefore, effectively, we only rotated by 180° which is the same as what a C_2^1 operation does. Because an S_4^2 can be expressed by a C_2^1, and an S_4^4 is the same as the identity, only the S_4^1 and the S_4^3 are unique symmetry operations.

The Symmetry of a Molecule

We have now discussed all types of symmetry elements and operations that can exist in an object. Next, let us think about how we can define the overall symmetry of an object. The **overall symmetry** of an object is defined as the sum of all the symmetry operations for this object. If two objects have exactly the same symmetry elements and operations then their symmetry is the same. Using the mathematical language of group theory, the mathematical theory for symmetry, we can say they belong to the same point group. The name point group comes from the fact, that it has at least one invariant point. The number of symmetry operations belonging to a point group is called the order of the point group. Let us see next what different point groups we know and how we can systematically classify them.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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2.2: Point Groups

The Low Symmetry Point Groups

C_1 Point Group

Overall, we divide point groups into three major categories: High symmetry point groups, low symmetry point groups, dihedral point groups, and rotational point groups. Let us begin with the low symmetry point groups. As the name says, these point groups only have few symmetry elements and operations. The point group C_1 is the point group with the lowest symmetry. Molecules that belong to this point group only have the identity as symmetry element.

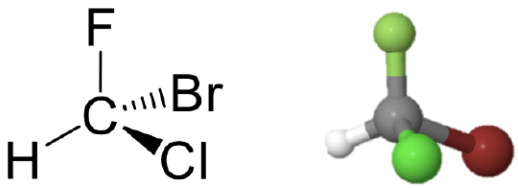


Figure 2.2.1 C_1 point group of bromochlorofluromethane (Attribution: symotter.org/gallery)

An example is the bromochlorofluromethane molecule (Fig. 2.2.1). It has no symmetry element, but the identity. The name C_1 comes from the symmetry element C_1. A C_1 operation is the same as the identity.

C_s Point Group

The point group C_s has a mirror plane in a addition to the identity. An example is the 1,2-bromochloroethene molecule (Fig. 2.2.2).

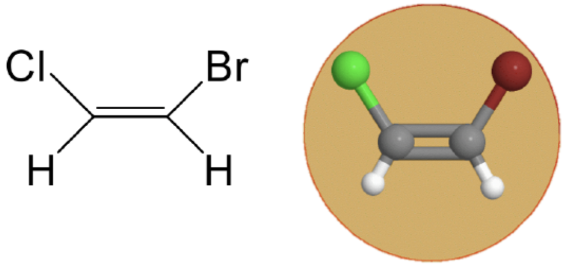


Figure 2.2.2 C_s point group of 1,2-bromochloroethene (Attribution: symotter.org/gallery)

This is a planar molecule and the mirror plane is within the plane of the molecule. This mirror plane does not move any atoms when the reflection operation is carried out, nonetheless it exists because any point of the molecule above the mirror plane will be found below the mirror plane after the execution of the operation. Vice versa, any point below the mirror plane will be above the mirror plane. This mirror plane does not have a vertical or horizontal mirror plane designation because no proper rotational axes exist.

C_i Point Group

The point group C_i has the inversion as the only symmetry element besides the identity. The point group C_i is sometimes also called S_2 because an S_2 improper rotation-reflection is the same as an inversion. An example is the 1,2-dibromo 1,2-dichloro ethane (Fig. 2.2.3).

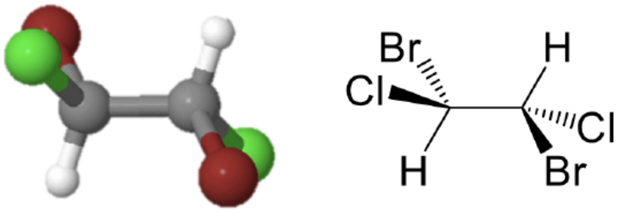


Figure 2.2.3 The C_i point group: 1,2-dibromo 1,2-dichloro ethane (Attribution: symotter.org/gallery)

This molecule looks quite symmetric, but it has inversion center in the middle of the carbon-carbon bond as the only symmetry element. Upon execution of the inversion operation, the two carbons swap up their positions, and so do the two bromine, the two chorine, and the two hydrogen atoms.

The High Symmetry Point Groups

The symmetry elements of the high symmetry point groups can be more easily understood when the properties of platonic solids are understood first. Platonic solids are polyhedra made of regular polygons. In a platonic solid all faces, edges, and vertices (corners) are symmetry-equivalent. We will see that this is a property that can be used to understand the symmetry elements in high symmetry point groups. There are only five possibilities to make platonic solids from regular polygons (Fig. 2.2.4).

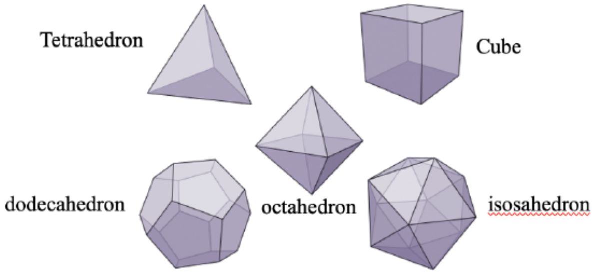


Figure 2.2.4 The platonic solids (Attribution: Drummyfish [CC0] https://commons.wikimedia.org/wiki/F...ransparent.svg)

The first possibility is to construct a tetrahedron from four regular triangles. The second platonic solid is the octahedron made of eight regular triangles. The third possibility is the icosahedron made of twenty triangles. In addition, six squares can be connected to form a cube, and twelve pentagons can be connected to form a dodecahedron. There are no possibilities to connect other regular polygons like hexagons to make a platonic solid.

The icosahedron is the most complex of all platonic solids. If you would like to see and study an icosahedron from the outside and inside, there is one for study on the playground of the Allentown Cedar Beach Park, in Allentown, Pennsylvania.

Figure 2.2.5 Icosahedron at Allentown Cedar Beach Park

The T_d Point Group

The tetrahedron, as well as tetrahedral molecules and anions such as CH_4 and BF_4- belong to the high symmetry point group T_d. Let us find the symmetry elements and symmetry operations that belong to the point group T_d. First, we should not forget the identity operation, E. Next, it is useful to look for the principal axes.

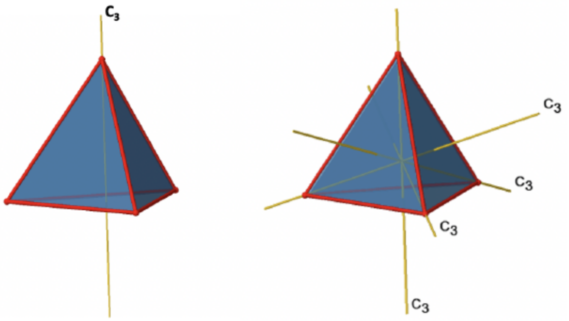


Figure 2.2.6 The C_3 axes in a tetrahedron (Attribution: symotter.org/gallery)

The tetrahedron has four principal C_3 axes (Fig. 2.2.6). It is a property of the high-symmetry point groups that they have more than one principal axis. The C_3 axes go through the vertices of the tetrahedron. Because each C_3 axis goes through one vertex, there are four vertices, and we know that in a platonic solid all vertices are symmetry-equivalent, we can understand that there are four C_3 axes. How many unique C_3 operations are associated with these axes? After three rotations around 120° we reach the identity. Therefore C_3^3=E, and we only need to consider the C_3^1 and the C_3^2 rotation about 120 and 240° respectively. Because there are four C_3 axes, there are four C_3^1 and four C_3^2 operations and eight C_3 operations overall. We can express this by writing the respective numbers as coefficients in front of the Schoenflies symbol for the operations (Fig. 2.2.7).

Symmetry operations: E, $8C_3$

Symmetry operations in detail: E, 4 C_3^1, 4 C_3^2 (C_3^3 = E)

Figure 2.2.7 Symmetry operations associated with the C_3 axes in the point group T_d

In addition to the C_3 axes there are C_2 axes (Fig. 2.2.8).

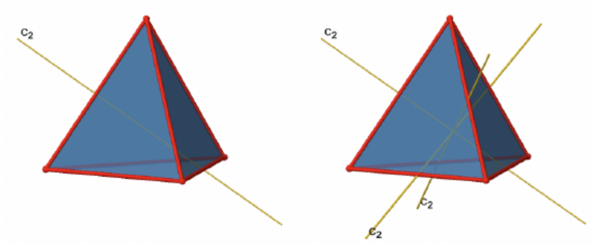


Figure 2.2.8 The C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

You can see that a C_2 axis goes through two opposite edges in the tetrahedron. Because a tetrahedron has six edges, and each C_2 axis go through two edges there are 6/2=3 C_2 axes. There is only one C_2 symmetry operation per C_2 axis because we produce the identity already after two rotations. Therefore there are three C_2^1 operations overall (Fig. 2.2.9).

Symmetry operations: $3C_2$

Symmetry operations in detail: 3 C_2^1

Figure 2.2.9 Symmetry operations associated with the C_2 axes in the point group T_d

In addition, the T_d point group has S_4 improper rotation reflections. Like the C_2 axes, they pass through the middle of two opposite edges. This also means that they are superimposing the C_2 axes. Because there are six edges, and two S_4 axes per edge there are 6/2=3 S_4 axes (Fig. 2.2.10).

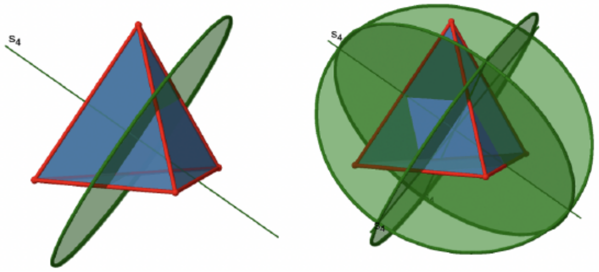
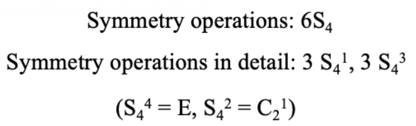


Figure 2.2.10 The S_4 axes in a tetrahedron (Attribution: symotter.org/gallery)

How many operations are associated with these S_4 axes? The order of the axes are even, and therefore we need four S_4 operations to produce the identity. The S_4^2 operation is the same as a C_2^1 operation because reflecting two times is equivalent to not reflecting at all, and rotating two times by 90° is the same as rotating about 180°. Therefore overall, only S_4^1 and S_4^3 operations are unique operations. S_4^2 and S_4^4 can be expressed by the simpler operations C_2^1 and E respectively. Because there are 3 S_4 axes, there are three S_4^1 and three S_4^3 operations. Overall there are six S_4 operations (Fig. 2.2.11).



Symmetry operations: $6S_4$

Symmetry operations in detail: 3 S_4^1, 3 S_4^3

($S_4^4 = E$, $S_4^2 = C_2^1$)

Figure 2.2.11 Symmetry operations associated with the S_4 axes in the point group T_d

There are also mirror planes (Fig. 2.2.11). The planes contain a single edge of the tetrahedron, thereby bisecting the tetrahedron. There a six edges in a tetrahedron, and therefore there are 6/1=6 mirror planes.

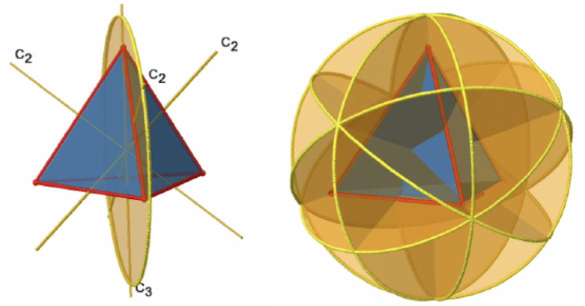
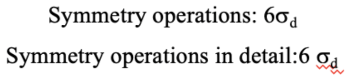


Figure 2.2.12 The mirror planes and C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

These planes are dihedral planes because each plane contains a C_3 principal axis and is bisects the angle between two C_2 axes. Overall, there are three C_2 axes and three C_2 operations. There is one reflection operation per mirror plane because reflecting two times produces the identity. Therefore, there are six σ_d reflection operations (Fig. 2.2.12, right and Fig. 2.2.13).



Symmetry operations: $6\sigma_d$

Symmetry operations in detail:6 σ_d

Figure 2.2.13 Reflection operations associated with the σ_d mirror planes in T_d

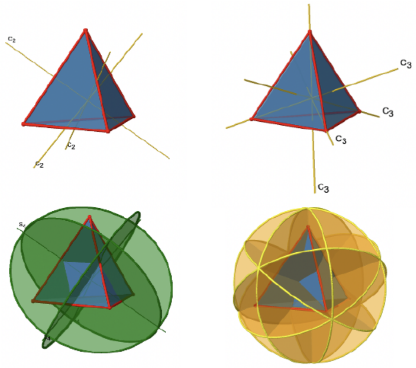
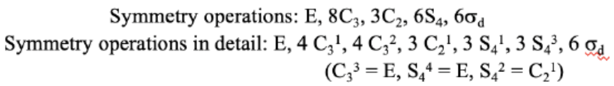


Figure 2.2.14 Summary of symmetry axes and planes in a tetrahedron with the point group T_d (Attribution: symotter.org/gallery)

In sum (Fig.2.2.14 and 2.2.15) we can denote the overall symmetry of the T_d point group the following way: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$. In detail the unique symmetry operations are E, $4C_3^1$, $4C_3^2$, $3C_2^1$, $3S_4^1$, $3S_4^3$, $6\sigma_d$.



Symmetry operations: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

Symmetry operations in detail: E, 4 C_3^1, 4 C_3^2, 3 C_2^1, 3 S_4^1, 3 S_4^3, 6 σ_d

($C_3^3 = E$, $S_4^4 = E$, $S_4^2 = C_2^1$)

Figure 2.2.15 Summary of the symmetry operations for the point group T_d

The Rotational Subgroup T

The high symmetry point group T is the so-called rotational subgroup of the point group T_d. A rotational subgroup is a point group in which all symmetry operations but the identity and the proper rotations have been removed from a high-symmetry point group.

For the point group T this leaves the 4C_3, the four C_3^2 and the three C_2 operations (Fig. 2.2.17). The S_4 rotation-reflections and the mirror planes have been removed. The point group T is rare.

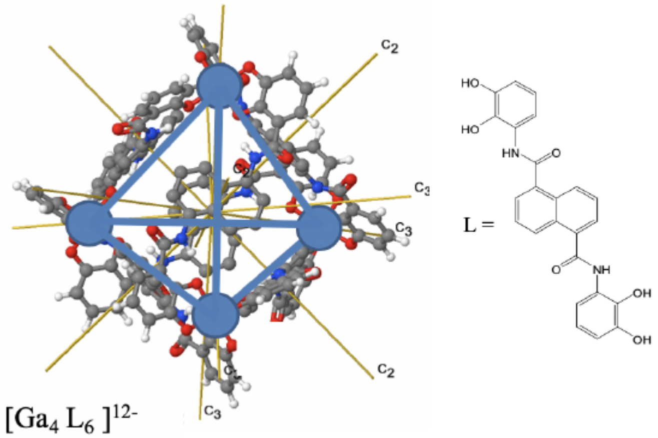


Figure 2.2.16 Symmetry elements in the Ga_4L_6 cage belonging to the point group T (Attribution: symotter.org/gallery)

An example is the depicted Ga_4L_6 cage (Fig. 2.2.16). The Ga atoms occupy the vertices of a tetrahedron, but the point group is not T_d but T because of the shape of the ligands that connect the four Ga atoms.

Symmetry operations: E, $4C_3$, $4C_3^2$, $3C_2$

Figure 2.2.17 Symmetry operations for the Ga_4L_6 cage

The Octahedral Point Group O_h

Another high symmetry point group is the point group O_h. Both the octahedron as well as the cube belong to this point group despite their very different shape (Fig. 2.2.18). Because they belong to the same point group they must have the same symmetry elements and operations. There are many octahedrally shaped molecules, such as the SF_6.

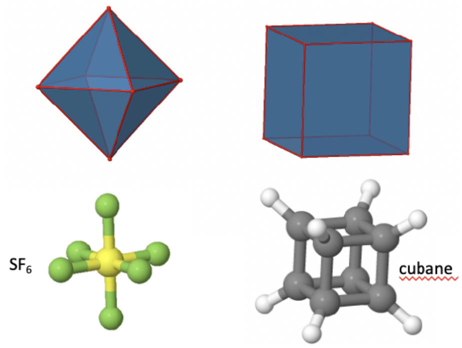


Figure 2.2.18 SF_6 and cubane with cubic and octahedral shape, respectively, belong to the point group O_h (Attribution: symotter.org/gallery)

Molecules with cubic shapes are far less common, because a cubic shape often leads to significant strain in the molecule. An example is cubane C_8H_8. Let us determine the symmetry elements and operations for the point group O_h using the example of the octahedron. If we used the cube, we would get exactly the same results.

There are three C_4 principal axes in the octahedron. They go through two opposite vertices of the octahedron (Fig. 2.2.19). There are three C_4 axes because an octahedron has six vertices which are all symmetry-equivalent because the octahedron is a platonic solid.

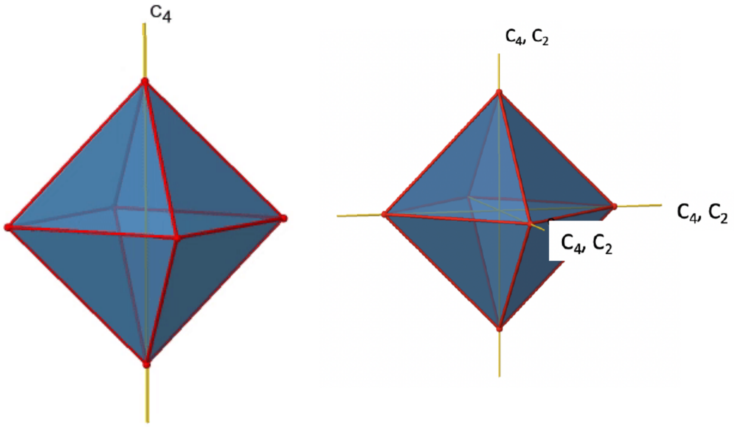


Figure 2.2.19 The C_4 and C_2 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

We can see that there are also C_2 axes where the C_4 axes run. This is because rotating two times around 90° is the same as rotating around 180°. What are the symmetry operations associated with these symmetry elements? Rotating four times around 90° using the C_4 axes produces the identity. So we have to consider the operations C_4^1, C_4^2, C_4^3 and C_4^4. How many of these are unique? C_4^4 is the same as the identity, so it is not unique, In addition a C_4^2 is identical to a C_2^1, and thus C_4^2 is also not unique, and can be expressed by the simpler operation C_2^1. That leaves the C_4^1 and the C_4^3 as the only unique symmetry operations. Because we have three C_4 axes, there are 2x3=6 C_4 operations, in detail there are $3C_4^1$ and three C_4^3 operations. In addition, there are the three C_2^1 operations belonging the the three C_2 axes (Fig. 2.2.20).

Symmetry elements: E, $3C_4$, 3 C_2

Symmetry operations: E, 6 C_4, 3 C_2
In detail: E, 3 C_4^1, 3 C_4^3
($C_4^2 = C_2^1$, $C_4^4 = E$)

Figure 2.2.20 C_4 and C_2 symmetry operations in the octahedral point group O_h

In addition, there are four C_3 axes (Fig. 2.2.21). They are going through the center of two opposite triangular faces of the octahedron.

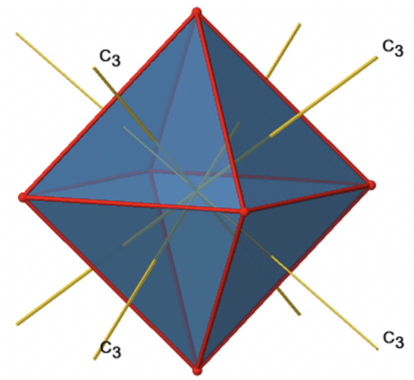


Figure 2.2.21 The C_3 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

You see above a single C_3 axis, and on the right hand side all four of these axes. How can we understand that there are four axes? An octahedron has overall eight triangular faces, and each C_3 axis goes through two opposite faces, so there are 8/2=4 C_3 axes. Each C_3 axis has the C_3^1 and the C_3^2 as unique symmetry operations. The C_3^3 is the same as the identity. So overall we have 4x2=8 operations, four of them are C_3^1, and four of them are C_3^2 (Fig. 2.2.22).

Symmetry elements: $4C_3$
Symmetry operations: $8\ C_3$
In detail: $4\ C_3^1$, $4\ C_3^2$
($C_3^3 = E$)

Figure 2.2.22 Symmetry operations of C_3 in the octahedral point group O_h

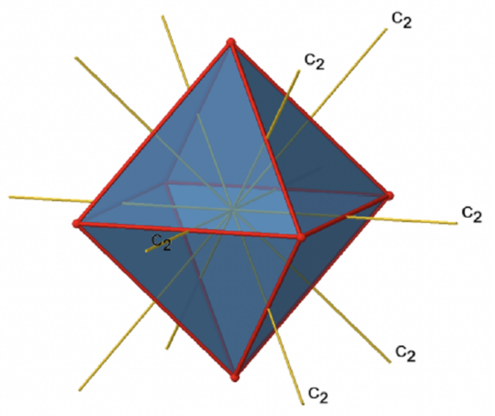


Figure 2.2.23 The C_2' axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

In addition to the C_2 axes that superimpose the C_4 axes, there are C_2' axes which go though two opposite edges of the octahedron (Fig. 2.2.23). How many of them are there? An octahedron has twelve edges, and because each C_2' passes through two edges, there must be 12/2=6 C_2' axes. These axes have primes because they are not conjugate to the C_2 axes that superimpose the C_4 axes. For each C_2' axis there is only the $C_2'^{\ 1}$ as the unique symmetry operation, and therefore there are overall 6 $C_2'^1$ symmetry operations (Fig. 2.2.24).

Symmetry elements: $6\ C_2'$
Symmetry operations: $6\ C_2'^1$

Figure 2.2.24 Symmetry operations of C_2' in the octahedral point group O_h

Let us look at the mirror planes next (Fig. 2.2.25). There are horizontal mirror planes that stand perpendicular to the C_4 principle axes. You can see a single one of them below on the left.

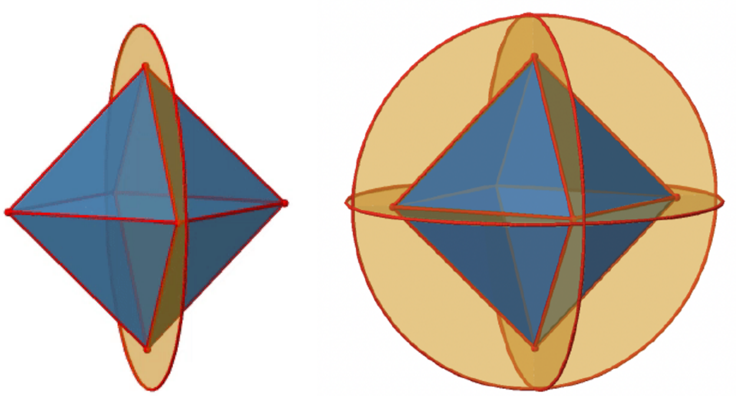


Figure 2.2.25 The horizontal mirror planes in the octahedral point group O_h (Attribution: symotter.org/gallery)

Note that this mirror plane also contains two axes, in addition to the one to which it stands perpendicular. Because it contains two principal C_4 axes, it has also properties of a vertical mirror plane. Nonetheless, we call it a horizontal mirror plane because it stands perpendicular to the third C_4. The horizontal properties trump the vertical ones, so to say. You can see that a single mirror plane contains four edges of the octahedron. Because there are twelve edges, there are 12/4=3 horizontal mirror planes. There is one mirror plane per principal C_4 axis. There are three horizontal reflection operations because there is always only one reflection operation per mirror plane (Fig. 2.2.26).

Symmetry elements: $3\sigma_h$
Symmetry operations: $3\sigma_h$

Figure 2.2.26 Symmetry operations associated with horizontal mirror planes in the octahedral point group O_h

Next let us look for vertical mirror planes (Fig. 2.2.27). A vertical mirror plane is depicted below on the left.

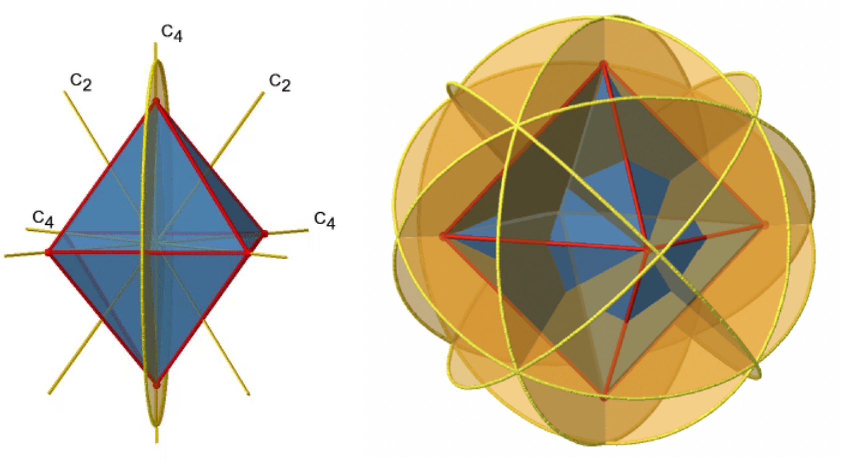


Figure 2.2.27 The vertical mirror planes in the octahedral point group O_h (Attribution: symotter.org/gallery)

You can see that - contrast to the horizontal mirror planes - it does not contain any edges. Rather, it cuts through two opposite edges. You can see that this plane contains a C_4 axis, but it does not stand perpendicular to the other two C_4 axes. Therefore it has only the properties of a vertical mirror plane. You can see however, that the mirror plane bisects the angle between two C_2' axes which also depicted. This makes the vertical mirror planes dihedral mirror planes, σ_d. How may of them do we have? As previously mentioned, each mirror plane cuts through two opposite edges. There are twelve edges in an octahedron, and thus there are 12/2=6 dihedral mirror planes. You can see all of them on the right side of Fig. 2.2.27. Each mirror plane is associated with one reflection operation, therefore there are six dihedral reflection operations (Fig. 2.2.28).

Symmetry elements: $6\ \sigma_d$
Symmetry operations: $6\ \sigma_d$

Figure 2.2.28 Symmetry operations associated with vertical mirror planes in the octahedral point group O_h

Next we can ask if the point group O_h has an inversion center? Yes, there is one in the center of the octahedron (Fig. 2.2.29)!

Figure 2.2.29 The inversion center of the octahedral point group O_h (Attribution: symotter.org/gallery)

Each point in the octahedreon can be moved through the inversion center to the other side, and the produced octahedron will superimpose the original one. There is always one inversion operation associated with an inversion center (Fig. 2.2.30).

Symmetry elements: i
Symmetry operations: i

Figure 2.2.30 Symmetry operations associated with the inversion center in the octahedral point group

Next, let us look for rotation-reflections. You can see an S_6 rotation-reflection operation below (Fig. 2.2.31, left).

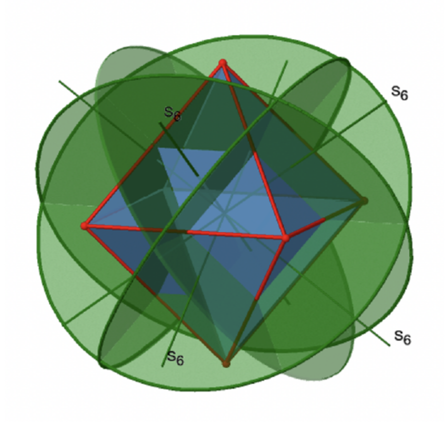


Figure 2.2.31 The S_6 rotation-reflection element of the octahedral point group O_h (Attribution: symotter.org/gallery)

The improper S_6 axis passes though the centers of two opposite triangular faces. One can see that rotation about 60° alone does not make the octahedron superimpose. The reflection at a plane perpendicular to the improper axis is required to achieve superposition. Overall, the rotation-reflection swaps up the position of the two opposite triangular faces. How many S_6 improper axes are there? Since each S_6 passes through two faces, and an octahedron has 8 faces there must be 8/2=4 S_4 axes. You can see all of them above (Fig. 2.2.31, right). Note that they are in the same position as the 4C_3 axes we previously discussed. How many unique operations are associated with them? For an S_6 axis we need to consider operations from S_6^1 to S_6^6. S_6^6 is the same as the identity so it is not unique. The S_6^2 is the same as a C_3^1 because rotating two times round 60° is the same as rotating around 120°, and reflecting twice is the same as not reflecting at all. Similarly, an S_6^4 is the same as an C_3^2. Rotating four time by 60° is the same as rotating two times by 120° and reflecting four times is the same as not reflecting at all. Further, an S_6^3 is the same as an inversion. After three 60° rotations we have rotated by 180°. If we reflect after that, then this is the same as an S_2^1 operation which is the same as an inversion. Therefore, only the S_6^1 and the S_6^5 operations are unique, all other operations can be expressed by simpler operations (Fig. 2.2.32).

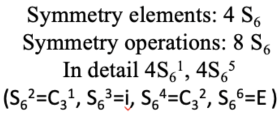

Symmetry elements: 4 S_6
Symmetry operations: 8 S_6
In detail 4S_6^1, 4S_6^5
($S_6^2=C_3^1$, $S_6^3=i$, $S_6^4=C_3^2$, $S_6^6=E$)

Figure 2.2.32 Symmetry operations of the rotation-reflection S_6 of the octahedral point group O_h

The octahedron also has S_4 improper axes, and you can see one of them below (Fig. 2.2.33, right).

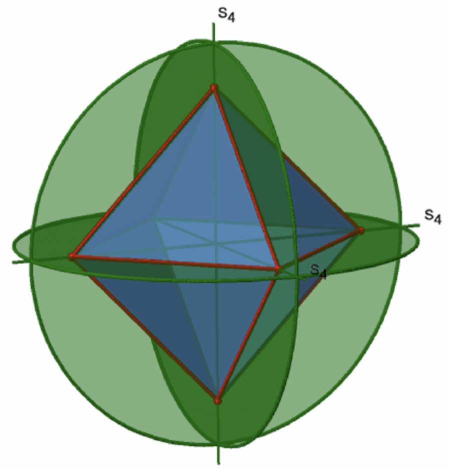


Figure 2.2.33 The S_4 improper axis of the octahedral point group O_h (Attribution: symotter.org/gallery)

It goes through two opposite corners of the octahedron. The S_4 improper axis seemingly does the same as the C_4 axis that goes through the same two opposite vertices, but actually does not. While rotating around 90° already makes the octahedron superimpose with its original form, executing the reflection operation after the rotation swaps up the position of the two vertices, and generally all points of the octahedron above and below the plane, respectively. Overall the S_4 moves the points within the object differently compared to the C_4 which makes it an additional, unique symmetry element. There are overall three S_4 improper axes because the octahedron has six vertices and one S_4 passes through two vertices (Fig. 2.2.34).

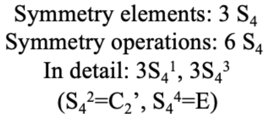

Symmetry elements: 3 S_4
Symmetry operations: 6 S_4
In detail: $3S_4^1$, $3S_4^3$
(S_4^2=C_2’, S_4^4=E)

Figure 2.2.34 Symmetry operations associated with the S_4 improper axis of the octahedral point group O_h

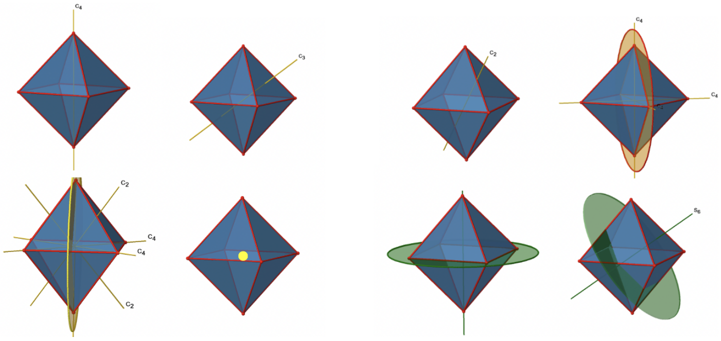


Figure 2.2.35 An overview over all symmetry elements in the octahedral point group O_h (Attribution: symotter.org/gallery)

Here is an overview over all the symmetry elements and operations (Fig. 2.2.35 and 2.2.36). Overall, there are 48 different unique operations that one can perform!

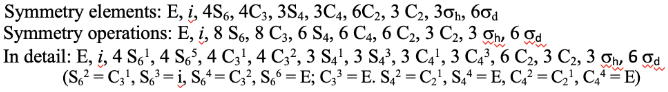

Symmetry elements: E, *i*, $4S_6$, $4C_3$, $3S_4$, $3C_4$, $6C_2$, 3 C_2, $3\sigma_h$, $6\sigma_d$
Symmetry operations: E, *i*, 8 S_6, 8 C_3, 6 S_4, 6 C_4, 6 C_2, 3 C_2, 3 σ_h, 6 σ_d
In detail: E, *i*, 4 S_6^1, 4 S_6^5, 4 C_3^1, 4 C_3^2, 3 S_4^1, 3 S_4^3, 3 C_4^1, 3 C_4^3, 6 C_2, 3 C_2, 3 σ_h, 6 σ_d
($S_6^2 = C_3^1$, $S_6^3 = i$, $S_6^4 = C_3^2$, $S_6^6 = E$; $C_3^3 = E$. $S_4^2 = C_2^1$, $S_4^4 = E$, $C_4^2 = C_2^1$, $C_4^4 = E$)

Figure 2.2.36 Summary over all symmetry operations and elements of the octahedral point group O_h

Like the point group T_d , also the point group O_h has a rotational subgroup, named O. It has the identity and the same proper rotations as the point group O_h, but no other symmetry operations (Fig. 2.2.38). An example is the polyoxometalate cluster core shown below (Fig. 2.2.37). Polyoxometalates are cluster anions of the group 5 and 6 elements.

Figure 2.2.37 Proper rotations in a $V_6P_8O_{24}$ polyoxometalate cluster core. The C_3 rotation is animated. (Attribution: symotter.org/gallery)

The point group O is generally rare.

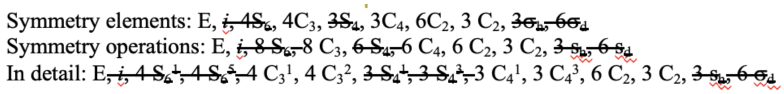

Symmetry elements: E, ~~*i*, $4S_6$~~, $4C_3$, ~~$3S_4$~~, $3C_4$, $6C_2$, 3 C_2, ~~$3\sigma_h$, $6\sigma_d$~~
Symmetry operations: E, ~~*i*, 8 S_6,~~ 8 C_3, ~~6 S_4,~~ 6 C_4, 6 C_2, 3 C_2, ~~3 s_h, 6 s_d~~
In detail: E~~, *i*, 4 S_6^1, 4 S_6^5,~~ 4 C_3^1, 4 C_3^2, ~~3 S_4^1, 3 S_4^3,~~ 3 C_4^1, 3 C_4^3, 6 C_2, 3 C_2, ~~3 s_h, 6 σ_d~~

Figure 2.2.38 Symmetry elements and operations in the point group O (relative to O_h)

Another high symmetry point group is the point group T_h. It can also be derived from the point group O_h. In this case the S_4, the C_4, the C_2’, and the σ_d operations are removed from the octahedral symmetry. An example is the hexapyridyl iron (2+) cation (Fig. 2.2.39).

Figure 2.2.39 The hexapyridyl iron (2+) cation and its S_6 and C_2 symmetry elements. An S_6 operation is animated.

You can see that the N-atoms of the pyridyl-ligands surround the Fe atoms octahedrally, but the symmetry is reduced from O_h to T_h because of the planar shape of the pyridyl-ligands. In particular the C_4 symmetry is reduced to C_2. This reduction in symmetry leads to elimination of the S_4, the C_2’, and the σ_d symmetry elements (Fig. 2.2.40).

T_h group (symmetry elements: E, *i*, $4S_6$, $4C_3$, $3C_2$, $3s_h$) can also be considered as a result of reducing **O_h** group symmetry (E, *i*, $4S_6$, $4C_3$, ~~$3S_4$, $3C_4$, $6C_2$,~~ 3 C_2, $3\sigma_h$, ~~$6\sigma_d$~~) by eliminating C_4, S_4 and some C_2 axes and s_d planes

Symmetry operations: *i*, 8 S_6, 8 C_3, 3 C_2, 3 σ_h,

Figure 2.2.40 Symmetry operations in $Fe(py)_6^{2+}$ in the point group T_h

The I_h Point Group

The two remaining platonic solids, the icosahedron and the dodecahedron, belong both to the icosahedral point group I_h. This is despite they are made of different polygons (Fig. 2.2.41).

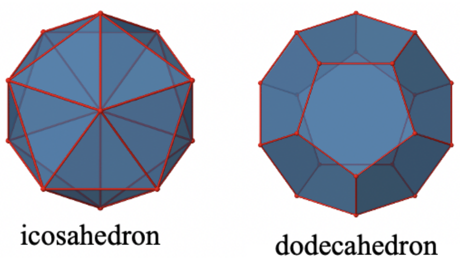


Figure 2.2.41 The icosahedron and dodecahedron of the I_h point group (Attribution: symotter.org/gallery)

Because they belong to the same point group, they have exactly the same symmetry operations. An example for a molecule with icosahedral shape is the molecular anion $B_{12}H_{12}^{2-}$. An example for a molecule with dodecahedral shape is the dodecahedrane $C_{20}H_{20}$.

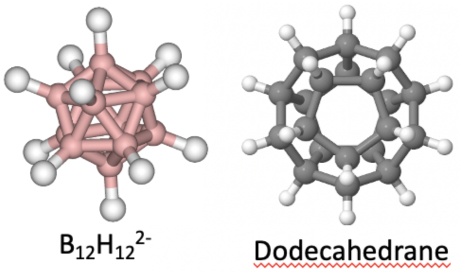


Figure 2.2.42 $B_{12}H_{12}^{2-}$ and the dodecahedrane (Attribution: wikiwand.com https://upload.wikimedia.org/Wikipedia/commons/thumb/9/97/Dodecaborane-3D-balls.png/640px-Dodecaborane-3D-balls.png)

Let us determine the symmetry elements and symmetry operations for the example of the icosahedron. We could also use the dodecahedron, and the results would be the same. The principal axes of the icosahedron are the C_5 axes. You can see one of them, going through the center of the pnetagon comprised of five triangular faces below (Fig. 2.2.43).

Figure 2.2.43 One of the C_5 axes of the icosahedron stands perpendicular to the paper plane going through the center of a pentagon of the icosahedron (Attribution: symotter.org/gallery)

You can understand that there is a C_5 when considering that there are five triangular faces making a pentagon. The C_5 axis sits in the center of the pentagon. We can see that when we rotate around this C_5 axis, then the produced icosahedron superimposes the original one. The C_5 axis goes through two opposite vertices of the icosahedron. Because an isosahedron has 12 vertices, there must be six C_5 axes overall. You can see all of them below (Fig. 2.2.44).

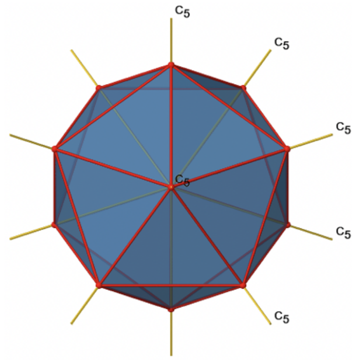


Figure 2.2.44 The C_5 axes of the icosahedron (Attribution: symotter.org/gallery)

There are four unique symmetry operations associated with a single C_5 axis, namely the C_5^1, the C_5^2, the C_5^3, and the C_5^4. The C_5^5 is the same as the identity. Because there are six C_5 axes, there are overall 6x4=24 C_5 symmetry operations (Fig. 2.2.45).

Symmetry elements: 6 C_5
Symmetry operations: 24 C_5
In detail: 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4 (C_5^5=E)

Figure 2.2.45 Symmetry operations associated with the C_5 axis of icosahedral point group

In addition, there are C_3 axes. One of them is shown below, and you can see that it passes through the centers of two opposite triangular faces (Fig. 2.2.46).

Figure 2.2.46 One of the C_3 axes of the icosahedral point group (Attribution: symotter.org/gallery)

As one rotates by 120° the atoms on the triangular faces change their position, and the resulting icosahedron superimposes the original one. As the name icosahedron says, there are twenty faces overall.

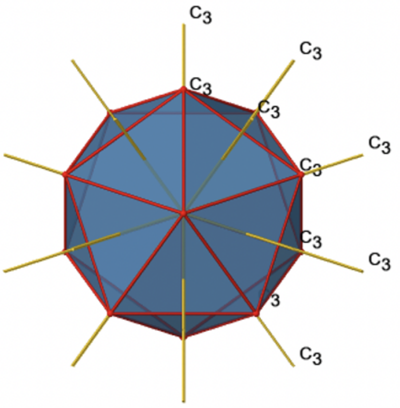
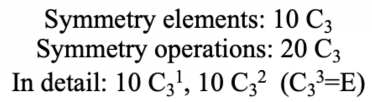


Figure 2.2.47 The C_3 axes of the icosahedral point group (Attribution: symotter.org/gallery)

Because one C_3 passes through two opposite axes, there are 20/2=10 C_3 axes overall (Fig. 2.2.47). Each C_3 axis is associated with two symmetry operations, namely C_3^1, and C_3^2. Thus, there are overall 10x2=20 C_3 symmetry operations.



Symmetry elements: 10 C_3
Symmetry operations: 20 C_3
In detail: 10 C_3^1, 10 C_3^2 (C_3^3=E)

Figure 2.2.48 Symmetry operations of the C_3 axes of the icosahedral point group

There are also C_2 axes (Fig. 2.2.49). They pass through the centers of two opposite edges of the icosahedron. Rotating around the C_2 axis shown makes the icosahedron superimpose.

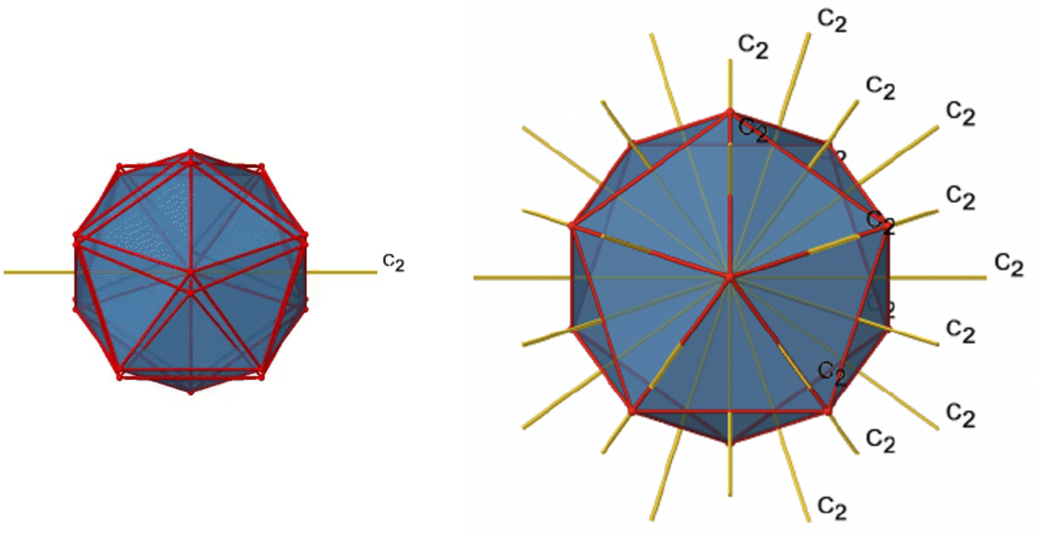
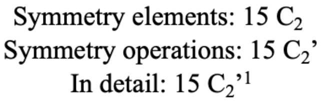


Figure 2.2.49 The C_2 axes of the icosahedral point group (Attribution: symotter.org/gallery)

An isosahedron has overall 30 edges. Because one C_2 axis passes through the centers of two opposite edges, we can understand that there are 30/2=15 C_2 axes. There is one unique C_2 operation per axis, and therefore there are 15 C_2 operations (Fig. 2.2.50).



Symmetry elements: 15 C_2
Symmetry operations: 15 C_2'
In detail: 15 $C_2'^1$

Figure 2.2.50 Symmetry operations associated with the C_2 axes of the icosahedral point group

We have now found all proper rotations. Let us look for mirror planes, next. You can see a mirror plane below (Fig. 2.2.51).

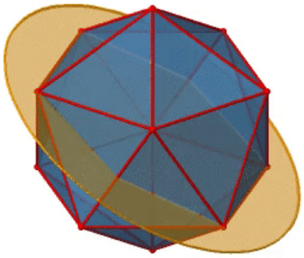


Figure 2.2.51 A mirror plane in the icosahedral point group (Attribution: symotter.org/gallery)

It contains two opposite edges. It also bisects two other edges. An icosahedron has overall 30 edges, therefore there are 30/2=15 mirror planes. You can see all of them below (Fig. 2.2.52 and Fig. 2.2.53)).

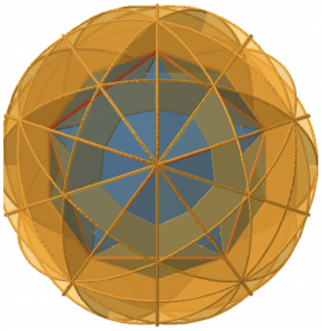


Figure 2.2.52 All the mirror planes in the icosahedral point group (Attribution: symotter.org/gallery)

Symmetry elements: 15 σ
Symmetry operations: 15 σ

Figure 2.2.53 Symmetry operations of the mirror planes in the icosahedral point group

The icosahedron also has an inversion center in the center of the icosahedron (Fig. 2.2.54 and Fig. 2.2.55)).

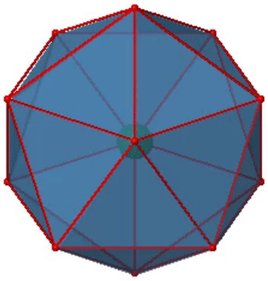


Figure 2.2.54 The inversion center in the icosahedron (Attribution: symotter.org/gallery)

As we carry out the associated, one symmetry operation, all points in the isosahedron move through the inversion center to the other side.

Symmetry elements: i
Symmetry operations: i

Figure 2.2.55 Symmetry operations of the inversion planes in the icosahedral point group

Let us now look for improper rotations. The improper rotational axes with the highest order are S_{10} axes. They are located in the same position as the C_5 axes, and go through two opposite corners (Fig. 2.2.56).

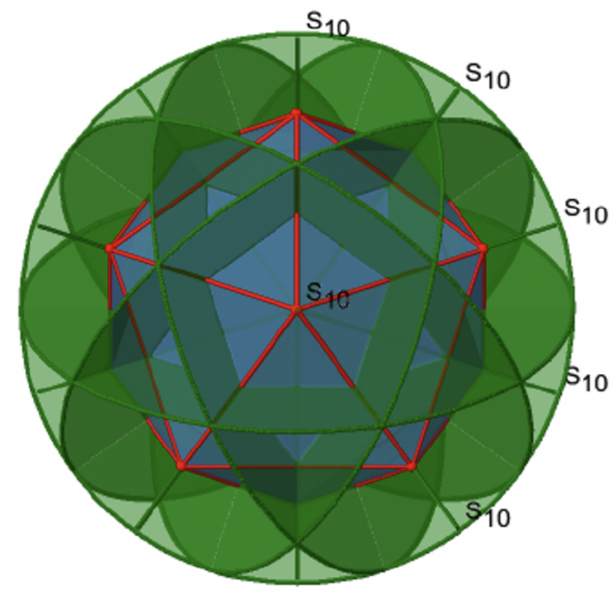


Figure 2.2.56 The S_{10} improper rotational axes in the icosahedral point group (Attribution: symotter.org/gallery)

The S_{10} exists because in an icosahedron there are pairs of co-planar pentagons that are oriented staggered relative to each other. The rotation around 36° brings one pentagon in eclipsed position relative to the other, but superposition is only achieved after the reflection at the mirror plane perpendicular to the rotational axis. Because one S_{10} passes through two opposite vertices, and there are 12 vertices there are 6 S_{10} improper axes. For each axis there are four unique symmetry operations, the S_{10}^1, the S_{10}^3, the S_{10}^7, and the S_{10}^9. Therefore, there are overall 4x6=24 operations possible (Fig. 2.2.57).

Symmetry elements: 6 S_{10}
Symmetry operations: 24 S_{10}
In detail: 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9 (S_{10}^2=C_5^1, S_{10}^4=C_5^2, S_{10}^5=i, S_{10}^6=C_5^3, S_{10}^8=C_5^4)

Figure 2.2.57 Symmetry operations associated with the S_{10} improper rotational axes of the icosahedral point group

Are the lower order improper rotational axes? Yes, there are S_6 axes that pass through the centers of two opposite triangular faces (Fig. 2.2.58). This symmetry element exists because the two triangular faces are in staggered orientation to each other. Rotation alone brings one face in eclipsed orientation relative to the other, but reflection at a mirror plane perpendicular to the axis is required to achieve superposition. The S_6 axes are in the same location as the C_3 axes.

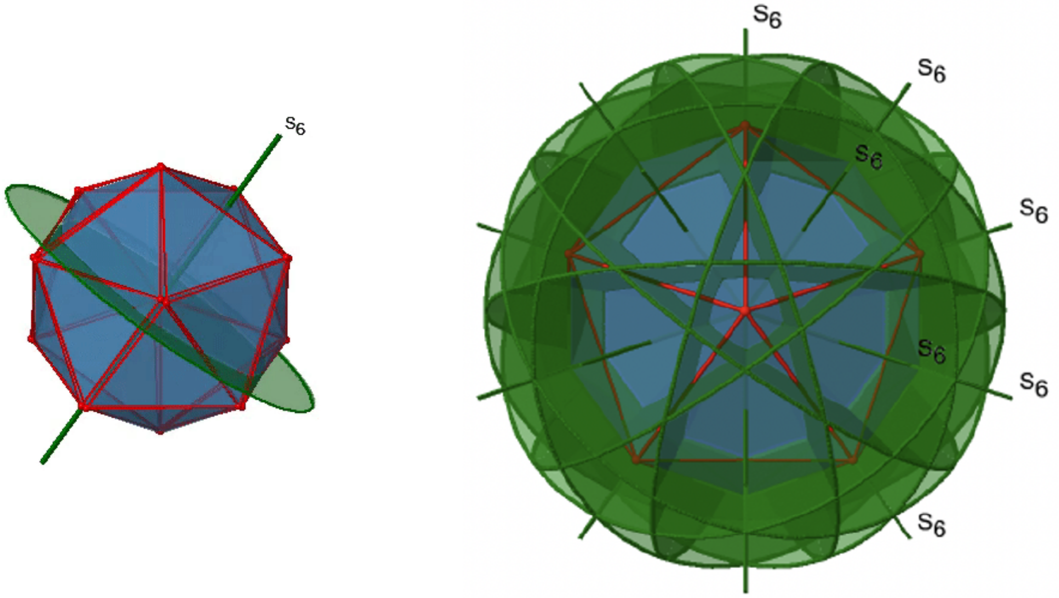
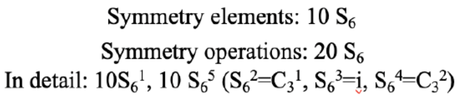


Figure 2.2.58 The S_6 rotation-reflections in the icosahedral point group (Attribution: symotter.org/gallery)

There are 10 S_6 axes because there are twenty faces and one axis passes through two opposite faces. Only the S_6^1 and the S_6^5 operations are unique S_6 operations, all others can be expressed by simpler operations. Therefore there are overall 10 S_6^1+10 S_6^5 = 20 S_6 operations (Fig. 2.2.59).



Symmetry elements: 10 S_6

Symmetry operations: 20 S_6

In detail: 10S_6^1, 10 S_6^5 (S_6^2=C_3^1, S_6^3=i, S_6^4=C_3^2)

Figure 2.2.59 Symmetry operations associated with the S_6 rotation-reflections in the icosahedral point group

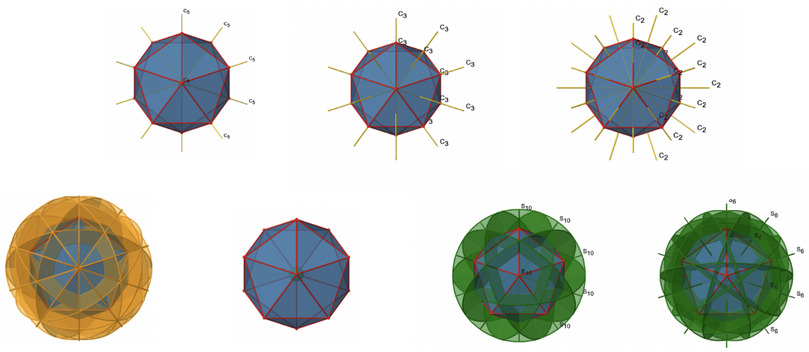
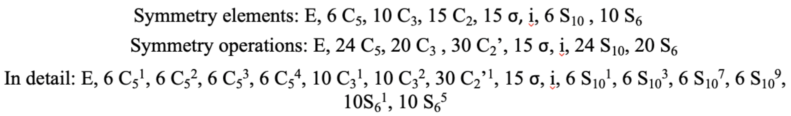


Figure 2.2.60 The symmetry elements of the icosahedral point group (Attribution: symotter.org/gallery)

We have now found all symmetry operations for the I_h symmetry. There are overall 120 operations making the point group I_h the point group with the highest symmetry (Fig. 2.2.60 and Fig. 2.2.61).



Symmetry elements: E, 6 C_5, 10 C_3, 15 C_2, 15 σ, i, 6 S_{10} , 10 S_6

Symmetry operations: E, 24 C_5, 20 C_3 , 30 C_2’, 15 σ, i, 24 S_{10}, 20 S_6

In detail: E, 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4, 10 C_3^1, 10 C_3^2, 30 C_2’^{1}, 15 σ, i, 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9, 10S_6^1, 10 S_6^5

Figure 2.2.61 Summary of the symmetry operations of the icosahedral point group

Also the point group I_h has a rotational subgroup.

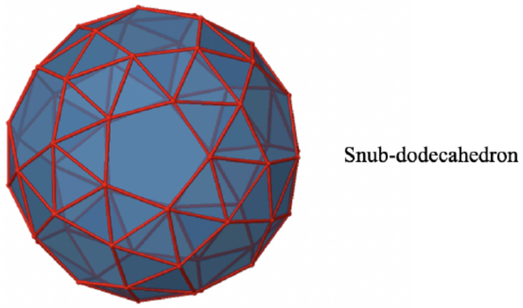
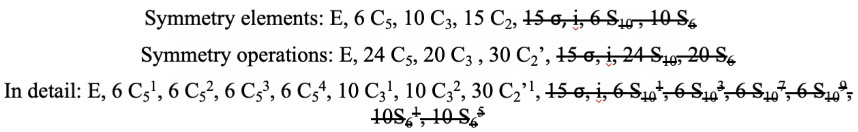


Figure 2.2.62 The snub-dodecahedron belonging to the point group I (Attribution: symotter.org/gallery)

It is called I. An example of an object with this symmetry is the snub-dodecahedron (Fig. 2.2.62). It has the identity, and all the proper rotation operations of the point group O_h, but the inversion, the rotation-reflections, and the mirror planes are eliminated (Fig. 2.2.63).



Symmetry elements: E, 6 C_5, 10 C_3, 15 C_2, ~~15 σ, i, 6 S_{10} , 10 S_6~~

Symmetry operations: E, 24 C_5, 20 C_3 , 30 C_2’, ~~15 σ, i, 24 S_{10}, 20 S_6~~

In detail: E, 6 C_5^1, 6 C_5^2, 6 C_5^3, 6 C_5^4, 10 C_3^1, 10 C_3^2, 30 C_2’^{1}, ~~15 σ, i, 6 S_{10}^1, 6 S_{10}^3, 6 S_{10}^7, 6 S_{10}^9, 10S_6^1, 10 S_6^5~~

Figure 2.2.63 Symmetry operations of the icosahedral rotational sub group I (relative to I_h)

Cyclic Point Groups

After having discussed high and low symmetry point groups, let us next look at cyclic point groups. They have the property that they have only a single proper n-fold rotational axis, but no other proper axes. In the most simple case they do not have any additional symmetry element such as mirror planes or rotation-reflections. These point groups are denoted C_n whereby n is the order of the proper axis. An example is the hydrogen peroxide molecule H_2O_2 (Fig. 2.2.64).

Figure 2.2.64 The C_2 rotational axis of hydrogen peroxide

It has a so-called roof-structure due to its non-planarity. One hydrogen atom points toward us, and the other points away from us. This structure is due to the two electron-lone pairs at each sp^3-hybridized oxygen atom. These electron-lone pairs consume somewhat more space than the H atoms, and there is electrostatic repulsion between the electron lone pairs. Therefore, the electron lone pairs at the different oxygen atoms try to achieve the greatest distance from each other. This forces the H-atoms out of the plane, leading to the roof-structure of the hydrogen peroxide. Because the H_2O_2 molecule is not planar, it only has a single C_2 axis, but no other symmetry element besides the identity. The C_2 axis passes through the center of the O-O bond. Execution of the C_2 operation swaps up both the O and the H atoms.

$$C_2 - H_2O_2 \ (\textbf{elements}: E, C_2)$$

Figure 2.2.65 Symmetry elements in the hydrogen peroxide molecule

Definition: Cyclic Groups C_n

Cyclic groups have one rotational axiPyramidal Groups

Another class of groups are the pyramidal groups, denoted C_{nv}. They have n vertical mirror planes containing the principal axis C_n in addition to the principal axis C_n. Generally molecules belonging to pyramidal groups are derived from an n-gonal pyramid. An n-gonal pyramid has an n-gonal polygon as the basis which is capped (Fig. 2.2.66).

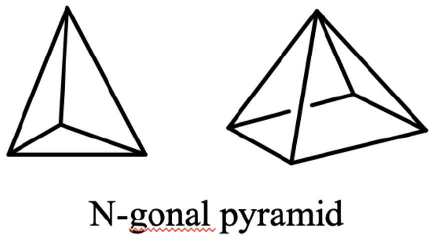


Figure 2.2.66 n-gonal pyramids (n=3,4)

For example a trigonal pyramid has a triangular basis which is capped, a tetragonal pyramid has a square which is capped, and so on. The proper axis associated with a specific pyramid has the order n and goes through the tip of the pyramid and the center of the polygon. An example of a molecule with a trigonal pyramidal shape is the NH_3 (Fig. 2.2.67).

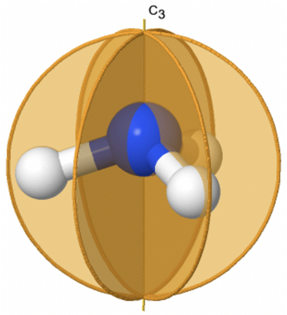


Figure 2.2.67 C_3 axis and vertical mirror planes in NH_3

The three H atoms form the triangular basis of the pyramid, which is capped by the N atom. The NH_3 molecule belongs to the point group C_{3v}. The C_3 axis goes though the N atom which is the tip of the pyramid, and the center of the triangle defined by the H atoms. There are three vertical mirror planes that contain the C_3 axis. Each of them goes through an N-H bond (Fig. 2.2.68).

$$C_{3v} - NH_3 \ (\textbf{elements}: E, C_3, 3\sigma_v)$$

Figure 2.2.68 Symmetry elements in NH_3

Definition: Pyramidal Groups C_{nv}

Pyramidal groups have n vertical plane(s) in addition to the principal axis C_n.

The Linear Group $C_{\infty v}$

A special n-gonal polygon is the cone. A cone can be conceived as an n-gonal pyramid with an infinite number *n* of corners at the base (Fig. 2.2.69).

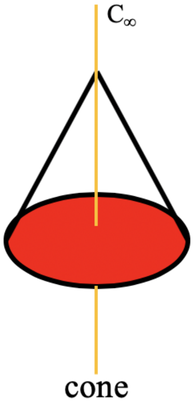


Figure 2.2.69 Cone having a proper rotational axis with infinite order.

In this case the order of the rotational axis that passes through the tip of the cone and the center of the circular basis is infinite. This also means that there is an infinite number of vertical mirror planes that contain the C_∞ axis (Fig. 2.2.71). The point group describing the symmetry of a cone is called the linear point group $C_{\infty v}$. Polar, linear molecules such as CO, HF, N_2O, and HCN belong to this point group. You can see the HCN molecule with its C_∞ axis and its infinite number of vertical mirror planes below (Fig. 2.2.70).

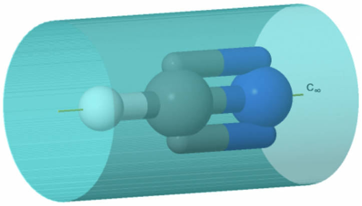


Figure 2.2.70 C_∞ axis of the HCN molecule

The infinite number of mirror planes, shown in blue are forming a cylinder that surround the molecule.

(**elements**: E, C_∞, $\infty\sigma_v$)

Figure 2.2.71 Symmetry elements of polar linear molecules

Definition: Linear group $C_{\infty v}$

The linear group $C_{\infty v}$ has an infinite number of vertical mirror planes containing a C_∞ axis

Reflection Groups

If we add a horizontal mirror plane instead of n vertical mirror planes to a proper rotational axis C_n we arrive at a the reflection point group type C_{nh}. The presence of the horizontal mirror planes also generates an improper axis of the order n. This is because when one can rotate and reflect perpendicular to the rotational axes independently, then it must also be possible to do it in combination. An example of a molecule belong to a reflection group is the trans-difluorodiazene N_2F_2 (Fig. 2.2.72).

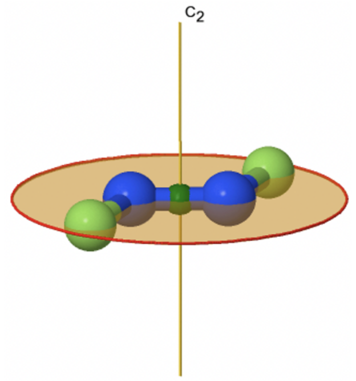


Figure 2.2.72 C_2 axis and horizontal mirror plane in trans-N_2F_2

It is a planar molecule with a C_2 axis going through the middle of the N-N double bond, and standing perpendicular to the plane of the molecule. The horizontal mirror plane stands perpendicular to the C_2 axis, and is within the plane of the molecule. There is an additional inversion center because an S_2 must exist which is the same as an inversion center. The inversion center is in the middle of the N-N bonds. Overall, the molecule has the symmetry C_{2h}.

C_{2h} – *trans*-F-N=N-F (**elements**: E, C_2, *i*, σ_h)

Figure 2.2.73 Symmetry elements in N_2F_2

Definition: Reflection Group C_{nh}

A reflection group has a horizontal plane perpendicular to the principal axis C_n

Dihedral Groups

Dihedral groups are point groups that have n additional C_2 axes that stand perpendicular to the principal axis of the order n. If there are no other symmetry elements, then the point group is of the type D_n.

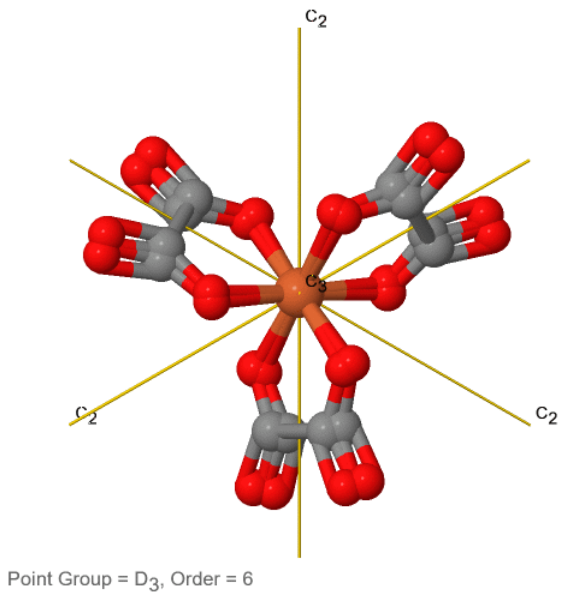


Figure 2.2.74 The tris-oxolato ferrate (3-) ion and its symmetry elements

For example in the point group D_3 there is a C_3 principal axis, and three additional C_2 axes, but no other symmetry element (Fig. 2.2.75). The tris-oxolato ferrate (3-) ion belongs to this point group (Fig. 2.2.75). You can see that the C_3 axis stands perpendicular to the paper plane, and there are three C_2 axes in the paper plane.

D_3 – (**elements**: E, C_3, $3C_2$)

Figure 2.2.75 Symmetry elements in the dihedral group D_3

Definition: Dihedral Groups D_n

In a point group of the type D_n there is a principal axis of order n, n C_2 axes, but no other symmetry elements.

If a horizontal mirror plane is added to the C_n axis and the n C_2 axes we arrive at the prismatic point groups D_{nh} (Fig. 2.2.76). The addition of the horizontal mirror plane generates further symmetry elements namely an S_n and n vertical mirror planes.

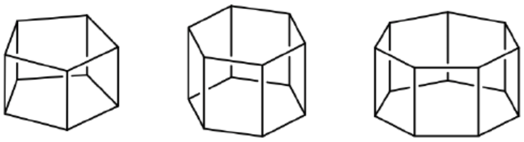


Figure 2.2.76 N-gonal prisms belong to the point group type D_{nh}

Generally, molecules belonging to this point group derive from n-gonal prisms. The order of the principal axis is the same as the number of corners of the polygons the prism are made of.

Definition: Prismatic Groups D_{nh}

In prismatic point groups there is a horizontal mirror plane perpendicular to the principal axis C_n. There are also n C_2 axes.

An example for a molecule belonging to a prismatic point group is PF_5 (Fig. 2.2.77).

Figure 2.2.77 The PF_5 molecule belonging to the point group D_{3h} and its symmetry elements.

It has a trigonal bipyramidal shape. The C_3 axis goes through the axial F atoms of the molecule, and the three C_2 axes go through the three equatorial F atom. The horizontal mirror plane stands perpendicular to the principal C_3 axis and is located within the equatorial plane of the molecule. In addition, there are the vertical mirror planes that contain the C_3 axis, and go through the three equatorial P-F bonds. There is also an S_3 axis which superimposes the C_3 axis. In sum:

$$D_{3h} - PF_5\ (\textbf{elements}: E, C_3, 3C_2, \sigma_h, S_3, 3\sigma_v)$$

Figure 2.2.78 Symmetry elements of PF_5

A special case of a D_{nh} group is the linear group $D_{\infty h}$. An object that has this symmetry is a cylinder. A cylinder can be conceived as a prism with an infinite number of vertices. Thus, the principal axis that passes through a cylinder has infinite order. Because of the infinite order of the principal axis, there is an infinite number of C_2 axes that stand perpendicular to the principal axis. You can see one such C_2 going though the cylinder (Fig. 2.2.79).

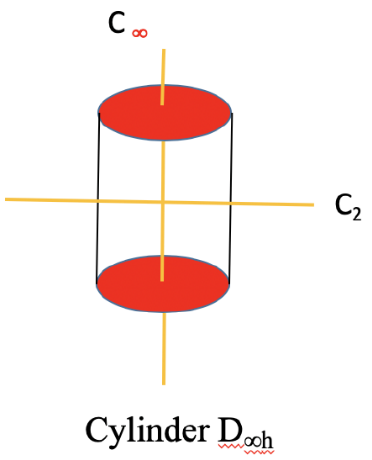


Figure 2.2.79 Cylinder as an example of linear group $D_{\infty h}$

There is now also an improper axis of infinite order, as well as an infinite number of vertical mirror planes. Non-polar linear molecules like H_2, CO_2, and acetylene C_2H_2 belong to the point group $D_{\infty h}$. You can see the C_∞ axis passing through a CO_2 molecule below (Fig. 2.2.80).

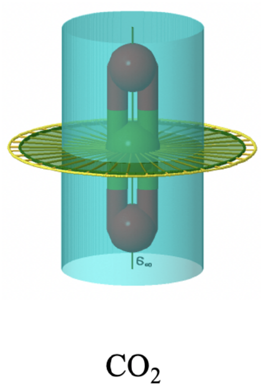


Figure 2.2.80 C_∞ in a CO_2 molecule

You can see the infinite number of vertical mirror planes as a blue cylinder. The infinite number of C_2 axes is shown a yellow lines going around the molecule. In sum:

$$E, C_\infty\ \infty\ C_2, \sigma_h, S_\infty, \infty\ \sigma_v, i$$

Figure 2.2.81 Symmetry elements of linear group $D_{\infty h}$

Definition: Linear Group D_{ooh}

In the point group $D_{\infty h}$ there is an infinite number of n C_2 axes in addition to the principal axis of infinite order, an infinite number of vertical mirror planes, and one horizontal mirror plane.

If we add n vertical mirror planes to the principal axis and the n C_2 axes, we arrive at the point group D_{nd}. The vertical mirror planes are dihedral mirror planes because they bisect the angle between the C_2 axes. An example is the ethane molecule in staggered conformation which has the symmetry D_{3d} (Fig. 2.2.82).

Figure 2.2.1 : Paste Caption Here

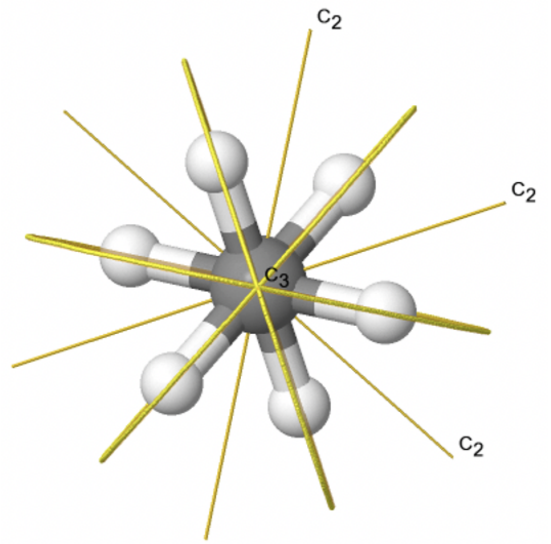


Figure 2.2.82 The ethane molecule in the staggered conformation belongs to the point group type D_{nd}

The C_3 axis goes along the C-C bond, and the $3C_2$ axes pass through the middle of the carbon-carbon bond, and bisect the angle between two hydrogens and one carbon atom. The three dihedral mirror planes pass through the C-H bonds. In addition, the ethane molecule has an S_6 axis, and an inversion center. In sum:

D_{3d} – ethane/staggered (elements: E, C_3, S_6, $3C_2$, 3 σ_d, i)

Figure 2.2.83 Symmetry elements in ethane

Definition: D_{nd}

In this point group type there are n dihedral mirror planes that contain the C_n and bisect the angle between adjacent C_2 axes

Improper Rotational Point Groups

The last class of point groups to be discussed are the improper rotation point groups. The only have one proper rotational axis, and an improper rotational axis that has twice the order of the proper rotational axis (Fig. 2.2.85). There may be an inversion center present depending on the order of the proper and improper axes. An example the tetramethylcycloocta-tetraene molecule (Fig. 2.2.84).

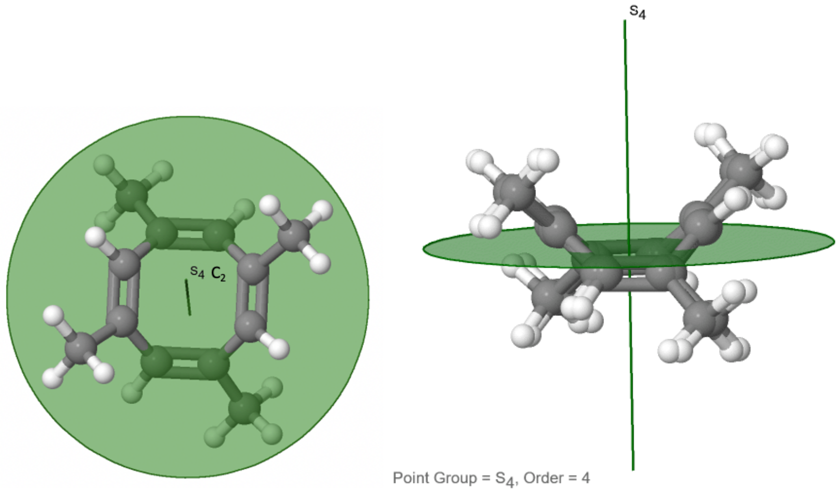


Figure 2.2.84 The S_4 and an C_2 axes of tetramethyl cycloocta-tetraene

It has an S_4 and an C_2 axis as the only symmetry elements besides the identity. Rotating by 90° alone does not superimpose the molecule because two C-C double bonds lie above the plane and two below the plane. In addition, two opposite methyl groups lie above and below the plane respectively. Therefore it needs the additional reflection to achieve superposition. There is also a C_2 axis which is in the same locations as the S_4 axis.

Symmetry elements: E, S_{2n}, C_n

May have inversion center *i*

Figure 2.2.85 Symmetry elements of improper rotational point groups

Guide for the Determination of Point Groups

With the knowledge you have, you can unambiguously identify the point group of a molecule. The key to success is that you are able to see the symmetry elements in the molecule. This takes practice. With enough practice you can identify the point group of a molecule immediately. Until, you can use guides, that you can follow to identify a point group. Such a guide asks systematic questions about the presence or absence of a symmetry element. Depending on whether you answer the question with yes or no you can follow the guide in a particular direction. Eventually, after having answered enough questions the guide will lead you to the respective point group. You can see such a chart below (Fig. 2.2.86).

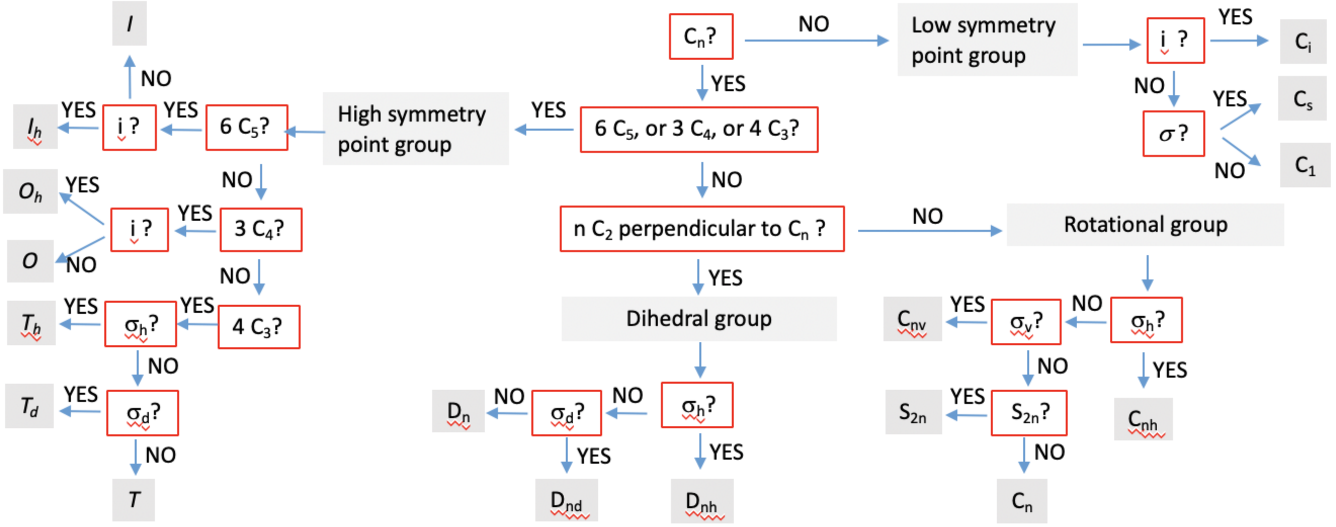


Figure 2.2.86 Guide for determination of point groups

You can first ask if there is at least one C_n present. If not, then the molecule must be in a low symmetry point group. If there is an inversion center, the point group is C_i. If not we can next ask, if there is a mirror plane. If yes it is C_s, and if not the point group is C_1. If a low symmetry point group can be ruled out, then we can ask next, if there is a high symmetry point group. This is the case when there are either $4C_3$, $3C_4$, or $6C_5$ rotational axes present, standing for tetrahedral, octahedral, and icosahedral symmetry, respectively. If there is an inversion center in case a C_5 is present, the point group is I_h. If not, it is I. Similarly, if there are $3C_4$ axes, and an inversion center, the point group must be O_h. If there is no inversion center the point group is O. If there are $4C_3$ axes, the point group must be T type. If there is a horizontal mirror plane in addition, then the point group must be T_h. If not, we can ask next is there are dihedral mirror planes. If yes, the point group is T_d, otherwise it is T. Now we have checked for all high symmetry point groups.

If a high-symmetry point groups can be ruled out, we ask if there are n C_2 axes in addition to the C_n principal axis. If this is so, then we must have a dihedral group of the D type. Next we ask, if there is a horizontal mirror plane. If yes, the point group must be D_{nh}. If not, we ask if there are dihedral mirror planes. If yes, the point group is D_{nd}. If there are no mirror planes at all, then the point group is D_n. If there are no n C_2 axes in addition to the C_n, the the group must be either a rotational group or an improper rotation group. We next ask, if there is a horizontal mirror plane. If yes, then the point group is of the type C_{nh}. If not, we ask if there are vertical mirror planes. If yes, then the point group is C_{nv}. If that is not the case, we ask if there is an S_{2n} in addition to the C_n. If yes, the point group is S_{2n}. If not, it is C_n.

Example: Dibromonaphtalene

Let us practice the point group guide by one example. Let us look at the dibromonaphtalene molecule (Fig. 2.2.87).

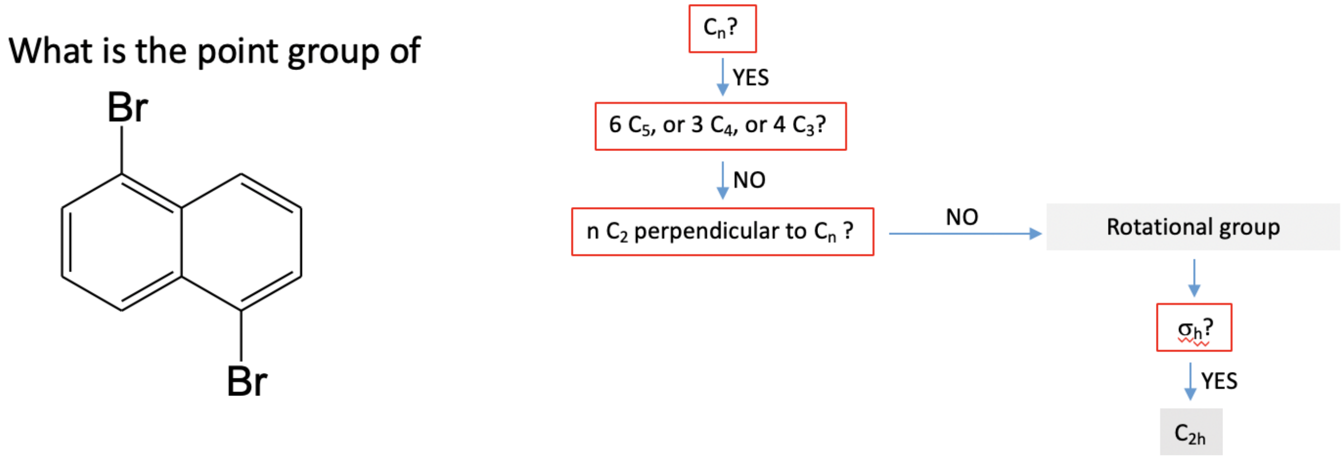


Figure 2.2.87 Guide for determining the point group of dibromonaphtalene

The first question we would ask is: Can you see at least one proper rotational axis? The answer is yes. There is a C_2 proper rotational axis that stands perpendicular to the plane of the molecule and goes through the center of the C-C bond that is shared by the two aromatic rings. Next we ask: Are the $6C_5$, $3C_4$ or $4C_3$ axes? That is clearly not the case, and thus we do not have a high symmetry point group. Next we can think about if the there are $2C_2$ axes in addition to the C_2 axes we already found. The answer is no, so the point group cannot be a dihedral group. Next, we would ask: Is there a horizontal mirror plane. This is indeed the case. There is a horizontal mirror plane in the plane of the molecule. It does not move any atoms around, but as we discussed before, a mirror does not need to do this to exist. This identifies the point group as C_{2h}.

Chiral Point Groups

A chiral point group is a point group that only has proper rotation operations in addition to the identity. This is equivalent to the statement that no improper rotations must exist in a chiral point group. This includes mirror planes and inversion centers because a mirror plane is the same as an S_1, and an inversion center is the same as an S_2. If a molecule belongs to a chiral point group, then it has a mirror image that cannot be superimposed with the original molecule. The two mirror images are called enantiomers. An example is the bromochlorofluoromethane. You can see two enantiomers separated by a dotted line (Fig. 2.2.88).

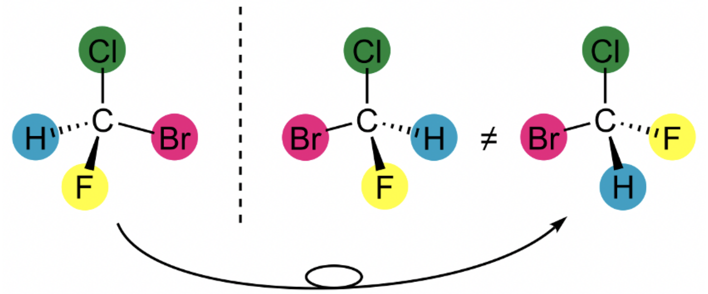


Figure 2.2.88 Chirality in bromochlorofluoromethane

The dotted line represents a mirror plane. Note that this mirror plane is not a mirror plane in the meaning of a symmetry element. You can see that the two molecules to the left and the right of the mirror plane are mirror images respective to each other. The molecules cannot be superimposed meaning that they are enantiomers. Note that the bromochlorofluoromethane molecule on the far right is not an enantiomer to the other two. It the same molecule as the enantiomer on the far left. We only need to rotate clockwise around the C-Cl axis to make the two molecules superimpose meaning that they are the same.

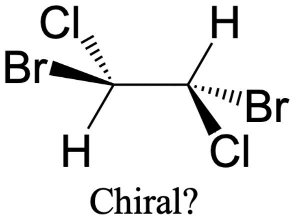


Figure 2.2.89 Dibromodichloroethane

It should be pointed out that the fact that a molecule has a carbon with four different substituents is not sufficient to make it a chiral molecule. The dibromodichloroethane molecule shown above (Fig. 2.2.89) has four different substituents around the carbon atom, but it is not chiral because there is an inversion center in the middle of the C-C bond.

Chiral High Symmetry Point Groups

Chiral groups not necessarily need to have low symmetry, in fact, the high symmetry rotational subgroups I, O, and T are chiral groups because they only have proper axes in addition to the identity (Fig. 2.2.90).

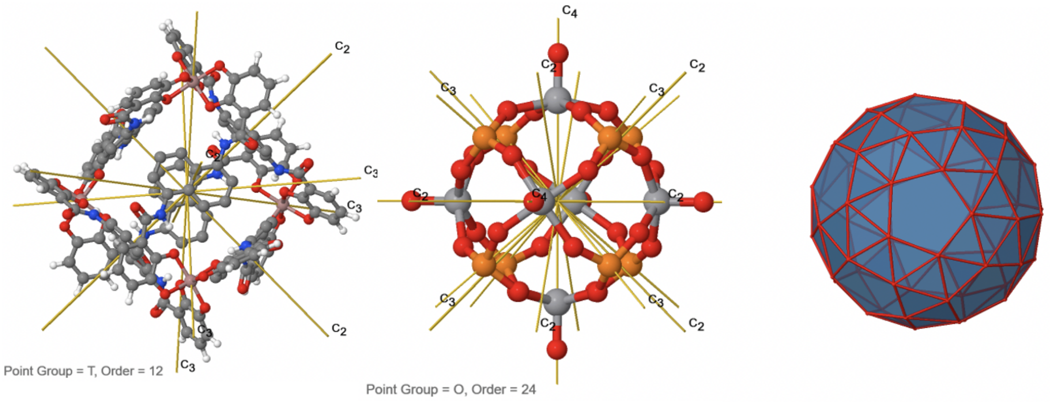


Figure 2.2.90 Objects belonging to chiral high symmetry point groups (T, O, and I from left to right).

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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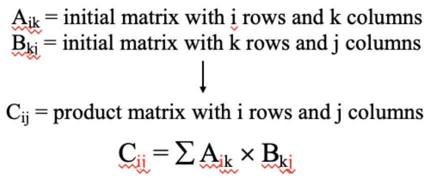
2.3: Matrix Representations of Symmetry Operations and Character Tables

Matrix Representations of Symmetry Operations

Thus, far we have looked at symmetry operations qualitatively, and determined their nature by inspection. Now let us have a look how we can describe symmetry operations from a more mathematical point of view. Why do we do this? We do this to be able to understand so-called character tables which we will later need to apply symmetry to molecular orbital theory. Generally, symmetry operations can be described by matrices. When a matrix representing a symmetry operation is multiplied with coordinates of an object, then this gives the new coordinates of the object after the symmetry operation was carried out. Therefore let us briefly review matrices, and matrix multiplications in particular. A matrix is nothing but an array of numbers arranged into rows and columns. When we multiply to matrices, we must multiply each row with each column of the matrix. When the first matrix A_{ik} has i rows and k columns and the second matrix B_{kj} has k rows and j columns, then the product matrix C_{ij} has i rows and j columns. A requirement for a matrix multiplication is that the number of columns of the first matrix is the same as the number of the rows of the second column. Otherwise, one can just not multiply each row with each column of the two matrices.



A_{ik} = initial matrix with i rows and k columns
B_{kj} = initial matrix with k rows and j columns

$\downarrow$

C_{ij} = product matrix with i rows and j columns

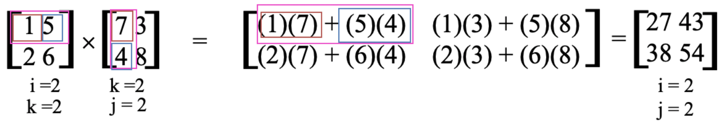
$$C_{ij} = \Sigma A_{ik} \times B_{kj}$$

Figure 2.3.1 Review on multiplying matrices

Let us do this by a few examples.

Example 1 of Matrix Multiplication

In the first example we multiply two 2x2 matrices, meaning that they both have two rows and two columns (Fig. 2.3.2). First, we need to check if the two matrices can be multiplied. We can see that the number columns of the first matrix is 2, and the number of rows of the second matrix is also 2. Therefore, we can multiply the two matrices.



$$\underset{\substack{i=2\\k=2}}{\begin{bmatrix}1&5\\2&6\end{bmatrix}} \times \underset{\substack{k=2\\j=2}}{\begin{bmatrix}7&3\\4&8\end{bmatrix}} = \begin{bmatrix}(1)(7)+(5)(4) & (1)(3)+(5)(8)\\(2)(7)+(6)(4) & (2)(3)+(6)(8)\end{bmatrix} = \underset{\substack{i=2\\j=2}}{\begin{bmatrix}27&43\\38&54\end{bmatrix}}$$

Figure 2.3.2 Example 1 of matrix multiplication

The product matrix is expected to be also a 2x2 matrix. Now we need to multiply the first row of the first matrix with the first column of the second matrix, and that means that we to multiply 1x7 and 5x4. The sum of 1x7+5x4=27 gives us the first character of the first row of the product matrix. Next, we multiply the first row of the first matrix with the second column of the second matrix. So we have to multiply 1x3 and 5x8. The sum of the two products gives the second character of the first row of the product matrix. Because the second matrix has no additional column, there is no further column with which the first row of the first matrix could be multiplied. Therefore, we now go to the second row of the first matrix, and multiply it with the first column of the second matrix. This gives the products 2x7 and 6x4. When added together, then this gives 38, and this is now the first character of the second row of the product matrix. Lastly, we multiply the second row of the first matrix with the second row of the second matrix. This gives 2x3 and 6x8 which gives 54 when added together. This is the second character in the second row of the product matrix.

Example 2 of Matrix Multiplication

In the next example, we multiply a 1x3 matrix with a 3x3 matrix (Fig. 2.3.3). This is possible because the number of the columns of the second matrix is 3, and the number of rows of the second matrix is also 3.

$$\underset{\substack{i=1\\k=3}}{[1\ 2\ 3]} \times \underset{\substack{k=3\\j=3}}{\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}} =$$

$$(1)(1)+(2)(0)+(3)(0)\quad (1)(0)+(2)(-1)+(3)(0)\quad (1)(0)+(2)(0)+(3)(1)$$

$$=\underset{\substack{i=1\\j=3}}{[1\ -2\ \ 3]}$$

Figure 2.3.3 Example 2 of matrix multiplication

The product matrix would be expected to have one row and three columns. The first matrix has only one row, so we multiply it with the three columns of the second matrix. Multiplying the first row of the first matrix with the first column of the second matrix gives (1)(1) + (2)(0) + (3)(0) = 1. This is the first character in the first, and only row in the product matrix. The multiplication of the first row of the first matrix with the second column of the second matrix is (1)(0) + (2)(-1) + (3)(0) = -2 which is the second character of the first row of the product matrix. The multiplication of the first row of the first matrix with the third column of the second matrix gives (1)(0) + (2)(0) + (3)(1) = 3. This is the third character of the first row of the product matrix. Overall, the product matrix is [1 -2 3].

Example 3 of Matrix Multiplication

In the last example let us multiply a 3x3 matrix with a 3x1 matrix (Fig. 2.3.4). Again, the number of the columns of the first matrix is the same as the number of the rows of the second matrix, they are both 3. Thus, we can multiply the two matrices.

$$\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \times \begin{bmatrix}1\\2\\3\end{bmatrix} = \begin{bmatrix}1\\-2\\3\end{bmatrix}$$

Figure 2.3.4 Example 3 of matrix multiplication

Multiplying the first row of the first matrix with the first, and in this case only column of the second matrix gives 1x1 + 0x2 + 0x3 = 1. This is the first and only character of the first row of the product matrix. The second matrix has only one column, therefore we multiply the second row of the first matrix with the only column of the second matrix in the next step. This gives 0x1 + (-1)x2 + 0x3 = -2. This the character of the second row of the product matrix. Lastly, we multiply the third row of the first matrix with the column of the second matrix. This gives 0x1 + 0x2 + 1x3 = 3. This is the character of the third row of the product matrix.

Applying Matrix Multiplications to Symmetry Operations

So what do symmetry operations have to do with the multiplication of matrices? The answer is that a symmetry operation can be described as a matrix, and the multiplication of this matrix with the matrix that represents the coordinates of the position of the points in an object, will give the new coordinates of the object after the symmetry operation has been carried out (Fig. 2.3.5).

[new coordinates] = [transformation matrix][old coordinates]

Figure 2.3.5 Relationships between symmetry operations and matrices

Example H_2O

A matrix that represents a symmetry operation is a 3x3 matrix and the matrix that describes coordinates is a 3x1 matrix. When two are multiplied then this gives a 3x1 matrix that describes the new coordinates of the object. For example, let us look at the water molecule H_2O.

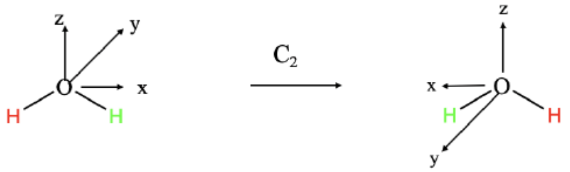


Figure 2.3.6 Transformation of coordinates in H_2O upon application of the C_2 symmetry operation

We can define a coordinate system in the water molecule so that the molecule is within the xz plane, whereby the z-axis is chosen so that it bisects the H-O-H bond angle. The y-axis would stand perpendicular and point into the board plane (Fig. 2.3.6). Any point within the water molecule, would have coordinates x,y,z that are defined by vectors $\vec{x}$, $\vec{y}$, $\vec{z}$ that point to these coordinates. For example, the center of a particular hydrogen atoms would have specific coordinates that would be described by three vectors that when added up, would point to the center of the hydrogen atom. Now let us think how the coordinates will change as we carry out a specific symmetry operations. For instance, take the C_2 symmetry operation that is carried out around the z-axis. How will the rotation change, the x,y, and z coordinates, respectively?

The x-coordinate is defined by a vector pointing into x-direction. As we rotate this vector 180° around the z-axis, it will retain its length but will point into the opposite direction (Fig. 2.3.6). Hence, we can say that the coordinate x has changed its algebraic sign, and is now –x. Now what about the y-coordinate? A vector pointing into y-direction will also be rotated around 180°, and point into the opposite direction. That means it is –y after the execution of the symmetry operation. Finally, how will the z-coordinate change? Because we rotate around z, there will not be any change to the z-vector, and thus the new coordinate z will be identical to the old coordinate z. If we represent the three vectors of the old coordinates by a 3x1 matrix $\vec{x}$, $\vec{y}$, $\vec{z}$, the new coordinates of the matrix $\vec{x}'$, $\vec{y}'$, $\vec{z}'$ are represented by the matrix -$\vec{x}$,- $\vec{y}$, $\vec{z}$. The matrix that when multiplied with the matrix for the old coordinates gives the matrix for the new coordinates, would be the matrix that would represent the symmetry operation C_2. In the case of the C_2 symmetry operation the matrix has the form below (Fig. 2.3.7).

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.7 C_2 symmetry operation for H_2O in matrix form

We can show that this matrix correctly represents the symmetry operation C_2 by applying the multiplication rules for matrices. Multiplying the first row of the matrix for C_2 with the only column of the matrix for the old coordinates would give (-1 x $\vec{x}$) + (0 x $\vec{y}$) + (0 x $\vec{z}$) = - $\vec{x}$ for the first character of the product matrix. Multiplying the second row of the matrix representation of C_2 with the only column of the matrix for the old coordinates gives (0 x $\vec{x}$) + (-1 x $\vec{y}$) + (0 x $\vec{z}$) = - $\vec{y}$ for the second character of the product matrix. Multiplication of the third row of the matrix for C_2 with the column of the matrix for the old coordinates gives (0 x $\vec{x}$) +(0 x $\vec{y}$) + (1 x $\vec{z}$) = $\vec{z}$ This proves that the matrix correctly represents the symmetry operation C_2.

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} -\vec{x} \\ -\vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.8 The symmetry operation C_2 in matrix form transforming the coordinates in H_2O

We can develop the matrix representation for the σ(xz) reflection operation along the same line we did for the C_2 operation. Let us first think about how the vectors representing the coordinate changes as the reflection operation is carried out. The vectors $\vec{x}$ and $\vec{z}$ do not change because they are within the xz mirror plane. However, the $\vec{y}$vector changes its direction as it is reflected to the other side of the mirror plane. Thus, the y-coordinate changes its algebraic sign.

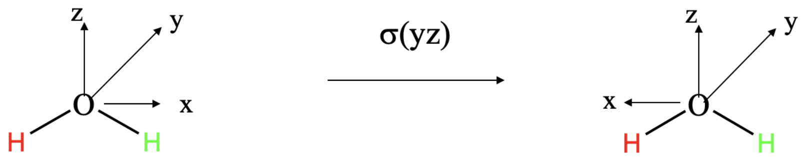


Figure 2.3.9 Transformation of coordinates of H_2O upon the application of the σ_{xz} symmetry operation

The matrix representing the new coordinates therefore has the form $\vec{x}$, - $\vec{y}$, $\vec{z}$. The matrix that when multiplied with the matrix of the old coordinates, gives the matrix of the new coordinates must be the matrix representing the symmetry operation σ_{xz}. It has the form below (Fig. 2.3.10).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.10 σ_{xz} symmetry operation in H_2O in matrix form

We could again show using the multiplication rules for matrices that multiplication of this matrix with the matrix for the old coordinates gives the matrix for the new coordinates (Fig. 2.3.11).

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x} \\ -\vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.11 the symmetry operation for σ_{xz} in matrix form transforming the coordinates of H_2O.

We can apply the same process for the σ(yz) symmetry operation. The σ(yz) mirror plane contains the coordinates y and z, and thus their vectors do not change upon the application of the symmetry operation. However, the vector $\vec{x}$ changes its direction upon reflection at the yz plane, and thus the algebraic sign of the x-coordinate changes (Fig. 2.3.12).

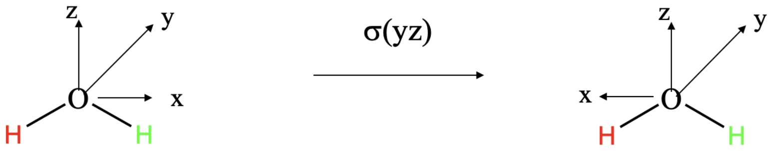


Figure 2.3.12 Transformation of the coordinates in H_2O upon the application of the σ_{yz} symmetry operation

The matrix for the new coordinates is thus $-\vec{x}$, $\vec{y}$, $\vec{z}$. In this case the matrix that when multiplied with the matrix of the old coordinates $\vec{x}$, $\vec{y}$, $\vec{z}$ gives the matrix with the new coordinates $-\vec{x}$, $\vec{y}$, $\vec{z}$ has the form below (Fig. 2.3.13).

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.13 σ_{yz} symmetry operation in H_2O in matrix form

We could again use the multiplication rules for matrices to show that the above matrix is the correct matrix representation of the symmetry operation σ(yz), Fig. 2.3.14.

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} -\vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.14 The multiplication of the σ_{yz} operation in matrix form with the coordinates of H_2O produces the new coordinates for H_2O

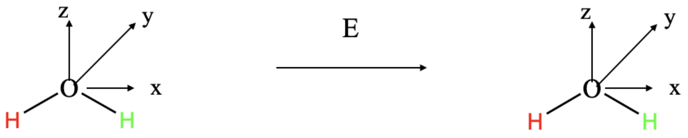


Figure 2.3.15 Transformation of the coordinates of H_2O by the E symmetry operation

Lastly, we can also determine the matrix representation of the identity operation (Fig. 2.3.15). It has the form below (Fig. 2.3.16).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.16 E symmetry operation in H_2O in matrix form

Like previously, we could use the multiplication rules to show that this matrix produces the correct matrix for the new coordinates. Since the identity does nothing to an object (Fig. 2.3.15), the new coordinates are the same as the old coordinates (Fig. 2.3.17).

$$\begin{bmatrix} \vec{x}' \\ \vec{y}' \\ \vec{z}' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix} = \begin{bmatrix} \vec{x} \\ \vec{y} \\ \vec{z} \end{bmatrix}$$

Figure 2.3.17 Multiplication of the symmetry operation E for H_2O with the coordinates of H_2O produces the correct, new coordinates for H_2O

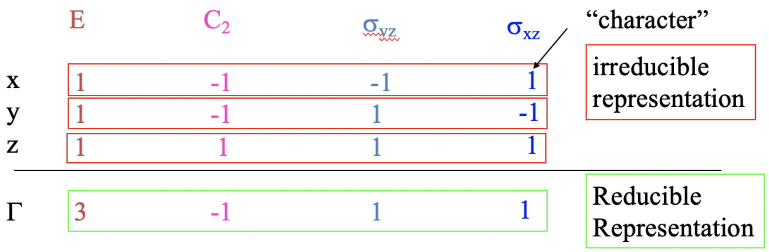
Reducible and Irreducible Representations

Let us look closer at the four matrices that we just derived (Fig. 2.3.18).

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Figure 2.3.18 The four matrices for the symmetry operations in the point group C_{2v}

It is noteworthy that all characters are zero, except those on a diagonal that goes from the top left corner in the matrix to the bottom right corner. This diagonal is called the trace of the matrix. With good justification we can say that the characters on the trace of the matrix tell us what the symmetry operation does with a coordinate. If it is a -1 the algebraic sign of the coordinate changes, if it is +1, it does not. If we write the characters of the trace of the matrices that belong to a specific coordinate on a line underneath the symmetry operations, we get what is called an irreducible representation for the specific coordinate (Fig. 2.3.19).



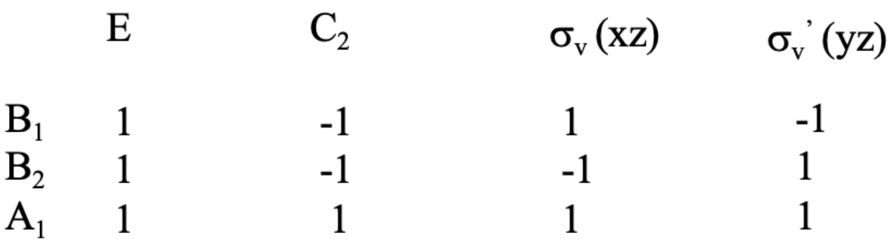
	E	C_2	σ_{yz}	σ_{xz}
x	1	-1	-1	1
y	1	-1	1	-1
z	1	1	1	1
Γ	3	-1	1	1

Figure 2.3.19 The irreducible and reducible representations associates with the coordinates in H_2O

For example, for the x-coordinate the characters of the traces of the matrices for the symmetry operations E, C_2, σ_{yz}, σ_{xz}, are 1, -1, -1, and 1, respectively. For the y-coordinate the characters would be 1, -1, 1, and -1, and for the z- coordinate they are 1, 1, 1, and 1. The use of an irreducible representation is that it tells us directly in a concise form what the symmetry operations do to a specific coordinate. The sum of two or more irreducible representations is a so-called reducible representation. If we sum up the three irreducible representations of Fig. 2.3.19, then this gives a reducible representation with the characters 1+1+1=3, (-1)+(-1)+1=-1, (-1)+1+1=1, and 1+(-1)+1=1. We will see about the use of reducible representations in a little bit.

Symmetry Types of Irreducible Representations

The specific characters in an irreducible representation determine the symmetry type of the irreducible representation. It is denoted by a capital letter with subscripts and/or superscripts. For example the irreducible representation for the x-coordinate is of the type B_1 (Fig. 2.3.20)



	E	C_2	σ_v (xz)	σ_v' (yz)
B_1	1	-1	1	-1
B_2	1	-1	-1	1
A_1	1	1	1	1

Figure 2.3.20 Symmetry types of of the irreducible representations associated with the coordinates of H_2O

B means that the symmetry is anti-symmetric with regard to the principal axis (Fig. 2.3.21).

“B” means *anti-symmetric* with regard to rotation about the principle axis.

Figure 2.3.21 The definition of the B irreducible representation

Anti-symmetric means that the algebraic sign of the coordinate changes as we rotate. In this case the principal axis is the C_2 axis. We can see that the algebraic sign changes because the character of the irreducible representation for the x-coordinate underneath C_2 is -1. The subscript 1 means that the representation is symmetric to a C_2 perpendicular to the principal axis, or if lacking to a vertical σ_v (Figure 2.3.22)

Subscript 1 means the representation is *symmetric* to a C_2 perpendicular to the principal axis or, if lacking, to a vertical plane σ_v.

Figure 2.3.22 The definition of the subscript 1 in an irreducible representation

In this case, we do not have a C_2 perpendicular to the C_2 which is our principal axis, but we have two vertical mirror planes. Symmetric means that the coordinate does not change its algebraic sign as the symmetry operation is carried out. We can see that this is true for the reflection with the lower number of primes which comes first in our considerations. It is indicated by the character +1 underneath the symmetry operation.

The irreducible representation of the y-coordinate has the symmetry type B_2 (Fig.2.3.20) The symmetry type is again B, because the character underneath C_2 is -1. The subscript is 2 in this case, and this means that the representation is *antisymmetric* to a C_2 perpendicular to the principal axis or, if lacking to a vertical plane σ_v (Fig. 2.3.23)

Subscript 2 means the representation is *antisymmetric* to a C_2 perpendicular to the principal axis or, if lacking to a vertical plane σ_v.

Figure 2.3.23 The definition of the subscript 2 in the irreducible representation

We can see that the $\sigma_v(xz)$ is anti-symmetric as indicated by the character -1 in the irreducible representation. Lastly, let us look at the symmetry type of the irreducible representation for the z-coordinate which is A_1 (Fig. 2.3.20) A means symmetric with regard to rotation around the principle axis (Fig. 2.3.24).

“A” means *symmetric* with regard to rotation about the principle axis.

Figure 2.3.24 The definition of the A irreducible representation

We can confirm the symmetric situation for the rotation around z by verifying that the character underneath the principal axis C_2 is +1.

Symmetry Types of Orbitals

Irreducible representations are more powerful than only telling you the symmetry type of a specific coordinate in a point group. More generally, they can tell the symmetry type of a mathematical function in a specific point group. Remember, that orbitals are mathematically wave functions. Thus, it should be possible to assign orbitals to a symmetry type within a given point group. Let us look for example, at the 2s and the 2p orbitals of the oxygen atom in the water molecule. Let us consider the 2s orbital first, and determine what the symmetry operations do with it. We can see that no symmetry operation changes the 2s orbital in any way, thus all characters of the irreducible representation that belongs to the orbital should be +1. We can see that this is only the case for the irreducible representation with the symmetry type A_1. Therefore we can say that the 2s orbital of the O-atom in the water molecule has the symmetry type A_1 (Fig. 2.3.25).

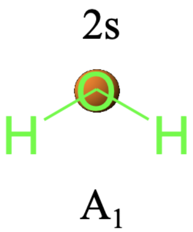


Figure 2.3.25 The 2s orbital of the O-atom in the water molecule has the symmetry type A_1

Next, let us determine the symmetry type of the $2p_z$ orbital. The $2p_z$ orbital is oriented along the z-axis around which we rotate. When carrying a C_2 operation we can see that this operation does not make any changes to the orbital. The same is true for the two reflection operations. Again, we can see that the symmetry operations do not change the $2p_z$ orbital in any way, and therefore it also must belong to the symmetry type A_1 (Fig. 2.3.26)

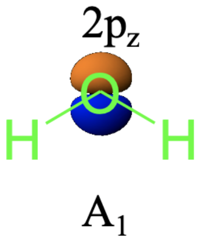


Figure 2.3.26 The 2p$_z$ orbital of the O-atom in the water molecule has the symmetry type A$_1$

For the 2p$_x$ orbital the situation is different though (Fig. 2.3.27). We can see that rotating around the C$_2$ axis changes the algebraic sign of the orbital. This means that the 2p$_x$ orbital should belong to a symmetry type which has a character of -1 for the C$_2$ operation. We can see that this can be the B$_1$ or the B$_2$ symmetry type, but not A$_1$. This rules out the A$_1$ symmetry type. We still need to decide if the symmetry type is B$_1$ or B$_2$. For B$_1$ reflection at the σ_v(xz) mirror plane would need to be symmetric, and for B$_2$ it would need to be anti-symmetric. We can see that the orbital does not change when we carry out the σ_v (xz) reflection, and thus the symmetry type must be B$_1$.

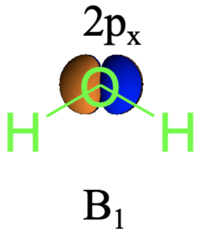


Figure 2.3.27 The 2p$_x$ orbital of the O-atom in the water molecule having the symmetry type B$_1$

Lastly let us determine the symmetry type of the 2p$_y$ orbital (Fig. 2.3.28). The 2p$_y$ orbital is oriented perpendicular to the paper plane, the blue lobe points to the front, and the orange one, hardly visible points to the back. We can see that when we rotate around 180° the orange lobe points to the front, and the blue one points to the back. That means that the wave function of the orbital has changed its algebraic sign. Therefore, it must be of B symmetry type. Which one is it? B$_1$ or B$_2$? We can see that in this case the σ_v(xz) does change the algebraic sign of the wave function because the front lobe of the orbital gets reflected to the back, and the lobe in the back gets reflected to the front. Thus, it is antisymmetric with respect to σ_v(xz) and thus it must belong to the symmetry type B$_2$.

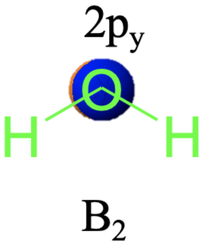
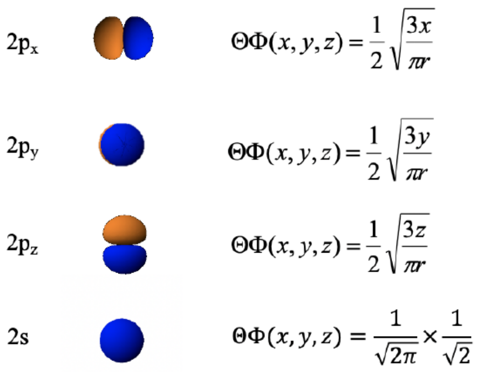


Figure 2.3.28 The 2p$_y$ orbital of the O-atom in the water molecule having the symmetry type B$_2$

We could have determined the symmetry types of the orbitals also from a more mathematical perspective. Remember when we discussed the atomic orbitals we saw that the wave function of a p$_z$ orbital is a linear function of the z-coordinate (Fig. 2.3.29). Therefore it has the same symmetry type as the z coordinate, namely A$_1$. A p$_y$ orbital is a linear function of y, therefore it has the same symmetry type as the coordinate y: B$_2$. A p$_x$ orbital is only a function of x, therefore its symmetry type is that of the coordinate x: B$_1$. The 2s orbital is not a function of any coordinate. Because of that it must belong to the symmetry type in which all characters are +1 which is the A$_1$ symmetry type in the point group C$_{2v}$.



$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{3x}{\pi r}}$$

$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{3y}{\pi r}}$$

$$\Theta\Phi(x,y,z)=\frac{1}{2}\sqrt{\frac{3z}{\pi r}}$$

$$\Theta\Phi(x,y,z)=\frac{1}{\sqrt{2\pi}}\times\frac{1}{\sqrt{2}}$$

Figure 2.3.29 The angular wave functions of the 2s and 2p orbitals in cartesian coordinates.

By the same means we can also determine the symmetry type of the d orbitals of the O atom in H_2O. They are not occupied, and not involved in the bonding, but nonetheless they are possible states for the electrons. Let us determine them using the table below (Fig. 2.3.30)

			xz	yz
C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Figure 2.3.30 Character table for the point group C_{2v}

Does the $3d_{z^2}$ – orbital change when the symmetry operations are carried out (Fig. 2.3.31)? No, it does not! Therefore, it has the symmetry type A_1.

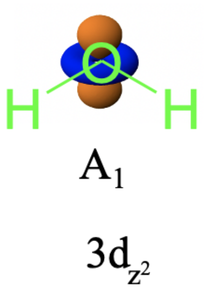


Figure 2.3.31 The $3d_{z^2}$ orbital of the O atom of the water molecule has the symmetry type A_1

What about the $3d_{xz}$? The $3d_{xz}$ orbital changes its algebraic sign when the C_2 operation is carried out, but not when the reflections are carried out. Therefore, it is of B_1 symmetry type (Fig. 2.3.32).

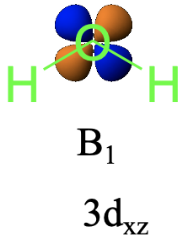


Figure 2.3.32 The $3d_{xz}$ orbital of the O atom of the water molecule has the symmetry type B_1

The $3d_{x^2-y^2}$-orbital also does not change when the symmetry operations are executed, thus it is of symmetry type A_1 (Fig. 2.3.33)

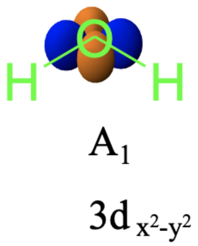


Figure 2.3.33 The $3d_{x^2-y^2}$ orbital of the O atom of the water molecule has the symmetry type A_1

For the d_{yz} orbital rotation and the $\sigma_v(xz)$ reflection changes the algebraic sign, therefore it is B_2 (Fig. 2.3.24).

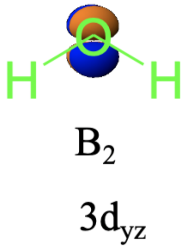


Figure 2.3.34 The $3d_{yz}$ orbital of the O atom of the water molecule has the symmetry type B_2

For the $3d_{xy}$ we can see that rotation does not change the orbital, but the $\sigma_v(xz)$ reflection does. This means that the symmetry type must be A_2 (Fig. 2.3.35).

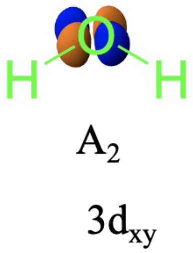


Figure 2.3.35 The $3d_{xy}$ orbital of the O atom of the water molecule has the symmetry type A_2

This is a new symmetry type which also belongs to the point group C_{2v}. No single coordinate is of this symmetry type, but mathematical functions that are the product of the coordinates x and y, such as the $3d_{xy}$ orbital are. Similarly, because the $3d_{z^2}$ orbital is a function of z^2 and the $3d_{z^2}$ has the symmetry type A_1 any function of z^2 has this symmetry type. Analogously, any function which is the product of the x and the z coordinate belongs to the symmetry type B_1, any function which is a function of x^2-y^2 belongs to the symmetry type A_1, and any function which is a product of y and z belongs to the symmetry type B_2.

Character Tables

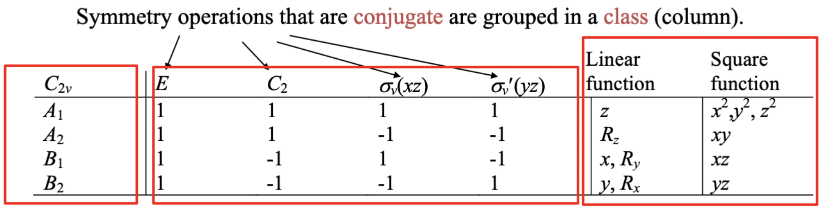
There is only a finite number of irreducible representations and symmetry types in a specific point group.

Generally, all the irreducible representations that are possible in a specific point group define the so-called *character table* of the point group Fig. 2.3.36).

Definition: Character Table

A complete set of irreducible representations in a point group defines its character table

Character tables describe what the symmetry operations of a point group do with a mathematical function. You can see the complete character table of the point group C_{2v} below (Fig. 2.3.36).



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Linear function	Square function
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Figure 2.3.36 Character table for the point group C_{2v}

It is made of several rows and columns. In the first column you can find the point group symbol to the very left, and then the symbols for the different symmetry types of the irreducible representations the point group has. Then, there are several columns with symmetry operations in the first row, and the characters for the irreducible representations below. Each of these columns is called a class. Symmetry operations that are conjugate are grouped into the same column, or the same class. For the point group C_{2v}, each operation gets its own column and that means that they are all non-conjugate. But this is not always true, in many other point groups there are several symmetry operations that are conjugate, and listed in the same column. We have already discussed qualitatively that conjugate operations transform the coordinates of an object in a similar way. Now we have a more exact definition which is that whenever the characters for the operations in their irreducible representations are the same, they belong to the same class.

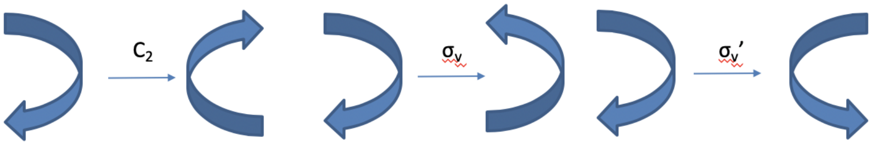


Figure 2.3.37 Transformation of a rotational vector rotating around z by the symmetry operations in the C_{2v} point group

The sum of characters underneath the identity operation E defines the dimension of the point group. For C_{2v} the dimension of the point group is 1+1+1+1=4. The order (h) of the point group is just the sum of all symmetry operations in the point group. For C_{2v} the order is 4. In the two far right columns of the character table you can find the mathematical functions that belong to the different irreducible representations. In the second column from the right linear and rotational functions are listed, and in the far right column square functions are listed. For example, the letter z is in the row associated with the symmetry type A_1. This means that any linear function of the z-coordinate has the symmetry type A_1. The letters x and y are in rows for the symmetry type B_1 and B_2 respectively. This means that any linear function of x and y has the symmetry type B_1 and B_2 respectively.

You can also see the symbols R_z, R_x, and R_y in the same column. These symbols stand for rotational functions around the z, x, and y axis respectively. R_z is in the row of the symmetry type A_2, which means that any rotational function of z has the symmetry type A_2. How can we understand that? Consider a rotational vector around z that indicates clockwise rotation (Fig. 2.3.37). If we rotate this vector by 180° counter-clockwise it will not change its direction, it will still point clock-wise, and thus the character underneath C_2 in the character table should be a 1. This rules out that the symmetry is B type, it must be either A_1 or A_2 type. We can further see that when we reflect this vector at the two vertical mirror planes, it reverses its direction, now pointing counter-clockwise. Therefore, the characters underneath the two mirror planes should be both -1. This means that the symmetry type must be A_2. If we did the same exercise with the R_x and the R_y rotational vectors we could show that they belong to the symmetry types B_2 and B_1 respectively. In the last column the square functions are listed. The row in which the function is located gives you the information about the symmetry type of the square function. For example any function of x^2, y^2, or z^2 has the symmetry type A_1, a function that is a product of x and y has the symmetry type A_2 and so forth.

Matrix Representations of Symmetry Operations in C_{3v}

Now let us go from the point group C_{2v} to the point group C_{3v} and determine the matrix representations of the symmetry operations. We will see that for this, and more generally for any point group with rotational axes with an order higher than 2, a symmetry degeneracy is possible, which means that two or even all three coordinates belong to the same symmetry type. The coordinates do not change independently upon the execution of a symmetry operation, they are linked to each other. Let us look at the ammonia molecule that belongs to the point group C_{3v}.

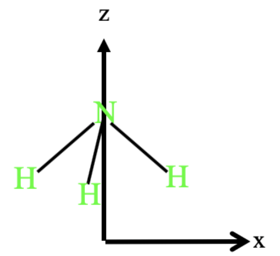
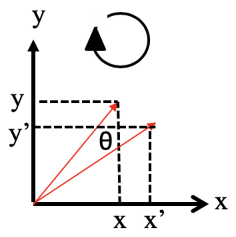


Figure 2.3.38 A suitable representation of the coordinate system in the ammonia molecule belonging to the C_{3v} point group

We can define the coordinate system so that the x-axis points to the right, the z-axis point to the to top , and the y-axis stands perpendicular to the paper plane (Fig. 2.3.38). The ammonia molecule is oriented so that its pyramid points into z-direction, and one of the three N-H bonds is within the xz plane.

Now let us see how the coordinates change when we rotate the molecule by an arbitrary general angle θ around the z-axis. In the diagram shown below, we now look along the z-axis, and the xy plane is within the paper plane (Fig. 2.3.39).



$$x' = x\cos\theta - y\sin\theta$$
$$y' = x\sin\theta + y\cos\theta$$

Figure 2.3.39 Transformation of x and y coordinates by rotation of the molecule of ammonia around an arbitrary angle θ

We can see that the rotation changes both the x and and the y coordinate together, but leaves the z-coordinate unaffected. According to trigonometry the new x-coordinate x' is x' = x cos θ - y sin θ. The new coordinate y' is y' = x sin θ + y cos θ.

The matrix representation of a symmetry operation that rotates around an arbitrary angle must be able to convert the old coordinates x,y,z into the new coordinates below (Fig. 2.3.40).

$$\begin{matrix} x\cos\theta - y\sin\theta \\ x\sin\theta + y\cos\theta \\ 1 \end{matrix}$$

Figure 2.3.40 The new coordinates (matrix form) of the NH_3 molecule after the rotation around an arbitrary angle θ

The matrix which is able to do this has the form below (Fig. 2.3.41)

$$\begin{matrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.41 Matrix representation for the rotation operation around an arbitrary angle θ

We could again use the multiplication rules for matrices to show that this matrix is the correct matrix.

The matrix that we just developed rotates around a general angle θ. What does this matrix look like in the point group C_{3v} where we rotate around 120° and 240°? Well, all we need to do is to insert the values of 120° and 240° for θ into the matrix. The sinus of 120° is -√3/2, and the sinus of 240° is √3/2. The cosinus of 120° and 240° are both -1/2 (Fig. 2.3.42).

$$\sin 120° = -\frac{\sqrt{3}}{2} \qquad \sin 240° = \frac{\sqrt{3}}{2} \qquad \text{(clockwise)}$$
$$\cos 120° = -\frac{1}{2} \qquad \cos 240° = -\frac{1}{2}$$

Figure 2.3.42 The values of sinus and cosinus for a 120° and 240° clockwise rotation

Note that these are the values for clockwise rotation. Because the C_3 operations rotate anti-clockwise, we must use the values for the 240° rotation for the C_3^1 and the values for the 120° rotation for the C_3^2 operation. Considering this, the matrix for the C_3^2 operation and the matrix for the C_3^1 operation are the matrices shown below (Fig. 2.3.43).

$$C_3^2 = \begin{matrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_3^1 = \begin{matrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.43 The matrices for the C_3^2 operation and the C_3^1 operation

We can see there is a significant difference to the all the matrices we saw before. There are non-zero characters not only on the trace of the matrix, but also on other positions within the matrix, in particular in the first two rows which represent the x and the y coordinates. This is a consequence of the fact that the x and the y coordinates are no longer independent in C_{3v}, they change in a dependent way. We say that they are degenerate.

Now can we determine the remaining symmetry operations in C_{3v}. There are three conjugate vertical mirror planes to consider. The first mirror plane stands within the xz plane and passes through the N-H bond that is within the xz plane. The matrix for it is simple. It has the form below (Fig. 2.3.44).

$$\text{1st } \sigma_v' = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.44 The matrix for the first mirror plane in the C_{3v} point group

It is straightforward to understand why the matrix has this form. Because the mirror plane is in the xz plane the coordinates x and z are not affected by the reflection at this plane. Therefore there are two +1 characters on the trace of the matrix in the rows for the x and the z coordinates, respectively, and all other characters in these rows are 0. The character in the second row on the trace of the matrix is -1 because the algebraic sign of the y-coordinate changes as we reflect at the xz plane. However, the other two mirror planes are not co-planar with any two coordinates, and for these planes the x and the y coordinates are dependent again. The matrix for the second mirror plane and the matrix for the third one are shown below (Fig. 2.3.45).

$$\text{2nd } \sigma_v' = \begin{matrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

$$\text{3rd } \sigma_v' = \begin{matrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

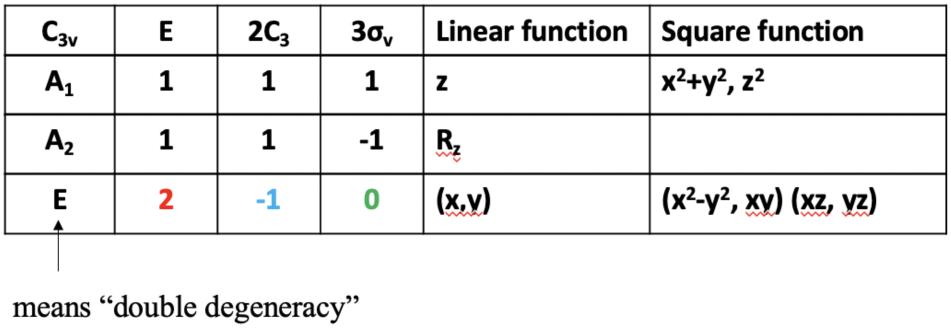
Figure 2.3.45 The matrices for the second mirror plane and the matrix for the third mirror plane in C_{3v}

We will not derive them in detail here. It is enough for us to understand here that these matrices have more complex forms with non-zero values outside the trace of the matrix because of the degeneracy of the x and y coordinates. Lastly, we should not forget the identity. Because the identity does nothing with an object, its matrix is always the matrix below in any point group (Fig. 2.3.46).

$$E = \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$$

Figure 2.3.46 The identity matrix for any point group

Because we know now the matrix representations of the symmetry operations we can understand the character table for the point group C_{3v} (Fig. 2.3.47)



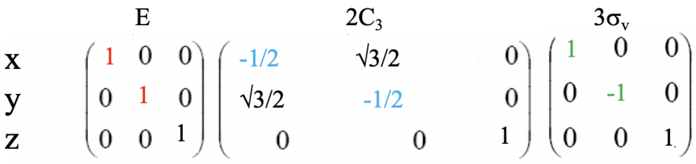
C_{3v}	E	$2C_3$	$3\sigma_v$	Linear function	Square function
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)	(x^2-y^2, xy) (xz, yz)

means “double degeneracy”

Figure 2.3.47 The character table for the point group C_{3v}

The character table has three classes for the three groups of non-conjugate symmetry operations. In the first class there is only the identity. You can see that the second class contains the C_3^1 and the C_3^2 operations, summarized as $2C_3$. The third class contains the 3 conjugate σ_v operations. In the point group C_{3v} there are three irreducible representations. The first two have the symmetry types A_1 and A_2 respectively, the third of is of type E. The last one is new to us. It stands for “double degeneracy”, and this symmetry type exists due to the double-degeneracy of the x and the y coordinate. You can see that the character table explicitly states that x and y are double-degenerate when you look into the last column of the character table. The letters x and y are in parentheses separated by a comma. The parentheses indicate the degeneracy of these two coordinates. More generally, any two functions that are linear functions of x or y are degenerate in C_{3v}. You can see that there are also other functions that are degenerate. For instance functions of x^2-y^2 and xy are degenerate. Also functions of xz and yz are degenerate.

You can see that the characters in the irreproducible representation of the E symmetry type are also unusual. Previously, we only encountered the characters 1 and -1. However, the character underneath the identity is 2, and the character in the class for the vertical mirror planes is 0. How can we understand these characters? The answer has to do with the double-degeneracy of the x and y coordinates. Because of this double-degeneracy, the characters in the irreducible representations are the sum of the characters on the trace of the matrices for the x and y coordinate. Let us check what they are. You can see the three matrices representing the three classes of the symmetry operations below (Fig. 2.3.48).



$$\begin{array}{cccc} & E & 2C_3 & 3\sigma_v \\ \begin{array}{c} x \\ y \\ z \end{array} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

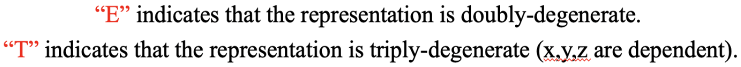
Figure 2.3.48 The three matrices representing the three classes of symmetry operations

For the identity the sum of the two characters is 1+1=2 which explains the character 2 in the irreducible representation E. For the matrix representing the C_3 operations the characters on the trace of the matrix for x and y are -1/2. When summed up -1/2 + (-1/2) gives -1 which explains the character -1 in the irreducible representation. Lastly for the matrix representing the vertical mirror planes the characters on the trace of the matrix for the x and y coordinates are 1 and -1, respectively. -1+1=0 which explains the character 0 in the irreducible representation of the symmetry type E.

The z coordinate has the symmetry type A_1 which is straightforward to understand because the characters for z on the trace of the matrices for the three different classes of symmetry operations are all 1. You can also see from the character table that there is again an irreducible representation to which no coordinate belongs to. It is the one with the symmetry type A_2. In C_{3v} only rotational functions around z have that symmetry type.

Symmetry Types of Degenerate Irreducible Representations

There are not only double-degenerate irreducible representations, denoted by a symbol E, there can also be triply-degenerate ones, indicated by a symbol T. In this case all three coordinates x, y, and z are degenerate. Triple-degeneracy does not appear in the point group C_{3v}, but in other point groups, in particular the high-symmetry point groups (Fig. 2.3.49).



“E” indicates that the representation is doubly-degenerate.
“T” indicates that the representation is triply-degenerate (x,y,z are dependent).

Figure 2.3.49 The definition of "E" and "D" irreducible representations

Both the E and T symbols can carry subscripts and primes that have specific meanings. The prime (‘) and (“) double prime in the symmetry representation label indicates “symmetric” or “anti-symmetric” with respect to σ_h, e.g. E\` or E\`\`(Fig. 2.3.50).

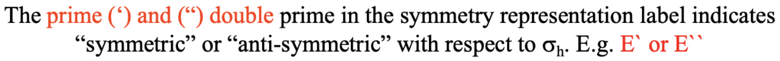

The prime (‘) and (“) double prime in the symmetry representation label indicates “symmetric” or “anti-symmetric” with respect to σ_h. E.g. E\` or E\`\`

Figure 2.3.50 The definition of prime (') and (") in irreducible representations

The subscripts g and u stand for the German words “gerade” and “ungerade” and a g and a u indicates “symmetric” or “anti-symmetric” with respect to inversion, *i*, respectively (Fig. 2.3.51).

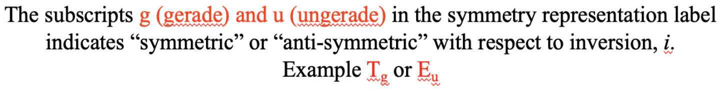
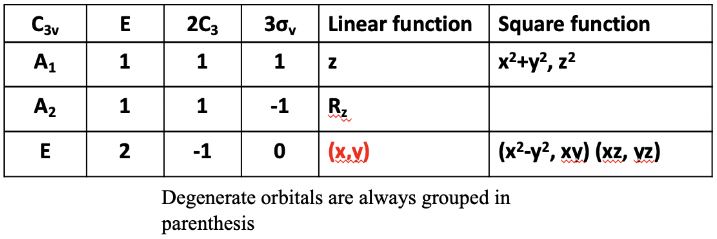

The subscripts g (gerade) and u (ungerade) in the symmetry representation label indicates “symmetric” or “anti-symmetric” with respect to inversion, *i*.
Example T_g or E_u

Figure 2.3.51 The definition of g (gerade) and u (ungerade) in irreducible representations

For example, there can be symmetry types like T_g or E_u. There are other subscripts possible, and we do not need to go through them exhaustively. It is enough to understand that they indicate a certain symmetry property in a symmetry type.

Character Tables and Degenerated Orbitals

One of the most useful properties of character tables are that one can identify degenerate orbitals very easily. For example, a quick look into the character table of the point group C_{3v} reveals that the $2p_x$ and the $2p_y$ orbital in NH_3 must be degenerate (Fig. 2.3.52).



C_{3v}	E	$2C_3$	$3\sigma_v$	Linear function	Square function
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)	(x^2-y^2, xy) (xz, yz)

Degenerate orbitals are always grouped in parenthesis

Figure 2.3.52 Character table of the C_{3v} point group

This is because the $2p_x$ orbital is a linear function of x, and the $2p_y$ orbital is a linear function of y, and linear functions of x and y are listed in parentheses in the double-degenerate irreducible representation of the type E. This double-degeneracy could also be derived by inspecting the orbitals in the NH_3 molecule, but this is not as easy as looking up the character table. You can see the $2p_x$ and the $2p_y$ orbitals in the ammonia molecule below (Fig. 2.3.53).

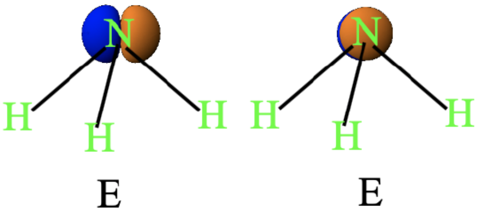


Figure 2.3.53 The $2p_x$ and $2p_y$ orbitals in ammonia

The two orbitals stand perpendicular to each other, but the NH_3 molecule has C_3 rotational symmetry. Therefore, why would the two orbitals be symmetry-degenerate? If they are degenerate, then there must be at least one symmetry operation that can interconvert the two orbitals. From the above depiction it not obvious what symmetry operation this could be.

Identifying the Double Degeneracy of $2p_x$ and $2p_y$ in NH_3

We can do a little trick to see that a reflection operation is the one that can interconvert the two orbitals. The trick is to rotate the coordinate system by 45°. You can see the ammonia molecule in the bird’s perspective below (Fig. 2.3.54).

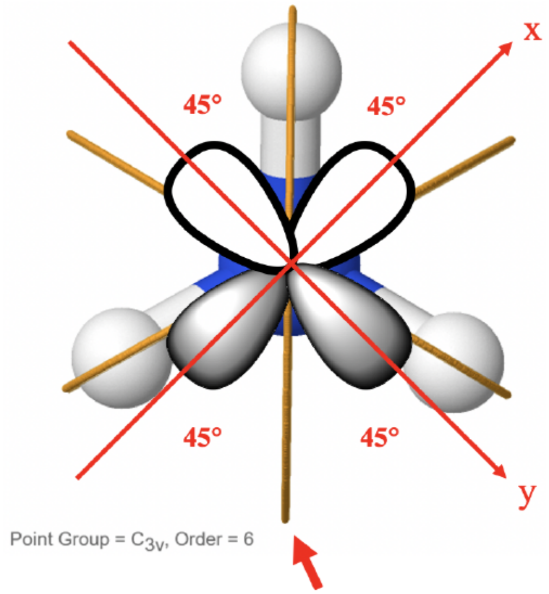


Figure 2.3.54 Ammonia in the bird's perspective with an arrow indicating the reflection plane that interconverts $2p_x$ and $2p_y$

This means that we look perpendicular to the base of the pyramid. You can see the NH_3 molecule with its three mirror planes above. Now we can choose our coordinate system so that the x and the y axes are rotated 45° with respect to one of the mirror planes. By definition, the $2p_x$ orbital must be oriented along the x-axis, and the $2p_y$ orbital must be oriented along the y-axis. You can see that one of the mirror planes, namely the one that oriented vertically, is able to interconvert the two orbitals. Upon reflection, the left and the right lobes of both orbitals will swap up their positions, so that after the symmetry operation is complete, the 2p orbitals are interconverted. Overall we can see that proving the degeneracy of two orbitals by inspection can be tricky. A quick look into the character table can tell us much more easily if two orbitals are degenerate.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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Concept Review Questions Chapter 2

Concept Review Questions

Section 1

1. What is the definition of symmetry, a symmetry operation, and a symmetry element?

2. There are five basic types of symmetry operations. Name them.

3. Of these five types of operations, two are not independent (i.e. they can be expressed by two of the three others). Name the two operations and explain why they are not independent.

4. What is the definition of the identity operation?

5. What is the definition of a proper rotational axis, and a proper rotation operation?

6. What is the definition of a mirror plane and a reflection operation?

7. What is the definition of an improper rotational axis and a rotation-reflection operation?

8. What is the definition of an inversion center and an inversion operation?

9. What is a principal axis?

10. What is the definition of a horizontal, vertical, and dihedral mirror plane, respectively?

11. What are the rules for giving axes and mirror planes primes?

12. How often do you have to carry out a proper rotation (order n), a reflection, an inversion, and a rotation-reflection (order n), respectively until you have reached the identity?

Section 2

1. What is a Platonic Solid?

2. Name the possible platonic solids.

3. Draw an icosahedron according to the rules that you have learned in class.

4. Which are the three low symmetry point groups? Which symmetry elements do they contain?

5. Name all high symmetry point groups.

6. What is a rotational subgroup?

7. What symmetry properties does a rotational point group have?

8. What symmetry properties does a dihedral point group have?

9. What different types of rotational point groups do you know?

10. What types of dihedral point group do you know?

Section 3

1. What is a matrix?

2. What are the multiplication rules for matrices?

3. Explain why transformation matrices represent symmetry operations?

4. What is an irreducible representation?

5. What is a reducible representation?

6. What is meant by an A and B symmetry type of an irreducible representation?

7. Explain briefly, why there are non-zero entries on positions other than those on the trace of the matrix for C_3 symmetry operations?

8. The x and y coordinates are dependent for C_3 rotations around the z axis in the point group C_{3v}. Explain.

9. The irreducible representation of the type E contains characters other than +1 and -1. Explain how these characters are generated?

10. Two orbitals are degenerate when a symmetry operation can interconvert them. Show how the double degeneracy of the $2p_x$ and the $2p_y$ orbitals in the point group C_{3v} can be demonstrated using this principle.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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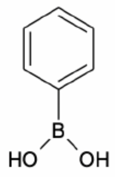
Homework Problems Chapter 2

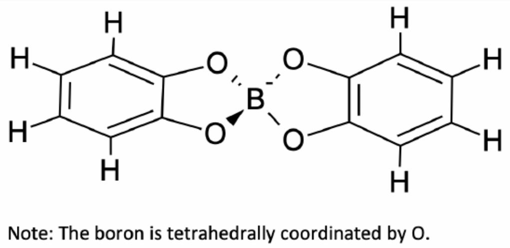
Homework Problems

Section 2

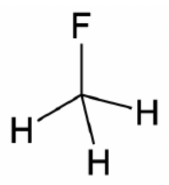
Exercise 1

Determine all symmetry elements and all unique symmetry operations of the following molecules:

a) 

b) 

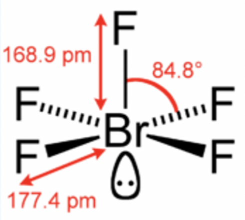
Note: The boron is tetrahedrally coordinated by O.

c) 

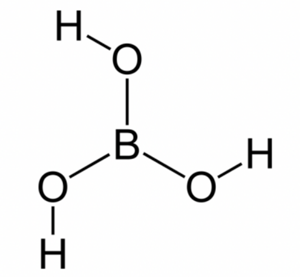
d) 

ethane (staggered conformation)

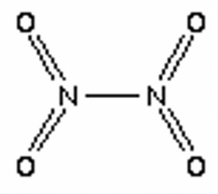
e) bromine tetrafluoride



f) Boric acid



g) Dinitrogen tetroxide



h) $PtCl_4^{2-}$ (square planar)

i) bromobenzene

j) SF_4

k) ClF_3

l) CO_2

m) benzene

Answer

a) Elements: E, C_2, σ_v, σ_v'

Operations: E, C_2, σ_v, σ_v'

b) Elements: E, S_4 C_2, $2\sigma_v$

Operations: E, S_4^1, S_4^3 C_2, $2\sigma_v$

c) Elements: E, C_3, $3\sigma_v$

Operations: E, C_3^1, C_3^2, $3\sigma_v$

d) Elements: E, C_3, 3 C_2,i, S_3, $3\sigma_d$

Operations: E, C_3^1, C_3^2, i, 3 C_2^1, S_6^1, S_6^5, $3\sigma_d$

e) Elements: E, C_4, C_2, 2 σ_v, 2 σ_v'

Operations: E, C_4^1 C_4^3, C_2^1, $2\sigma_v$, 2 σ_v'

f) Elements: E, C_3, σ_h, S_3

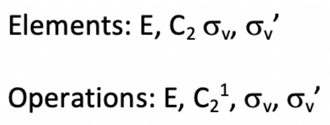
Operations: E, C_3^1, C_3^2, σ_h, S_3^1, S_3^5

g) Elements: E, C_2, C_2', C_2'', i, σ_h, $2\sigma_v$

Operations: E, C_2^1, $C_2^{\prime 1}$, $C_2^{\prime\prime 1}$, i, σ_h, $2\sigma_v$

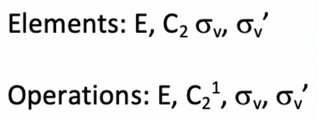
h) Elements: E, C_4, C_2, $2C_2'$. $2C_2''$, i, S_4, σ_h, $2\sigma_v$, $2\sigma_d$

Operations: E, C_4^1, C_4^3, C_2^1, $2C_2^{\prime 1}$, 2 $C_2^{\prime\prime 1}$, i, S_4^1, S_4^3, σ_h, $2\sigma_v$, $2\sigma_d$

i) 

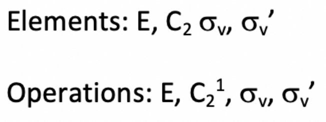
Elements: E, C_2 σ_v, σ_v'

Operations: E, C_2^1, σ_v, σ_v'

j) 

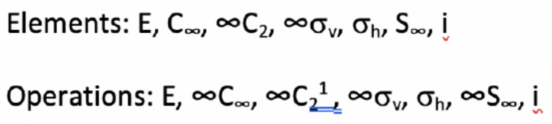
Elements: E, C_2 σ_v, σ_v'

Operations: E, C_2^1, σ_v, σ_v'

k) 

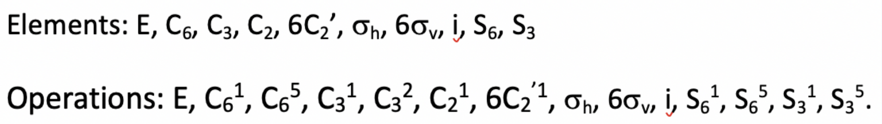
Elements: E, C_2 σ_v, σ_v'

Operations: E, C_2^1, σ_v, σ_v'

l) 

Elements: E, C_∞, ∞C_2, $\infty\sigma_v$, σ_h, S_∞, i

Operations: E, ∞C_∞, ∞C_2^1, $\infty\sigma_v$, σ_h, ∞S_∞, i

m) 

Elements: E, C_6, C_3, C_2, $6C_2'$, σ_h, $6\sigma_v$, i, S_6, S_3

Operations: E, C_6^1, C_6^5, C_3^1, C_3^2, C_2^1, $6C_2'^1$, σ_h, $6\sigma_v$, i, S_6^1, S_6^5, S_3^1, S_3^5.

Exercise 2

When is a molecule chiral?

a) It has no mirror planes

b) It is has no inversion center

c) It has no principal axis

d) It has no rotation reflections (improper rotations)

Answer

d) It has no rotation reflections (improper rotations)

Exercise 3

If a molecule has a principal axis C_n , and n additional C_2 axes standing perpendicular to C_n then it belongs to

a) A dihedral point group

b) A rotational point group

c) A low symmetry point group

d) A high symmetry point group

Answer

a) A dihedral point group

Exercise 4

Which of the following molecules are chiral:

a) CH_4

b) $CHCl_3$

c) HCFClBr

d) HOF

e) BHFCl

Answer

c) HCFClBr

Exercise 5

Determine the point groups of the molecules at symmetry.otterbein.edu/challenge/index.html until you feel that you can determine point groups effortlessly

Section 3

Exercise 1

Can the following matrices be multiplied and if so what is the product matrix?

a)

$$\begin{bmatrix} 2 & 1 & 0 \\ 5 & 9 & 1 \\ 2 & 2 & 3 \end{bmatrix}\begin{bmatrix} 0 & 3 & 1 \\ 4 & 1 & 2 \\ -1 & -1 & 3 \end{bmatrix}$$

b)

$$\begin{bmatrix} 3 & 1 & 0 \end{bmatrix}\begin{bmatrix} 4 \\ 2 \\ 1 \end{bmatrix}$$

c)

$$\begin{bmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 2 & 1 \end{bmatrix}\begin{bmatrix} 1 & 4 \\ 2 & 3 \\ 3 & 2 \\ 4 & 1 \end{bmatrix}$$

d)

$$\begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix}\begin{bmatrix} 1 & 5 & 8 \\ 2 & 2 & 4 \\ 1 & 8 & 1 \end{bmatrix}$$

Answer

a)

$$\begin{bmatrix} 2 & 1 & 0 \\ 5 & 9 & 1 \\ 2 & 2 & 3 \end{bmatrix}\begin{bmatrix} 0 & 3 & 1 \\ 4 & 1 & 2 \\ -1 & -1 & 3 \end{bmatrix} = \begin{bmatrix} 2\times0+1\times4+0\times(-1) & 2\times3+1\times1+0\times(-1) & 2\times1+1\times2+0\times3 \\ 5\times0+9\times4+1\times(-1) & 5\times3+9\times1+1\times(-1) & 5\times1+9\times2+1\times3 \\ 2\times0+2\times4+3\times(-1) & 2\times3+2\times1+3\times(-1) & 2\times1+2\times2+3\times3 \end{bmatrix} = \begin{bmatrix} 4 & 7 & 4 \\ 35 & 23 & 26 \\ 5 & 5 & 15 \end{bmatrix}$$

b)

$$\begin{bmatrix} 3 & 1 & 0 \end{bmatrix}\begin{bmatrix} 4 \\ 2 \\ 1 \end{bmatrix} = \begin{bmatrix} 3\times4+1\times2+0\times1 \end{bmatrix} = \begin{bmatrix} 14 \end{bmatrix}$$

c) $$\begin{bmatrix}1&2&3&4\\4&3&2&1\end{bmatrix}\begin{bmatrix}1&4\\2&3\\3&2\\4&1\end{bmatrix}=\begin{bmatrix}1\times1+2\times2+3\times3+4\times4 & 1\times4+2\times3+3\times2+4\times1\\4\times1+3\times2+2\times3+1\times4 & 4\times4+3\times3+2\times2+1\times1\end{bmatrix}=\begin{bmatrix}30&20\\20&30\end{bmatrix}$$

d) $$\begin{bmatrix}2&-1\\1&1\end{bmatrix}\begin{bmatrix}1&5&8\\2&2&4\\1&8&1\end{bmatrix}$$

These two matrices cannot be multiplied.

Exercise 2

Determine the irreducible representations for the following orbitals in the point group D_{2h}.

The z axis is defined as the axis of the principal C_2 axis. C_2’ is defined as the axis rotating around y. σ_v is defined as the xz plane.

	E	C_2	C_2'	C_2''	i	σ_h	σ_v	σ_v'
a) 2s								
b) $2p_x$								
c) $2p_y$								
d) $2p_z$								
e) $3d_{z2}$								
f) $3d_{x2-y2}$								
g) $3d_{xy}$								
h) $3d_{yz}$								
i) $3d_{xz}$								

Answer

	E	C_2	C_2'	C_2''	i	σ_h	σ_v	σ_v'
a) 2s	1	1	1	1	1	1	1	1
b) $2p_x$	1	-1	-1	1	-1	1	1	-1
c) $2p_y$	1	-1	1	-1	-1	1	-1	1
d) $2p_z$	1	1	-1	-1	-1	-1	1	1
e) $3d_{z2}$	1	1	1	1	1	1	1	1
f) $3d_{x2-y2}$	1	1	1	1	1	1	1	1
g) $3d_{xy}$	1	1	-1	-1	1	1	-1	-1
h) $3d_{yz}$	1	-1	-1	1	1	-1	-1	1
i) $3d_{xz}$	1	-1	1	-1	1	-1	1	-1

Exercise 3

Determine the matrix representations of the symmetry elements of the following point groups:

a) D_2

Define principal C_2 axis as the axis running along z. C_2' runs along x.

b) C_3

If we define the principal C_3 axis running along the z axis:

Answer

a)

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_2\!: \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_2'\!: \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$C_2''\!: \begin{matrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

b)

$$E\!: \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_3^1\!: \begin{matrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix} \qquad C_3^2\!: \begin{matrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

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CHAPTER OVERVIEW

3: Molecular Orbitals

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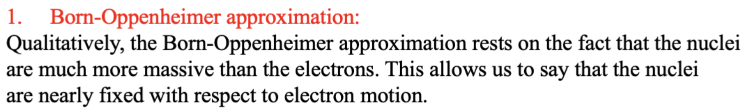
3.1: Introduction into Molecular Orbital Theory

Covalent Bonding: Molecular Orbital Theory

Now that we have thoroughly studied symmetry, we can next apply symmetry to molecular orbital theory. Molecular orbital theory is a bonding theory that has been developed to explain covalent bonding, but as we will see in a bit, it can also make statements about ionic bonding. We will see that the application of symmetry to molecular orbital theory will greatly help us to understand molecular orbitals, in particular for more complex molecules. Before we apply symmetry to molecular orbital theory, however, let us briefly review the principles of molecular orbital theory.

Like all theories it is based on a few basic assumptions, also called axioms. The first assumption is the **Born-Oppenheimer approximation**. It says that the position of the nuclei are nearly fixed relative to electron motion (Fig. 3.1.1).

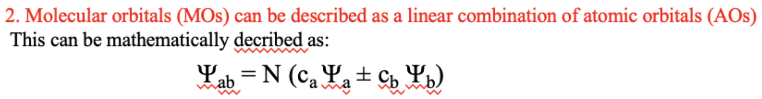


1. Born-Oppenheimer approximation:

Qualitatively, the Born-Oppenheimer approximation rests on the fact that the nuclei are much more massive than the electrons. This allows us to say that the nuclei are nearly fixed with respect to electron motion.

Figure 3.1.1 The Born-Oppenheimer approximation

This is a good approximation because the nuclei are much more massive than the electrons. The second axiom is that molecular orbitals can be described as a linear combination of atomic orbitals (Fig. 3.1.2). Linear combination means a vectorial addition or subtraction.



2. Molecular orbitals (MOs) can be described as a linear combination of atomic orbitals (AOs)

This can be mathematically decribed as:

$$\Psi_{ab} = N\,(c_a\,\Psi_a \pm c_b\,\Psi_b)$$

Figure 3.1.2 The second axiom of molecular orbital theory.

Since orbitals are so-called vector functions they can be added and subtracted like vectors. Any orbital is a wave function that has a specific amplitude at a particular point in space. A point in space is defined by a vector that points from the origin to that point in space. Therefore, there is an amplitude associated with each vector that is associated with the wave function. In mathematical form we can say that a molecular orbital $\Psi_{ab} = N\,(c_a\Psi_a \pm c_b\Psi_b)$, whereby Ψ_a is the atomic orbital *a* of atom *a*, and Ψ_b is the atomic orbital *b* of atom *b*. The coefficients c_a and c_b determine how much the specific atomic orbitals *a* and *b* contribute to the molecular orbitals. The larger the coefficient, the greater the contribution of the particular atomic orbital to the molecular orbital.

N is the so-called **normalization factor**. The normalization factor has a value so that the probability to find the electron anywhere within the molecular orbital is 100%. Like in atomic orbitals, the square of the wave function for a molecular orbital reflects the probability to find the electron at a particular position, when we view the electron as a particle. Therefore, the integral of the square of the wave function over space must be 1, and the normalization factor is chosen so that it is 1. The number of orbitals that can be combined to molecular orbitals is not restricted to two. Also three, four or more orbitals can be combined. The number of molecular orbitals that results from a combination of atomic orbitals is always the sum of the atomic orbitals. So when two atomic orbitals are combined, two molecular orbitals must result, when three atomic orbitals are combined, three molecular orbitals must result, and so forth.

How can we qualitatively understand that the vectorial addition of atomic orbitals to form molecular orbitals explains covalent bonding? The nature of the covalent bond is that electrons are being shared between and that the bonds are directional. If we bring two atomic orbitals closer together they will start to interfere.

For example, two 1s orbitals of two hydrogen atoms will start to interfere as we bring the two atoms closer together. If that interference is constructive then the amplitudes of the two wave functions will add up and result in an increased amplitude between the atoms. This addition of amplitudes can be mathematically described by the vectorial addition of the atomic orbital amplitudes. An increased amplitude is associated with an increased electron density between the atoms. Because this electron density is located in between the atoms it can be interpreted as "shared" electron density explaining a directional, covalent bond. The molecular orbital can be called a *bonding* molecular orbital (Fig. 3.1.3).

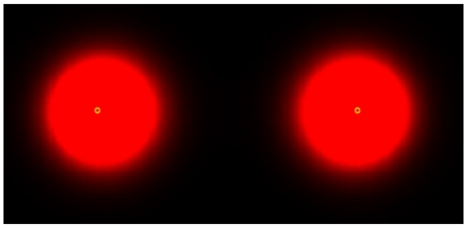


Figure 3.1.3 Bonding molecular orbital of the 2s orbitals of two hydrogen atoms (Attribution: www.falstad.com/qmmo/)

However, we must also consider that negative interference can occur which can be described by vectorial subtraction of the amplitudes of the atomic orbitals. In this case the electron-density is depleted in between the atoms, and there is actually a node in between the atoms where the wave function of the molecular orbital changes its algebraic sign. This molecular orbital can be called an *anti-bonding* molecular orbital (Fig. 3.1.4).

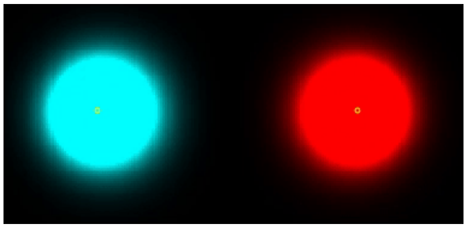


Figure 3.1.3 Anti-bonding molecular orbital of the 2s orbitals of two hydrogen atoms (Attribution: www.falstad.com/qmmo/)

The anti-bonding orbital has a higher energy than the bonding molecular orbital. This can be qualitatively understood from the fact that the energy of wave functions increases with the number of nodes. We have seen this principle before when we discussed atomic theory, and now we meet it again in molecular orbital theory. If a covalent bond forms will depend how many the electrons will be in the bonding or anti-bonding orbitals.

Electrons tend to occupy the lower energy states first, and therefore bonding orbitals will be filled first. However, the Pauli principle holds for molecular orbitals as it holds for atomic orbitals, and therefore we cannot fill more than two electrons in one molecular orbital. Once the bonding molecular orbital is filled, we must start to fill the anti-bonding orbital.

$$\text{Bond Order} = \frac{\text{No. } e^{-} \text{ in bonding MOs - No. } e\text{- in antibonding MOs}}{2}$$

Figure 3.1.5 Equation for the calculation of bond order

We can define a bond order in the molecule by subtracting the number of electrons in anti-bonding orbitals from the number of bonding orbitals, and divide the resulting number by two (Fig. 3.1.5).

If we stick to our example, the two H atoms, then we have two electrons overall to consider. We can fill both electrons into the bonding molecular orbital, and the anti-bonding molecular orbital remains empty. This gives a bond order of (2-0)/2=1. Therefore, we can say that one covalent bond has formed between the H atoms, have we have produced an H_2 molecule.

Generally we can say that a molecule would expected to be stable when the bond order is larger than 0. That would mean that an H_2^+ molecular ion should be stable because its bond order would be (1-0)/2=½. The H_2^+ ion has only one electron which would be in the bonding orbital. However, this bond order is smaller than that of H_2, and thus it should be less stable than H_2. This is in accordance with experimental observations. Also an H_2^- ion should be stable. In this case, one of the three overall electrons would be in the anti-bonding orbital. The bond order would be (2-1)/2=1/2. An H_2^{2-} anion, however would be expected to be unstable because there would be two electrons in bonding molecular orbitals, and two in anti-bonding ones, resulting in a bond order of (2-2)/2=0 (Fig. 3.1.6).

H_2: BO = (2-0)/2 = 1

H_2^+: BO = (1-0)/2 = 1/2

H_2^-: BO = (2-1)/2 = 1/2

H_2^{2-}: BO = (2-2)/2=0

Figure 3.1.6 Bond order calculations for H_2, H_2^+, H_2^- and H_2^{2-}

Molecular Orbital Diagram of H_2

The covalent bonding in a molecule can be described by a molecular orbital diagram. Let us briefly review the principles of its construction for the example of the H_2 molecule (Fig. 3.1.7).

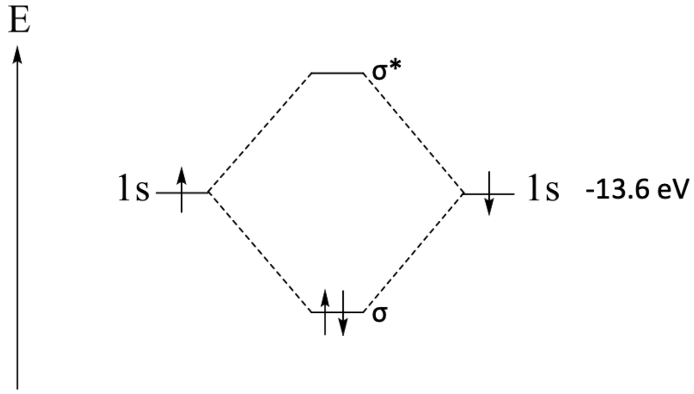


Figure 3.1.7 Molecular orbital diagram of H_2

Firstly, we write an arrow to the left. It indicates the relative energies of the orbitals, and is labeled with an E, standing for energy.

Next, we indicate the two 1s atomic orbitals by two horizontal lines, and give them appropriate labels. The lines must be at the same energy levels in the diagram, as both 1s orbitals have the same energy. If you know the exact energy of the orbitals you can write the exact energy next to the orbital name. In the case of the 1s orbitals this would be -13.6 eV.

Next we write the two molecular orbitals as horizontal lines at the appropriate energy levels into the middle of the diagram. The bonding orbital must have a lower energy than the atomic orbitals, and the anti-bonding orbital must have a higher energy. The energy difference between the molecular orbitals and the atomic orbitals must be approximately the same. Typically, the bonding orbital is slightly less bonding than the anti-bonding orbital is anti-bonding. When constructing qualitative molecular orbital diagrams, we do not know the exact energy values for the molecular orbitals, but we can estimate the relative energies of the orbitals according to the arguments just discussed. In the case of the H_2 molecule the two 1s atomic orbitals overlap in σ-fashion, we can therefore denote the molecular orbitals with a σ symbol which we can write next to the lines for the orbitals. The anti-bonding MO gets a * in addition to indicate its anti-bonding nature. We connect the molecular orbitals with atomic orbitals by dotted lines to indicate that the molecular orbitals have been constructed from the 1s atomic orbitals.

In the last step, we fill the electrons into the atomic and molecular orbitals. Each hydrogen has one 1s electron, and we write the electrons as arrows in the 1s orbitals. One electron should be spin up and the other one spin down, because the electrons must have paired spins in the molecular orbital, and spin-reversal is quantum-mechanically forbidden. Lastly, we fill the two electrons into the molecular orbitals according to energy. This means we must write them with with paired spins into the bonding molecular orbital. Now our molecular orbital diagram is complete.

Factors Influencing the Degree of the Covalent Interaction

Now let us refine our understanding of molecular orbitals and molecular orbitals diagrams. Not all atomic orbitals can be combined to form molecular orbitals, and the degree of covalent interaction between two atomic orbitals can vary lot. What are the criteria according to which we can decide if covalent interaction between two atomic orbitals is possible, and if so how much? There are three criteria to consider.

The symmetry criterion, the overlap criterion, and the energy criterion. The symmetry criterion says that if there is a combination of atomic orbitals with bonding and the antibonding interactions that do not cancel out then there is a bonding interaction. We will discuss in a moment what this means.

Definition: Symmetry Criterion

If there is a combination of atomic orbitals with bonding and the antibonding interactions that do not cancel out then there is a bonding interaction.

The overlap criterion states that the better the atomic orbitals (of appropriate symmetry!) overlap the stronger the covalent interaction.

Definition: Overlap Criterion

The better the atomic orbitals (of appropriate symmetry!) overlap the stronger the covalent interaction.

The energy criterion states that the closer the orbitals are in energy the more covalent interaction between them.

Definition: Energy Criterion

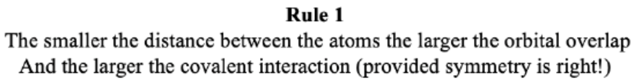
The closer the atomic orbitals in energy the stronger the covalent interaction.

The Overlap Criterion

Let us now look at each criterion in more detail. Let us start with the one we can probably most easily understand, the overlap criterion. The greater the overlap the greater the covalent interaction. The overlap can be estimated according to three rules.

Rule 1

The first rule says that the overlap is the greater the smaller the distance between the two orbitals (Fig. 3.1.8).



Rule 1

The smaller the distance between the atoms the larger the orbital overlap

And the larger the covalent interaction (provided symmetry is right!)

Figure 3.1.8 Rule 1 for the overlap criterion

This means that a small distance between the orbital leads to a strongly bonding and a strongly anti-bonding orbital, respectively while a large distance leads to a weakly bonding and a weakly anti-bonding orbital. When the distance is small then there is a large energy difference between the bonding and the anti-bonding molecular orbital, when the distance is large then the energy difference is small (Fig. 3.1.9).

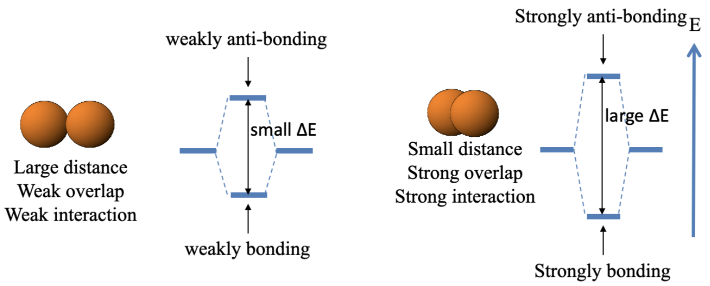
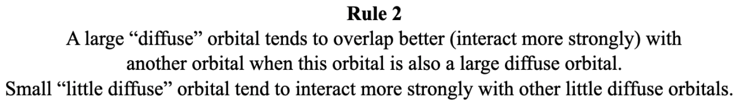


Figure 3.1.9 The effect of the distance between atomic orbitals on the energy difference of the resulting molecular orbitals.

Rule 2

Rule 2 states that a large “diffuse” orbital tends to overlap better (interacts more strongly) with another orbital when this orbital is also a large diffuse orbital. Small “little diffuse” orbital tend to interact more strongly with other little diffuse orbitals. If we combine a large orbital with a small orbital however, then this typically does not lead to good overlap and thus weak interaction (Fig. 3.1.10).



Rule 2

A large “diffuse” orbital tends to overlap better (interact more strongly) with another orbital when this orbital is also a large diffuse orbital.

Small “little diffuse” orbital tend to interact more strongly with other little diffuse orbitals.

Figure 3.1.10 Rule 2 for the overlap criterion

We can qualitatively understand this by looking at the image below (Fig. 3.1.11).

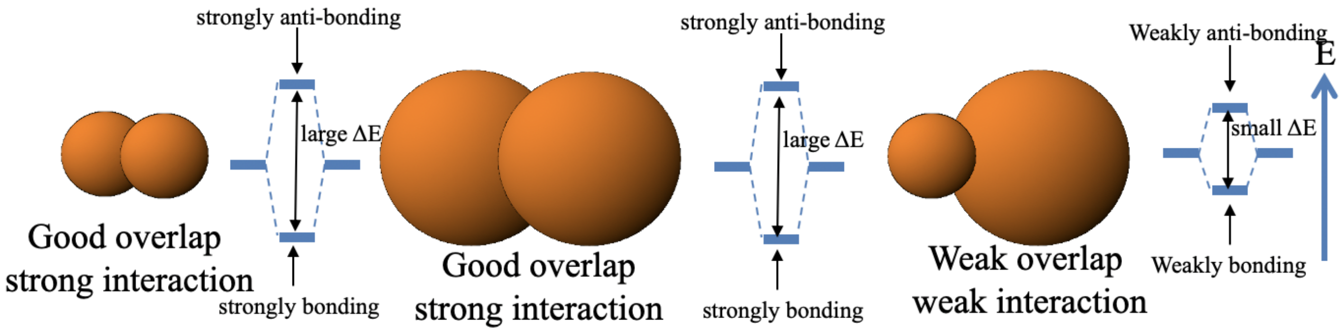


Figure 3.1.11 Relationships between orbital size and covalent interactions.

Only a small volume fraction of the large orbital can overlap with the small orbital due to the small size of the small orbital. Due that small overlap the bonding orbital is only weakly bonding, and the anti-bonding is only weakly anti-bonding. The energy difference between the bonding and the anti-bonding orbital is small. In the other two cases, the bonding orbitals tend to be strongly bonding, and the anti-bonding ones strongly anti-bonding. The energy differences between the orbitals tend to be large.

Rule 3

Rule 3 says that that orbitals that overlap in σ-fashion tend to interact more strongly than orbitals that overlap in π-fashion (Fig. 3.1.12).

Rule 3
There is a tendency that orbitals that overlap in σ-fashion interact more strongly than orbitals that overlap in π-fashion.

Figure 3.1.12 Rule 3 for the overlap criterion

One can see easily from the image below that two p orbitals that have the same distance *d* from each other overlap much more when they overlap in σ-fashion compared to π-fashion (Fig. 3.1.13).

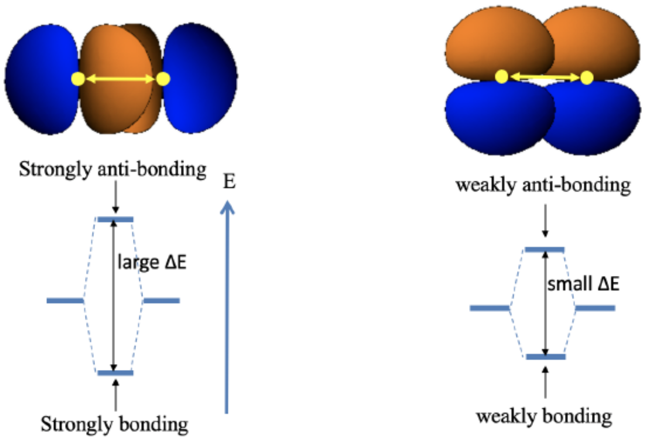


Figure 3.1.13 Visual representation of orbitals overlapping in σ-fashion vs orbitals overlapping in π-fashion

This is because in the first case they point toward each other, and the orbital overlap is on the bond axis, while in the latter case they are oriented parallel to each other, and the orbital overlap is above and below the bond axis. This implies that the σ-overlap leads to more bonding and anti-bonding orbitals with a larger energy gap between them compared to the π-overlap.

The Energy Criterion

The energy criterion states that the covalent interaction is the larger the smaller the energy difference between the atomic orbitals. We can understand this qualitatively when considering that orbitals are waves, and waves of similar energy interfere more significantly with each other than waves with different energies. Just imagine two waves with very different wavelengths associated with very different energies. Would they interfere effectively? No, they wouldn’t. Rather, two waves with very similar wavelengths would interfere better. Because greater energy difference means less interaction, molecular orbitals that result from the interaction of two atomic orbitals with large energy difference are much more similar in shape, size, and location compared to molecular orbitals that result from atomic orbitals with similar energy.

The greatest covalent interaction is expected when the energy between the two orbitals is exactly the same. This is only possible when two, same orbitals A of the two same atoms overlap. In this case we form a perfect covalent bond with electrons exactly equally shared between the orbitals. The maximum of the amplitude of the bonding molecular orbital is exactly in the middle between the two atoms. In the molecular orbital diagram the energy difference between the bonding MO and the AOs is about the same as the energy difference between the anti-bonding MO and the AOs. Assuming that each atomic orbital is filled with one electron the two electrons are in the bonding molecular orbital where they are equally shared between the atoms (Fig. 3.1.14)

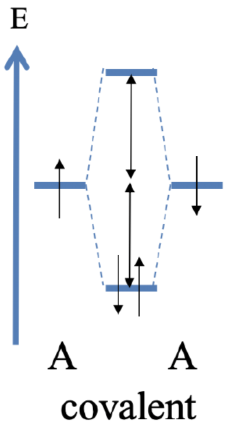


Figure 3.1.14 Covalent interaction occurring when the energy between the two atomic orbitals is exactly the same

Now let us make the energy of the two atomic orbitals somewhat different. Because they are different we denote the atomic orbitals A and B now, whereby we choose the energy of orbital A to be somewhat higher than that of orbital B. Overlap between the atomic orbital still produces covalent interaction yielding a bonding and an anti-bonding molecular orbital. However, the energy difference of the molecular orbitals to the two atomic orbitals is no longer the same. The anti-bonding MO is now closer to the AO with the higher energy, and the bonding MO is now closer in energy to the AO with the lower energy. This has another consequence. The bonding molecular orbital is now localized primarily at atom B, and the anti-bonding orbital is located primarily at atom A. If we again assume that each AO contributed one electron to the covalent bond, then the two electrons will be in the bonding MO. Because the bonding MO is now primarily localized at atom B, the bonding electrons are primarily localized at atom B. This means they are no longer exactly equally shared, and we have a polar, covalent bond which his polarized toward atom B (Fig. 3.1.15).

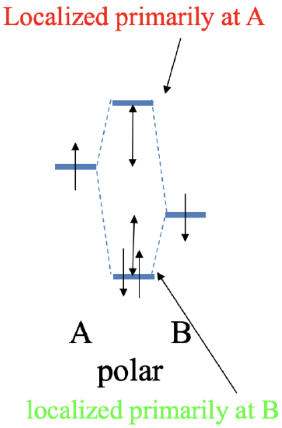


Figure 3.1.15 An example of covalent interaction occurring when the energy between the two atomic orbitals is somewhat different

Now let us make the energy difference between the two atomic orbitals of the atoms A and B very large (Fig. 3.1.16). In this case, the bonding MO is energetically very close to the AO of atom B, and is localized almost exclusively at atom B. Actually, the bonding MO closely resembles the AO of atom B in shape, size and localization. In other words, the AO of B has hardly changed due to the very weak covalent interaction resulting from the large energy difference between the atomic orbitals. Vice versa, the anti-bonding orbital is energetically very close to the AO of atom A, and is localized almost completely at atom A. The anti-bonding MO is very close to the AO in shape, size, and location. Due to the weak covalent interaction, there is almost no change to the atomic orbital of A. Assuming that each atomic orbital contributes two electrons, the bonding orbital will be filled. The two electrons will be almost exclusively located at atom B. This means that we have effectively transferred one electron from atom A to atom B in a redox process, and have produced an ionic bond. Atom A has now effectively a 1+ charge, and atom B has a 1- charge.

This shows that molecular orbital theory, although designed for covalent bonding, can also make statements about ionic bonding. We can also see that a 100% ionic bond is not possible. To achieve 100% iconicity the energy difference between the two atomic orbitals would need to be infinitely large. This is practically impossible. However, a 100% covalent bond is possible because two electrons can be exactly equally shared between two atoms when the energy of the atomic orbitals is exactly zero.

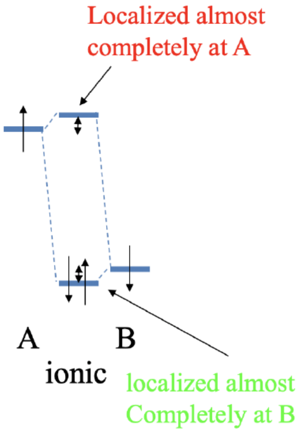


Figure 3.1.16 Covalent interaction occurring when the energy difference between two atomic orbitals is very large.

Another conclusion that we can draw is that bonding electrons are located at the atom with the atomic orbital of lower energy, and anti-bonding electrons are located at the atoms with the atomic orbital of higher energy. Orbital energy is correlated with electronegativity. For orbitals of the same type and the same elements, orbitals with higher electronegativity have lower energy. For example, a 2s orbital of fluorine has a lower energy than a 2s orbital of oxygen because the electronegativity of fluorine is higher. Bonding electrons are therefore located primarily at the more electronegative atom, while anti-bonding electrons are located primarily at the less electronegative atom (Fig. 3.1.7). When there are enough anti-bonding orbitals occupied it is possible that the overall polarity in the molecule is such that the dipole moment points toward the more electro-positive atom. An example is carbon monoxide which is slightly polarized toward the carbon atom. We will discuss the MO diagram of the carbon monoxide in detail later.

Bonding electrons are located at the more electronegative atom.
Antibonding electrons are located at the more electropositive atom.

Figure 3.1.17 Relationship between orbital energy and electronegativity

The Symmetry Criterion

Lastly, let us look at the symmetry criterion. The symmetry criterion tells us if a covalent interaction between orbitals is possible based on the relative orientation of the orbitals. Only if bonding and anti-bonding interactions do not cancel out, a bonding interaction is possible, and we can construct molecular orbitals from atomic orbitals. Bonding and anti-bonding interactions cancel out when positive and negative interferences due to orbital overlap are exactly equal. This can be determined by inspection of orbital overlap.

For example, let us look at the orbital overlap between the 1s orbitals of hydrogen and the $2p_z$ orbital of oxygen in the water molecule (Fig. 3.1.18).

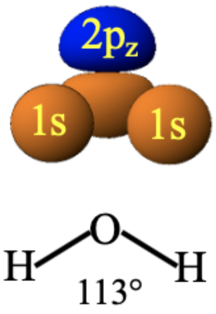


Figure 3.1.18 The orbital overlap between the 1s orbitals of hydrogen and the $2p_z$ orbital of oxygen in the water molecule

In the water molecule the orbitals are oriented to each other in a specific way because of the bent structure of the water molecule. Due to the bent structure of the water molecule the 1s orbitals overlap differently with the two lobes of the $2p_z$ molecule. The lobe that points downward overlaps more strongly than the lobe that points upward. The two lobes must have different algebraic sign. Now we choose the algebraic sings of 1s orbitals so that bonding is maximized. This means that we choose the algebraic signs so that they are the same as the those of the lobe that points downward. We can see that now the overlap of the 1s with the $2p_z$ orbital produces more positive than negative interferences. The blue lobe is further away from the 1s orbitals than the orange lobe and thus positive and negative interferences do not cancel out. This is equivalent to saying that bonding and anti-bonding interactions do not cancel out. Therefore, the symmetry is “right”, we can construct molecular orbitals from this combination of atomic orbitals.

Can the $2p_x$ orbital of oxygen also combined with the 1s orbitals of the hydrogen atom to form molecular orbitals? The $2p_x$ orbital is oriented differently relative to the 1s orbitals in the H_2O molecule (Fig. 2.1.19).

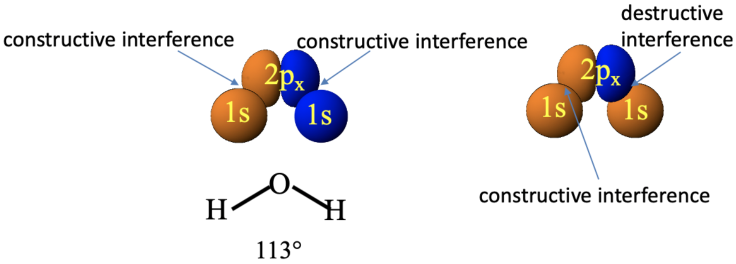


Figure 3.1.19 The orbital overlap between the 1s orbitals of hydrogen and the $2p_x$ orbital of oxygen in the water molecule shown in two different orientations

In this case, we must choose the algebraic signs of the two 1s orbitals to be different so that bonding interactions are possible. The bonding and the antibonding interactions only do not cancel out if the left 1s orbital has the same algebraic sign as the left lobe of the $2p_x$ orbital and the right 1s orbital has the same algebraic sign as the right lobe of the $2p_x$ orbital. If, for instance, we chose both 1s orbitals to be orange, then the bonding interactions between the left lobe and the left 1s orbital would be canceled out by the equally strong anti-bonding interactions between the right lobe and the right 1s orbital. Overall, we see however, that if we select the color (meaning algebraic sign) of the 1s orbitals appropriately then the symmetry is “right” and we can create molecular orbitals from the atomic orbitals.

What about the combination of the 2s of the oxygen with the 1s orbitals of the hydrogens (Fig. 3.1.20)?

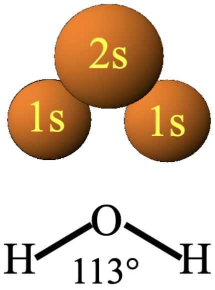


Figure 3.1.20 The orbital overlap between the 1s orbitals of hydrogen and the 2s orbital of oxygen in the water molecule

We can see that is very easy to construct a combination in which there are bonding interactions. If we choose the algebraic sign of all atoms to be the same, then certainly bonding and anti-bonding interactions do not cancel out. The symmetry is “right”, and the construction of atomic orbitals from molecular orbitals is possible.

What about the interactions between the 1s orbitals and the $2p_y$ orbital (Fig. 3.1.21)?

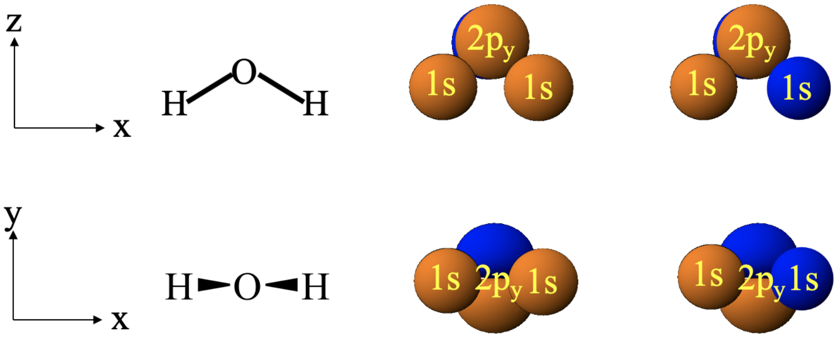


Figure 3.1.21 The orbital overlap between the 1s orbitals of hydrogen and the $2p_y$ orbital of oxygen in the water molecule shown in two different orientations

In this case, the two 1s orbitals are in the paper plane, and the $2p_y$ orbital stands perpendicular to it. That makes a 1s orbital to overlap equally with both lobes of the $2p_y$ orbital. Because the two lobes of a $2p_y$ orbital must have different algebraic sign, the constructive and the destructive interferences will cancel out, no matter how we chose the algebraic signs of our 1s orbitals. That means there is no possibility to create orbital overlap in which bonding an anti-bonding interactions do not cancel out. Therefore, we cannot produce molecular orbitals from a combination of 1s and $2p_y$ orbitals. The $2p_y$ must remain non-bonding. You may be able to see the cancelation of the bonding and antibonding orbital overlap better if you choose your coordination system differently. Let us have the y-axis point up, and the x-axis point right (Fig. 3.1.21, bottom). Now we look at the H_2O molecule from the bird perspective, and the $2p_y$ orbital is oriented vertically. The 1s orbitals are still on the x-axis. You can see the overlap between the 1s orbitals and the $2p_y$ orbital more clearly now. No matter how we choose the algebraic sign of our orbitals, the bonding and the anti-bonding interactions cancel out.

We have seen thus far that is is possible to decide about “right” and “wrong” symmetries by inspection, but we have noticed that this is not trivial. Generally, the more complex a molecule gets the more difficult it is to decide about “right” and “wrong” symmetry. As we will see in the following, group theory can greatly help us decide about “right” and “wrong” symmetry. It provides a formal pathway to unambiguously make such a decision.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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3.2: The Symmetry Adapted Linear Combination of Atomic Orbitals Method

Rules for the Symmetry-Adapted Linear Combination of Atomic Orbitals (SALC)

The construction of molecular orbitals using group theory follows a method called “Symmetry-adapted linear combination of atomic orbitals”. This method follows the following **steps**.

1. Firstly, we determine the point group for the molecule.
2. Secondly, we determine the axes of the coordinate system in a useful way.
3. Thirdly, we determine the ligand atomic orbitals that can be combined to form so-called ligand group orbitals (LGOs). These are usually orbitals of the same kind that a symmetry operation can interconvert. The number of LGOs is always the number of the ligand atomic orbitals.
4. In the next step, we determine the symmetry types of the ligand group orbitals, and we will talk in a moment how this works.
5. Finally, we determine the symmetry type of the atomic orbitals of our central atom, and combine ligand group orbitals and central atom orbitals of the same symmetry type. If they have the same symmetry type their symmetry is “right”. The MOs resulting from this combination will have the same symmetry type as the orbitals from which they have been made. Also the number of MOs must be the same as the number of LGOs and central atom AOs.

Now you can construct a molecular orbitals diagram using the MOs that you have constructed using SALC. After you have constructed the MO diagram, always check that the number of MOs is equal to the number of AOs. If not, you must have made a mistake and you have to go back and find the mistake.

Example - H_2O

Let us carry out these steps using our water molecule as an example. As we determined previously, the point group of the water molecule is C_{2v}. A sensible way to define the coordinate system is to have the x-axis point to the right, the z-axis point to the top, and the y-axis point out of the paper plane (Fig. 3.2.1). The water molecule would be in the xz plane pointing into z-direction. The next step is to define the ligand atoms and ligand orbitals. It is easy to see that the H atoms would be ligand atoms, and the O atom would be the central atom. The ligand atomic orbitals that would be combined to form ligand group orbitals would be the 1s orbitals of the hydrogen atoms. We would expect two ligand group orbitals because we combine two atomic orbitals.

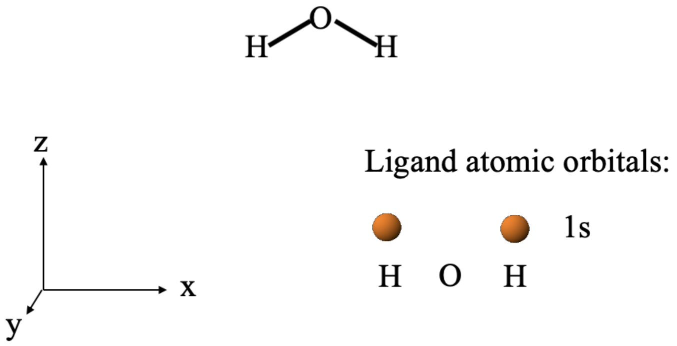


Figure 3.2.1 SALC for the water molecule (step 1 and 2)

Determination of LGO Symmetry Types

Next, we need to determine the symmetry types of the ligand group orbitals (LGOs). We can do this in two steps.

In the first step, we determine the reducible representation for the ligand group orbitals by a method called the “orbital swapping method”, and in the second step we determine the irreducible representations for the ligand group orbitals from the reducible representation. The irreducible representations will give us the symmetry type of the ligand group orbitals. Let us do the first step, and carry out the orbitals swapping method to determine the reducible representation. To do so, let us first denote the two 1s orbitals Ψ1 and Ψ2, respectively (Fig. 3.2.2).

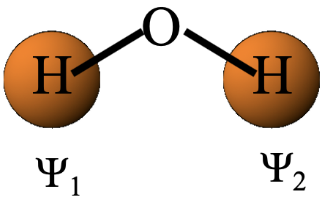
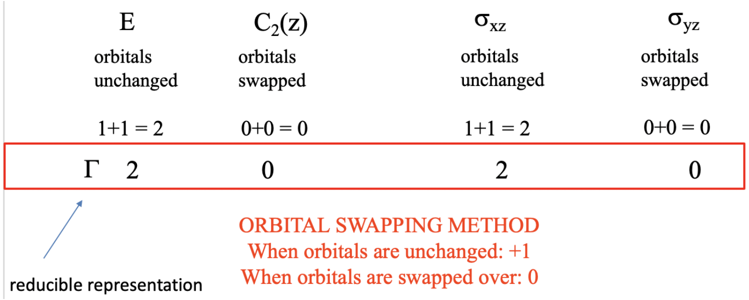


Figure 3.2.2 The 1s orbitals of the hydrogen atoms of the water molecule denoted as Ψ1 and Ψ2

Then, we decide if Ψ1 and Ψ2 get swapped up when a particular symmetry operation is carried out. If so, each gets a character zero, if not, they get a character +1 each. The sum of these characters give the character in the reducible representation for the particular symmetry operation. After we have applied orbital swapping for all symmetry operations, we know all the characters of the reducible representation. The E symmetry operation does not swap the orbitals, hence the character in the reducible representation is 1+1=2 (Fig. 3.2.3). The C_2 symmetry operation does swap the orbitals, hence the character in the reducible representation is 0+0=0. The xz mirror plane leaves the orbitals at their positions, therefore the character in the reducible representation is 1+1=2. the yz mirror plane swaps the orbitals, hence the character is 0+0=0 (Fig. 2.3.2).



	E	$C_2(z)$	σ_{xz}	σ_{yz}
	orbitals unchanged	orbitals swapped	orbitals unchanged	orbitals swapped
	1+1 = 2	0+0 = 0	1+1 = 2	0+0 = 0
Γ	2	0	2	0

reducible representation

ORBITAL SWAPPING METHOD
When orbitals are unchanged: +1
When orbitals are swapped over: 0

Figure 3.2.3 Using the orbital swapping method to determine the reducible representation for the LGOs of the water molecule

You may ask: Why does the orbital swapping method work? What deeper principle is behind it? The answer is. The orbital swapping method is a short-cut for getting the sum of the characters on the trace of a transformation matrix that converts the two wave functions. Before the symmetry operation is carried out the two wave functions can be described by a matrix of of the form below (Fig. 3.2.4).

$$\begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix}$$

Figure 3.2.4 Matrix that represents the two 1s orbitals.

When the orbitals are swapped, Ψ1 and Ψ2 on the matrix are swapped, and the matrix takes the form below (Fig. 3.2.5).

$$\begin{bmatrix} \Psi_2 \\ \Psi_1 \end{bmatrix}$$

Figure 3.2.5 Matrix that represents the two 1s orbitals after the orbitals haven been swapped

The transformation matrix when multiplied with the matrix in Figure 3.2.4 gives the matrix in Figure 3.2.5 which is the transformation matrix for the operation(s). This matrix has the form below (Fig. 3.2.6),

$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

Figure 3.2.6 The transformation matrix for C_2 and σ_{yz}

and we could use the multiplication rules to show that this matrix is the correct matrix. This means the transformation matrix for C_2 and σ_{yz} is the matrix shown in Figure 3.2.6.

$$C_2,\ \sigma_{yz}$$

$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} \longrightarrow \begin{bmatrix} \Psi_2 \\ \Psi_1 \end{bmatrix}$$

Figure 3.2.7 Multiplication of the matrix representing the 1s orbitals with the matrix representation for C_2 and σ_{yz}

For the operations E and σ_{xz} the orbitals do not get swapped, and the final matrix is the same as the initial matrix in Figure 3.2.4. Thus, the transformation matrix has the form below (Fig. 3.2.8). For the matrix in Figure 3.2.6 the sum of the characters on the trace of the matrix is zero. For the matrix below

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Figure 3.2.8 Transformation matrix for E and σ_{xz}

this sum is 2. These are the characters of the reducible representation that we previously determined using the orbital swapping method. Using the multiplication rules we can show that the matrix of Fig. 3.2.8 is the correct transformation matrix (Fig. 3.2.9)

$$E,\ \sigma_{xz}$$

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} \longrightarrow \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix}$$

Figure 3.2.9 Multiplication of the matrix for the 1s orbitals with the matrix representation for E and σ_{xz}

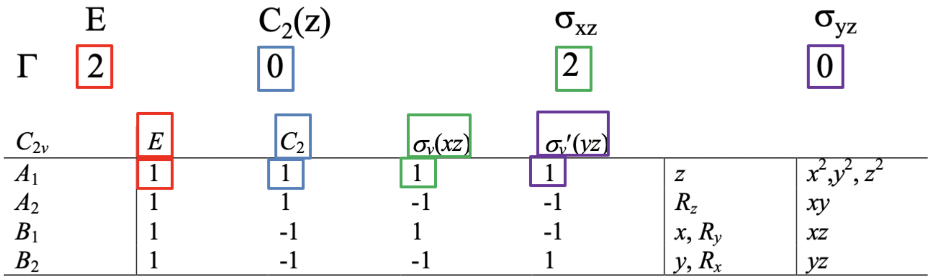
In the next step we need to determine the irreducible representations from the reducible representation. Remember, a reducible representation is the sum of two or more irreducible representations. Thus, a reducible representation contains the information about the irreducible representations it is composed of, and we need to find a tool to extract that information.

The tool to do this is a formula from group theory called the reduction formula. You can see the reduction formula below (Fig. 3.2.10).

$$\begin{pmatrix} \text{Number of irreducible} \\ \text{representations of} \\ \text{a given type} \end{pmatrix} = \frac{1}{\text{order}} \sum_R \left[\begin{pmatrix} \text{number} \\ \text{of operations} \\ \text{in the class} \end{pmatrix} \times \begin{pmatrix} \text{character of} \\ \text{reducible} \\ \text{representation} \end{pmatrix} \times \begin{pmatrix} \text{character of} \\ \text{irreducible} \\ \text{representation} \end{pmatrix} \right]$$

Figure 3.2.10 The reduction formula

It says that the number of irreducible representations of a given symmetry type is one over the order of the point group times the sum of the products of the number of operations in a specific class in the character table of the point group times the character of the reducible representation for a given symmetry operation times the character of the irreducible representation for a given symmetry operation. The "sum of products" means the sum of the products for all classes of symmetry operations in the point group. The number of operations in a class and the character of the irreducible representation can be read from the character table for the point group. Here we see for the first time the utility of character tables for molecular orbital theory. The characters of the reducible representation can be read from the reducible representation previously determined by the orbital swapping method.



	E	$C_2(z)$	σ_{xz}	σ_{yz}
Γ	2	0	2	0

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Figure 3.2.11 The reducible representation of the LGOs of the water molecule and the character table of C_{2v}

For clarity, let us use the reduction formula for the determination of the irreducible representations of the ligand group orbitals for the example of the water molecule. Our task is to find the number of irreducible representations of each possible symmetry type in the point group. In the point group C_{2v}, these are the symmetry types A_1, A_2, B_1, and B_2. Let us start with A_1. The number of irreducible representations of the type A_1 is: A_1 = 1/4 (1x2x1 + 1x0x1 + 1x2x1 + 1x0x1) = 1 (Fig. 3.2.12).

$$\#A_1 = 1/4\ (1x2x1 + 1x0x1 + 1x2x1 + 1x0x1) = 1$$

Figure 3.2.12 Calculation of the number of irreducible representations A_1

The result means that one of the two ligand group orbitals has the symmetry type A_1. The factor ¼ is because the order of the point group is 4. We can determine the order just by counting the number of symmetry operations in the character table for C_{2v}. The first product 1x2x1 (red) is the product for the identity E. The number of operations in the column for E is 1, there is never another conjugate operation in the class for the identity. Note that the number "1" is not explicitly spelled out. The number of operation within a class of a character table is only spelled out when the number is larger than 1. The character in the reducible representation for E is 2, and the character for the irreducible representation for the A_1 symmetry type underneath E is also 1. The second product is 1x0x1 (blue) because the number of operations in the class of for C_2 is 1, the character in the reducible representation for C_2 is 0, and the character of the irreducible representation underneath C_2 is 1. The third product for the σ_{xz} operation is 1x2x1 (green) because the character for the class σ_{xz} is 1, the character in the reducible representation for σ_{xz} is 2, and the character of the irreducible representation under σ_{xz} is 1. Lastly, the product for the operation σ_{yz} is 1x0x1 (black) because the number of operations in the class for σ_{yz} is 1, the character in the reducible representation under σ_{yz} is 0, and the character of the irreducible representation under σ_{yz} is 1 (purple).

Using the same procedure, we can also determine the number of ligand group orbitals that have the symmetry types, A_2, B_1, and B_2.

$$\#A_2 = 1/4\ (1x2x1 + 1x0x1 + 1x2x(-1) + 1x0x(-1)) = 0$$

$$\#B_1 = 1/4\ (1x2x1 + 1x0x(-1) + 1x2x(1) + 1x0x(-1)) = 1$$

$$\#B_2 = 1/4\ (1x2x1 + 1x0x(-1) + 1x2x(-1) + 1x0x1) = 0$$

Figure 3.2.13 Calculation for the number of irreducible representations for A_2, B_1, and B_2, respectively

The result (Fig. 3.2.13) is that the second ligand group orbital has the symmetry type B_1, and the number of ligand group orbitals with the symmetry type A_2 and B_2 is 0. We have determined that the reducible representation is the sum of the two irreducible representations A_1 and B_2 (Fig. 3.2.14).

$$\Gamma = A_1 + B_1$$

Figure 3.2.14 The reducible representation shown as the sum of the two irreducible representations

The result means that one ligand group orbital has A_1 symmetry, the other B_1 symmetry. The one with A_1 symmetry reflects the combination of two 1s orbitals with the same algebraic sign, the one with B_1 symmetry reflects the combination of two 1s orbitals with opposite algebraic sign.

We encountered the LGOs already previously by inspection. Here we see that group theory can formally derive them. We can also verify that the two LGOs have A_1 and B_1 symmetry, respectively, by carrying out the symmetry operations and see what they do to the respective LGO. For the LGO with A_1 symmetry, no symmetry operation changes the LGO (Fig. 3.2.15). This is consistent with the symmetry type A_1 for which all characters on the irreducible representation are 1.

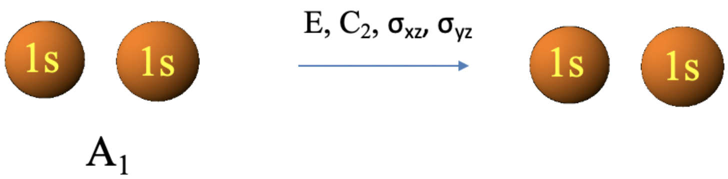


Figure 3.2.15 Verifying the A_1 symmetry by carrying out the symmetry operations

For the LGO with B_1 symmetry type we see that the C_2 operation and the σ_{yz} operations reverse the algebraic sign of the wave function, while the identity and the σ_{yz} operations don't (Fig. 3.2.16). This is consistent with the irreducible representation of the B_1 symmetry type which has the characters +1 for E and σ_{xz}, and -1 for the operations C_2 and σ_{yz}.

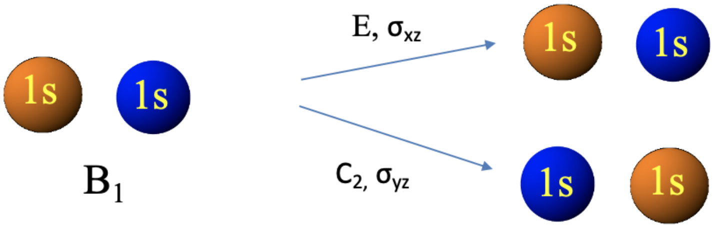
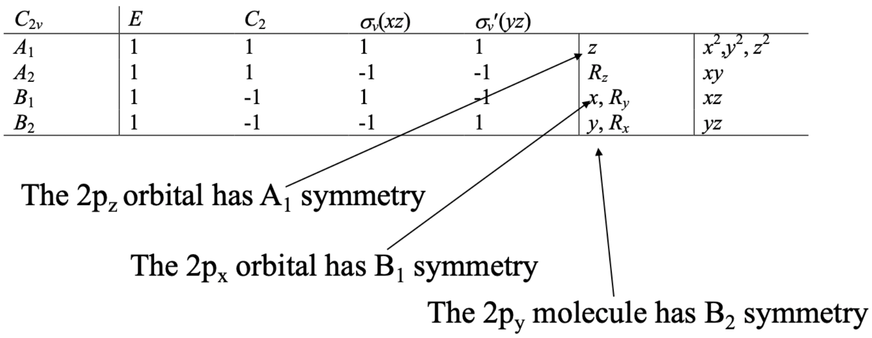


Figure 3.2.16 Verifying the B_1 symmetry of the second LGO by carrying out the symmetry operations

Symmetry Type Determination of Central Atom Orbitals

In the next step we have to find out the symmetry types of the central atom valence orbitals. In the case of the water molecule the central atom valence orbitals are the 2s, and the three 2p orbitals. We can easily read the symmetry types of these orbitals from the character table of the point group C_{2v} (Fig. 3.2.17).



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The $2p_z$ orbital has A_1 symmetry

The $2p_x$ orbital has B_1 symmetry

The $2p_y$ molecule has B_2 symmetry

Figure 3.2.17 The character table of the point group C_{2v} and the symmetry types of the central atom valence orbitals

An s orbital is always of the totally symmetric symmetry type in the point group. This is the symmetry type with all characters having a +1 value. In the point group C_{2v} this is the symmetry type A_1. The symmetry type of the $2p_z$ orbital is also A_1. This is because the letter *z* is in the row for the symmetry type A_1. Similarly, the $2p_x$ and the $2p_y$ orbitals have the symmetry type B_1 and B_2 respectively because the letters *x* and *y* are in the rows for the symmetry types B_1 and B_2, respectively.

Combination of AOs and LGO to form MOs

When central atom AOs have the same symmetry type then they have the "right" symmetry to be combined to form molecular orbitals. The molecular orbitals will have the same symmetry type than the AOs and LGOs from which they have been made. The number of MOs of a specific symmetry type must be equal to the sum of the LGOs and AOs that have the same symmetry type. When an orbital does not find a partner orbital of the same symmetry type then it is non-bonding.

Let us apply these ideas to the example of the water molecule. We saw that there were two AOs that had the symmetry type A_1, namely the 2s and the $2p_z$ orbital. There was also an LGO with A_1 symmetry. We can therefore combine these three orbitals to form molecular orbitals. They also must have the symmetry type A_1 (Fig. 3.2.18).

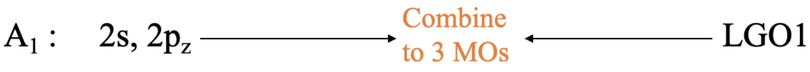


Figure 3.2.18 Combination of A_1 AOs and LGOs to create MOs

Next, let us think about orbitals of the symmetry type A_2. No AO and no LGO has this symmetry type. Therefore, there are also no MOs of this symmetry type (Fig. 3.2.19).

A_2: ----------

Figure 3.2.19 AOs and LGOs of the A_2 symmetry type

For the symmetry type B_1 we find that there is one AO, namely the $2p_x$ orbital and one LGO that have this symmetry type. This means that these two orbitals can be combined to form two MOs of the same symmetry type (Fig. 3.2.20).

B_1: $2p_x$ $\longrightarrow$ Combine To 2 MOs $\longleftarrow$ LGO2

Figure 3.2.20 Combination of the AOs and LGOs of the B_1 symmetry type

For the B_2 symmetry there is only the $2p_y$ AO, but no LGO it could be combined with. Thus, the $2p_y$ orbital remains non-bonding (Fig. 3.2.21).

B_2: $2p_y$ (non-bonding; has no partner)

Figure 3.2.21 AOs and LGOs of the B_2 symmetry type

Remember, we got the same result when we analyzed the orbitals by inspection. Here, group theory give us the same result through a formalism. This has the advantage that ambiguity and mistakes are avoided. Nonetheless, it should be kept in mind what the group-theoretical result means, and for that it is useful to have previously analyzed the interactions of the 2p orbitals with the 1s orbitals by inspection.

The MO Diagram of H_2O

Now we can construct the molecular orbital diagram of H_2O. As always we first draw a vertical arrow for the energy axis (Fig 3.2.22). Next we indicate the atom symbols on the left and the right side of the diagram. By convention, the the central atom is on the left side. After that we can write the atomic orbitals into the molecular orbital diagram according to approximate relative energy, and indicate their names and symmetry.

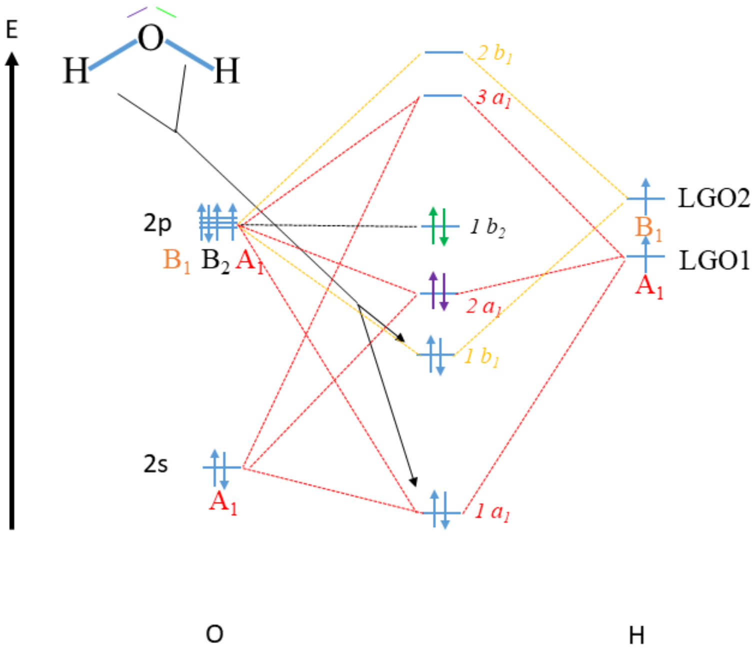


Figure 3.2.22 MO diagram of H_2O and its relationship to the valence bond structure of H_2O

We know that the 2s orbitals of O must be lower in energy than the 2p orbitals of O, and we write them accordingly. We also know that the 2p orbitals all have the same energy, and so we write them together as close as possible. For the H orbitals we write the ligand group orbitals and indicate them LGO1 and LGO2. We do not know the exact energy of the LGOs relative to the 2p and 2s orbitals of oxygen, but we would expect that it is similar to the them, otherwise we could not make covalent bond. We also know that the O-H bonds are polarized toward O, so we would suspect that the LGOs are more similar to the 2p orbitals in energy compared to the 2s orbitals. We write the LGO2 somewhat above LGO1 to indicate the LGO2 has a slightly higher energy because it has a node. It is also ok though to write them out with the same energy, both methods are common in the literature. We indicate that LGO1 has the symmetry type A_1 and LGO2 has the symmetry type B_1.

Now we need to write out the molecular orbitals in the middle of the diagram. We go systematically through all the symmetry types as we construct the MOs. For example, we can start with the symmetry type A_1. Because we combine three orbitals of this symmetry type we need to write three MOs into the middle of the diagram, and indicate the symmetry type. When we combine three orbitals the following approximation holds. There will be one bonding orbital of low energy, one anti-bonding orbital of high energy, and a third one of intermediate energy that is approximately non-bonding. We do not know if it is exactly non-bonding, slightly bonding or slightly anti-bonding. Exact quantum-mechanical calculations could determine this as well as the exact energy of the orbital, but here our focus is on the qualitative construction and understanding of molecular orbital diagrams. Therefore, we must leave this question unanswered. The bonding orbital should be written below the lowest energy atomic orbital which contributes to the MO, in this case the 2s orbital of O. The anti-bonding orbital should be drawn at an energy level above the highest-energy orbital that contributes to it, in this case the A_1-type 2p orbital. You can draw the approximately non-bonding a_1-type MO at approximately half the distance between the bonding and the anti-bonding MO into the diagram. The lowest energy orbital gets the label $1a_1$, the second-lowest, the label $2a_1$, and the highest energy orbital gets the label $3a_1$. Note that for the MOs we use lower case letters to indicate the symmetry type. The coefficients in front of the symmetry type numbers the orbitals according to increasing energy. In the last step we connect all A_1-type AOs and LGOs with the a_1-type MOs by dotted lines. This is indicated by the dotted, red lines in Fig. 3.2.22.

Next, we can draw the b_1-type MOs. We expect two MOs, because there is one AO of this symmetry type, and one LGO of this symmetry type. One MO is expected to be bonding and should have low energy, the other one must be anti-bonding, and have high energy. The energy of the bonding MO should be lower than the energy of the lowest energy orbital that contributes to it, in this case the B_1-type 2p orbital. The anti-bonding orbital should have a higher energy than the highest energy AO/LGO that contributes to it, in this case the LGO2. The bonding MO gets the label $1b_1$ and the anti-bonding orbital the label $2b_1$. We do not exactly know the energy of the b_1-type MOs relative to the a_1 type AOs when qualitatively drawing the MO diagram. For example, the anti-bonding $2b_1$ orbital is drawn with a higher energy than the anti-bonding $3a_1$ orbital, but we would not that for sure (only exact quantum-mechanical calculations could tell). We would however suspect, that the bonding $1b_1$ orbital has a higher energy than the bonding $1a_1$ orbital because the energy of the 2s orbital is significantly lower than the energy of the B_1-type 2p orbital. We would also suspect that the $1b_1$ orbital is lower in energy than the $2a_1$ orbital because we know that the $1b_1$ is bonding, while the $2a_1$ is approximately non-bonding. Finally, we connect the AOs and LGOs with B_1 symmetry with the MOs of b_1 symmetry with dotted lines, indicated orange in Fig. 3.2.22.

Lastly, we still have to decide what to do with the $2p_y$ orbital that has the symmetry type B_2. This orbital has no partner of the same symmetry type, and thus remains exactly non-bonding. Therefore, we write the $2p_y$ orbital as a b_2-type orbital with unchanged energy in the middle of the MO diagram, and interconnect the two orbitals with a horizontal, dotted line, Fig. 3.2.22.

Now let us fill the electrons into the orbitals. The O atom has six valence electrons, two of them are in the 2s orbitals and four of them are in the 2p orbitals. The 2p orbitals are filled according to Hund's rule. Because each H atom contributes one electron, the LGOs are both considered half-full with one electron each. Now we can fill the MOs according to increasing energy. Overall we have 6+2=8 electrons to fill into the MOs. Consequently, the $1a_1$ gets filled first, then the $1b_1$, then the $2a_1$, and finally the $1b_2$. The $1b_2$ is called the highest occupied molecular orbital, abbreviated HOMO. The next higher orbital, the $3a_1$ orbital is called the lowest unoccupied orbital, also called LUMO. HOMOs and LUMO are important for the chemistry of a molecule because the HOMO electrons are the most reactive electrons, and the LUMO is the orbital that easiest to fill with an electron coming from a co-reactant.

Now our MO diagram is complete. It is insightful to compare the MO diagram of water with the Lewis-dot structure of the water molecule to understand what additional information we can gain from the MO diagram compared to the Lewis dot structure. In the Lewis dot structure there, are two localized O-H bonds, so overall we have four bonding electrons. Can we we see these bonding electrons also in the MO diagram? Well, we recognize that there are two bonding molecular orbitals that are filled, the $1a_1$ and the $1b_1$. Therefore, also in the MO diagram there are four bonding electrons. You can see however, that the two MOs are not energetically equal, thus two electrons have a higher energy than the other two. This is something that we do NOT see in the Lewis-dot structure. According to the Lewis dot structure all four electrons are equivalent. The bonding MOs in water are delocalized over the entire molecule. In contrast to that in the Lewis dot structure two electrons are localized in the first O-H bond, and the other two in the second O-H bond. This is another difference between the Lewis-dot and the MO picture of the covalent bonding in water.

Next, let us see if there is an equivalent of the two electron lone pairs at O in the Lewis dot structure in the MO diagram. We can see that there are two filled, non-bonding MOs, the $1b_2$ is completely non-bonding, and the $2a_1$ is approximately non-bonding. We can argue that these non-bonding electrons are the counterparts of the four electrons in the two electron lone pairs. However, in the Lewis-dot structure the two electron lone pairs appear equivalent. In the MO picture we can see that the two non-bonding electrons have a higher energy than the other two.

Overall, we can say that the MO diagrams gives us a more refined picture of the covalent bonding compared to the Lewis dot structure. This however comes at the price of constructing a complicated MO diagram compared to a simple Lewis dot structure. Therefore, our decision to construct or not construct an MO diagram depends on how much detail we need to know in the context of a chemical problem that we want to solve. For example, light absorption due to electron transitions cannot be explained via a Lewis-dot structure, we need an MO diagram to understand that.

The MO Diagram of NH_3

Let us do another, more complex example to enhance our understanding of MO theory, the example of the MO diagram of NH_3. The NH_3 molecule belongs to the point group C_{3v}. The coordinate system can be chosen so that the z-axis points vertically, and the x-axis points to the right. The y-axis stands perpendicular to the paper plane. The NH_3 molecule is oriented with the tip of the pyramid pointing up and one N-H bond being in the xz plane (Fig. 3.2.23).

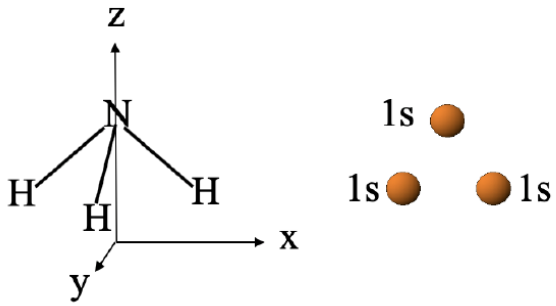
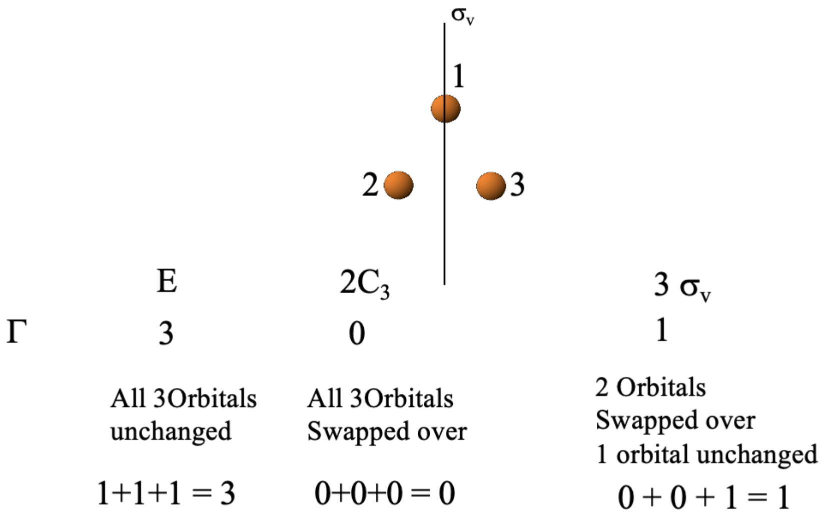


Figure 3.2.23 The chosen coordinate system and the ligand orbitals of NH_3

We would choose the N atom as the central atom and the H atoms the ligand atoms. The relevant ligand orbitals for bonding would be the 1s orbital of the H atoms. We would group them to form ligand group orbitals. Three LGOs would be expected as three 1s orbitals would be combined.

The Reducible Representation of the LGOs of NH_3

The next step is to determine the reducible representation of the LGOs using the orbital swapping method, Fig. 3.2.24.



	E	$2C_3$	$3\ \sigma_v$
Γ	3	0	1
	All 3Orbitals unchanged	All 3Orbitals Swapped over	2 Orbitals Swapped over 1 orbital unchanged
	$1+1+1 = 3$	$0+0+0 = 0$	$0 + 0 + 1 = 1$

Figure 3.2.24 Orbital swapping method for the 1s LGOs of NH_3

We can see that the identity leaves all three orbitals unchanged, hence the character on the reducible representation for E is 1+1+1=3 (Fig. 3.2.24).

Next we need to see what a C_3 operation does. It changes the position of all three orbitals, so the character on the reducible representation is 0+0+0=0.

Finally, we need to see what a vertical mirror plane does. We have three conjugate mirror planes and can select any one of the three. For example we can select the one that passes through orbital 1. Reflection at this plane does not change the position of orbital 1, but swaps up the positions of orbitals 2 and 3. Thus, orbital 1 gets a character 1, the other ones get the character 0. The character of the reducible representation is the sum of these three characters, and thus 1+0+0=1. Now, we have found all the characters of the reducible representation.

The Irreducible Representations for the LGOs of NH_3

Next, we can determine the irreducible representations from the reducible representation using the reduction formula. In this case the number of A_1 –type irreducible representations is 1, the number of E type irreducible representations is 1, and the number of A_2-type irreducible representations are 0 (Fig. 3.2.25).

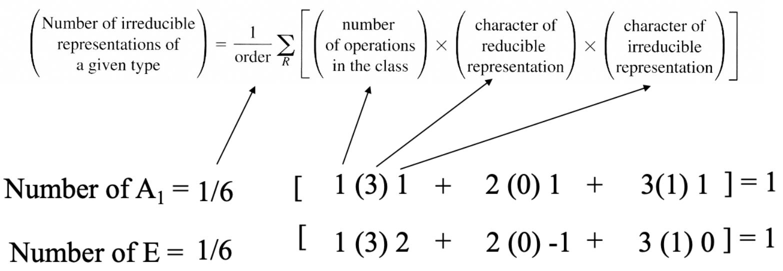
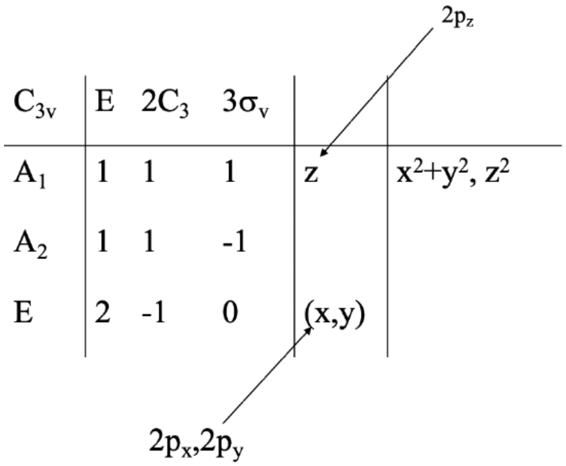


Figure 3.2.25 Calculation for the number of irreducible representations of the A_1 and E symmetry type of NH_3

At first glance it looks as though we had found only two of the three expected irreducible representations. However, we need to consider that the symmetry type E is double-degenerate, so it counts like two irreducible representations. Consequently, two of the three ligand orbitals belong to this symmetry type, and are double-degenerated. The third one has the symmetry type A_1.

Symmetry types of Central Atom Orbitals of NH_3

Next, we need to determine the symmetry type of the central atom orbitals. A quick look into the character table can tell us that (Fig. 3.2.26).



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	

Figure 3.2.26 Character table for C_{3v} and the symmetry types of the N valence orbitals.

The 2s orbital must have the totally symmetric symmetry type, thus it must have the symmetry type A_1. The $2p_x$ and the $2p_y$ orbitals are found in the row for the symmetry type E. They are double-degenerated as one can see from the fact that the letters x and y are in parentheses. The $2p_z$ orbital has A_1 symmetry, because the letter z can be found the row of the symmetry type A_1.

Combination of the AOs and LGOs of NH_3 to form MOs

Now we must again combine central atom AOs and LGOs of the same symmetry type to form molecular orbitals. The molecular orbitals will have the same symmetry type than the AOs and LGOs from which they have been made. The number of MOs of a specific symmetry type must be equal to the sum of the LGOs and AOs that have the same symmetry type. When an orbital does not find a partner orbital of the same symmetry type, then it is non-bonding.

Let us apply these ideas to the ammonia molecule. We saw that there were two AOs that had the symmetry type A_1, namely the 2s and the $2p_z$ orbitals. There was also an LGO with A_1 symmetry. We can therefore combine these three orbitals to form molecular orbitals. They also must have the symmetry type a_1.

$$A_1:\quad 2s,\ 2p_z \longrightarrow \begin{matrix}\text{Combine}\\ \text{to 3 MOs}\end{matrix} \longleftarrow \text{LGO1}$$

Figure 3.2.27 Combination of the AOs and LGOs of the A_1 symmetry type in NH_3

Next, let us think about orbitals of the symmetry type A_2. No AO and no LGO has this symmetry type. Therefore, there are also no MOs of this symmetry type. For the symmetry type E we find that there are two AOs, namely the $2p_x$ and the $2p_y$ orbital and two LGOs that have this symmetry type. This means that these two orbitals can be combined to form four MOs of the E symmetry type (Fig. 3.2.28).

$$E: 2p_x, 2p_y \longrightarrow \begin{matrix}\text{Combine}\\ \text{To 4 MOs}\end{matrix} \longleftarrow \text{LGO2 and LGO3}$$

Figure 3.2.28 Combination of the AOs and LGOs of the E symmetry type

The MO Diagram of NH_3

Now we can construct the MO diagram of NH_3 (Fig. 3.2.29).

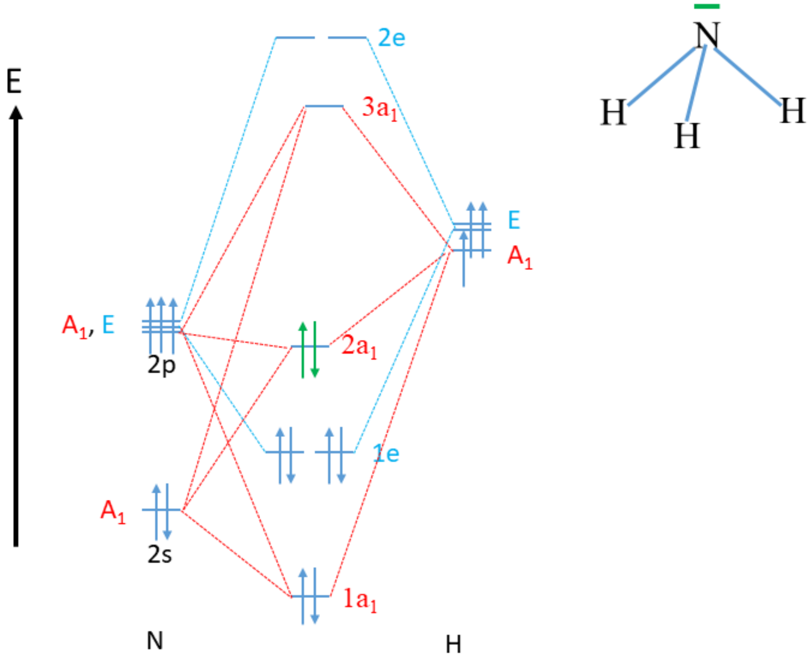


Figure 3.2.29 MO diagram of NH_3

First, we draw the energy axis and indicate the atoms N and H on the left and the right side of the diagram. In the next step we draw the atomic orbitals for the N atom and indicate the symmetry type. The 2s orbital must be drawn below the 2p orbitals to indicate their lower energy.

Then, we can draw the ligand group orbitals on the right side of the diagram and indicate the the symmetry. We can draw the A_1-type LGO somewhat below the E-type orbitals because it has a somewhat lower energy, but this is optional. We know that three MOs with a_1 symmetry must form. When three MOs form then we can estimate that one will be a low-energy bonding one, one will be a high-energy anti-bonding one, and the third one will be an approximately non-bonding one of intermediate energy. Therefore, we will draw the bonding $1a_1$-orbital below the 2s orbital, and the anti-bonding $3a_1$ orbital above the A_1-type LGO, and the $2a_1$ orbital about half-way in between. We also label the MOs according to the energy with the labels $1a_1$, $2a_1$, and $3a_1$, respectively. Lastly, we interconnect the AO and LGOs of the symmetry type A_1 with the a_1-type MOs through dotted lines. They are shown in red (Fig. 3.2.29).

Then, we draw the four E-type MOs. Because the symmetry type E implies that the orbitals are double-degenerate, we know that there must be two double-degenerate bonding MOs and two double-degenerate anti-bonding MOs of the symmetry type E. A valuable property of group theory is that double-degeneracy in symmetry also implies double-degeneracy in energy, and this means that we know that the two bonding MOs have the same energy, and the anti-bonding MOs also have the same energy. We must also draw them this way into the MO diagram. The bonding pair is labeled 1e and the anti-bonding pair is labeled 2e. We cannot know this for sure based on qualitative inspection, but we can suspect that the two bonding e-type orbitals have an energy in between the $1a_1$ and the $2a_1$ orbital. The $2a_1$ orbiital is higher than the 1e orbital because the former is approximately non-bonding, and the latter is bonding. The $1a_1$ orbital is likely lower in energy than the 1e orbital because the $1a_1$ orbital has a contribution from the low-energy 2s orbital, while the 1e orbital only has contributions from the energetically higher 2p orbitals. By similar arguments we can explain that the 2e orbital has a somewhat higher energy than the $3a_1$.

Now we still need to fill the electrons into the orbitals. The N atom has five valence electrons, two being in the 2s, and three being in the 2p orbitals. The three LGOs of H contain one electron each. This gives overall 5+3=8 electrons that we need to fill into the MOs according to energy. That fills the $1a_1$ orbital first, then the two $1e_1$ orbitals, and finally the $2a_1$ orbital. This makes the $2a_1$ orbital the HOMO in the molecule, and the $3a_1$ the LUMO in the molecule.

We can also make again a comparison of the MO and the Lewis-dot picture of the covalent bonding. We can view the non-bonding HOMO the equivalent of the electron-lone pair at N. There are six electrons in bonding MOs which is the equivalent of the six bonding electrons in the Lewis-dot structure. However, in the MO diagram we can see that the six electrons are not equivalent in energy. We are not able to see that in the Lewis-dot structure. Again, we can conclude that the MO diagram gives us more information about the bonding, which comes at the expense of the increased effort to construct an MO diagram.

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Concept Review Questions Chapter 3

Concept Review Questions

Section 1

1. What are the assumptions (axioms) of molecular orbital (MO) theory?

2. Explain qualitatively why the vectorial addition of atomic orbitals creates molecular orbitals (which underlying physical phenomenon is described by the vectorial addition?).

3. Explain qualitatively why molecular orbital theory is suitable to describe covalent bonding.

4. What are the three criteria that determine the degree of covalent interaction in MO theory?

5. Which three rules determine the degree of orbital overlap in MO theory?

6. Explain why the combination of a large, diffuse orbital and a small orbital produces only weak covalent interaction?

7. Explain why sigma-interactions between atomic orbitals typically produce larger orbital overlaps than pi-interactions?

8. Explain why the combination of orbitals of the same energy leads to the largest degree of covalent interaction?

9. What can be said about energy and location of a bonding and an anti-bonding molecular orbital that are made from atomic orbitals of large energy difference?

10. MO theory – even though designed for covalent bonding – can also make statements about ionic bonding. Explain why.

11. Explain the principles of SALC.

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Homework Problems Chapter 3

Homework Problems

Section 1

Exercise 1

What will lead most likely to the smallest covalent interaction:

a) Overlap of a small and a large orbital.

b) Overlap of two small orbitals.

c) Overlap of two large orbitals.

Answer

a) Overlap of a small and a large orbital.

Exercise 2

What will lead most likely lead to the largest covalent interaction:

a) orbital overlap in sigma-fashion

b) orbital overlap in pi-fashion

c) orbital overlap in delta fashion

Answer

a) orbital overlap in sigma-fashion

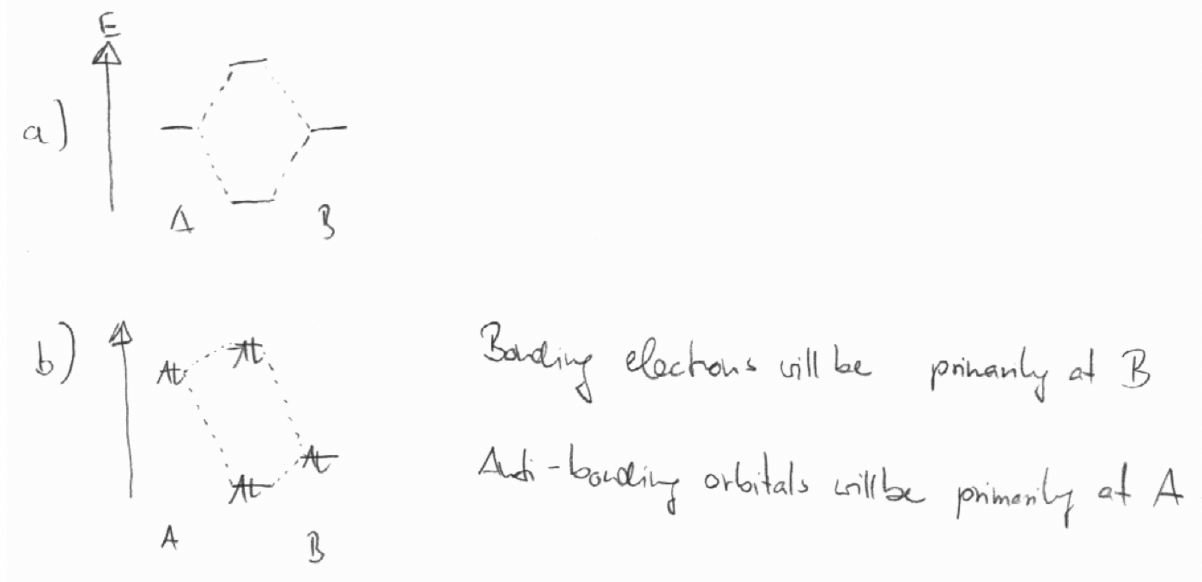
Exercise 3

Qualitatively construct the MO diagrams composed of

a) two 2s atom orbitals A and B of equal energy.

b) The orbital energy of atom A is significantly higher than that of B. Assuming both the bonding and the antibonding MO are filled with electrons: Where will bonding and antibonding electrons primarily be located. Explain briefly your decision.

Answer



Bonding electrons will be primarily at B

Anti-bonding orbitals will be primarily at A

Exercise 4

Decide by “inspection” which of the following combinations of orbitals have the “right” symmetries to form molecular orbitals.

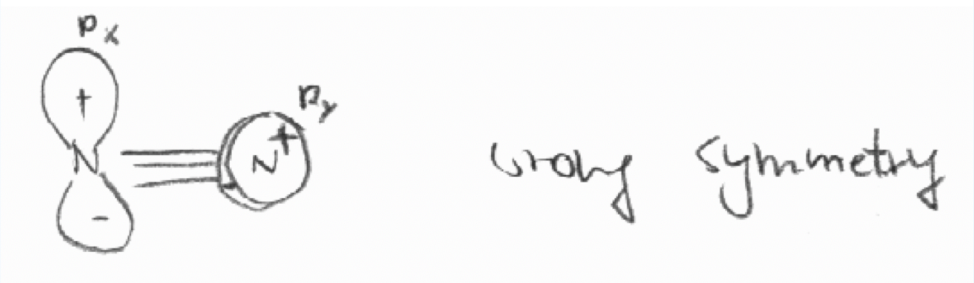
a) The $2p_x$ orbital of the first N atom and the $2p_y$ orbital of the second atom in the molecule N_2. The z axis is defined as the bond axis in N_2.

b) The $2p_x$ (of F) and the 1s orbital (of H) in the HF molecule. The z axis is defined as the bond axis.

c) The $2p_z$ orbital of F and the 1s orbital in the HF molecule: The z axis is defined as the bond axis.

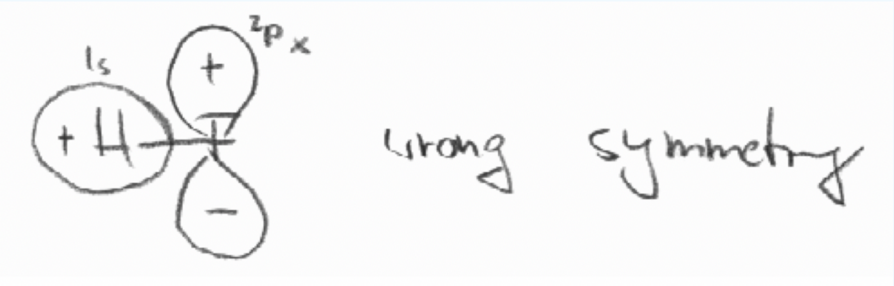
Answer

a)



wrong symmetry

b)



wrong symmetry

c) 

Exercise 5

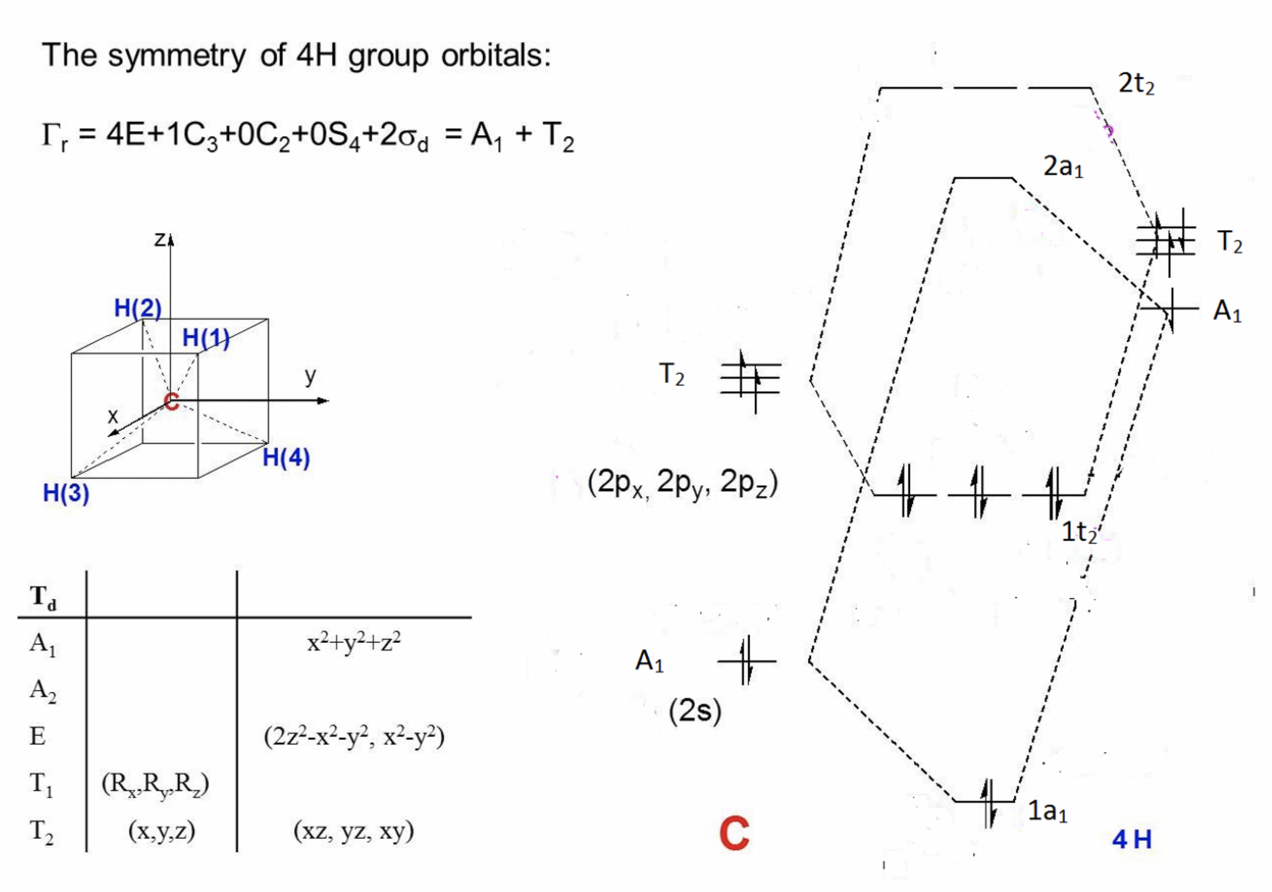
The CH_4 molecule belongs to the point group T_d. You can find the character table of the point group in the internet.

a) Calculate the reducible representation for the ligand group orbitals (LGOs).

b) Calculate the irreducible representations of the ligand group orbitals (LGOs).

c) Draw a qualitative molecular orbital diagram for CH_4.

Answer



The symmetry of 4H group orbitals:

$$\Gamma_r = 4E+1C_3+0C_2+0S_4+2\sigma_d = A_1 + T_2$$

T_d		
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x,R_y,R_z)	
T_2	(x,y,z)	(xz, yz, xy)

Exercise 6

Which are the symmetry types of the central atom orbitals in the PCl_5 molecule?

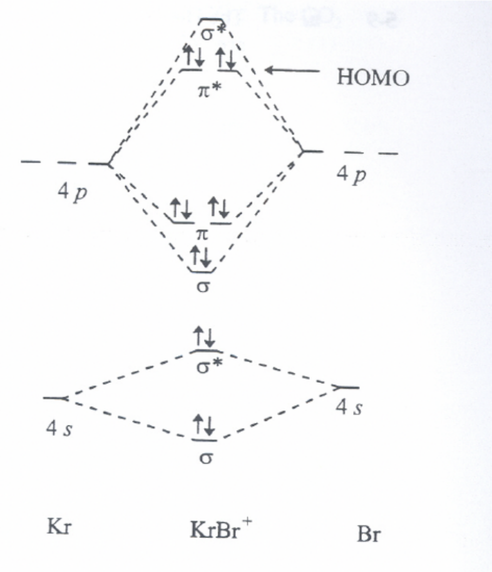
Answer

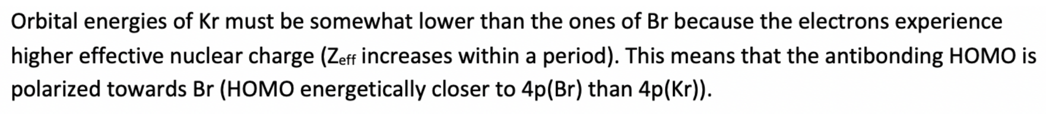
1. Determine point group of PCl_5. --> D_{3h}.
2. Decide what are the valence orbitals of the central atom: 3s, 3p
3. Look up the character table of D_{3h}, eg. in the internet. You will find their symmetries to be: A_1' (3s), A_2'' ($3p_z$), E'($3p_x$, $3p_y$)

Exercise 7

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer





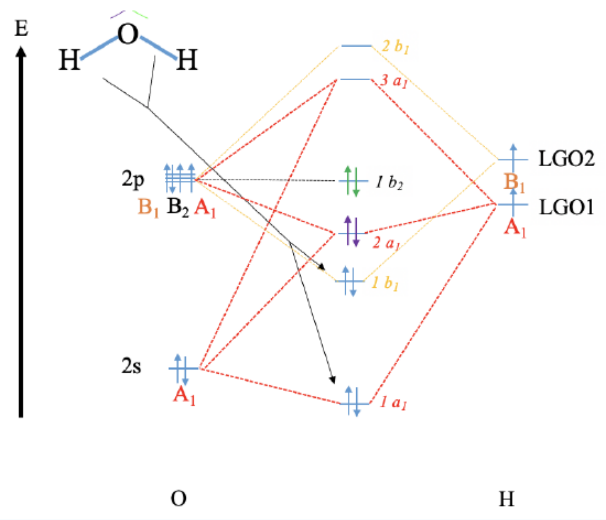
Orbital energies of Kr must be somewhat lower than the ones of Br because the electrons experience higher effective nuclear charge (Z_{eff} increases within a period). This means that the antibonding HOMO is polarized towards Br (HOMO energetically closer to 4p(Br) than 4p(Kr)).

Exercise 8

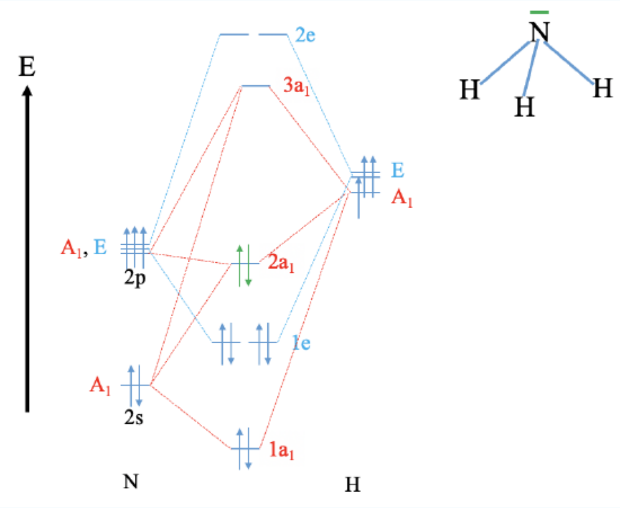
Reconstruct the MO diagram for water and NH_3 (repeat what we did in class without looking at your notes (only use the respective character tables).

Answer

Water



NH_3



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CHAPTER OVERVIEW

4: Lewis Acid-Bases and The Hard and Soft Acid-Base Concept

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4.1: Molecular Orbital Theory & Lewis acid-base reactions

A brief review of the Lewis acid-base theory

In this chapter we will discuss Lewis-acid base reactions from the perspective of molecular orbital theory. The Lewis acid-base concept has been developed by Gilbert Lewis (Fig. 4.1.1).

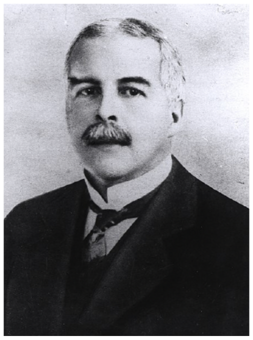

Figure 4.1.1 Gilbert Lewis (1875-1946) (Attribution: es una imagen de licencia libre, no tiene autor / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0) https://commons.wikimedia.org/wiki/F...wton-Lewis.jpg)

It is a very general acid-base concept, and includes the Broensted and Arrhenius acid-base concepts. It is very important for coordination chemistry. Let us briefly review what a Lewis acid, a Lewis base, and a Lewis acid-base reaction is.

A Lewis acid is defined as an electron pair acceptor.

Definition: Lewis Acid

A Lewis acid is an electron pair acceptor

A Lewis base is defined as an electron pair donor.

Definition: Lewis Base

A Lewis base is an electron pair donor

An example of a Lewis acid is BH_3, and an example for a Lewis base is NH_3. What happens in a Lewis-acid base reaction?

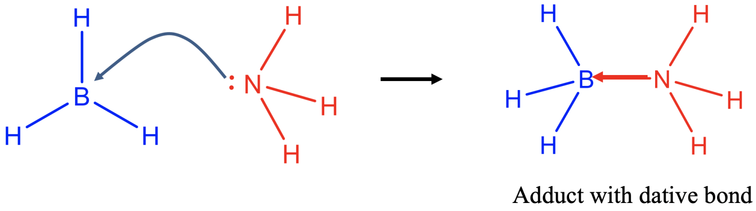

Figure 4.1.2 Acid-base reaction between NH_3 and BH_3

The Lewis base donates an electron pair to form a covalent bond with the Lewis acid (Fig. 4.1.2). A covalent bond formed in a Lewis acid-base reaction is usually called a dative bond because both electrons in the covalent bond come from a single partner. In a "conventional" covalent bond both partners contribute one electron to the covalent bond. There is however no fundamental difference between a “conventional” covalent bond and a dative covalent bond, it is just a matter of perspective. To indicate a dative bond one can draw an arrow pointing from the donor to the acceptor atom, instead of just a line. The reaction product of a Lewis acid-base reaction is called an adduct.

As mentioned previously, the Lewis acid-base concept is quite general and can explain the bonding in quite different compounds. It includes the Broensted acid-base concept, meaning that any Broensted acid is also a Lewis acid, and any Broensted base is also a Lewis base. However, the reverse is not true. Not every Lewis acid is a Broensted acid, and not every Lewis base is a Broensted base.

Here are a few examples that can illustrate the generality of the Lewis acid-base concept.

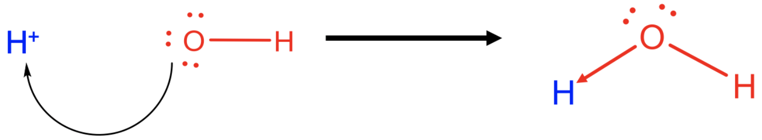

Figure 4.1.3 Acid-base reaction between H^+ and OH^-

For example, an H^+ ion is a Lewis acid and an OH^- anion is a Lewis base, and the two can react to form water as a Lewis-acid base adduct. In this case one of the O-H bonds in the water molecule would be viewed as a dative bond, while the other one would be viewed as a “regular” covalent bond. Of course, there is no actual difference between the two bonds, we just have a different perspective on them. The same reaction could also be viewed as a Broensted acid base reaction with the OH^- ion as the proton acceptor, and the H^+ ion as the proton donor.

The Lewis acid-base concept also explains bonding in coordination compounds, and the formation of coordination compounds from metal ions and ligands. The ligand is the Lewis base and the metal ion is the Lewis acid, the coordination compound is the Lewis acid-base adduct. The bond between the metal ion and ligand is a dative bond pointing from the ligand to the metal.

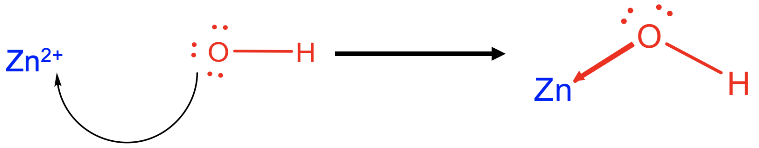

Figure 4.1.4 Acid-base reaction between Zn^{2+} and OH^-

For example, Zn^{2+} acts as a Lewis acid when reacting with 4 OH^- as a Lewis base to form tetrahydroxo zincate (2-) anions (Fig. 4.1.4). The formed Zn-O bonds are dative bonds indicated as arrows pointing from the O to the Zn.

The Lewis acid-base concept can even be used to explain bonding in ionic crystals. In this case the anion would be the donor and the cation the acceptor.

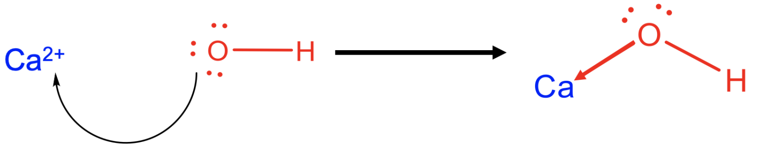

Figure 4.1.5 Acid-base reaction between Ca^{2+} and OH^-

For example Ca^{2+} can be viewed as a Lewis acid, and OH^- as a Lewis base in a reaction that forms calcium hydroxide $Ca(OH)_2$ as the Lewis acid-base adduct. The bonds between Ca^{2+} and OH^- would be viewed as a dative bonds indicated as arrows pointing from O to Ca. In this case the ionic bonds would be interpreted as highly polar dative bonds. You may want to remember in this context that completely ionic bonds are not possible in general, and there must also be some degree of covalency due to the finite electronegativity difference between two elements.

MO theory and Lewis Bases

MO theory is a theory designed to explain covalent bonding. Because dative bonds are covalent bonds, MO theory should be able to explain dative bonds. So how can Lewis acids and bases and their reactions be viewed from an MO theory perspective? MO theory states that a molecule is a Lewis base when its HOMO is approximately non-bonding (Fig. 4.1.6).

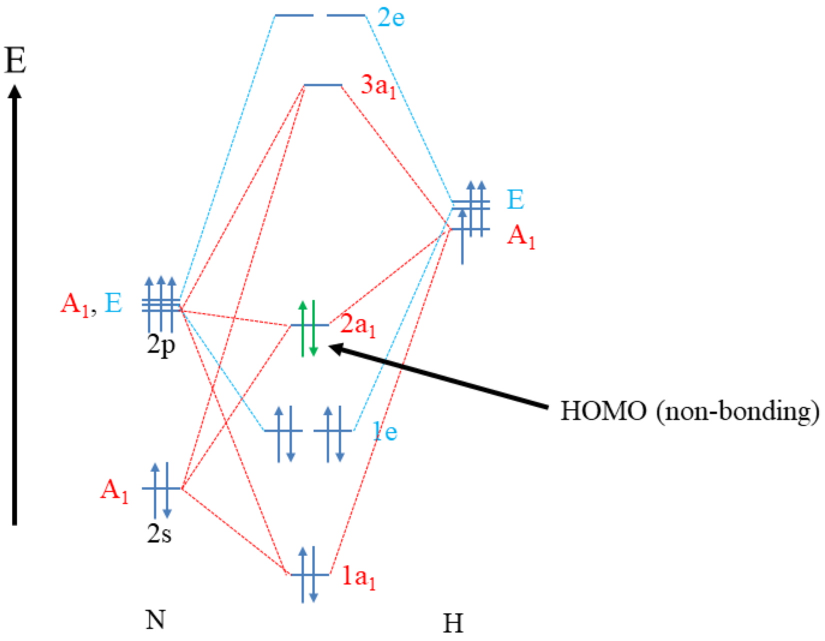

Figure 4.1.6 Molecular orbital diagram of NH_3

This explains, for example, that NH_3 is a Lewis base. Remember, its HOMO, the $2a_1$ orbital, is approximately non-bonding. Why does an approximately non-bonding HOMO make a molecule a Lewis base? Firstly, because the HOMO electrons are the highest energy electrons and thus the most reactive electrons, they get donated preferentially over all other electrons. The non-bonding nature of the HOMO is ideal, because if the HOMO was anti-bonding, the electrons would be so reactive, so that they would likely get completely transferred to the reaction partner. In this case we would not have a Lewis acid-base reaction, but a redox reaction. We would not form a covalent bond, but an ionic bond. If the HOMO was bonding, then the energy of the electrons would be too unreactive, simply no reaction would likely be observed.

MO theory and Lewis Acids

So what is then a Lewis acid according to MO theory? A Lewis acid, from the MO theory perspective, is a molecule that has an approximately non-bonding lowest unoccupied molecular orbital. The orbital needs to unoccupied, otherwise no electrons could be donated into it. For energy minimization arguments, electrons would be donated into the unoccupied orbital that has the lowest energy, which is the LUMO. So why is it ideal if the LUMO is non-bonding? If it was anti-bonding, its energy would likely be too high, and the donor would be unable to donate its electrons. There would not be a stabilization of electrons due to the high energy of the LUMO. The molecule would remain unreactive. If the LUMO was a bonding orbital, then its energy would likely be so low so that the electrons would likely be completely transferred to the Lewis acid. In this case we would not form a dative bond but an ionic bond via a redox reaction.

An example of a Lewis acid is the BeH_2 molecule. It is a linear molecule belonging to the point group $D_{\infty h}$. The character table of this point group is a bit unusual because the principal axis has infinite order, and there is an infinite number of C_2 axes and mirror planes (Fig. 4.1.7). Therefore, the symmetry types of this point group are not of the type we previously encountered. We do not want to understand the character table and its symmetry types in detail here, but just extract the information that is relevant for us to construct the molecular orbitals.

$D_{\infty h}$		
Σ_g^+		x^2+y^2, z^2
Σ_u^+	z	
Π_u	(x,y)	

Figure 4.1.7 $D_{\infty h}$ character table (simplified)

The central atom of the molecule is the Be atom, and its valence orbitals are the 2s and the 2p orbitals. According to the character table of $D_{\infty h}$ the 2s orbital has the symmetry type Σ_g^+, the $2p_z$ orbital has the symmetry Π_u, and the $2p_x$ and the $2p_y$ orbitals are double-degenerated, and have the symmetry type Σ_u^+.

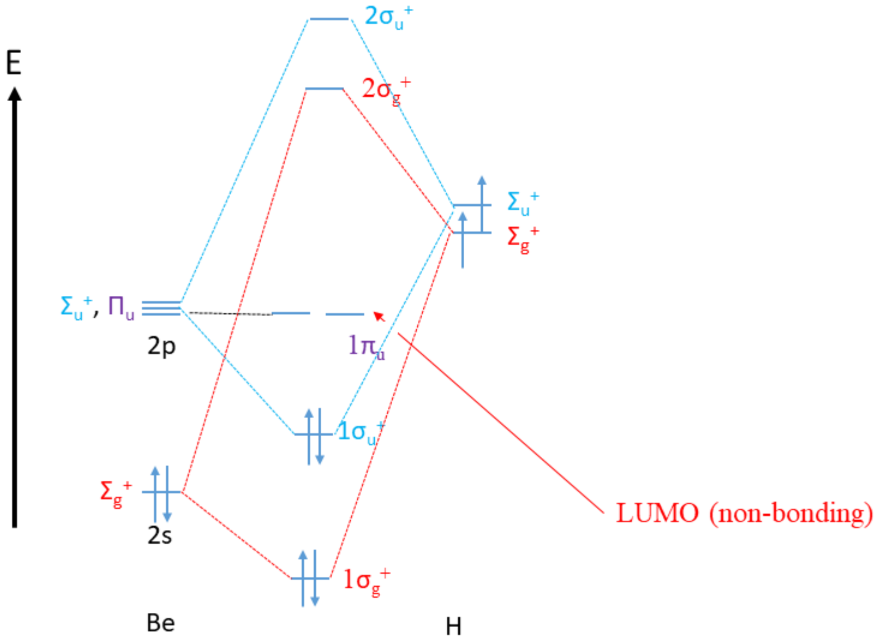

Figure 4.1.8 Molecular orbital diagram for BeH_2

The two 1s orbitals of H make two ligand group orbitals. Determination of the reducible and the irreducible representation of the the LGOs via SALC would give the symmetry types of the LGOs which in this case are Σ_g^+ and Σ_u^+. We therefore expect that there is a bonding and an anti-bonding orbital of σ_g^+ type, and a bonding and an anti-bonding orbital are of the σ_u^+ type. The $2p_x$ and the $2p_y$ orbitals remain non-bonding. The Be atom has two valence electrons in the 2s orbital, and the 2 H atoms contribute two valence electrons each, so there are overall four electrons that we need to fill into the MOs. This fills the bonding σ_g^+ and the σ_u^+, making the σ_u^+ the HOMO. You see that we have a bonding HOMO here, which would argue that BeH_2 is not a Lewis base. However, we see that the LUMOs are the non-bonding $2p_x$ and $2p_y$ orbitals. This explains the Lewis-acidic character of the molecule.

Bonding in Lewis Acid Base Adducts

The greatest covalent interaction between two orbitals it is achieved when both orbitals have the same energy. We learned this previously in Chapter 3 when we discussed the energy criterion. The same holds for dative bonds. The more similar the energies of the donor HOMO and the LUMO acceptor, the greater the covalent interaction. Ideally, the energies are exactly same. In this case we form a perfect covalent bond with the electrons equally shared between the donor and the acceptor. We can graphically illustrate this in an MO diagram the following way (Fig. 4.1.9).

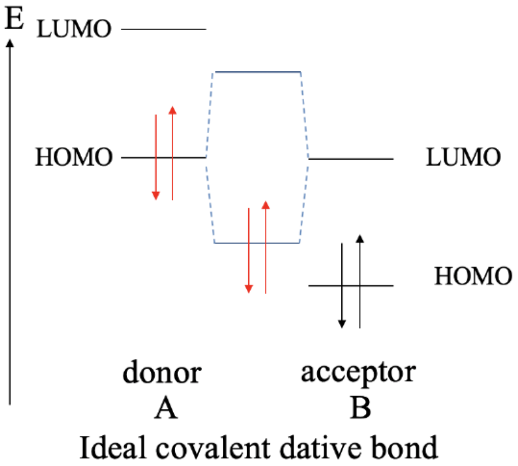

Figure 4.1.9 Covalent interaction between the HOMO of donor A and the LUMO of acceptor B with the same energy

Let us assume a molecule A that acts as a donor and a molecule B that acts as an acceptor. The donor A has a HOMO and a LUMO that have a certain energy. The acceptor molecule B also has a HOMO and a LUMO with the LUMO having the same energy as the HOMO of A. The molecule B will also have HOMO which is energetically below that LUMO. Because their identical energies the combination of the HOMO of A with the LUMO of B leads to a bonding MO and an anti-bonding MO with equally shared electron density. Both MOs have equidistant energy from the HOMO of A and the LUMO of B. The electrons coming from the HOMO of A will be in the bonding MO. They will be equally shared, and the dative bond is an ideal covalent bond.

The exact match of the HOMO and LUMO energies of the donor and acceptor is rarely achieved. Let us consider a number of scenarios in which these energies are not the same, and what consequences this has for the dative bond.

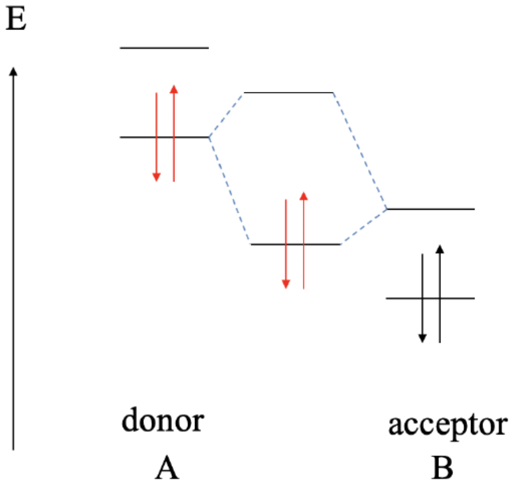

Figure 4.1.10 Covalent interaction between a LUMO of acceptor B that has somewhat lower energy than the HOMO of donor A

Let us assume next, that the LUMO of the acceptor B is somewhat lower than the HOMO of donor A. In this case, we can still form a bonding MO and an anti-bonding MO due to covalent interaction between the HOMO of A and the LUMO of B. However, now the bonding MO will be localized primarily at B, and the anti-bonding MO will be localized mostly at A. The electrons from the HOMO of A will be in the bonding MO, and thus the bonding electrons in the dative bond will be localized mostly at B. This means that the dative bond is polar, and polarized toward the acceptor.

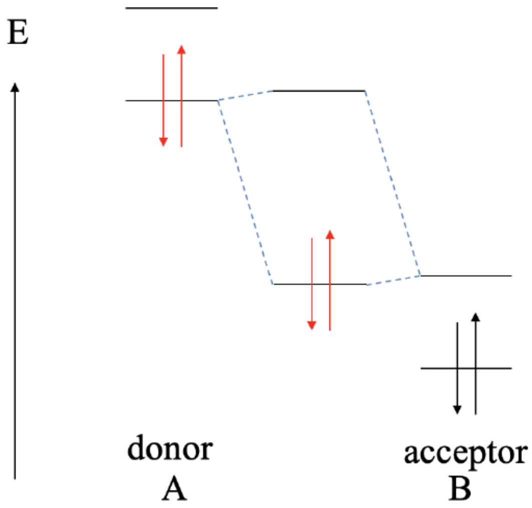

Figure 4.1.11 Covalent interaction between a LUMO of the acceptor that is much lower energy than the HOMO of the donor

Let us consider next, what the bonding will be if the LUMO of the acceptor is much lower than the HOMO of the donor (Fig. 4.1.11). In this case, there is still the possibility to form a bonding MO and an anti-bonding MO, but the bonding MO will be localized practically exclusively at the acceptor, and the anti-bonding MO will be localized practically completely ar the donor. The electrons from the donor will be in the bonding MO, but because the bonding MO is located almost entirely at the acceptor, the electrons are transferred completely from A to B in a redox reaction, and the bonding will be ionic, and we have an ionic compound AB made of A^{2+} cations and B^{2-} anions. This reaction would no longer be considered a Lewis acid-base reaction, and the reaction product will no longer be considered a Lewis acid-base adduct.

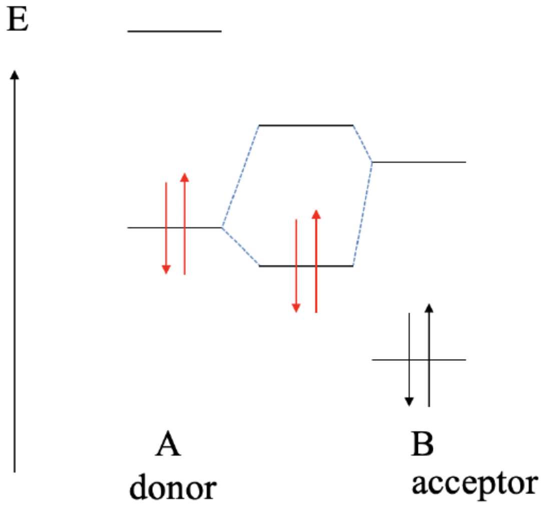

Figure 4.1.12 Covalent interaction when the LUMO of the acceptor B is higher in energy than the HOMO of donor A

The next possibility to consider is that the LUMO of B is higher in energy than the HOMO of A (Fig. 4.1.12). In this case the bonding MO will be localized primarily at the donor A and the electrons in the dative bond will be predominantly at A. We have a polar, dative bond which is polarized toward A.

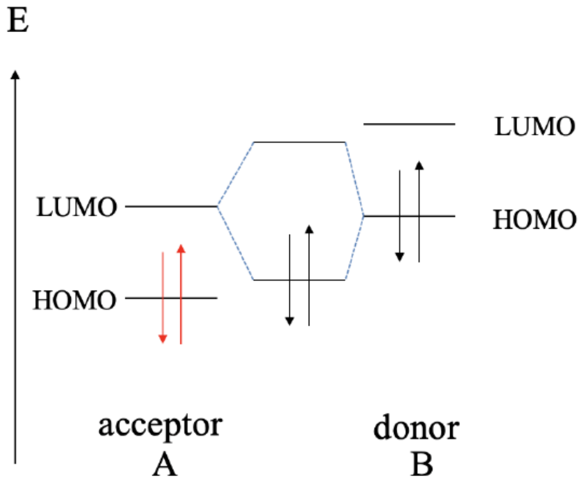

Figure 4.1.13 Covalent interaction when the LUMO of A is of similar energy compared to the HOMO of B and the LUMO of B is energetically much higher than the LUMO of A.

Next, let us raise the energy of the HOMO and the LUMO of B even higher. This leads to the fact that now the HOMO of B is energetically closer to the LUMO of A, compared to the energy difference between the HOMO of A and the LUMO of B. This results in the fact that the interaction will be mostly between the HOMO of B and and the LUMO of A. As a consequence, B will act now as the donor, and A will act as the acceptor. The dative bond may be polarized toward A or B, or not be polar at all depending on the relative energy of the HOMO of B and the LUMO of A.

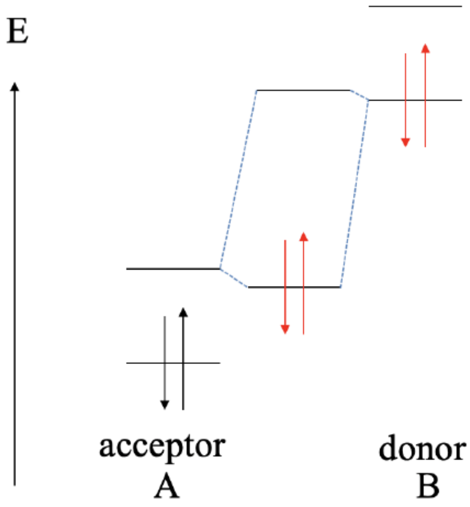

Figure 4.1.14 Covalent interaction between LUMO of acceptor A and HOMO of donor B, when the HOMO of B is much higher in energy than the HOMO of A

If we raise the orbital energies of B even further, and the HOMO of B is much higher than the HOMO of A, then we will get a redox reaction. B gets oxidized, and A gets reduced. B^{2+} cations and A^{2-} anions will form an ionic compound of the composition AB.

Examples

Generally spoken, the relative HOMO and LUMO energies of reaction partners decide if a Lewis acid-base, or a redox reaction takes place, and what the polarity of the bond is. Here are a few examples that will illustrate our general considerations (Fig. 4.1.15).

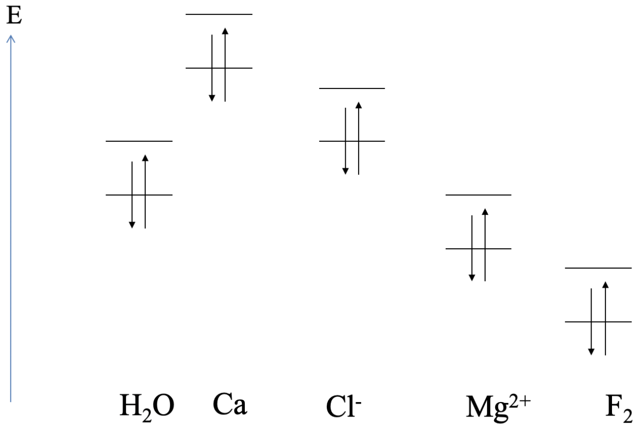

Figure 4.1.15 Practical examples of covalent Lewis acid-base reactions

The relative orbital energies of the highest occupied atomic orbitals and the lowest unoccupied atomic orbitals of calcium, and the HOMO and LUMO energies of H_2O are shown (Fig. 4.1.15). Can we predict the type of reaction? We can see that the highest occupied Ca orbital has a much higher energy than the LUMO of water. We would therefore expect that Ca gets oxidized, and water gets reduced. An ionic compound would be expected. This is what actually happens in experiment. The reaction of water and calcium yields calcium hydroxide and hydrogen gas.

Next, let us consider a possible reaction between water and chloride. We can see that the HOMO of Cl^- is similar in energy compared to the LUMO of H_2O. We would therefore expect a Lewis acid-base interaction with Cl^- as the donor and H_2O as the acceptor. Such an interaction indeed occurs in aqueous solutions containing Cl^- in the form of weak hydrogen bonding between Cl^- and H_2O.

Next, let us consider the interactions between Mg^{2+} and H_2O. In this case the LUMO of Mg^{2+} has about the energy of the HOMO of the water molecule. We would therefore expect that the water molecule acts as the donor and the Mg^{2+} acts as the acceptor. Indeed, Mg^{2+} forms a hexaaqua complex with water, which has the composition $Mg(H_2O)_6{}^{2+}$. The bonding should be very little polar.

Lastly, what are the interactions between F_2 and H_2O? The HOMO of H_2O is much higher than the LUMO of F_2. We would therefore expect a redox reaction in which F_2 is reduced, and H_2O is oxidized. In reality F_2 can oxidize H_2O to form OF_2 and HF.

From the above examples it becomes also clear that we cannot necessarily predict the strength of the Lewis-acid base interactions. For example, the hydrogen bonding between H_2O and Cl^- is much weaker than the dative bonds between H_2O and Mg^{2+}. Other factors such as orbital overlap also need to be taken into consideration to make statements about the strength of the interactions.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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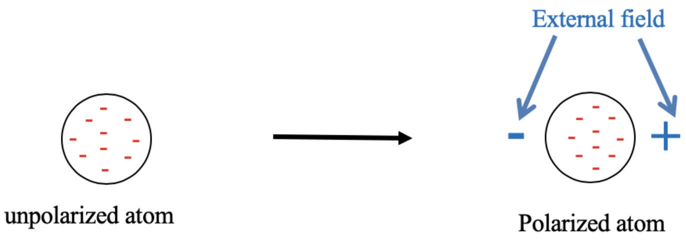
4.2: Hard and Soft Acids and Bases

The Hard and Soft Bases Concept (HSAB)

The hard and soft acid and base concept (HSAB) can be conceived as a refinement of the Lewis-acid and base concept. Its most useful feature is that it can make predictions about the strength of the acid-base interactions. It can also estimate if the interactions are more ionic or more more covalent.



4.2.1 Visual representation of a unpolarized atom and an atom polarized in an electric field.

Let us first clarify what is meant by hard and soft, respectively. These terms refer to the polarizability of the electrons in an atom or a molecule (Fig. 4.2.1). An atom is soft when its electrons are easily polarizable. This means that the electron cloud easily deforms in an electric field. Easy deformation is consistent with the term "soft". In an electric field the negatively charged electrons are attracted to the positive pole of the electric field. Therefore, the electron cloud distorts toward the positive end of the electric field, and the atom is polarized. Vice versa, when the electron cloud is not easily polarizable, we say the atom is hard. What is then meant by a hard and a soft acid or base? A hard or soft acid is a hard or soft Lewis acid, and a hard or soft base is a hard or soft Lewis base. As mentioned previously, the HSAB concept is useful because it make statements about the strength of the acid-base interactions, and thus the strength of the bonds. It can also make statements on whether the bonding is more covalent or more ionic (Fig. 4.2.2).

Hard-hard interactions: strong (mostly ionic)
Soft-soft interactions: strong (mostly covalent)
Hard-soft interactions: weak

Figure 4.2.2 Relationships between the hardness of acids and bases, and the strength and nature of the acid-base interactions

Generally, hard-hard interactions, meaning the interactions between a hard acid and a hard base, tend to be strong. The bonding is more likely ionic. Soft-soft interactions also tend to be strong, but they are more likely covalent. Hard-soft interactions tend to be weak.

Species with large donor/acceptor atoms: soft
Species with small donor/acceptor atoms: hard

Figure 4.2.3 Size of donor atoms affect on hard-soft behavior

Why are soft-soft and hard-hard interactions strong, while hard-soft interactions are weak? To answer this question, we must first understand what makes and acid or base hard or soft. Generally, we can say that the more delocalized the electrons are, the softer the species. For a single atom or ion this means that the larger the atom or ion is the softer the species. The larger the atom size, the more delocalized are its valence electrons. The size of a neutral atom is defined by its position in the periodic table. Generally, the higher the period, the softer the atom (Fig. 4.2.3).

For cations:
Higher positive charge → smaller radius → higher hardness

For anions:
Higher charge → larger radius → smaller hardness

Figure 4.2.4 Effect of charge on hard-soft behavior

For ions, also the charge plays a role. For cations, a higher positive charge makes a cation harder, for anions a higher negative charge makes the anion softer (Fig. 4.2.4).

If species is large, then it can nonetheless be hard if no orbitals are available for π-bonding
(e.g. Cs$^+$ is hard acid).

If species is small, then it can be soft when orbitals for π-bonding is available
(e.g. d orbitals can be used for π-bonding: Cu$^+$ is soft acid,
or π-orbitals can be used, e.g. CN$^-$,CO are soft bases).

Figure 4.2.5 π-bonding effect on hard-soft behavior

The size of the donor/acceptor atom is not the only factor that determines the hardness. Also the ability of the species to make π-bonding is important. Species that have orbitals suitable for π-bonding tend to be soft even if size arguments suggest that they are hard. This is because π-bonding increases electron delocalization (Fig. 4.2.5).

For example, transition metals have d-orbitals available which are suitable for π-bonding with ligands, while alkali metals do not. Therefore, a relatively small transition metal cation such as Cu$^+$ is softer than large alkali metal ions such as Cs$^+$. For anions π-bonding is also important. For instance, CN$^-$ anions are soft bases even though the donor carbon atom is small because the CN$^-$ ligand has π-orbitals available for π-bonding with Lewis acids.

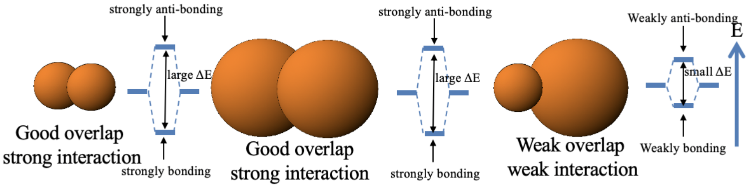


Figure 4.2.6 Orbital overlap criterion

So back to the question: Why are soft-soft and hard-hard interactions strong, but hard-soft interactions weak? This essentially boils down to rule 2 of the orbital overlap criterion (see chapter 3 on MO theory). Two small orbitals have typically good overlap, and two large orbitals also have good orbital overlap, and thus the interaction is strong. However, large and small orbitals tend to have weak orbital overlap, and thus the bonding weak.

Now to the question of why soft-soft interactions tend to be more covalent, while hard-hard interactions tend to be more ionic. The answer has to do with the fact that in smaller atoms the energy differences between atomic orbitals tends to be larger compared to large atoms. As a consequence, it is statistically more likely that the HOMO and LUMO of two soft species have more similar energies compared to two hard species. When the HOMO and LUMO of a Lewis acid and a Lewis base are similar in energy, then the bonding is more covalent. When they are significantly different, then the bonding is more ionic.

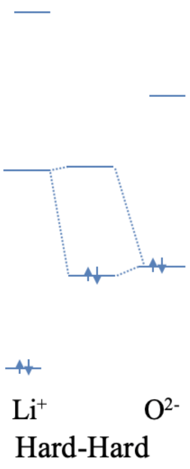


Figure 4.2.7 Hard-hard covalent interactions in lithium oxide

Let us illustrate this by two qualitiative examples. Lithium oxide is made of O^{2-} anions and Li$^+$ cations. If we view the ionic bonding between the O^{2-} and the Li$^+$ ions as an extreme case of a polar, dative bond, then oxide anion acts as a Lewis base, and the Li$^+$ ion acts as a Lewis acid. How can the high ionicity be explained? Both the Li$^+$ and the O^{2-} are small ions, thus they are both hard. The small size also implies that the energy differences between the atomic orbitals are large. Because of this, it is unlikely that the highest occupied atomic orbital of the O^{2-} ion has a similar energy than the lowest unoccupied atomic orbital of the Li$^+$ ion. Due to the large energy difference, the bonding MO will be localized almost completely at the O^{2-} anion, and the bonding will be ionic (Fig. 4.2.7).

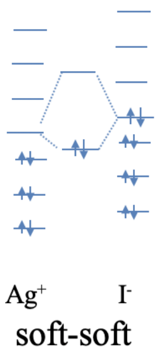


Figure 4.2.8 Soft-soft covalent interactions in silver iodide

An example of a compound with strong soft-soft-interactions is silver iodide. While AgI is considered an ionic compound, the interactions have a significantly stronger covalent character. The soft nature of Ag^+ is readily understood from the fact that Ag^+ is a period 5 transition metal ion with low positive charge, and d-orbitals available for π-bonding. Iodine is a period 6 element, thus iodide is quite soft. Because Ag and I are elements of period 5 and 6, respectively, their orbital energy differences are significantly smaller than those of O and Li which are period 2 elements. Thus, the HOMO of I^- and the LUMO of Ag^+ are naturally closer in energy resulting in a more covalent interaction (Fig. 4.2.8).

We should be aware that we need to treat these considerations with caution. For example, B-O bonds are fairly covalent bonds despite the fact that B and O are both quite hard. The HOMO of the donor and the LUMO of the acceptor of hard species are not necessarily much different. Other parameters such as electronegativity differences also weigh in and must be taken into account to correctly predict the nature of the chemical bond.

Examples - Bases

To get a feeling for correctly estimating the hardness of a species let us consider a few examples. Let us start with some bases.

$$F^- \qquad Cl^- \qquad Br^- \qquad I^-$$

Figure 4.2.9 Example of bases

What statements about hardness can you make for the series F^-, Cl^-, Br^-, I^- (Fig. 4.2.9). They are all halogenide ions with the same negative charge. The size increases from fluoride to chloride, to bromide to iodide. Thus, the softness should increase in the same order. F^- is a small ion with a small negative charge and should be be hard, I is a very heavy element therefore I^- is very soft. Cl^- and Br^- are moderately hard, and soft ions, respectively.

$$H_2O \qquad OH^- \qquad O^{2-} \qquad CH_3O^- \qquad PhO^-$$

Figure 4.2.10 Example series with O donor atoms

Next, consider the series H_2O, OH^-, O^{2-}, CH_3O^-, and PhO^-. All of the species contain small O donor atoms, so all of them should be considered hard. The OH^- ion is somewhat softer than the H_2O because of the negative charge that increases the size of the donor O atom. For the same reason O^{2-} is somewhat softer than OH^-. CH_3O^- is somewhat softer than O^{2-} because of the positive inductive effect of the methyl group. The phenolate ion is the softest because the negative charge at O can be delocalized in the aromatic ring. The delocalization of the negative charge leads to a greater polarizability, and thus softness. We could also think about if F^- would likely be harder or softer than H_2O. F is a little smaller than O, but F carries a negative charge, so the case is ambiguous.

$$NH_3 \qquad CH_3NH_2 \qquad PhNH_2$$

Figure 4.2.11 Example series with N donor atoms

Next, let us look at the series NH_3, CH_3NH_2, and $PhNH_2$ (Fig. 4.2.11). The N donor atom is a small, little polarizable atom, thus the species should be regarded hard. N is somewhat larger than O though, which means that NH_3 is somewhat softer than H_2O. CH_3NH_2 would be a bit softer than NH_3 because the positive inductive effect of the methyl group, and aniline would be a bit softer than methyl amine because of possibility to delocalize the lone pair at N in the aromatic ring.

$$H_2S \qquad RSH,\ RSR$$

Figure 4.2.12 Example series with S donor atoms

What about H_2S, alkyl thiols and di alkyl thiols (4.2.12)? The S donor atom is in the 3rd period, and large enough to be considered soft. The softness would be expected to somewhat increase from H_2S to R-SH to R-S-R because of the positive inductive effect of the alkyl group.

$$PR_3$$

Figure 4.2.13 Example of PR_3

The next example is a phospine of the general formula PR_3 (4.2.13). Like sulfur, phosphorus is a period 3 donor atom, and phosphines are generally soft.

$$CO \qquad CN^-$$

Figure 4.2.14 Example series with C donor atoms

Lastly, let us look at carbon monoxide and cyanide (Fig. 4.2.14). At first glance these species appear like hard bases because of the small carbon donor atoms. However, they are actually quite soft because of their ability to use their π and π^* orbitals in π-bonding with Lewis acids, in particular transition metal ions. We will look closer at this issue later when we discuss the bonding in transition metal complexes in detail.

Example - Acids

Now let us think about the hardness of acids.

$$H^+ \qquad Li^+ \qquad Na^+ \qquad K^+$$

Figure 4.2.15 Example series of alkali metal cations

In the series H^+, Li^+, Na^+, K^+: Are these hard or soft acids and how does the hardness change within this series (Fig. 4.2.15)? The answer is: All alkali metal cations are considered hard acids, even the relatively large K^+ cation in the 4th period. This is because alkali metal cations have only s-valence orbitals and thus a lack of orbitals suitable for π-bonding. Within the series H^+ is the hardest and K^+ is the softest because the ionic radius increases with increasing period.

$$Be^{2+} \qquad Mg^{2+} \qquad Ca^{2+}$$

Figure 4.2.16 Example series of earth alkali metal cations

Similarly, the earth alkaline metals Be^{2+}, Mg^{2+}, and Ca^{2+} are hard cations with the hardness decreasing from Be^{2+} to Ca^{2+}. Due the the 2+ charge earth alkaline metal cations are expected harder than alkali metal cations of the same period, for example Be^{2+} should be estimated harder than Li^+.

$$BF_3 \qquad BCl_3 \qquad B(CH_3)_3 \qquad BH_3$$

Figure 4.2.17 Example series with boron

In the next series BF_3, BCl_3, $B(CH_3)$, and BH_3 the hardness declines from BF_3 to BH_3 (Fig. 4.2.17). BCl_3 is a softer than BF_3 because of the smaller electronegativity of Cl versus F. The more electronegative F withdraws more electron density from the boron making it smaller, and thus harder. Because of the positive inductive effect, the $B(CH_3)_3$ is softer than BCl_3. The BF_3 and BCl_3 molecules are considered hard acids overall, the $B(CH_3)_3$ is an intermediate case. At first glance, it would appear that BH_3 is harder than $B(CH_3)_3$, nonetheless it acts more like a soft acid, possibly because of the hydride-like character of the compound.

$$Fe^{2+} \qquad Fe^{3+} \qquad Co^{2+} \qquad Co^{3+} \qquad Rh^{3+} \qquad Ir^{3+}$$

Figure 4.2.18 Example series with transition metal ions

Next let us consider the transition metal ion series Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+} (Fig. 4.2.18). These cations have the ability to make π-bonding, but because of the higher 2+ and 3+ charge respectively, none of them are soft. All period 4 cations with a 3+ charge, namely Fe^{3+} and Co^{3+} are hard acids, the Fe^{2+} and Co^{2+} ions are at the borderline between hard and soft due to their lower charge. Rh^{3+} and Ir^{3+} are also at the borderline. They have a higher positive charge, but are in period 5 and 6, respectively. Rh^{3+} would be expected to be harder than Ir^{3+} because it is in a lower period.

$$Ti^{4+} \qquad Si^{4+}$$

Figure 4.2.19 Example series of transition metals with 4+ charges

Ti^{4+} and Si^{4+} are both hard acids (Fig. 4.2.19). Generally, all ions with a charge of +4 or higher are hard acids.

Cu^{+} Cd^{2+} Hg^{2+} Pd^{2+} Pt^{2+}

Figure 4.2.20 Example series of period 4 transition metal ions

What about the last series Cu^+, Cd^{2+}, Hg^{2+}, Pd^{2+}, and Pt^{2+} (Fig,. 4.2.20)? Think about it. They are all considered soft acids. Cu^+ is a relatively low period 4 element, but has only a 1+ charge, and has d-orbitals for π-bonding. Hg^{2+}, Pd^{2+}, and Pt^{2+} have a somewhat higher 2+ charge, but are period 5 and 6 elements, and also have d-orbitals for π-bonding. Pt^{2+} would be expected softer than Pd^{2+} because of its higher period.

Quantitative Measures for Hardness

From the previous considerations we have seen that it is possible to make qualitative, and in some cases semi-quantitative estimates about the hardness of acids and bases, but they are not a quantitative measure for hardness. A hardness scale that allows for quantitative measure of hardness is Pearson's concept of absolute hardness (Equ. 4.2.1).

$$\text{Hardness: } \eta = \frac{\mathrm{I}-\mathrm{A}}{2}$$

Equation 4.2.1 Equation for the quantitative calculation of absolute hardness

It relates the hardness to the difference between the ionization energy and the electron affinity over 2.

$$\text{Softness: } \sigma = 1/\eta$$

Equation 4.2.2 Equation for the quantitative calculation of softness

The softness is then defined as the inverse of the absolute hardness (Eq. 4.2.2).

$$\chi = \frac{\mathrm{I}+\mathrm{A}}{2}$$

Equation 4.2.3 Equation for Mulliken's electronegativity

We can immediately see that the absolute hardness is related to Mulliken's electronegativity scale which is the ionization energy + the electron affinity over 2 (4.2.3).

What is the idea behind this definition? We have previously qualitatively discussed that hard species tend to have large orbital energy differences, while soft species tend of have small orbital energy differences. Therefore, it makes sense to define the energy difference between the highest occupied atomic or molecular orbital and the lowest unoccupied atomic or molecular orbital a quantitative measure for the hardness of a species (Eq. 4.2.4).

$$\text{Hardness: } \eta = \frac{\mathrm{I}-\mathrm{A}}{2} = \frac{\boldsymbol{E(HOMO)-E(LUMO)}}{\mathbf{2}}$$

Equation 4.2.4 Extended equation for the calculation of absolute hardness

The first ionization energy IE is minus the energy of the highest occupied atomic/molecular orbital: IE=-E(HOMO or HOAO) and the electron affinity is minus the energy of the lowest unoccupied molecular or atomic orbital: EA=-E(LUMO/LUAO). Therefore, the difference between the HOMO/HOAO and the LUMO/LUAO is the same as the difference between the ionization energy and the electron affinity.

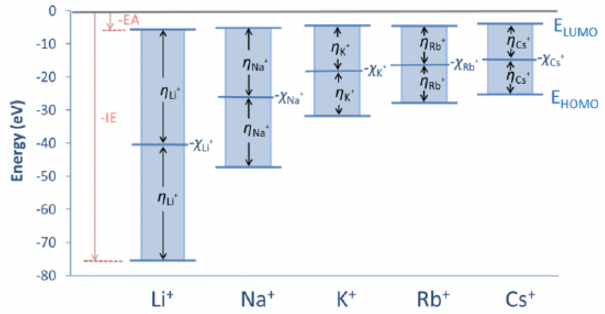
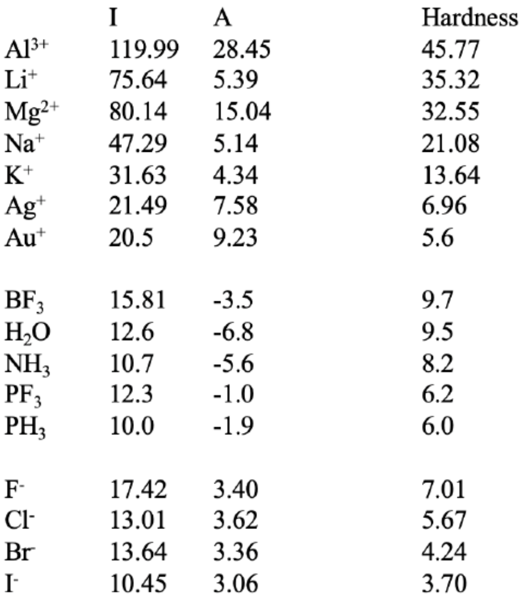


Figure 4.2.21 Absolute hardness for the alkali metal cations (Attribution: https://chem.libretexts.org/@api/deki/files/253564/clipboard_e58063ab90ddeb5e676c4fcf93712d0f4.png?revision=1&size=bestfit&width=781&height=422 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

Figure 4.2.21 illustrates the concept of absolute hardness for the example of the alkali metal cations. You can see that the lowest unoccupied atomic orbitals are fairly similar in energy, but the energy of the highest occupied atomic orbital increases significantly from the Li^+ to the Cs^+. Thus, the energy differences decrease from the Li^+ to the Cs^+, and the absolute hardness η is just half the value. The energy on the y-axis half-way between the HOMO and the LUMO energy is minus the energy associated with the Mulliken electronegativity.



	I	A	Hardness
Al^{3+}	119.99	28.45	45.77
Li^+	75.64	5.39	35.32
Mg^{2+}	80.14	15.04	32.55
Na^+	47.29	5.14	21.08
K^+	31.63	4.34	13.64
Ag^+	21.49	7.58	6.96
Au^+	20.5	9.23	5.6
BF_3	15.81	-3.5	9.7
H_2O	12.6	-6.8	9.5
NH_3	10.7	-5.6	8.2
PF_3	12.3	-1.0	6.2
PH_3	10.0	-1.9	6.0
F^-	17.42	3.40	7.01
Cl^-	13.01	3.62	5.67
Br^-	13.64	3.36	4.24
I^-	10.45	3.06	3.70

Figure 4.2.22 Acids and bases and their absolute hardness (Attribution: R.G. Pearson, Inorg. Chem. 1988, 27, 734)

In the table above (Fig. 4.2.22) you can see a number of acids and bases together with their hardness calculated from ionization energies and electron affinities. Let us check if the calculated values are in line with expectations and see what additional value the absolute hardness concept brings. For example, we can see that Li^+ is harder than Na^+ which is harder than K^+. This is what we expected.

We can also see that we can determine relative hardness not possible by qualitative inspection. For example, we can see that Al^{3+} is harder than Li^+. From atomic size perspective a neutral Al is larger than a neutral Li, and from that perspective the Li^+ should be harder. On the other hand the positive charge is higher on Al compared to Li. From that point of view the Al should be harder. By qualitative inspection we could not tell which parameter dominates the overall hardness. The absolute hardness concept shows that (for this case) the charge is more important than neutral atom size. Similarly we could not decide by inspection that Mg^{2+} was softer than Li^+ because charge arguments would suggest that Mg^{2+} is harder while neutral atom size arguments would say that Li^+ should be harder. We can see that in this case neutral atom size has a larger impact, albeit only slightly. According to our expectations Mg^{2+} is harder than Na^+ as both ions are neighbored in the same period, and thus very similar in atomic radius, but the Mg has the higher positive charge. We can also see that Ag^+ and Au^+ have much lower hardness than K^+ which we would expect. We would also understand the Au^+ has a lower value than Ag^+ because these elements are in the same group, and Au^+ is in period 6, while Ag^+ is in period 5.

Below Au^+ you can see a group of neutral molecules. Only the BF_3 molecule is a Lewis acid, other molecules are Lewis bases. We can see that BF_3 has a relatively high hardness, but is softer than K^+. Of the bases, H_2O is the hardest base, followed by NH_3, followed by PF_3 followed by PH_3. This is what we expected. O is the smallest donor atom, followed by N, followed by P. PF_3 is harder than PH_3 because of the higher electronegativity of fluorine versus hydrogen.

The last group are the halogenide anions. According to expectations F^- is the hardest and I^- is the softest. We can see that Cl^- has a lower hardness value than PH_3. The chemical behavior of latter is that of a soft base, while the former is still regarded a relatively hard base. We can see that we also need to treat the absolute hardness values with some caution, it is not an omnipotent method, other factors but HOMO and LUMO energy values can also influence polarizability.

When comparing the three groups we see that the cations tend to have the highest hardness values, followed by the neutral molecules. The anions tend to have the lowest values. This means that a hard acid tends to have a higher absolute hardness value than a hard base. To interpret the values meaningful we should therefore only compare acids with acids and bases with bases.

The HSAB Concept and Solubilities

Because the HSAB concept can estimate the strength of the interactions between Lewis acids and Lewis bases, it can also estimate a number of other properties that derive from this strength of interactions. For example, it can be used to estimate solubilities. When the Lewis acid-base interaction between cation and anion is strong we would expect low solubility, when the interaction is weak then we would expect high solubility.

$$\text{Solubility in } H_2O: AgI < AgBr < AgCl < AgF$$

Figure 4.2.23 Solubility of silver halogenides

For example, it is know that the solubility of silver halogenides in water increases from AgI to AgBr to AgCl to AgF (Fig. 4.2.23). This is in accordance with the HSAB concept. Ag^+ is considered soft, and thus it would make the strongest interactions with the softest anion, the iodide I^-. Ag^+ would make the weakest interactions with F^-, because it is the hardest.

$$\text{HSAB would expect } LiI > LiBr > LiCl > LiF$$
$$\text{Found: } LiBr > LiCl > LiI > LiF$$

Figure 4.2.24 Solubility of lithium halogenides

What would be our expectations for the lithium halogenides (Fig. 4.2.24)? In this case, we would expect the solubility to decline from LiI to LiBr, to LiCl, to LiF. Why? This is because Li^+ is a hard cation, and thus the strongest interactions should result with F^-. Consequently, LiF would have the lowest solubility. I^- is the softest anion, thus it should make the weakest interactions with Li^+.Consequently, the LiI would have the highest solubility. Is this what we observe experimentally? The experimentally greatest observed solubility is that of LiBr, followed by LiCl, followed by LiI. LiF has the lowest solubility. We can see that the LiI solubility is not what we expected. Instead of having the highest solubility, it has the second-lowest solubility. We can see here the limitations of the HSAB concept. There are also other factors that determine solubility, in particular solvation enthalpy. I^- has a very low hydration enthalpy, which explains the lower than expected LiI solubility. In a way, the HSAB concept is able to explain the low hydration enthalpy of I^- because it is based on the strength of interaction between I^- and water. The water is a hard acid and therefore interacts only weakly with a soft base like I^-. This can serve as an explanation for the low hydration enthalpy.

Another good example to illustrate the effects of solvation enthalpy on solubility is the solubility of the silver halogenides in liquid ammonia (not aqueous ammonia). It is actually reversed, the AgF has the smallest solubility , and the AgI has the highest solubility. The HSAB interaction between Ag^+ and the halogenide ions are the same no matter of the solvent. Therefore, they cannot serve as an explanation. Rather, we can argue that the reverse enthalpies of solvation in liquid ammonia compared to liquid water are responsible for the inverse behavior. From the standpoint of HSAB, the ammonia molecules are already significantly softer than the water molecules, therefore interactions with the soft anions become significantly stronger.

The HSAB Concept and Stability

The HSAB concept can also be used to estimate thermodynamic stabilities of compounds, such as decomposition points, melting points etc. Generally, the greater the acid-base interactions the greater the expected thermodynamic stability. Let us do couple of exercises to practice this concept.

$$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$$

Figure 4.2.25 Thermodynamic stability for alkali oxides

What order of thermodynamic stability would you expect for the alkali oxides (Fig. 4.2.25)? The answer is: The stability declines with increasing period of the alkali metal. Why? The oxide anion is considered a hard base due to its relatively small radius. Thus, the strongest interactions are expected with the Li^+ which is the hardest alkali metal, and the weakest interactions would be expected for the Cs^+ which is the softest alkali metal. This is in line with experimental observations. Only Li gives Li_2O when burned in O_2, Na gives sodium peroxide and the remaining alkali metals give superoxides.

$$BeO > MgO > CaO > SrO > BaO$$

Figure 4.2.26 Thermodynamic stability for earth alkali oxides

We can ask the same question for the earth alkaline oxides (Fig. 4.2.26). Similarly, the stability of BeO is the highest because Be has the highest hardness. BaO has the lowest stability because Ba^{2+} is the softest earth alkali cation. Ba gives barium peroxide instead of barium oxide when burned in O_2.

The HSAB Concept and Acidity

The HSAB concept can also explain Brønsted acidity. How?

$$\text{Acidity: } H_2O < H_2S < H_2Se$$

Figure 4.2.27 Acidity of the series of H_2O, H_2S, and H_2Se

Let us look at the series H_2O, H_2S, and H_2Se (Fig. 4.2.27). The Brønsted acidity increases from H_2O to H_2S to H_2Se. Why? H^+ is a hard acid, and therefore the strongest interactions would be expected with the hardest base, the oxide ion, and the weakest interactions would be expected with the softest base, the Se^{2-} anion. Therefore, H_2Se loses a proton most easily, making it the strongest acid. For H_2O the acidity is the smallest because the interactions between H^+ and O^{2-} are the greatest.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Figure 4.2.28 Acidity of the series of $HClO_4$ to $HClO_3$ to $HClO_2$ to HClO

Let us go to a somewhat more complicated example (Fig. 4.2.28). The acidity of perchloric acid, chloric acid, chlorous acid, and hypochlorous acid declines from $HClO_4$ to $HClO_3$ to $HClO_2$ to HClO. In this case all protons are bound to oxygen, so we cannot argue as before. However, we can argue that the negative charge in the anions of the acids is most delocalized in the case of the perchloric acid because the greatest number of resonance structures can be drawn for perchloric acid. Because the negative charge is most delocalized, the electron is most polarizable, and thus the softest. For the hypochloric acid we have the opposite case. There is no electron delocalization possible and only one resonance structure can be drawn for the hypochlorite anion. It is therefore the hardest, interacting the strongest with the proton.

$$NH_3 < PH_3 < AsH_3$$

Figure 4.2.29 Basicity of the series of NH_3, PH_3, and AsH_3

Lastly, let us think about the relative basicity of NH_3, PH_3, and AsH_3 (Fig. 4.2.29)? The N atom is the hardest base, and the interactions with protons are the strongest. Therefore, NH_3 is the strongest base. AsH_3 is the weakest base because As is the softest atom making the weakest interactions with protons.

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Concept Review Questions Chapter 4

Concept Review Questions

Section 1

1. What is the definition of a Lewis acid and a Lewis base?

2. What is a Lewis acid-base adduct?

3. What is a dative bond?

4. A Lewis base is typically a molecule with an approximately non-bonding HOMO? Explain why.

5. A Lewis acid is typically a molecule with an approximately non-bonding LUMO. Explain why.

Section 2

1. What is meant by a “soft” and a “hard” atom?

2. What is the influence of donor atom size on the hardness of a base?

3. What is the influence of acceptor atom size on the hardness of an acid?

4. What is the influence of positive charge on the hardness of an acid?

5. What is the influence of negative charge on the hardness of a base?

6. Explain the concept of Pearson’s absolute hardness.

7. The CH_4 molecule does not make significant hydrogen bonding with Cl^-. Explain this using Lewis acid/base and molecular orbital theory arguments.

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Homework Problems Chapter 4

Homework Problems

Section 2

Exercise 1

Decide if the following species are acids or bases according to Lewis theory. Order them with respect to their hardness and polarizability.

Ti^{3+}, Ti^{4+}, Zr^{3+}, Hf^{3+}

Answer

Hardness: $Ti^{4+} > Ti^{3+} > Zr^{3+} > Hf^{3+}$

Polarizability: $Hf^{3+} > Zr^{3+} > Ti^{3+} > Ti^{4+}$

Exercise 2

Decide if the following species are acids or bases according to Lewis theory. Order them with respect to their hardness and polarizability.

NH_3, PH_3, AsH_3, SbH_3.

Answer

Bases.

Hardness: $NH_3 > PH_3 > AsH_3 > SbH_3$

Polarizability: $SbH_3 > AsH_3 > PH_3 > NH_3$

Exercise 3

CsI is much less soluble in water than CsF. Why?

Answer

Cs-F hard-hard interactions are stronger than Cs-I hard-soft interactions. Nonetheless, CsI is less soluble because of the small solvation enthalpy for I^- (weak hard-soft interaction between water and I^-).

Exercise 4

Order the following species with regard to their expected solubility in water: ZnS, CdS, HgS.

Answer

ZnS> CdS>HgS

Exercise 5

AlF_3 is insoluble in liquid HF but dissolves when NaF is present. When BF_3 is added to the solution, AlF_3 precipitates. Explain.

Answer

Hard-Hard interactions between H and F in H-F stronger than Hard-Hard interactions between Al^{3+} and F^-. Consequence: no reaction occurs (no formation of AlF_4^-).

Hard-Hard interactions between Al^{3+} and F^- are stronger than hard-hard interactions between Na^+ and F^-. Consequence: AlF_3 dissolves to form AlF_4^-.

AlF_3 precipitates upon addition of BF_3 because Al-F hard-hard interactions are weaker than B-F hard-hard interactions (B^{3+} is harder than Al^{3+}). AlF_4^- (aq) + BF_3 (aq) --> BF_4^- (aq) + AlF_3(s).

Exercise 6

Why were most of the metals used in early prehistory soft metals (in HSAB terminology)?

Answer

Because oxygen is the most abundant element in the earth crust. Thus most hard metals have formed oxides with oxygen. Soft metals do not easily combine with oxygen to form oxides. Therefore, they can be found more often in elemental form in nature. Because of that they have been used more often.

Exercise 7

Which of the following ions is the softest according to HSAB theory:

a) oxide (O^{2-})

b) peroxide (O_2^{2-})

c) ozonide (O_3^-)

Answer

c) ozonide (O_3^-)

Exercise 8

The oxidation of barium with oxygen gas yields barium peroxide while the oxidation of strontium with oxygen gas yields strontium oxide. Explain this from the standpoint of the HSAB theory.

Answer

Barium is softer, so it has a greater tendency to combine with the peroxide ion which is relatively soft compared to the oxide ion.

Exercise 9

A molecule with an electron pair in an antibonding HOMO will most likely undergo a reaction in which

a) this molecule will get oxidized

b) this molecule will be reduced

c) this molecule will act as a donor in a Lewis acid base reaction.

d) this molecule will act as an acceptor in a Lewis acid base reaction.

Answer

a) this molecule will get oxidized

Exercise 10

When a dative bond is polarized toward the acceptor this indicates that

a) the HOMO energy of the donor is higher than the LUMO energy of the acceptor.

b) the HOMO energy of the donor is lower than the LUMO energy of the acceptor.

c) the HOMO energy of the donor is equal to the LUMO energy of the acceptor.

Answer

a) the HOMO energy of the donor is higher than the LUMO energy of the acceptor.

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CHAPTER OVERVIEW

5: Coordination Chemistry I - Structures and Isomers

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5.1: History

Coordination Chemistry

Now let us direct our focus toward actual coordination chemistry, also often called complex chemistry. In the following, we will apply the previously learned concepts about atomic theory, symmetry, molecular orbital theory, and acid-base chemistry to coordination compounds. Let us first ask: How are coordination compounds, or complexes defined? They are typically Lewis-acid base adducts between a metal atom or a metal ion as the Lewis acid and one or more ligands as a Lewis base. These ligands can be inorganic ligands such as halogenide ions, water, and ammonia molecules, or organic ligands like amines or alcohols. Coordination compounds are known since the antique due to their often intense color, and are used as a pigment or dye, for example Prussian Blue ($KFe[Fe(CN)_6]$ or tetrammine copper, both of which are intensely blue. You can see a few examples of coordination compounds below, namely the hexahydrate of copper (II) sulfate which is blue, iron (III) chloride, which is yellow, and nickel sulfate which is greenish-blue. Because of their intense color they have also attracted the attention of modern chemists from the early on, but the chemical bonding in these compounds remained a mystery for a relatively long time. The bonding in these compounds seemed more complex, hence the name complex compounds.

Figure 5.1.1 $Cu(SO_4)$ x 5 H_2O (Attribution: No machine-readable author provided. Yuvalif assumed (based on copyright claims). / Public domain https://commons.wikimedia.org/wiki/F...er-Sulfate.JPG), $FeCl_3$ x 6 H_2O (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg) and $NiSO_4$ x 6 H_2O (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg), respectively

History on Coordination Compounds

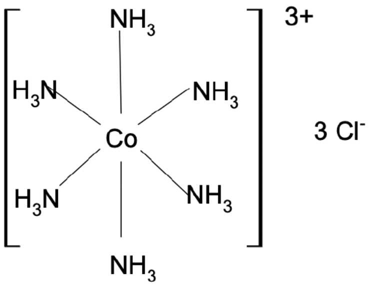
What was the problem with the bonding in coordination compounds? Their empirical formulas could be easily determined by element analysis, but the results could not be explained with the concept of valence. In the early days of modern chemistry it was believed that the number of bonds in a compound could not exceed the valence. For example, in the compound of the formula $Co(NH_3)_6Cl_3$ the valence of Co would be +3, therefore cobalt could not make more than three bonds. Assuming that the Co^{3+} ion would make three bonds to the 3 Cl^- ions, how would one involve the six NH_3 molecules in the bonding?

Figure 5.1.2 Alfred Werner (1866-1919) (Attribution: ETH Zürich / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...ortr_09965.jpg)

The chemist who solved this mystery was Alfred Werner. He correctly suggested that the number of bonds would not be restricted to the valence, but that more bonds would be allowed. It would be possible that the six NH_3 molecules bind directly to Co^{3+} forming a so-called complex cation. They would be in the so-called first coordination sphere around the Co. The three chloride ions would then be bound loosely to the complex cation balancing the charge of the complex cation. They would be in the second coordination sphere.

Formula Writing in Coordination Chemistry

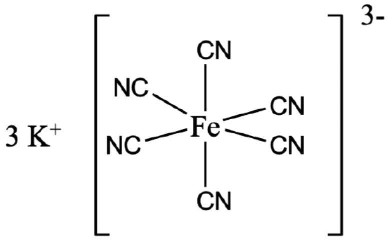
How can we write a formula of a coordination compound that contains complex ions?



$[Co(NH_3)_6]Cl_3$

Figure 5.1.3 Example of complex cation notation

For complex cations we write the element symbol for the metal ion first followed by the formula for the ligands. If there is more than one ligand, then we will place the ligands in parentheses, and indicate their number by a subscript behind the parentheses. The entire complex cation is placed in brackets. The formula for the anion in the second coordination sphere is placed behind the brackets and the number of anions is indicated by a subscript (Fig. 5.1.3).



$K_3[Fe(CN)_6]$

Figure 5.1.4 Example of a formula for a complex with a complex anion

For complex anions, we write the formula for the counter cation first, followed by the complex anion in brackets. You can see two examples above (Fig. 5.1.3 and 5.1.4). We have complex cations of Co with six NH_3 ligands coordinated to it in the first coordination sphere. Three Cl^- ions are in the second coordination sphere. Hence the formula is $[Co(NH_3)_6]Cl_3$. The second example is the coordination compound with the complex anion having a 3- charge in which six cyanide anions bind to a central Fe^{3+} ion. The K^+ ion in the second coordination sphere compensates the charge of the complex anion. Hence the formula is $K_3[Fe(CN)_6]$.

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5.2: Nomenclature

Classification of Ligands

Let us look a little closer at ligands and see how we can classify them. One way is to categorize them into monodentate and multi-dentate ligands.

Monodentate ligands have only one point of attachment to the metal ion.

Definition: Monodentate ligand

Monodentate ligands have only one point of attachment to the metal ion

Examples for such ligands are halogenide ligands, ammonia as ligand, and water as ligand. The molecules often have different names when acting as ligands, and you must know these names. For example, water as a ligand is called an aqua ligand, ammonia as a ligand is called an ammine ligand, chloride as a ligand is called a chloro ligand.

Ligands with more than one point of attachment are called multidentate ligands, or chelate ligands.

Definition: Multidentate ligands

Multi-dentate ligands have two or more points of attachment to the metal ion

Complexes with chelate ligands are called chelate complexes. Greek prefixes indicate how many points of attachment the ligand has (Fig. 5.2.1).

2: bi-dentate
3: tri-dentate
4: tetra-dentate
5: penta-dentate
6: hexa-dentate

Figure 5.2.1 Greek prefixes indicating how many points of attachment the chelating ligand has

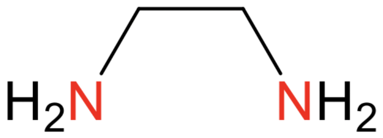
If there are two, then we have a bidentate ligand, when there are three, we have a tridentate ligand. We use the prefixes tetra, penta, and hexa to indicate four, five, and six points of attachment, respectively. Multi-dentate ligands with more than six points of attachment are rare.

Figure 5.2.2 Visual representation of the origin of the word chelate (Attribution: Junior Libby https://www.publicdomainpictures.net...503683515x.jpg)

The name chelate ligand comes from the Greek word chela, meaning great claw of the lobster. We can see that our lobster in Figure 5.2.2 happily chelates a Ni^{2+} ion with its two great claws!

Common Bidentate Ligands

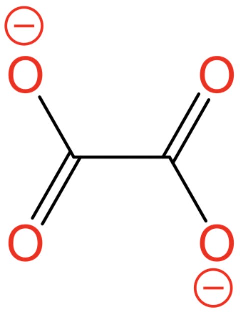
A few common bidentate ligands are shown below.



Ethylenediamine (en)

Figure 5.2.3 The ethylenediamine (en) ligand. Donor atoms are denoted red.

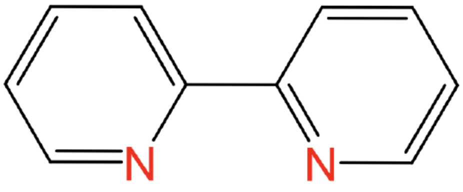
The first one is ethylene diamine. It has two nitrogen donor atoms that can bind to the metal, and they are separated by an ethylene group (Fig. 5.2.3).



Oxalate (ox)

Figure 5.2.4 The oxalate (ox) ligand. Donor atoms are denoted red.

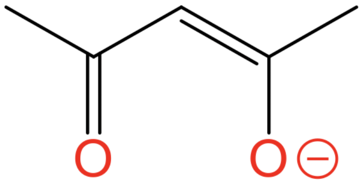
Another common ligand is the oxalate ligand. It has two O donor atoms separated by two carbon atoms. There are two negative charges that are delocalized over the four O atoms (Fig. 5.2.4).



bipyridyl (bipy)

Figure 5.2.5 The Bipyridyl (bipy) ligand. Donor atoms are denoted red.

As a third example you can see the bipyridyl ligand having two N donor atoms as part of two aromatic rings. The two N atoms are separated by two carbon atoms (Fig. 5.2.5).



acetylacetonate (acac)

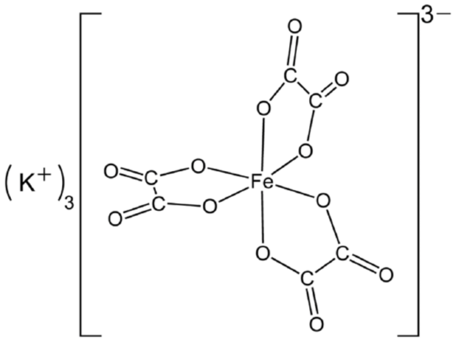
Figure 5.2.6 Acetylacetonate (acac). Donor atoms are denoted red.

Lastly, there is the acetyl acetonate ligand with two O donor atoms separated by three C atoms (Fig. 5.2.6). The acetyl acetonate carries a negative charge that is delocalized between the two O atoms. In this case the donor atoms are separated by three carbons.

Common ligands often have specific abbreviations. They are often used in the formulas of coordination compounds with these ligands. For example, the ethylene diamine ligand is abbreviated *en*, the oxalate ligand is abbreviated *ox*, the bipyridyl ligand is abbreviated *bipy*, and the acetyl acetonate ligand is abbreviated *acac*. There are not only bidentate ligands with O and N donor atoms, but also with others such as P and S.

Rings in Complexes with Chelate Ligands

In most chelating ligands the donor atoms are separated by two or three other atoms, mostly carbon atoms. This is because in this case the chelate ligands can form five- and six-membered rings with the metal ion (Fig. 5.2.7).



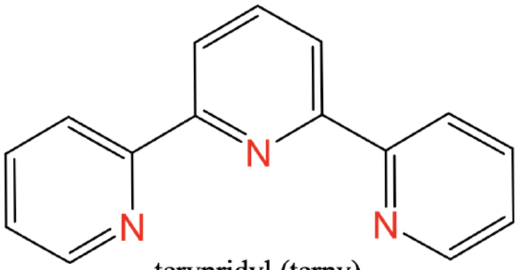
$[Fe(ox)_3]^{3-}$

Figure 5.2.7 Trioxolato iron complex (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...oxalate-2D.png)

You can see that the trioxolato iron complex above has three five-membered rings containing one Fe, two O, and two C atoms. These ring sizes are particularly stable because they have the least ring strain. As a consequence, the respective chelate complexes are particularly stable.

Tridentate Ligands

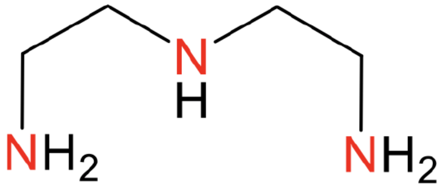
Here are a couple of examples for tridentate ligands.



terypridyl (terpy)

Figure 5.2.8 Terypridyl (terpy). Donor atoms are denoted red.

The first one is terpyridyl, abbreviated “Terpy”(Fig. 5.2.8), the second one is bisethylenetriamine, abbreviated “tris” (Fig. 5.2.9).

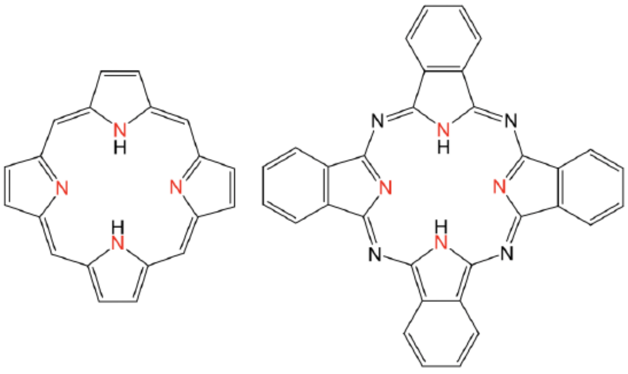


Bisethylenetriamine (tris)

Figure 5.2.9 Bisethylenetriamine (tris). Donor atoms are denoted red.

Both of them have three N-donor atoms separated by two carbon atoms. In the “tris”-ligand there are two ethylene groups between the N atoms, in the case of the “terpy”-ligand the N-atoms are part of three aromatic rings (Fig. 5.2.8. and Fig. 5.2.9)

Tetradentate Ligands



Porphyrine

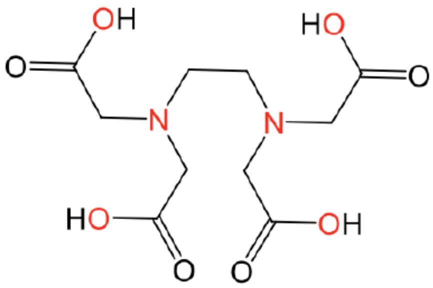
Phtalocyanine

Figure 5.2.10 Porphyrine (left) and Phtalocyanine (right). Donor atoms are denoted red.

Two common tetradentate ligands are porphyrine and phtalocyanine (Fig. 5.2.9 and 5.2.10). Both are co-called macrocyclic ligands because they are large cycles. They both have four N-donor atoms pointing inside of the cycle. The phtalocyanine ligand has four additional N atoms connecting the five-membered rings via imine-linkages. Further the phtalocyanine has four benzene rings fused to the four five-membered rings. The porphyrine ligand is very important in biological systems. For example, it is part of the protein hemoglobin. In this case a an Fe^{2+} ion sits in the center of the porphyrin ring. It is also a component of chlorophyll in which case an Mg^{2+} ion sits in the center of the ring. Phtalocyanine ligands are important as components of dyes.

Hexadentate Ligand, EDTA

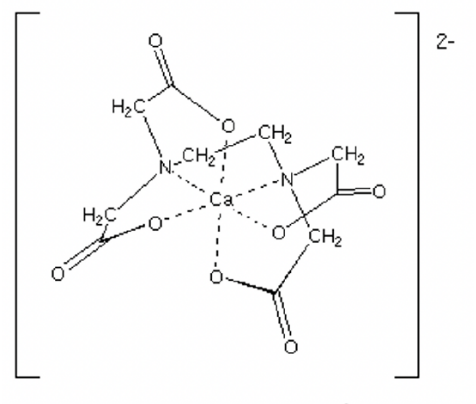
A very common hexadentate ligand is the ethylenediamine tetraacetic acid (EDTA) ligand. You can see its structure below (Fig. 5.2.11).



ethylene diamine tetraacetic acid (EDTA)

Figure 5.2.11 Structure of EDTA (donor atoms are denoted red)

It has two N-donor atoms separated by an ethylene group. Each N-atom is further connected to two acetyl groups. The overall four acetyl groups carry four O-donor atoms. Overall, there are six donor atoms. The six donor atoms can coordinate octahedrally to a metal ion such as a Ca^{2+} ion (Fig. 5.2.12).



EDTA complex with Ca^{2+}

Figure 5.2.12 EDTA complex with Ca^{2+}

In coordinated form the EDTA ligand is deprotonated, and the O donor atoms carry a negative charge. Therefore an EDTA complex with a divalent cation such as Ca^{2+} has a 2- charge.

Nomenclature of Complexes

Now let us develop a nomenclature for coordination chemistry so that we can communicate them in an educated manner. One important aspect is that we name the number of ligands. To indicate the number of a particular ligand we use Greek prefixes (Fig. 5.2.13).

2	di
3	tri
4	tetra
5	penta
6	hexa
7	hepta
8	octa

Figure 5.2.13 Greek prefixes associated with the number of ligands in a coordination compound.

These are the same prefixes we got to know when we discussed multidentate ligands. If there are two ligands we use the prefix di, if there are three we use the prefix tri- and so fourth.

Nomenclature of Complexes with Anionic Coordination Spheres

We can now develop the full name of a coordination compound. Let us consider compounds with complex anions first. We can name them according to three steps.

In the first step we name the counter cation. We do not account for the number of counter cations in the name.

Next, we determine the name and the number of ligands. If the ligand is anionic it gets the suffix “o”. Note that sometimes for ease of pronunciation abbreviations are used. For example a Cl^- is a chloro-ligand, and not a chlorido ligand. You must memorize these shorter forms. Generally, when an anion ends with “ide”, the “ide” is omitted, and replaced by “o”.

The third step is to name the metal ion and add the suffix “ate” to the name. You can either add the oxidation number of the metal in roman numerals or the charge of the complex anion in parentheses after the name of the metal. The first nomenclature is called the “Stock” system, the latter the “Ewing-Bassett” system. Note that if the element symbol of the metal is derived from a latin name then the latin name is used. For example if silver is the metal then the complex anion is an argentate, if lead is the metal the complex anion is a plumbate. Also here abbreviations are often used to make pronunciation easier. If the name ends with “um” that ending is replaced by “ate”.

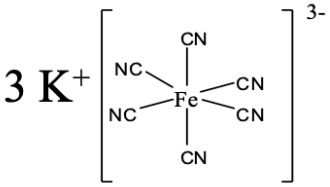


Figure 5.2.14 Example of a complex with a complex anion

An example for coordination compounds with a complex anion is shown above (Fig. 5.2.14). What is its name? There are three K^+ cations, so the name starts with potassium. We realize next, that there are six cyanide anions as ligands, so the name continues “hexacyano”. The name of the metal is iron, but we use the latin name ferrum, and replace the ending “um” with the ending “ate”. The oxidation number of the iron is +3. We can see that from the fact that the complex ion has a 3- charge, and the six cyano ligands have a 1- charge each. If we used the Stock system we would therefore place the roman numerals for +3 in parentheses behind the name. If we used the Ewing-Bassett system, we would place the (3-) for the negative charge of the complex behind the name. So overall it would be either a potassium hexacyanoferrate (III) or a potassium hexacyanoferrate (3-).

Exercises

How would you name the following two compounds?

$$H_2[PtCl_6]$$

Figure 5.2.17 Example 1

Let us look at the first example (Fig. 5.2.17). First, we need to name the cation. What is it? It is just “hydrogen”. Next we need to determine the name and number of ligands. We have six chloro ligands, so the name continues with “hexachloro”. The name of metal is platinum. We replace the ending “um” by “ate”. In the Stock system the roman numeral would be (IV) because the oxidation state of the Pt is +4. We can see this from the fact that the complex anion has a 2- charge, and the six chloro ligands have a 1- charge each. We must add +4 to -6 to get to -2. Therefore, in the Stock system, the name would be hydrogen hexachloroplatinate (IV), and in the Ewing-Bassett system it would be hydrogen hexachloroplatinate (2-).

$$K_3[Ag(S_2O_3)_2]$$

Figure 5.2.18 Example 2

The second example (Fig. 5.2.18) has three K^+ cations, so the name starts with potassium. What is the name of the ligand? The name of the anion is thiosulfate. In this case we replace the ending “e” by the ending “o”. We have two ligands, so it is a “dithiosulfato”. The metal is silver, but we use the latin name “argentum”, and replace the ending “um” by the ending “ate”. So it is an “argentate” . Fusing the parts together gives “potassium dithiosulfato argentate”. The oxidation number of Ag is +1, the charge at the anion is -3. So put either (I) in roman numerals or 3- in parentheses behind the name.

Nomenclature of Complexes with Cationic Coordination Spheres

Now let us name complexes with complex cations. We name the complex cation first, and then the anion. Then, we determine the name and the number of the ligands and prefixes accordingly. If there is an anionic ligand we give it the suffix “o” again. Then, we name the metal. In this case, we always use English names. We place the oxidation number in roman numerals or the charge of the complex cation behind the name, depending on whether we want to use the Stock or the Ewing-Bassett system.

$$[H_3N—Ag—NH_3]^+ \qquad Cl^-$$

Figure 5.2.19 Example of a complex with a complex cation

For example, how would you name the complex depicted above (Fig. 5.2.19)? There are two NH_3 ligands which are neutral. We have to consider that NH_3 as a ligand is called an “ammine” ligand. Note that it is spelled with two “m” in the middle. So the name starts “diammine”. The name of the metal is silver, and the oxidation state of silver is +1. This is because the complex has a 1+ charge and the ammine ligands are neutral. The anion is a chloride anion.

Diamminesilver(I) chloride

Figure 5.2.20

Therefore, the name in the Stock system would be “diamminesilver(I) chloride (Fig. 5.2.20).

Diamminesilver(1+) chloride

Figure 5.2.21

In the Ewing-Bassett system it would be “Diamminesilver (1+) chloride” (Fig. 5.2.21)

Exercises

What would be the names of the two compounds listed below.

$$[Pt(NH_3)_4]\ Cl_2$$

Figure 5.2.22 Example 1

The first example, Fig. 5.2.22, has four NH_3 ligands, so the name starts with tetraammine. Platinum is the metal, so the name continues “platinum”. The oxidation state of Pt is +2 because the complex cation has a 2+ charge, and the ligands are charge-neutral. The name of the anion is “choride”. So overall it is a “tetraammineplatinum(II) chloride” according to the Stock system or a “tetrammineplatinum(2+) chloride according to the Ewing-Bassett system.

$$[Ni(H_2O)_6]\ Cl_2$$

Figure 5.2.23 Example 2

The second compound (Fig. 5.2.23) has six water ligands, therefore the name starts with “hexaaqua” followed by the name of the metal with is “nickel”. The oxidation state of Ni is 2+ because the charge at the complex cation is +2, and the ligands are charge-neutral. The name of the anion is “chloride”. Therefore, the name is either hexaaaqua nickel (II) chloride or “hexaaquanickel (2+) chloride.

Nomenclature of Complexes with Cationic and Anionic Coordination Spheres

There is also the possibility that a coordination compound is made of a complex cation and a complex anion. In this case, the rules discussed previously hold, the only new thing to learn is that we name the complex cation first and the complex anion second.

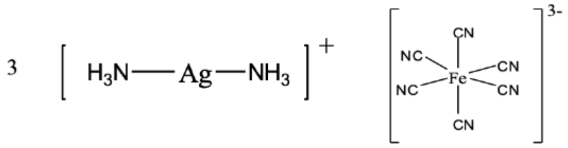


Figure 5.2.24 Coordination compound made of both a complex cation and complex anion

In the compound depicted (Fig. 5.2.24) we have a diammine silver (I) cation and a hexacyanoferrate (III) anion.

Diamminesilver(I) hexacyanoferrate (III)
or
Diamminesilver(1+) hexacyanoferrate(3-)

$$[Ag(NH_3)_2]_2\ [Fe(CN)_6]$$

Figure 5.2.24

Hence the name is diammine silver (I) hexacyanoferrate (III) in the Stock system or diammine silver(1+) hexacyanoferrate (3-), Fig. 5.2.24.

Nomenclature of Complexes with More Than One Ligand of the Same Kind

What if there are different ligands in a coordination compound? In this case, we name the ligands in alphabetical order, and give each ligand a prefix according to its number.

$$[Co(NH_3)_4Cl_2]NO_3$$

Figure 5.2.26 Example 1

For example: What is the name of $[Co(NH_3)_4Cl_2]NO_3$, Fig. 5.2.26? This is a compound with a complex cation containing ammine and chloro ligands. Because “a” comes before “c” in the alphabet we have to name the ammine ligand first. There are four ammine ligands and two chloro ligands. Therefore, we use the prefixes “tetra” in front of “ammine” and “di” in front of “chloro”. So the name starts “tetraamminedichloro”. Then, we name the metal which is cobalt. The oxidation number of cobalt is +3 because there are four charge-neutral ammine ligands, two anionic chloro ligands, and the charge at the complex cation is +1. +3 -2 = +1. So in the Stock system the compound is called tetramminedichlorocobalt(III) nitrate, in the Ewing-Basset system it is called tetramminedichlorocobalt(1+) nitrate.

$[Pt(NH_3)BrCl(H_2O)]SO_4$

Figure 5.2.27 Example 2

Let us do one more example, Fig. 5.2.27. In the compound $[Pt(NH_3)BrCl(H_2O)]SO_4$ there is a complex cation with four different ligands: an “ammine” ligand, a “bromo”-ligand, a "chloro"-ligand, and an "aqua" ligand. What is the order of them? According to the alphabet, “ammine” comes first, “aqua” is second, “bromo” is third, and “chloro” is fourth. They do not get a prefix because there is just one of them for each. The metal is platinum, and its oxidation state is +4 because the complex cation has a 2+ charge, and there are two neutral ligands, namely the aqua and the ammine ligands, and two anionic ones, namely the bromo and the chloro ligands: +4 - 2 = +2.

Ammineaquabromochloroplatinum(IV)sulfate
or
ammineaquabromochloroplatinum(2+)sulfate

Figure 5.2.28

Therefore, the name is ammineaquabromochloroplatinum(IV)sulfate in the Stock system, and ammineaquabromochloroplatinum(2+)sulfate in the Ewing-Bassett system, 5.2.28.

Nomenclature of Complexes with Complicated Ligands in a Coordination Sphere

So far we only considered relatively simple ligands that were either monoatomic, or contained a few atoms only. However, many ligands, in particular chelating ligands, contain more atoms, and have more complex names. These names may already contain prefixes that we use to number ligands. For example the ethylenediamine ligand is a chelating ligand with a longer name that already contains the prefix “di”. In such cases, to avoid ambiguity, we put the ligand name in parentheses, and place a somewhat different prefix in front of it to account for the number of the ligands.

“Tris” instead of “tri”
“tetrakis instead of “tetra”
“pentakis” instead of “penta”
etc.

Figure 5.2.29 Prefixes used for complicated ligands

Instead of “di” we use “bis”, instead of “tri” we use “tris”, instead of “tetra” we use “tetrakis”, instead of “penta” we use “pentakis”, and so on, Fig. 5.2.29.

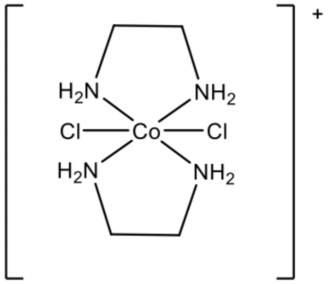


Figure 5.2.30 Example of a complex cation with more complicated ligands.

For example, what is the name of the complex cation depicted above (Fig. 5.2.30)? We first need to realize that there are two different ligands: chloro ligands and ethylenediamine ligands. We need to name the chloro ligands first, because they come first in the alphabet. Because there are two chloro ligands we use the prefix “di”. The ethylenediamine ligand is placed in parentheses, and the prefix “bis” is used instead of “di”. The metal is cobalt in the oxidation state +3 because the complex cation has a 1+ charge, and there are two chloro ligands with a 1- charge each, and two charge-neutral ethylenediamine ligands: +3 -2 = +1.

Dichlorobis(ethylenediamine)cobalt(III)
Dichlorobis(ethylenediamine)cobalt(1+)

Figure 5.2.31

Therefore, the name is dichlorobis(ethylenediamine)cobalt(III) in the Stock system and dichlorobis(ethylenediamine)cobalt(1+) in the Ewing-Bassett system (Fig. 5.2.31).

Nomenclature of Complexes with Bridging Ligands

Ligands cannot only be terminal, they can also bridge two metal centers. To indicate that a ligand is a bridging ligand we give it a prefix μ. Bridging ligands are named before terminal ligands, and the name of the molecular fragments with the terminal ligands and metal ions is placed in parentheses after the name of the bridging ligand.

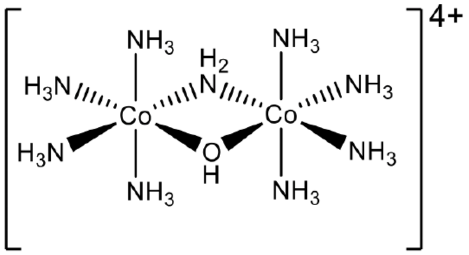


Figure 5.2.32 Complex with bridging ligands

So what is the name of the complex cation depicted above (Fig. 5.2.32)? We can see that there are two different bridging ligands, one is a hydroxo-ligand OH^-, and the other is called an amido ligand NH_2^-. These bridging ligands bridge two identical molecular fragments containing a Co atom and four ammine ligands each. The two bridging ligands need to be named first, and we have to name them according to alphabetic order. Hence, the name starts " μ-amido- μ-hydroxo". Then, we need to name the two fragments which are bridged. Because there is one Co and four NH_3 ligands, the name of the fragment is "tetraamminecobalt". Because this is a more complex name we need to put it into parentheses. There are two fragments, therefore we need to use the prefix "bis". The oxidation state of Co is +3. This is because there are two anionic ligands, the hydroxo, and the amido ligand which have both a 1- charge. The other ligands are neutral. The complex cation carries a 4+ charge: +6-2=+4. Because there are two Co atoms, they have an oxidation number of +6/2=+3.

μ-amido-μ-hydroxobis(tetraamminecobalt)(III)

Figure 5.2.33

Hence, the overall name according to the Stock system is " μ-amido-μ-hydroxobis(tetraamminecobalt)(III)", Fig. 5.2.33.

μ-amido-μ-hydroxobis(tetraamminecobalt)(4+)

Figure 5.2.34

In the Ewing-Bassett system it is μ-amido- μ-hydroxobis(tetraamminecobalt)(4+), Fig. 5.2.34. Now we have completed the chapter on nomenclature.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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5.3: Coordination Numbers and Structures

Coordination Numbers (CN) and Structures of Complexes

Coordination compounds have many different structures or shapes, and therefore it is important that we are able to categorize the structures of coordination compounds, understand why a particular structure forms, and why certain structures are more common than others.

A central parameter that determines the structure is the coordination number. A coordination number is the number of points of attachment between the ligands and the metal.

Definition: Coordination Number

The coordination number is the number of points of attachment between the ligands and the metal

What are the main factors that are associated with the coordination number? Some of them are associated with the metal ion, and some of them are associated with the ligands. The shape and the size of a ligand greatly influences the coordination number. Generally, the bulkier the ligand the smaller than coordination number. With regard to the metal ion, the size of the metal ion plays an important role. The larger the metal ion, the more ligands fit around it, and the coordination number increases. In addition, the electron configuration of the metal ion plays a role. For certain electron configurations certain coordination numbers are preferred because these coordination numbers stabilize electron energies. Lastly, there are intermolecular interactions to consider. In solid state they occur between neighbored complexes, in solution they occur between the complex and solvent molecules. This can lead to different coordination numbers and structures in the solid state, and in solution, respectively.

Main Factors Determining CNs

1. Shape and size of ligands
2. Size of metal ion
3. Electron configuration of metal ion
4. Intermolecular interactions (solution vs. solid state)

As you can see, there are many factors that influence the coordination number, and the shape of the complexes. These factors are sometimes opposing, which makes the prediction of structures difficult. Nonetheless, there are a number of rules that allow for a fair accuracy in structure prediction, and we will go through these rules in the following.

Low Coordination Numbers (CN)

CN = 1

The coordination number 1 is very rare. When there is one point of attachment, then there are usually reactive coordination sites at the metal ion that lead to cluster formation. This reduces the energy and increases the coordination number. For example, in methyl lithium (MeLi) the Li appears to have the coordination number 1 because you may think that there is only a single, covalent Li-C bond. However, there is actually a tetrahedral cluster Li_4Me_4.

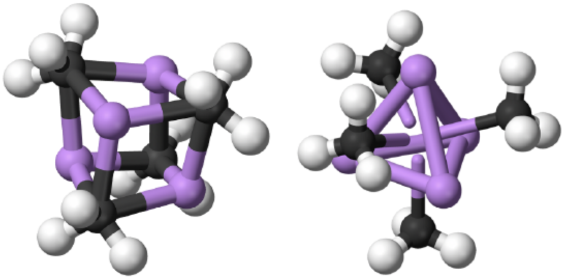

Figure 5.3.1 Two different views on the structure of MeLi tetrameric cluster (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...2-3D-balls.png)

The four Li atoms build a tetrahedron and the methyl groups are placed above the faces of the tetrahedron (Fig. 5.3.1). One can also think of MeLi as a near cubic molecule in which the Li atoms occupy every other vertice of the cube, and methyl groups the remaining vertices of the cube (Fig. 5.3.2). The cluster formation avoids the coordination number 1, and stabilizes the methyl lithium. In addition to a tetrameric cluster there is also a hexameric cluster for Me-Li known.

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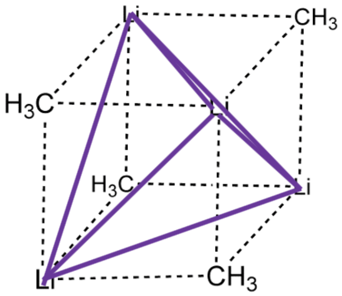

Figure 5.3.2 Structure in methyllithium inscribed into a cube. (https://commons.wikimedia.org/wiki/File:MeLi.png)

The coordination number 1 is only possible when a large metal ion is surrounded by a very bulky ligand that suppresses cluster formation, and there is no coordination of solvent molecules to the metal.

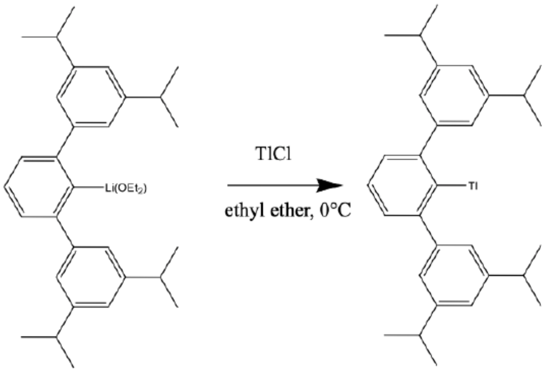

Figure 5.3.3 2,6,-Trip$_2$C$_6$H$_3$Tl (Attribution: Niemeyer, M., and Power, P. P., J. Angew. Chem., Int. Ed., 1998, 37, 1277.)

An example the the cluster 2,6,-Trip$_2$C$_6$H$_3$Tl. (Trip = 2,4,6, i-Pr$_3$C$_6$H$_2$), Fig. 5.3.3. It has a Tl$^+$ coordinated to a bowl-shaped, bulky ligand via a Tl-C bond. The Tl fits exactly into the bowl-shaped cavity in the ligand, thereby preventing cluster formation. The compound can be prepared from its lithium derivative and thallium chloride in diethyl ether at 0°C.

CN = 2

The coordination number 2 is also rare, but already a lot more common than the coordination number 1. Generally, d^{10} metal ions have a tendency to make structures with CN=2. These structures are linear structures. An example of a d^{10} ion is Ag$^+$. Why is it d^{10}? Ag is located in group 11, so it has 11 valence electrons. If we remove one, there are ten. The energy of the Ag$^+$ ion is minimized when the 4d-subshell is full, and the 5s-subshell is empty. Ag$^+$ makes many linear structures with ligands, example ammine ligands or cyano ligands. In an oversimplified picture, we may explain the structure using VSEPR arguments assuming there is an sp-hybridization of the 5s and one 5p orbital, and the two electron lone pairs at the two ligands get donated into the sp-hybridized orbitals. What other d^{10}-ions can you think of? There would be the higher and lower homologue of the Ag$^+$ ion, the Cu$^+$, and the Au$^+$ ion.

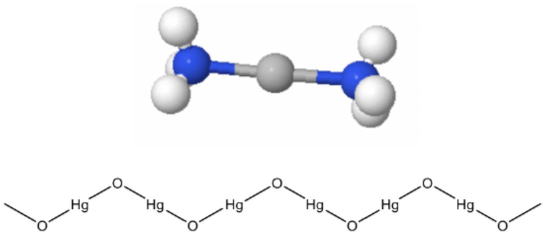

Figure 5.3.4 Linear structures formed with a coordination number of 2: [Ag(NH$_3$)$_2$]$^+$ and HgO (Attribution: https://chem.libretexts.org/@api/deki/files/18507/2.bmp?revision=2&size=bestfit&width=243&height=134 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

They make linear complexes such as $CuCl_2^-$ and $Au(CN)_2^-$. Hg^{2+} is also a d^{10} ion that often makes linear complexes, for example $Hg(CN)_2^-$. This linear coordination is not only found in molecular compounds but also in extended solids. For example, HgO and HgS make zig-zag chains of linearly coordinated Hg^{2+} (Fig. 5.3.4). The bending of the chain occurs at the oxide anions, because of the electron lone pairs at O. Other metal ions but d^{10} ions make linear structures only when the ligands are very bulky. These examples are rare.

CN = 3

The coordination number 3 is also rare for coordination compounds. They are most common for d^{10} ions, especially when the ligands are bulky. In most cases the trigonal planar structure, or a structure close to that is adopted.

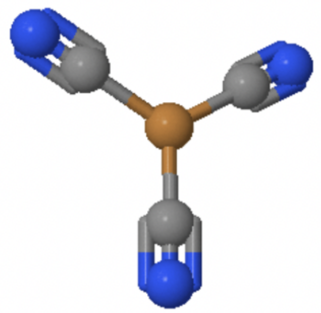

Figure 5.3.5 The $Cu(CN)_3^{2-}$ anion (Attribution: ▯ https▯ ://chem.libretexts.org/@▯ api/deki/files/18508/3.bmp?revision=1 http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

An example is the $Cu(CN)_3^{2-}$ anion in which Cu^+ is surrounded by three cyanide anions in a trigonal planar fashion (Fig. 5.3.5).

CN = 4

The coordination number 4 is a very common coordination number. It is actually the second-most common coordination number, only surpassed by the coordination number 6. The by far most common structure associated with the coordination number 4 is the tetrahedral structure. Why? It is because the ligands have the greatest distance from each other, and the smallest steric repulsion. Generally, smaller ions and/or larger ligands favor the coordination number 4 over the coordination number 6.

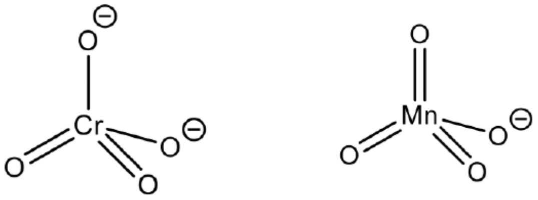

Figure 5.3.6 Permanganate anion and the chromate anion

This is the case in the permanganate anion and the chromate anion, for example. Here, the oxidation state of Mn and Cr are +7 and +6 respectively, making the ionic radius very small.

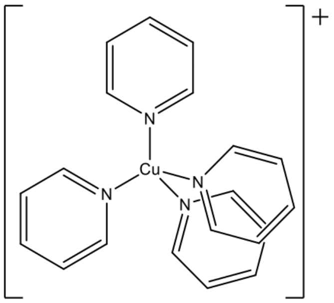

Figure 5.3.7 The tetrakis(pyridyl) copper(1+) ion

Another example is the tetrakis(pyridyl) copper(1+) ion. Here, the ligands are fairly bulky. The tetrahedral structure is particularly common for d^0 and d^{10} ions, and mostly favored over the octahedral structure. All examples above have either d^0 or d^{10} ions. Cr(VI) and Mn(VII) are d^0 and Cu(I) is d^{10} thus fulfilling this requirement as well.

The second-most common structure after the tetrahedral structure is the square planar structure. It is only common for ions with d^8 electron configuration. What are common d^8 ions? Examples are the ions Ni^{2+}, Pd^{2+}, and Pt^{2+}. We can find these elements in group 10 of the periodic table. Therefore, they must have ten valence electrons in the neutral state. Because of the 2+ charge, two electrons are removed leaving eight electrons. All eight electrons are in the d-valence subshell, therefore the ions are called d^8 ions.

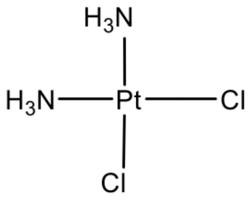

Figure 5.3.8 Cis-platinum

The arguably most well known square planar complex is cis-platinum. It has two chloro and two ammine ligands attached to Pt in cis-position. It is known as anti-cancer drug.

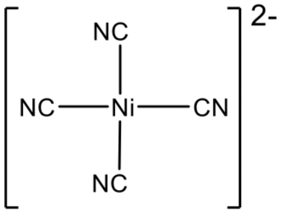

Figure 5.3.9 $Ni(CN)_4^{2-}$

$Ni(CN)_4^{2-}$ is another example of a group 10 square planar complex.

Can you think of other d^8 ions? The group 11 elements Cu, Ag, and Au have eleven valence electrons in the neutral state. In this case we need to remove three electrons to get to eight electrons, meaning that Cu^{3+}, Ag^{3+}, and Au^{3+} are d^8 ions. Cu and Ag are not very stable in the oxidation state +3, therefore examples of square planer Cu(III) and Ag(III) are fairly rare.

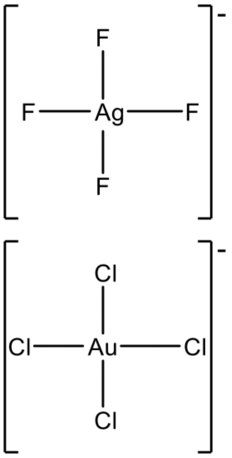

Figure 5.3.10 Structures of AgF_4^- and $AuCl_4^-$, respectively

Examples are AgF_4^- and CuF_4^-, Fig. 5.3.10. However Au^{3+} is more common and there is a relatively large number of Au(III) complexes, e.g. $AuCl_4^-$.

Because group 12 elements are not stable in the oxidation state 4, there are no group 12 d^8 ions. However group 9 d^8 ions are known. In this case the ions must be in the oxidation state +1 in order to have eight d electrons. Cobalt is not stable in the oxidation state +1, but Rh and Ir are, and square planar Rh(I) and Ir(I) complexes are common.

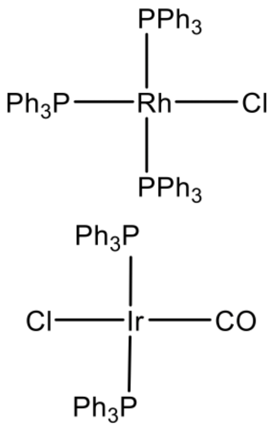

Figure 5.3.11 Structures of $Rh(PPh_3)_3Cl$ and $Ir(CO)(PPh_3)_2Cl$.

For example Rh makes a $Rh(PPh_3)_3Cl$ complex (Fig. 5.3.11). It is a common hydrogenation catalyst. Vasca's complex $Ir(CO)(PPh_3)_2Cl$ is another example (Fig. 5.3.11). It has the property to reversibly bind oxygen.

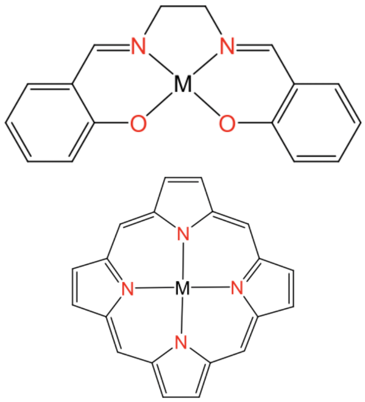

Figure 5.3.12 A generic salen complex (top) and a porphyrin complex (bottom). M = metal.

The square planar coordination is possible also with metal ions other than d^8 ions, but only when the ligand forces the metal ion into this coordination. Ligands that do this are for example the porphyrin ligand and the salen ligand. They are tetradentate ligands with donor atoms that form a square forcing the metal ion to adopt a square-planar coordination (Fig. 5.3.12).

A last possibility is the seesaw structure. It is know for main group elements, but not for transition metal elements.

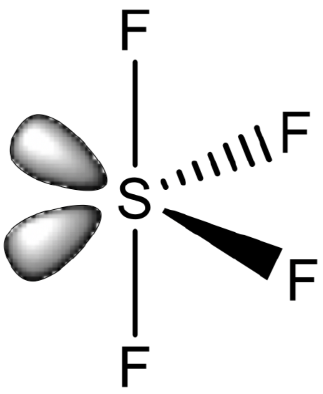

Figure 5.3.13 Structure of SF_4

An example is SF_4 (Fig. 5.3.13). The seesaw structure is derived from the octahedral structure whereby two adjacent corners of the octahedron are occupied by electron lone pairs. Formally one could consider a compound like SF_4 as a coordination compound in which four F^- ligands bind to an S^{4+} cation. However, this view is commonly not adopted, and the S-F bonds are not viewed as dative covalent bonds.

CN = 5

For the coordination number 5, the two most common structures are the trigonal bipyramid and the square pyramid. They are about equally common because they have very similar energies. Which one is preferred, depends on the particular circumstances, the nature of the metal, the ligands, the solvent, etc. Many molecules have structures in between, mostly described as distorted trigonal bipyramids. Distortion is even more common in solid state due to packing effects. Packing effects minimize the void space in the crystal.

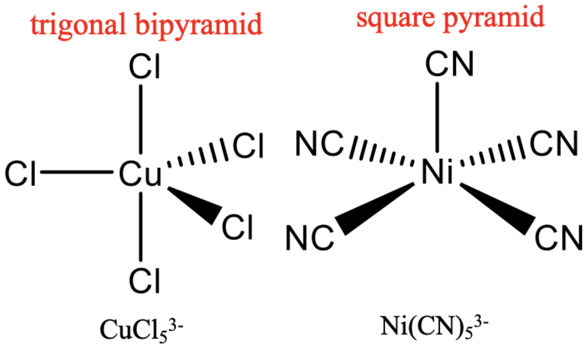

Figure 5.3.14 Structures of $CuCl_5^{3-}$ and $Ni(CN)_5^{3-}$, respectively

An example for a trigonal bipyramidal structure is $CuCl_5^{3-}$, an example for a square-pyramidal structure is $Ni(CN)_5^{3-}$ (Fig. 5.3.14). The pentagon, another conceivable structure, is not known. Five-coordinate compounds are known for the full range of transition metals. A difference compared to the structures with the coordination numbers 2 to 4 is, that in the structures with the coordination number 5 not all ligands are symmetry-equivalent. For the trigonal bipyramidal shape we distinguish between axial and equatorial ligands. In square-pyramidal complexes, the fifth ligand at the tip of the pyramid is symmetrically different to the other four at the base of the pyramid.

Because the energy difference between the trigonal bipyramidal and the square pyramidal structure is small, and there is only a small activation barrier between the two structures, they are often fluxional. This means that they can dynamically interconvert.

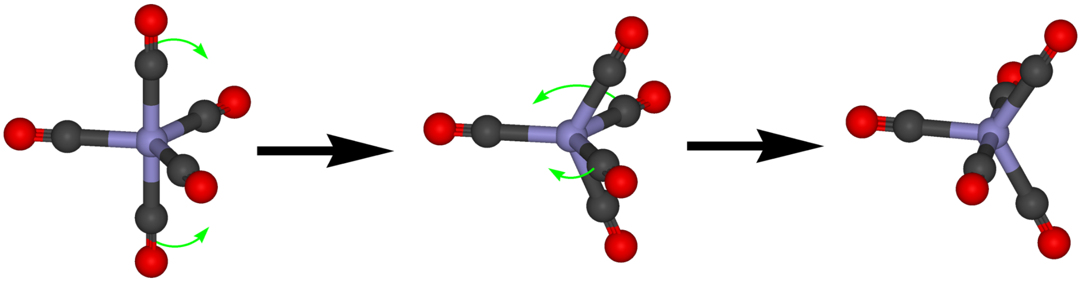

Figure 5.3.15 Berry pseudo rotation illustrated for the iron pentacarbonyl molecule. (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...-mechanism.png)

This interconversion occurs according to a mechanism called the Berry pseudo rotation. In the Berry pseudo-rotation one 120° bond angle between two ligands in equatorial position increases until it is eventually 180°. The initial 180° angle between two ligands in axial position decreases until it is 120°. This means that the two previously equatorial ligands are now axial ligands, and the two axial ligands are now equatorial ligands. As the Berry pseudo rotations occurs, the complex moves from a trigonal bipyramidal structure through a square-pyramidal intermediate to another trigonal bipyramidal structure. The Berry pseudo rotation happens often very fast, therefore in many measurements the five ligands appear identical. For example, the PF_5 molecule shows only one signal in the ^{19}F NMR because the movement of F atoms from the equatorial to the axial position and vice versa is too fast for the NMR time scale. At low temperatures, the Berry pseudo rotation may be slow enough so that axial and equatorial positions can be resolved. In compounds with larger ligands the pseudo rotation may also be slow enough so that axial and equatorial positions are resolved in the NMR.

CN = 6

The most common coordination number is the coordination number 6. This coordination number exists for all transition metal electron configurations from d^0 to d^{10}. We can explain this by the fact that many metal ions have the right size to support six ligands around them, and there are many ligands that have the right size to surround a metal ion in the coordination number 6. The by far most common shape for the coordination number 6 is the octahedral shape. It is the shape for which the ligands have the largest distance from each other thereby minimizing steric repulsion. A second reason is that the orientation of atomic orbitals supports the octahedral shape, as many orbitals point along the x,y, and z axes, in particular the p orbitals, and the d_{z^2} as well as the $d_{x^2-y^2}$.

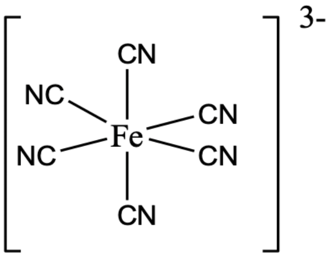

Figure 5.3.16 Structure of the hexacyanoferrate(3-) anion

An example is the hexacyanoferrate(3-) anion in which six cyano ligands surround the metal ion octahedrally (Fig. 5.3.16).

Distortions of Complexes with CN = 6

Octahedral complexes can distort in two basic ways. The first common distortion is the so-called tetragonal distortion. Tetragonal distortion can be achieved either via elongating an octahedron along two opposite vertices, or compressing the octahedron along two opposite vertices.

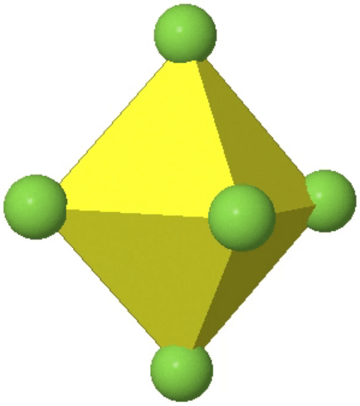

Figure 5.3.17 Tetragonal distortion (elongated octahedron) (Attribution:Chemtube3d.com)

In the first case, two opposite vertices are further away from the center of the octahedron compared to the other four corners (Fig. 5.3.17).

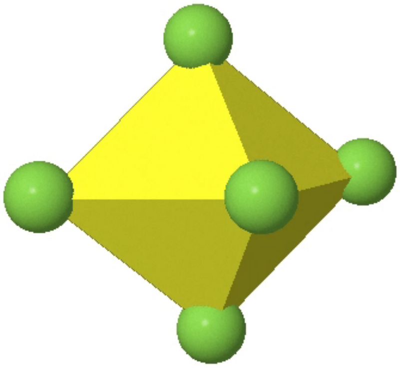

Figure 5.3.18 Tetragonal distortion (compressed octahedron) (Attribution:Chemtube3d.com)

In the compressed octahedron two opposite corners are closer to the center compared to the four other corners (Fig. 5.3.18). Both the elongated and the compressed octahedron have the same symmetry, meaning they belong to the same point group. Which point group is it? We still have a C_4 principal axis, but one only. It goes through the corners of the two opposite vertices along which we distorted. There is a horizontal mirror plane perpendicular to the C_4 axis, as well as an inversion center. Thus, the point group must be D_{4h}. In tetragonally distorted octahedra all faces are equivalent, but the distances of the ligands from the center of the octahedron are not the same.

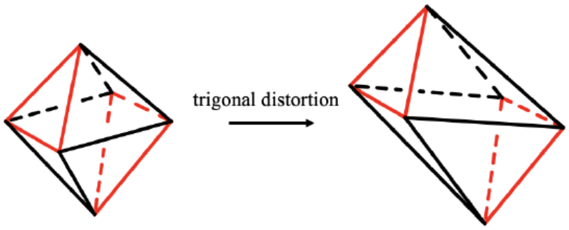

Figure 5.3.19 Trigonal distortion of an octahedron

When you elongate or compress the octahedron along to opposite faces you create a trigonal antiprism (5.3.19). It is called antiprism because the two opposite regular triangular faces, shown here in red are oriented in staggered fashion. This type of distortion is called trigonal distortion. The point group of a trigonal antiprism is D_{3d}. The C_3 axis goes through the two opposite regular triangular faces of the antiprism. There are three C_2 axes standing perpendicular, and going through the centers of the six remaining distorted triangular faces. There are three vertical mirror planes also that bisect the angle between the C_2 axes. In a trigonal antiprism the faces are not all equal, but the distance of the vertices are all the same.

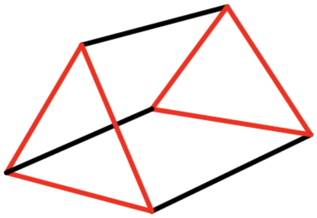

Figure 5.3.20 Trigonal prism

When we rotate one of the two opposite triangular faces of an antiprism by 60°, the two faces become eclipsed and a trigonal prism results (Fig. 5.3.20). Trigonal prismatic compounds are mostly observed when there are three bidentate ligands connecting the top and bottom triangular faces. What is the point group? It is D_{3h}. There is a C_3 axes going through the two opposite triangles. 3 C_2 axes are going through the centers of the three rectangles, and there is a horizontal mirror plane perpendicular to the C_3 axis. Does an elongation or compression along the two opposite triangular faces change the symmetry? Think about it. No, it does not change it.

CN = 7

Coordination numbers higher than 6 are considered high coordination numbers. They are significantly less common than the coordination numbers, 4, 5, and 6. A simple explanation is that large coordination numbers require a very large cation or a very small anion of the combination of both to avoid steric repulsion. These conditions are statistically less likely. In addition, large coordination numbers are not so favorable from the stand point of orbital orientation.

Let us first look at the coordination number 7 in more detail. There are three structures possible which are about equally common in nature.

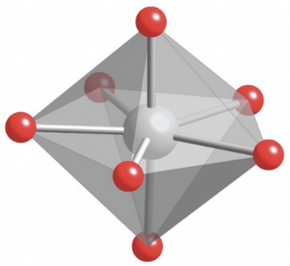

Figure 5.3.21 Pentagonal bipyramid, ZrF_7^{3-} (Attribution: chemtube3d.com https://www.chemtube3d.com/images/ga...s/I607ST22.jpg)

The first one is the pentagonal bipyramid of which ZrF_7^{3-} is an example (Fig. 5.3.21).

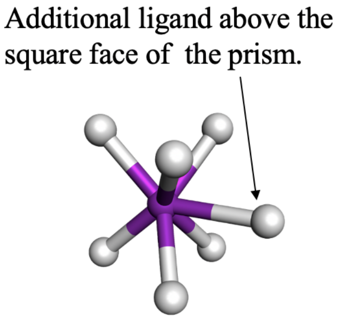

Figure 5.3.22 Trigonal prism, TaF_7^{2-} (Attribution: J3D3 / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...CapRightps.png)

The second one is the capped trigonal prism. TaF_7^{2-} is an example for it (Fig. 5.3.22). The seventh ligand is placed above a square face of the prism, not a triangular face. Can you imagine why? Think about it for a moment. The answer is that the square face is larger than the triangular face, and thus there is less steric repulsion.

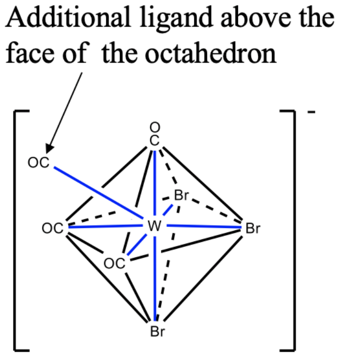

Figure 5.3.23 Capped octahedron, tribromotetracarbonyltungstate(IV)

The third structure is the capped octahedron. An example is the tribromotetracarbonyltungstate(IV). In this compound three bromo ligands and three carbonyl ligands occupy the vertices of two opposite faces in the octahedron. The fourth carbonyl ligand is placed above the triangular face with the carbonyl ligands. You can see that like for the coordination number 5, the ligands are not symmetrically equivalent.

CN = 8

Now, let us go to the coordination number 8. What shapes could you imagine that adopt the coordination number 8? The most symmetric, and simple shape is the cube (Fig. 5.3.24).

Figure 5.3.24 Transformation of a cube into a square antiprism. No cubic complexes are known.

However, complexes with cubic shapes are not observed. This is because there is another related structure which is energetically more favorable. It is the square antiprism (Fig.5.3.25). In a square antiprism, two opposite square faces are oriented in staggered fashion relative to each other. Relative to the cube one face of the cube is rotated by 45° relative to the opposite face, and the two opposite square faces are interconnected with each other to form triangular faces. The square antiprism is preferred over the square prism because the vertices where the ligands sit have a greater distance to each other compared to the cube.

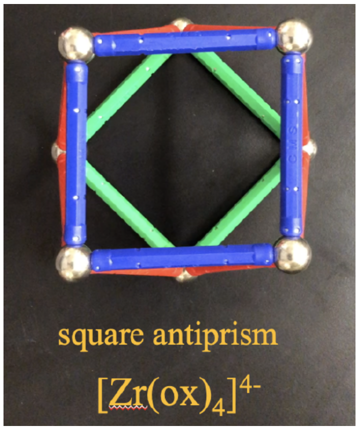

Figure 5.3.25 Square antiprism. The tetraoxolato zirconate(4-) anion has square anti-prismatic shape.

An example of a coordination compound that makes a square antiprism is the tetraoxolato zirconate(4-) anion.

A structure related to the square antiprism is the dodecahedron. Note that we are not talking about the dodecahedron that is a platonic solid here. We can derive the dodecahedron by squeezing on the two opposite corners of the two squares. This distorts and bends a square to form two additional triangular faces. This produces the dodecahedron (Fig. 5.3.26).

A video of the square antiprism to dodecahedron transformation can be accessed through the link below:

https://www.youtube.com/watch?v=A8G7...ature=youtu.be

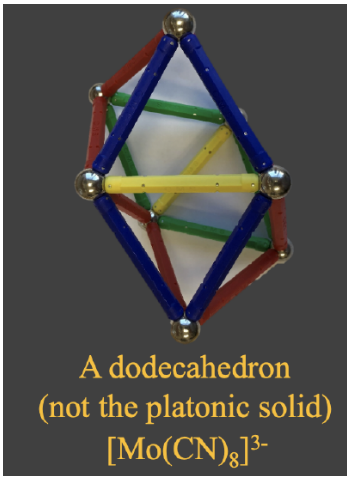

Figure 5.3.26 Dodecahedron. The octacyanomolybdate (3-) anion is an example for this shape.

An example for this shape is the complex octacyanomolybdate (3-), (Fig. 5.3.26). As you can see from the examples, all metal ions are large metal ions, and the ligands a small, confirming that structures with large coordination numbers are favored by large metal ions and small ligands.

CN = 9

Finally, let us think about shapes associated with the coordination number 9.

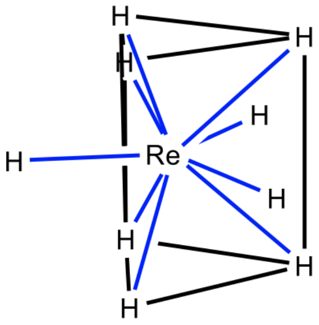

Figure 5.3.27 Tricapped prism of the nonahydridorhenate anion.

One possible shape is the tricapped trigonal prism for which the nonahydridorhenate is an example (Fig. 5.3.27). Here three additional ligands are placed above the three rectangular faces of the trigonal prism. Unsurprisingly, the ligands are small, and the metal ion is large.

Another example is the tricapped antiprism. The nonaammine lanthanum(3+) cation is an example. In this case the three additional ligands are placed above three triangular faces of an antiprism. The coordination number 9 is not the upper limit for coordination numbers. Coordination numbers up to 16 have been observed, but they are rare.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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5.4: Isomerism

This section will be about isomerism in coordination compounds. You may know isomerism already from your organic chemistry classes. Here, we will apply isomerism to coordination chemistry. Some forms of isomerism in organic and coordination chemistry are the same, but there are some forms of isomerism that only occur in coordination chemistry.

Let us first briefly review the definition of isomerism: Isomerism is when two or more compounds have identical empirical formulas but different structures.

Definition: Isomerism

When two or more compounds have identical empirical formulas but different structures they are called isomers.

We distinguish between two basic types of isomerisms: Constitutional isomerism and stereoisomerism. What is the difference? In constitutional isomerism the bonds are not between the same atoms.

Definition: Constitutional Isomers

In constitutional isomers the bonds are not between the same atoms.

In stereoisomerism, the bonds are between the same atoms, but ligands are at different coordination sites.

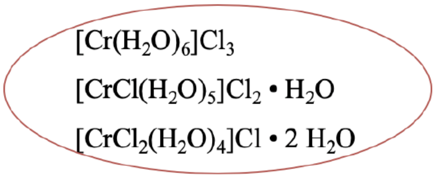
Definition: Stereoisomers

In stereoisomers, the bonds are between same atoms, but the ligands are at different coordination sites.

Forms of Constitutional Isomerism

Hydrate Isomerism

First, let us look more closely at hydrate isomerism. In hydrate isomerism, in one isomer a water ligand is in the first coordination sphere, and in the other isomer it is in the second coordination sphere. A water molecule in the second coordination sphere is only defined for the solid state, but not in solution. This is because in solution the water molecule would become part of the solvent. Here are a few examples for hydrate isomers.



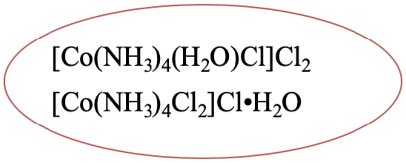
$[Cr(H_2O)_6]Cl_3$

$[CrCl(H_2O)_5]Cl_2 \bullet H_2O$

$[CrCl_2(H_2O)_4]Cl \bullet 2\ H_2O$

Figure 5.4.1 Two hydrate isomers of the complex $[Cr(H_2O)_6]Cl_3$

In the complex $[Cr(H_2O)_6]Cl_3$ there are six aqua ligands in the first coordination sphere (Fig. 5.4.1). In one hydrate isomer, there are only five water molecules in the first coordination sphere, the sixth one is in the second coordination sphere. One chloride anion has moved from the second to the first coordination sphere. There is a third hydrate isomer which has four aqua ligands in the first coordination sphere and two water molecules in the second coordination sphere. Two chloro ligands are now in the first coordination sphere, and one in the second coordination sphere. More hydrate isomers would be possible theoretically, but for some reason nature does not make them.



$[Co(NH_3)_4(H_2O)Cl]Cl_2$

$[Co(NH_3)_4Cl_2]Cl \bullet H_2O$

Figure 5.4.2 The hydrate isomers of the complex $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Another example is $[Co(NH_3)_4(H_2O)Cl]Cl_2$. It has a hydrate isomer in which one aqua ligand has moved to the second coordination sphere, and one chloride anion has moved from the second to the first coordination sphere (Fig. 5.4.2).

Ionization Isomerism

A second form of isomerism is the ionization isomerism. In this case an ion moves from the first to the second coordination sphere and/or vice versa.

$$[Co(NH_3)_5NO_3]SO_4$$
$$[Co(NH_3)_5SO_4]NO_3$$

Figure 5.4.3 Two ionization isomers of the complex $[Co(NH_3)_5NO_3]SO_4$

For example, in the compound $[Co(NH_3)_5NO_3]SO_4$ there is a nitrate ion in the first coordination sphere, and a sulfate ion in the second coordination sphere (Fig. 5.4.3). There is an ionization isomer to this compound, in which the sulfate ion is now in the first coordination sphere, and the nitrate is in the second coordination sphere.

Coordination Isomerism

Another form of constitutional isomerism is coordination isomerism. In this isomerism, ligands are bound to different metal ions. Naturally, this implies that this form of isomerism can only exist if at least one isomer has two distinguishable metal ions.

For example, the compound $Pt(NH_3)_2Cl_2$ has two different coordination isomers. At first glance, they do not seem to be isomers at all. However, we can verify that they have the same empirical formula than the first compound (Fig. 5.4.4).

$$Pt(NH_3)_2Cl_2$$
$$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3] \quad [Pt(NH_3)_4][PtCl_4]$$

Figure 5.4.4 Two different coordination isomers for the complex $Pt(NH_3)_2Cl_2$

$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ has two Pt atoms, four NH_3 units and four Cl atoms. That makes $Pt_2(NH_3)_4Cl_4$. This formula can be divided by 2 to to give $Pt(NH_3)_2Cl_2$. We can now easily see that the two compounds are isomers. The third isomer also has two Pt atoms, four NH_3 units, and four chloro atoms, so it must be an isomer as well.

Why are they coordination isomers? This is because in the first complex all ligands are bound to the same metal atom, whereas in the other two the ligands are bound to different metal atoms. In these compounds, one Pt atom belongs to a complex cation, and the other one to a complex anion. In the second isomer, three ammine ligands and one chloro ligand are bound to the first Pt atom, and one ammine and three chloro ligands are bound to the second Pt atom. In the third isomer, four ammine ligands are bound to the first platinum atom, and four chloro ligands belong to the second platinum atom.

Coordination isomerism is also possible for metal ions of different elements.

$$[Co(en)_3]Cr(CN)_6] \text{ and } [Cr(en)_3][Co(CN)_6]$$

Figure 5.4.5 Example of two coordination isomers with metal ions of different elements

In the example shown (Fig. 5.4.5), the first isomer has ethylenediamine bound to Co and cyanide bound to Cr, whereas in the second isomer ethylenediamine is bound to Cr and the cyano ligand is bound to Co.

$$[Pt(NH_3)]_4[PtCl_6] \text{ and } [Pt(NH_3)_4Cl_2][PtCl_4]$$

$$Pt(II) \quad Pt(IV) \qquad Pt(IV) \quad Pt(IV)$$

Figure 5.4.6 Two coordination isomers with metal ions in different oxidation states (Oxidation states noted below each coordination sphere)

Further, in coordination isomers metal ions can be in different oxidation states. We can see that in the two depicted isomers there are complex cations, and complex anions with Pt in in different oxidation states (Fig. 5.4.6). In the first isomer Pt(II) makes the complex cation having four ammine ligands attached to it. Pt(IV) is part of the complex anion being surrounded by six chloro ligands. In the second isomer Pt(IV) forms the complex cation having four ammine and two chloro ligands in the first coordination sphere, and Pt(II) forms the complex anion having four chloro ligands.

Linkage isomerism

Linkage isomerism, also called ambidentate isomerism, is an isomerism that can be observed for ligands that have more than one reactive end. In two linkage isomers, the ligands will bind with different ends to the metal. Which end is reactive depends on the effective HOMO-LUMO interactions. Soft donor atoms tend to bind to soft metals, and hard donor atoms tend to bind to hard metals. Also the solvent can play a big role.

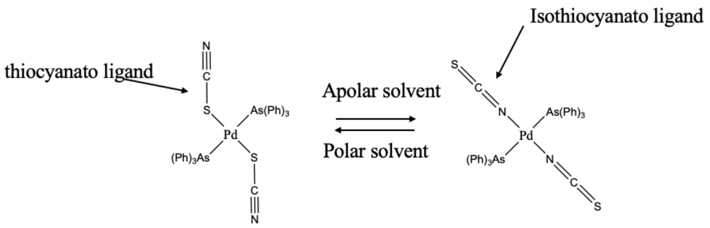


Figure 5.4.7 Two ambidentate isomers of thiocyanate

An example of an ambidentate ligand is the thiocyanate anion (Fig. 5.4.7). It can bind either with the sulfur or with the nitrogen end to a metal ion. When it binds with the S-end it is called the thiocyanato-ligand, when it binds with the N-end it is called the isothiocyanato ligand. Which atom binds to the metal can depend on the solvent. In the example shown, thiocyanate binds with S to Pd in polar solvents, but with N in apolar solvents. We could try to rationalize why. A possibility is that in polar solvents the more electronegative N atom can engage in hydrogen bonding which is not possible in apolar solvents. Steric arguments could also play a role. You can see that the triphenyl arsine ligands are fairly bulky. When the ligand binds with the nitrogen, then it binds in linear fashion avoiding steric interference with one of the arsine ligands. So it may be that in apolar solvents steric interactions dominate the behavior, while in polar solvents solvent-ligand interactions are in control.

It is even possible that two, same ambidentate ligands bind with opposite ends to the metal in one and the same molecule.

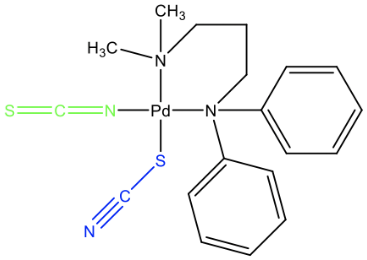


Figure 5.4.8 An example of two, same ambidentate ligands binding with opposite ends to the metal in one and the same molecule.

An example is the complex shown (Fig. 5.4.8). In this molecule, there is a thiocyanato and an isocyanato ligand binding to Pd. What arguments would we have to explain this ambidentate isomerism? Think about it for a moment. We can see that the two methyl groups are far less bulky than the two phenyl groups. When thiocyanate binds with the S-atom, then it can bend away from the two bulky phenyl groups. The second thiocyanate anion binds with the N atom because there is no significant interference between the methyl groups and the linear isothiocyanate ligand. This behavior indicates that thermodynamically, the Pd-N interaction is stronger, but only a little bit stronger because other factors such as steric interference can easily reverse the behavior.

Thio- and isothiocyanato ligands are not the only examples of ambidentate ligands.

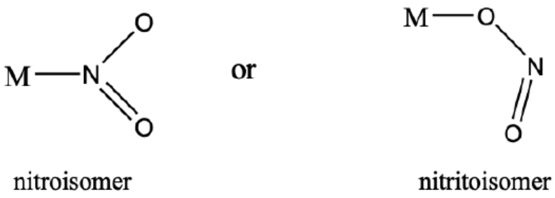


Figure 5.4.9 Two linkage isomers of the nitrite anion

Another example is the nitrite anion. It can either bind with the N- end or the O-end to a metal. In the first case it is called a nitroisomer, in the latter it is called a nitrito isomer (Fig. 5.4.9). Nitritoisomers are usually more stable.

Stereoisomers (Configuration Isomers)

Now let us discuss the second major type of isomerism: Stereisomerism. As mentioned previously, in stereoisomerism the bonds are between the same atoms, but the positions at which the ligands bind, the coordination sites, are different. There are two basic types of stereoisomerism: diastereomerism, and enantiomerism (Fig. 5.4.10).

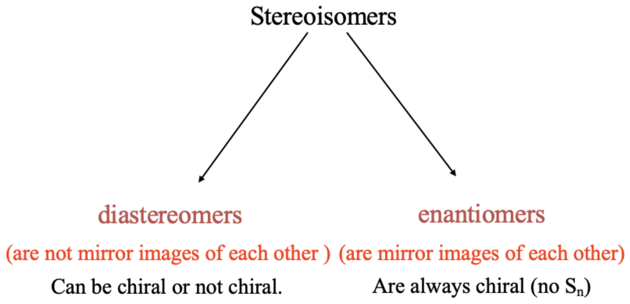


Figure 5.4.10 Types of stereoisomerism

In diastereomerism, the diastereomers are not mirror images to each other.

Definition: Diastereomers

Diastereomers are stereoisomers that are not mirror images of each other. They can be chiral or not chiral.

In enantiomerism, the enantiomers are mirror images to each others. Enantiomers are always chiral molecules.

Definition: Enantiomers

Stereoisomers that are mirror images of each other. They are always chiral.

Diastereomers can be chiral, but do not have to be chiral. Remember, a molecule is chiral when it does not have an improper rotational axis.

Example - Diastereomers and Enantiomers

Let us take an example from organic chemistry to illustrate the difference between enantiomerism and diastereomerism.

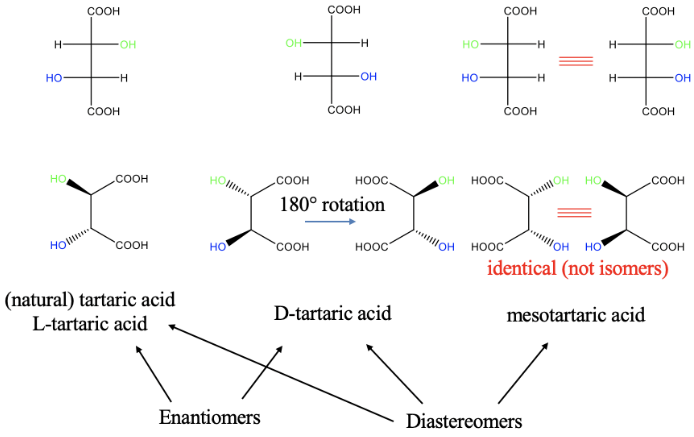


Figure 5.4.11 Example of diastereomers and enantiomers

Above (on the top left of Fig. 5.4.11) you see the Fischer projection an isomer of a compound called tartaric acid, it is called L-tartraric acid. The first OH group from the top points to the left, and the second one points to the right. This is the natural form of tartaric acid. The real structure of L-tartaric acid is depicted below (bottom left). You can see the the OH group that points to the right in the Fischer projection points toward us, while the other one, that points to the left in the Fischer projection, points away from us.

In the D-tartaric acid isomer, the first OH group in the Fischer projection points to the left, and the second one points to the right. For the real structure this means that the first OH-group points away from us, and the second one points toward us. These two isomers are mirror images to each other, and thus they are enantiomers. You may not immediately see in the real structure that the two are mirror images, but you can see it when you rotate the molecule around the C-C bond axis so that the carboxylic acid groups point to the the left (Fig. 5.4.11). Can you see it now?

There is a third isomer which is the so-called mesotartraric acid. We can draw its Fischer projection with both OH groups pointing to the right side (Fig. 5.4.11). In the real structure now both hydroxo groups point to the front. Is this molecule a mirror image of one of the two previous molecules? No, it is not! Therefore, it is a diasteromer relative to the other two. At first glance it seems that we can draw another molecule which is the mirror image of the mesotatraric acid. It would have two hydroxo groups pointing to the left in the Fischer projection, and two hydroxo groups pointing away from us in the real structure. However, the two molecules can be rotated so that they superimpose, and therefore they are not isomers, but identical molecules.

Cis-Trans Isomerism

Let us now discuss some common forms of stereoisomerism. The cis-trans isomerism is one very common stereoisomerism. It occurs when two, same ligands are in adjacent or opposite positions. For example, in a square planar complex two ligands can be adjacent or in opposite positions. When in adjacent position, the bond angle is 90° and we have a cis-isomer, when in opposite position, the bond angle is 180° and we have a trans-isomer.

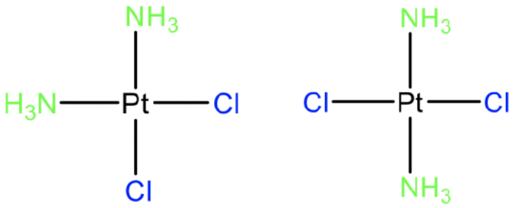


Figure 5.4.12 Cis-platinum and trans-platinum, respectively

The probably most well known example of a cis-isomer in coordination chemistry is cis-platinum which is an anti-cancer drug (Fig. 5.4.12). Its trans-isomers does not have these pharmaceutical properties showing that cis-trans isomerism can have a profound impact on the properties of a molecule. Overall cis-trans isomerism in Pt(II) complexes have been most intensely studied, but cis-trans isomerism is also known for other d^8 metal ions in square planar complexes. We can also ask if cis- and trans isomers are diastereomers or enantiomers. Let us look at the example of cis- and trans-platinum to answer this question. Clearly, these two isomers are not mirror images to each other, so they must be diasteromers. Generally, cis- and trans- isomers are diastereomers.

Cis-trans isomerism extends beyond square planar complexes, and is also known for other shapes, for example, the trigonal bipyramidal shape, and the octahedral shape. In the cis-isomer of an octahedral complex two ligands occupy positions on the same face of the octahedron, whereas in the trans-isomer they occupy opposite position of the octahedron.

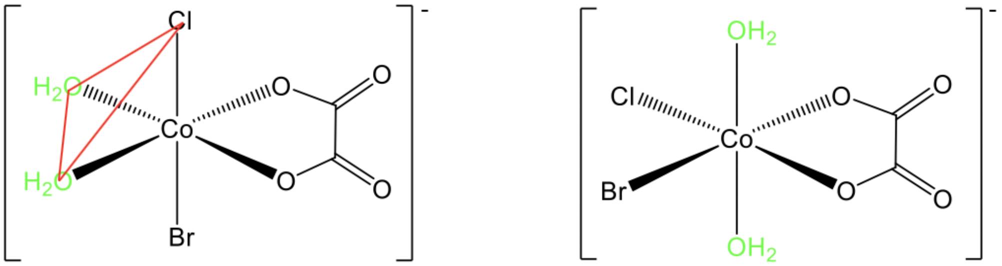


Figure 5.4.13 Cis and trans isomers of the diaquabromochlorooxalato cobalt(1-) complex, respectively

For example, in the complex diaquabromochlorooxalato cobalt(1-) there are cis and trans isomers known (Fig. 5.4.13). In the trans-isomer the two aqua-ligands stand in opposite position, and there is a 180° angle between them. In the cis-isomer they are in adjacent position, and the angle is 90°. We can see that the two ligands are on the same triangular face of the octahedron, shown in red.

Are there rules that can help us to decide if a cis- or a trans- complex will form? As you might suspect, the largest ligands usually go in trans-position due to steric repulsion arguments. Bidentate ligands usually form the cis-isomer because bidentate ligands are usually designed to make five- or six-membered rings with the metal ion. Are cis-trans isomers chiral? If the ligands are simple, then they are usually not, but if they are more complicated, then they can be. In this context it needs to be said that ideal structures are rarely observed. For example, a square planar complex is rarely an ideal square plane e.g. because the bond angles may be somewhat distorted from the 90° angle due to the fact that the ligands have unequal steric requirements. A slight distortion actually can remove one or many symmetry elements, leading to chirality, however, such small deviations are usually ignored.

Fac-mer Isomerism

Another common type of stereoisomerism in coordination chemistry is fac-mer isomerism. Fac stands for facial and mer stands for meridional. In a fac-isomer the same ligands are on a common face of a polyhedral complex, in the mer isomer they are on a plane that bisects the polyhedron. This kind of isomerism is very common for octahedral complexes, but not restricted to those.

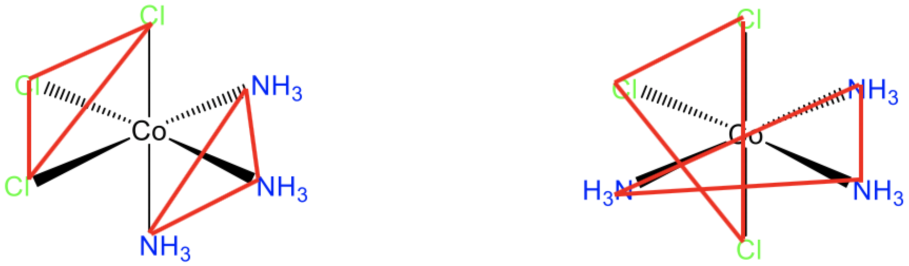


Figure 5.4.14 Fac- (left) and mer-isomers (right) of the triammine trichloro cobalt(III) complex.

For example the complex triammine trichloro cobalt(III) has a fac- and a mer-isomer. You can see that in the fac-isomer the identical ligands are on two opposite triangular faces of the octahedron. In the mer-isomers they lie on two planes that bisect the octahedron. We can again ask if they are diastereomers or enantiomers? The answer is: They are not mirror images to each other, so they are not enantiomers, but diastereomers.

Fac-mer Isomerism with Tridentate Ligands

Fac-mer isomerism is also common for octahedral complexes with tridentate ligands, for example the ligand diethylenetriamine (Fig. 5.4.15).

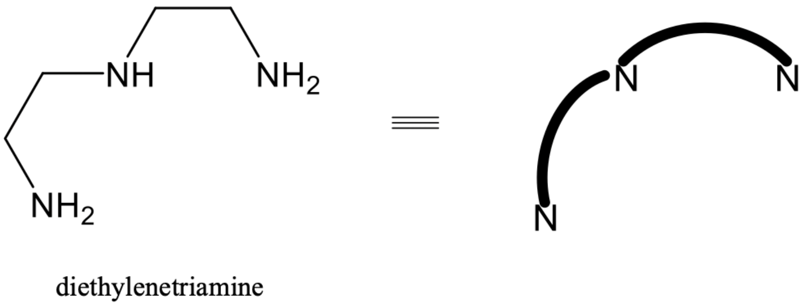
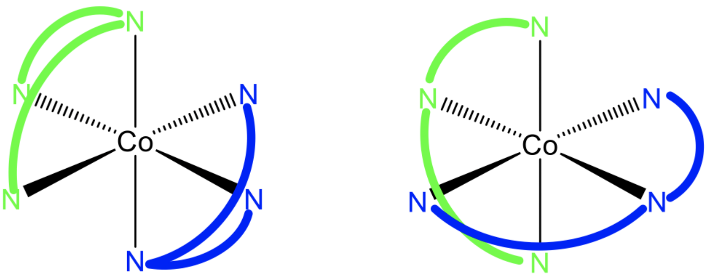


Figure 5.4.15 Diethylenetriamine

In this ligand two NH_2 groups and one NH group are interconnected by two ethylene units. For clarity reasons, in complexes with this ligand, often only the N donor atom of the NH_2 and NH groups is depicted, and the ethylene diammine units are simplified as bent lines interconnecting the N-atoms. We will use this simplification in the following (Fig. 5.4.16).



fac-isomer mer-isomer

Figure 5.4.16 Fac-mer isomers of the bis(diethylenetriamine) cobalt complex.

Here is an example of bis(diethylenetriamine) cobalt complexes that are fac-mer isomers (Fig. 5.4.16). One ethylenediamine ligand is shown in green, the other one is shown in blue. You can see that the left isomer is the fac-isomer with all three donor atoms of a ligand placed on the same face of the octahedron. On the right side is the mer-isomer, with all donor atoms of the same ligand placed on planes that bisect the octahedron. Also in this case the two isomers are not mirror images and are diasteromers to each other.

Triethylenetetramine Complexes

There is isomerism similar to fac-mer isomerism in octahedral complexes with the tetradentate ligand triethylenetetramine (Fig. 5.4.17).

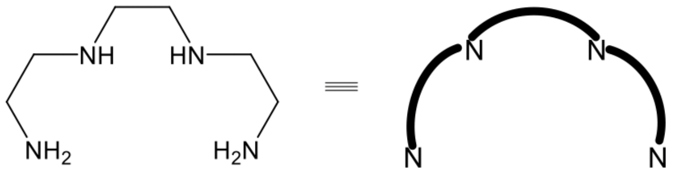


Figure 5.4.17 Triethylenetetramine

In this ligand, two NH and two NH_2 groups are bridged by four ethylene groups. We can again depict the ligand in a simplified way by just showing the N donor atoms, and by simplification of the ethylene groups as bent lines.

One possibility to realize an octahedral complex with triethylenetetraamine ligands is to orient all three rings in the same plane, we can also say we have an octahedral complex with three coplanar rings. This is shown below (Fig.5.4.18).

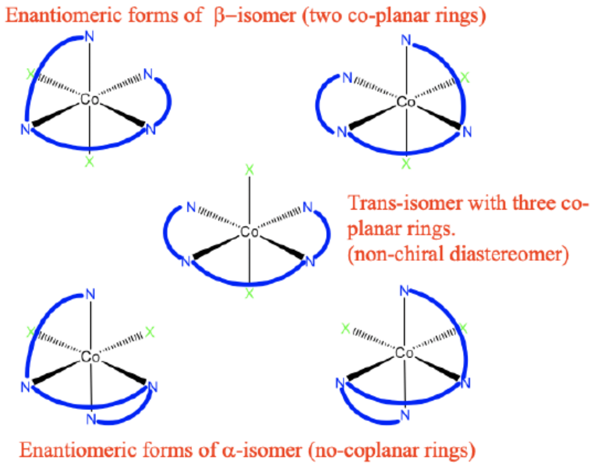


Figure 5.4.18 Octahedral complex with triethylenetertraamine ligands

The three ethylenediamine units make three five-membered rings which are co-planar to each other. The N-atoms occupy overall four vertices of the octahedron. There are two other generic ligands X located at to opposite vertices of the octahedron. Therefore, this isomer is called the trans-isomer.

We can ask if this molecule is chiral? The answer is no, because there is a mirror plane which is co-planar with the three five-membered rings. In addition to this trans-isomer, there are also two cis-isomers, one is called the α-isomer, the other one is called the β-isomer. In the β-isomer, there are now only two co-planar rings, the third one is now out of plane. The two ligands X are in cis-position relative to each other. Is the trans-isomer a diastereomer or enantiomer to the β -isomer? They are clearly not mirror images to each other, therefore they must be diasteromers. Is this β-isomer chiral? Yes, it is! There is no improper rotational axis. Therefore, an enantiomer must exist, and this enantiomer must be a mirror image of the β-form. Here it is! Naturally, it must also have two co-planar rings, and two ligands X in cis-position. It is therefore also considered a β-isomer.

Now let us discuss the α-isomerism. In an α-isomer no two ligands are co-planar any more. This isomer is a diasteromer to the trans- and the β-form because the isomers are not mirror images. Also the α-isomer is chiral. Therefore, there must be another α-isomer which is the mirror image to the first α-isomer. It is shown in the bottom right of **Figure 5.4.18**.

Nomenclature for Propeller Complexes

Complexes with two or more non-coplanar rings that are non-adjacent are always chiral and are called “propeller complexes”. There is a special nomenclature for propeller complexes that we will briefly discuss in the following.

Let us first understand why these complexes are propeller complexes? They are called like that because the non-coplanar rings are oriented relative to each other similarly to propeller blades. A propeller must have at least two blades, but can also have more than that. We distinguish between so-called left handed propellers and right-handed propellers. A left-handed propeller has the property to move away from you in a medium like air or water when rotated counter-clockwise.

Definition: Left-Handed Propeller

Counterclockwise rotation moves a left-handed propeller away

A right handed propeller moves away from you when rotated clock-wise.

Definition: Right-Handed Propeller

Clockwise rotation moves a right-handed propeller away

The tip of one blade of a left-handed propeller describes a left-handed helix as it moves away, the tip of a blade of a right-handed propeller describes are right-handed helix as it moves away.

Determining the Handedness of "Propeller Compexes"

How can we determine the handedness of a propeller molecule? Let us determine it using the example of the tris(oxalato) ferrate(III) anion. Fig. 5.4.19.

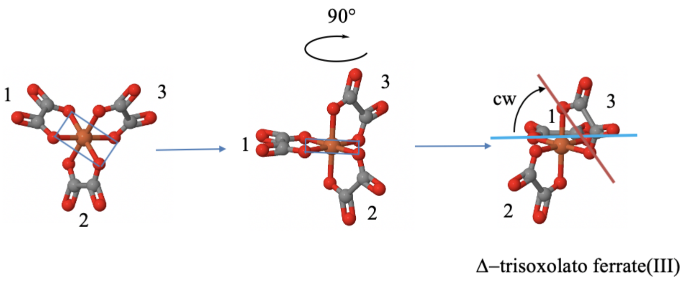


Figure 5.4.19 The tris(oxalato) ferrate(III) anion. The molecule is rotated in two steps so that ring 1 is oriented horizontally, and points to the back. The horizontal blue line needs to be rotated counter-clockwise to make it parallel to the brown line.

It is a three-bladed propeller molecule because it has three five-membered rings between the three oxolato ligands and the iron center. Each ring is considered a blade. None of the rings are co-planar and none of them are adjacent, meaning that the rings do not share a donor atom.

In order to determine the handedness, we can first rotate the molecule so that one of the rings is oriented horizontally and points to the back. Unless we have a three-dimensional model, we need to do this in our mind. Once that is accomplished we can draw a horizontal line between the two donor atoms of that ring. Next we can draw a line between two donor atoms of another ring. If necessary, we extend the line so that the line crosses the horizontal line. Next, we determine the smallest angle between the two lines, and rotate the non-horizontal line until it becomes horizontal. We can do this just in our mind. If we need to rotate anti-clockwise, the propeller is considered left-handed, we call it a Λ -isomer. If we need to rotate clock-wise, the the propeller is right-handed, we call it Δ-isomer.

Determining Handedness for Propeller Molecules Requiring More Than One Label

In some cases coordination compounds have multiple non-adjacent, non-coplanar ring combinations, and the handedness must be determined for each combination. Examples are octahedral EDTA complexes.

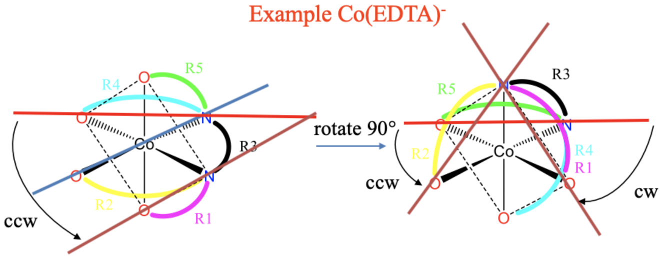


Figure 5.4.20 An octahedral EDTA Co complex. Rotation around the blue line moves the green ring into horizontal position, pointing to the back.

In those complexes there are overall five different rings which we can label R1 to R5. You can see the different rings in different colors (Fig. 5.4.20) For clarity we have abbreviated the linkers between the donor atoms by bent lines in different colors. Each color represents a different linker making a different ring.

We realize that ring R3 is shared with all other rings, therefore it is adjacent to all other rings and does not need to be considered. R1 is adjacent to R2, and R3, but not adjacent and not co-planar with R4 and R5. Therefore we need to consider the R1-R4 and R1-R5 combinations. Further, R2 is coplanar with R3 and R4, and adjacent to R3, but is not coplanar and not adjacent to R5. Therefore, we need to consider the R2-R5 combination as well. R4 and R5 are adjacent, so we do not need to consider this combination. We have found all combinations we need.

We now need to rotate the complex so that one relevant ring is oriented horizontally and points to the back. We can for example choose the ring R4. Luckily, is already correctly oriented. Next, we can connect the donor atoms of the ring R4 to produce a horizontal line. Now let us draw a line between the donor atoms of the ring R1. We see that we need to rotate the horizontal line counter-clockwise to make it parallel to this line, thus the R1-R4 ring combination is a Λ-configuration.

We can next determine the R1-R5 handedness by first reorienting the molecule so that R5 points to the back. R1 could also be chosen. However, R5 is part of two relevant ring combinations, and so we can kill two bird with one stone if we choose R5. We can move ring R5 to the back by rotating 90° counter-clockwise around the blue axis shown in Fig. 5.4.20. In goes through an O atom, the cobalt atom, and an N atom. This axis stands perpendicular to the square indicated by dotted lines. The square has four donor atoms on the four vertices, and these donor atoms move 90° counter-clockwise as the rotation is carried out. The orientation of the rings follow the movement of the donor atoms. The O-donor atom of the ring R5 moves so that R5 is now horizontal, and points to the back. Next we can interconnect the donor atoms of R5, and the donor atoms of R1 by lines. We can see that the horizontal line must be rotated clockwise so that it becomes parallel with the other one. Therefore, the R1-R5 configuration is a Δ-configuration.

For the determination of the combination R2-R5 the complex does not need to be reoriented again. We can directly draw a line through the donor atoms of R2, and determine the direction of rotation. This time we need to rotate counter-clockwise again, meaning the R2-R5 combination is in Λ-configuration.

Overall, we have a $\Lambda\Delta\Lambda$-(ethylenediamine tetracetato)cobaltate(III). Note that the order of designation is arbitrary, we could have named the molecule a $\Lambda\Lambda\Delta$-complex or a $\Delta\Lambda\Lambda$-complex also.

Exercise

Let us practice this by one more example.

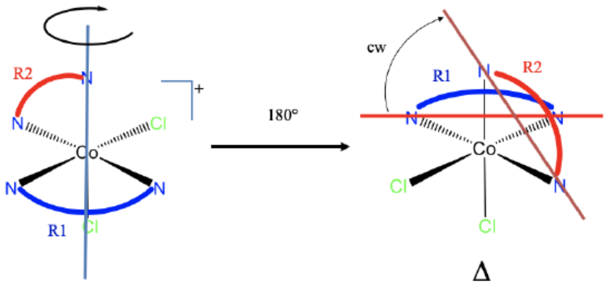


Figure 5.4.21 Example to determine handedness

What is the handedness of the complex shown? First of all: Does it meet the criteria for a propeller complex? The answer is yes. There are two rings, R1 and R2, and they are both not coplanar, and non-adjacent.

To determine handedness we need to first move the molecule so that one ring is oriented horizontally and points to the back. We could choose any of them, but it seems easier to rotate the ring R1 that points to the front and is oriented horizontally by 180° around an axis that is defined by one N and on Cl atom (shown in blue in Fig. 5.4.21)), and is oriented vertically. This rotation moves one of the donor atoms of the other ring by 180°, which defines the new orientation of the ring. Now we can draw a horizontal line through the donor atom of ring 1, and a line through the donor atoms of ring R2. We can see that we must rotate clock-wise, and the propeller complex is right-handed.

Ring Conformations

In addition to isomerism, also conformerism has an influence on the structure of a coordination compound. There may be two or more conformers possible for a particular isomer. As an example, let us consider a ring between a metal ion and an ethylenediamine ligand (Fig. 5.4.22).

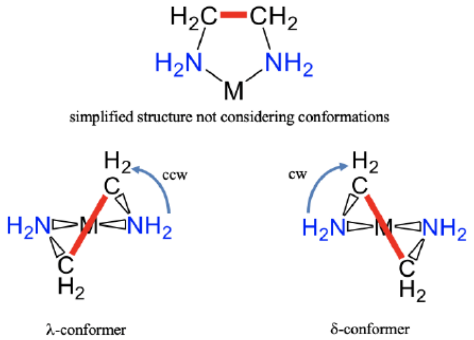


Figure 5.4.22 Ring structure between a metal ion and an ethylene diamine ligand

In contrast to simplified depictions often used, it is not planar, because of the sp^3-hybridization of the carbon and nitrogen atoms. There are two different conformations possible that differ in the orientation of the C-C bond within the ring. They are shown above (Fig. 5.4.22). In the conformation shown left we must rotate a thought horizontal line going through the two nitrogen donor atoms counterclockwise so that it becomes parallel to the C-C bond. For the other conformer, we need to rotate the thought horizontal line clockwise. We call the first conformer the λ-conformer, and the second one the δ-conformer. In this case we use lower case letters to indicate conformerism and not isomerism.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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Concept Review Questions Chapter 5

Chapter 5

Section 1 & Section 2

1. Explain how the name “chelate” ligand originates.

Section 3

1. What are the main factors determining coordination numbers?

2. Is the coordination number 1 common? Explain.

3. For which electron configuration are the coordination numbers 2 and 3 common?

4. What is the structure of methyl lithium?

5. What electron configuration is common for square planar shapes?

6. What is the most common shape for the coordination number 4?

7. Which are the most common shapes for the coordination number 5?

8. What is the Berry pseudo rotation? Describe its mechanism.

9. What are the most common shapes of coordination compounds with the coordination number 7? What are the point groups associated with these shapes.

10. Explain briefly, why molecular coordination compounds with cubic shapes are not known, while square anti-prisms are relatively common.

11. Explain why coordination compounds with high coordination numbers (7 and larger) are not very common.

12. Name an example of a coordination compound with the coordination number 9.

Section 4

1. What is the difference between a constitutional isomer and a stereoisomer.

2. Name four types of constitutional isomerism.

3. What is the definition of hydrate isomerism?

4. Why is hydrate isomerism only possible in solid state?

5. What is the definition of ionization isomerism?

6. What is the definition of coordination isomerism?

7. What is the definition of linkage (ambidentate) isomerism?

8. What is the difference between a diasteromer and an enantiomer?

9. What is the definition of cis-trans isomerism?

10. What is the definition of fac-mer isomerism?

11. What is the definition of a propeller complex?

12. What is the definition of a left-handed/right-handed propeller?

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Homework Problems Chapter 5

Homework Problems

Exercise 1

Name the following compounds:

a. $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5\,]^{4+}$
b. $Na[Fe(NH_3)_3Cl_3]$
c. $VOCl_3$
d. Na_2PdCl_4
e. $[Ni(NH_3)_3(NMe_3)](PF_6)_2$

Answer

a) μ-oxo bis(pentaamminechromium (III)) (or 4+)

b) sodium triammine trichloroferrate (II) (or (1-))

c) trichlorooxo vandadium(V) (or (0))

d) sodium tetrachloropalladate (II) (or (2-))

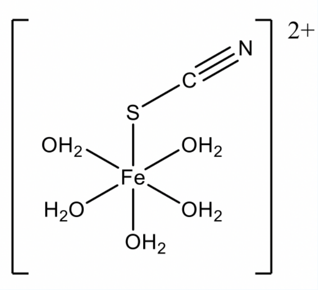
e) triammine (trimethylamine) nickel (II) hexafluorophosphate or triammine (trimethylamine) nickel (2+) hexafluorophosphate

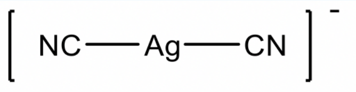
Exercise 2

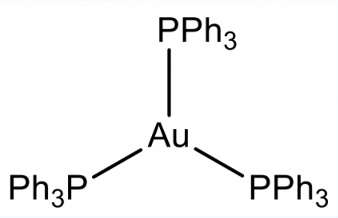
Write a plausible structural formula for

a. pentaaquathiocyanatoiron(III).
b. dicyanoargentate (I)
c. Tris(triphenylphosphine)gold(I)

Answer

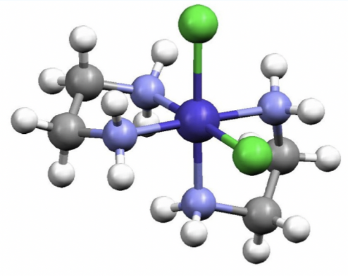
a) 

b) 

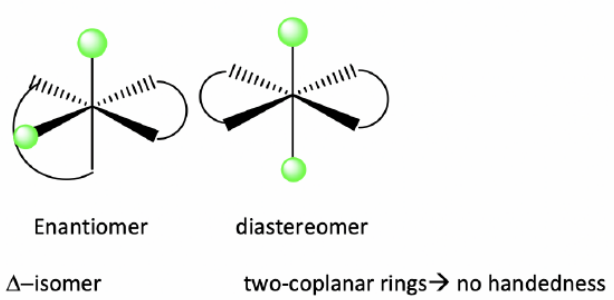
c) 

Exercise 3

What other stereoisomers can you draw for the complexes depicted below. Are they diasteromers or enantiomers? Determine the handedness of all isomers.

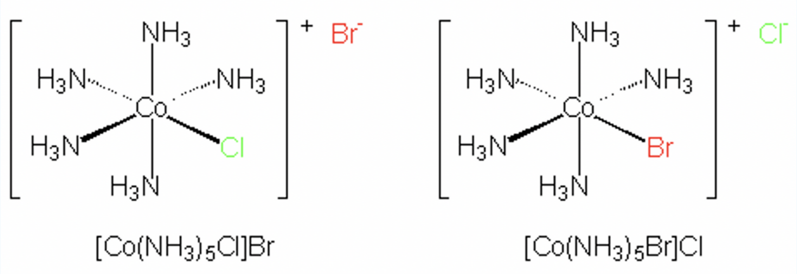


Answer



Exercise 4

What type of isomerism is present between the following molecules:



Answer

Ionization isomerism

Exercise 5

How many hydrate isomers are theoretically possible for $[Al(H_2O)_6]Cl_3$. Write down their formulas.

Answer

$[Al(H_2O)_5Cl]Cl_2$ x H_2O

$[Al(H_2O)_4Cl_2]Cl$ x 2 H_2O

$[Al(H_2O)_3Cl_3]$ x 3 H_2O

Exercise 6

What isomerisms do you see between the following two compounds:

$[M(H_2O)_4Cl_2]Br_2$ and $[M(H_2O)_3ClBr_2]Cl \times H_2O$.

Answer

Hydrate isomerism and ionization isomerism

Exercise 7

What distortions are common for the octahedral shape?

Answer

Tetragonal and trigonal distortions

Exercise 8

Which coordination number and shape would you most likely expect for a complex between Ag^+ and $S_2O_3^{2-}$?

Answer

CN = 2, linear shape.

Exercise 9

Which of the following complexes are most likely square planar:

a. $AuCl_4^-$
b. $ZnCl_4^{2-}$
c. $TiCl_4$
d. $FeCl_4^{2-}$

Answer

a) $AuCl_4^-$

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CHAPTER OVERVIEW

6: Coordination Chemistry II - The 18 Electron Rule

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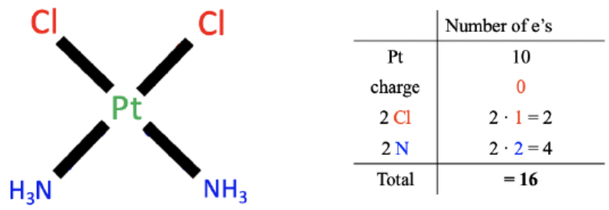
Chapter 6.1: The 18 Electron Rule

Electron Counting In Transition Metal Complexes

In this chapter we will learn how to count valence electrons in coordination compounds. Electron counting is important because the number of electrons in a complex can tell us a lot about the stability and reactivity in a coordination compound. In addition, it allows us to predict and understand structures to a certain extent. Electron counting sounds trivial, but it is not as trivial as it seems, actually there are even two different methods for electron counting. Each method leads to the same result. Which method you prefer is "personal taste", but each method is about equally common in the literature, so you need to know both of them.

The Neutral Atom Method

The first method is called the "neutral atom method". As the name suggests, we will break up the complex into neutral fragments, and count the electrons that contribute to the bonding in each of the fragments. The neutral atom method is carried out according to the following three steps. First, we count the number of the valence electrons of the metal. We consider the metal as neutral atom. The number valence electrons is the same as the group number of the transition metal in the periodic table. For transition metals the group number varies from 3 to 12. In the second step, we account for the ionic charge of the complex, if the complex is not neutral. This will reduce the number of electrons for a complex cation, and increase the number of valence electrons for a complex anion. In the third step, we need to determine how many electrons are contributed by each ligand. This is the most complicated step. To determine the number of electrons must cleave each metal-ligand bond so that a ligand fragment results that is neutral. We then count the number of electrons at the ligand that contributed to the bond. The number of electrons contributed by each ligand is then summed up. This is sum is then added to the number of electrons determined by the previous steps. This is gives the overall number of valence electrons.



	Number of e's
Pt	10
charge	0
2 Cl	$2 \cdot 1 = 2$
2 N	$2 \cdot 2 = 4$
Total	**= 16**

Figure \(\PageIndex{1}\): Example of neutral atom method

Let us apply these rules by an example, the cis-platinum complex (Figure \(\PageIndex{1}\)). We first need to count the number of electrons of the metal. The metal is platinum which is located in group 10 of the periodic table. Therefore, a neutral platinum atom has ten valence electrons.

Next, we look at the charge of the complex. In this case, there is no charge, and therefore no electrons are added or subtracted.

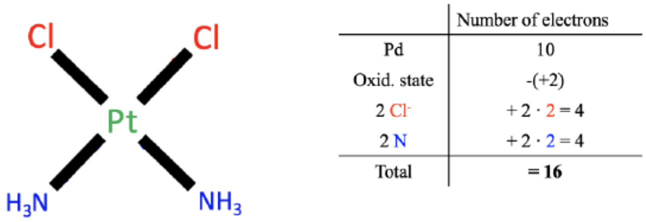
Lastly, we count the electrons of the ligands. There are two types of ligands, the chloro-ligands and the ammine ligands. Now, our task is to cleave the Pt-ligand bond so that neutral ligand fragments result. We can see that for the chloro-ligands we must cleave the Pt-Cl bond, homoleptically, meaning in the middle, assigning one electron to the Pt and one electron to Cl, because doing so creates a neutral chlorine atom. The fact that we cleaved the bond homoleptically, means that the chloro ligand contributed one electron. Because we have two chloro ligands, there are overall two electrons.

Now, let us think about how many electrons the ammine ligands contribute. In this case we need to cleave the metal-ligand bond heteroleptically to produce a neutral ligand fragment. Both bonding electrons are assigned to the ligand. This produces a neutral NH_3 molecule. This means that each ammine ligand contributes two electrons. Overall, that makes four electrons, because we have two ammine ligands.

Finally, we need to sum up the electrons from all three steps. That is ten electrons from Pt, zero electrons due to charge, two electrons from the chloro ligands, and four electrons from the ammine ligands equaling 16 valence electrons total. This is the final result.

"Oxidation State" Method

The oxidation state method is also comprised of three steps. The first step is the same as in the neutral atom method. We determine the number of electrons of the neutral metal which the same as its group number in the periodic table. The next step is different though. It requires the determination of the oxidation state of the metal. How can we determine it? First, we cleave the metal-ligand bonds heteroleptically so that all bonding electrons are assigned to the ligands. Then we determine the charge of the ligands. Ligands can either be neutral or negatively charged. We determine the overall number of charges at the ligands. The difference between that number and the charge of the complex is the oxidation state of the metal. We either add or subtract electrons depending on the oxidation state of the metal. If the oxidation state is positive we subtract electrons, if it is negative, which is rare, then we add electrons. The third step counts the number of the electrons contributed by the ligands. Because we cleaved all bonds heteroleptically, all bonding electrons are considered to be contributed by the ligands, and we count them accordingly. Finally, we sum up the electrons of all three steps which gives the total number of electrons.



	Number of electrons
Pd	10
Oxid. state	-(+2)
2 Cl^-	$+2 \cdot 2 = 4$
2 N	$+2 \cdot 2 = 4$
Total	**= 16**

Figure \(\PageIndex{2}\): Example of the oxidation state method

Let us apply the method to the previous example cis-platinum. Applying the first step gives us 10 valence electrons for the platinum.

Next, we need to determine the oxidation state of Pt. To do so, we must now cleave all metal-ligand bonds heteroleptically, so that all bonding electrons are assigned to the ligand. By the way, this is equivalent to saying that we treat all the bonds as dative bonds with all electrons coming from the ligands as the donors. When we do this for the chloro ligands we see that this created chloride anions with a 1- charge. Cleaving the Pt-N bonds heteroleptically leads to neutral NH_3 molecules. Therefore the overall number of charges at the ligands is 2x(-1)+2x0=-2. The charge at the complex is zero, therefore the oxidation state of Pt is 0-(-2)=+2. We must therefore subtract two electrons from the 10 electrons of the platinum.

Now we must determine the number electrons coming from the ligands. Because all bonds are considered as dative bonds, the chloro ligands contribute two electrons each, and the ammine ligands contribute two electrons each. That makes overall eight electrons.

In sum, 10 electrons from the neutral Pt atom minus two electrons due to the +2 oxidation state of Pt plus 2x2=4 electrons from Cl plus 2x2=4 electrons from NH_3 gives 16 electrons total. We can see that we have arrived at the same results as in the case of the oxidation state method.

We can discuss the advantages and disadvantages of both methods, also. The neutral atom method has the advantage that we do not have to think about charges at ligands and oxidation states. However, we have to think about how to cleave bonds to create neutral fragments. We may need to cleave bonds in an way that is not reflecting the donor-acceptor nature of a coordination compound. The oxidation method does account for the donor-acceptor nature of a coordination compound because the bonds are considered dative bonds, and the electrons are assigned to the ligands and metals accordingly. We do not need to think how to cleave bonds, because we cleave the bonds always heteroleptically. However, it requires us to think about charges at the ligands to determine oxidation states which is an additional, non-trivial step.

Counting Electrons: Ligand Contributions

The most difficult step in electron counting is usually the determination of the number of electrons a ligand provides. Therefore, let us practice this by a few examples.

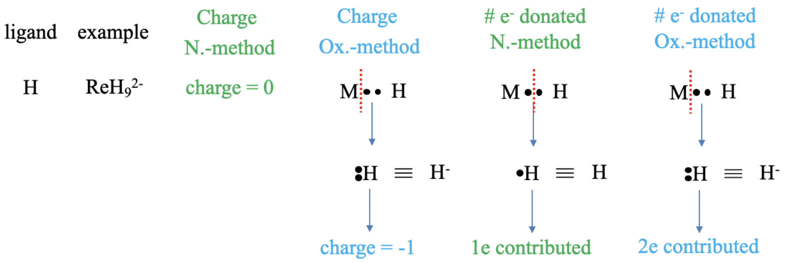


Figure \(\PageIndex{3}\): Counting electrons in a hydrido ligand

Let us first look at an hydrido ligand which is for example present in the nonahydridorhenate(2-) complex anion (Figure \(\PageIndex{3}\)). What is the charge at the ligand in the two methods? In the neutral atom method, the charge is always zero, this is a no-brainer. In the case of the oxidation statement method, we need to treat the bond as a dative bond, and that means that we must cleave the bond heteroleptically, so that both bonding electrons can be assigned to the ligand. An H atom with two electrons is a hydride anion with a -1 charge. Next, let us think about the number of electrons donated. In the neutral atom method we need to produce neutral ligand fragments. To do so we must cleave the M-H bond homoleptically, because this will create a neutral hydrogen atom. How many electron will it contribute? It will contribute one electron, because we cleaved the bond homoleptically assigning only one of the two bonding electrons to H. In the oxidation state method, the hydrido ligand contributes two electrons because the bond was considered dative and therefore cleaved heteroleptically. Both bonding electrons were assigned to the ligand, therefore the ligand contributes two electrons.

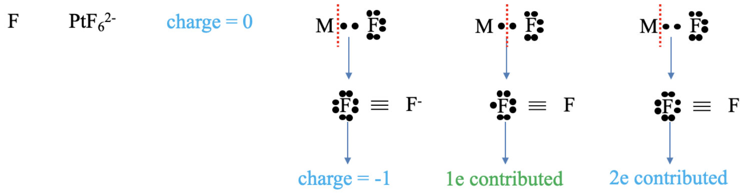


Figure \(\PageIndex{4}\): Counting electrons in a halogenide as ligand

Next, let us consider a halogenide ligand (Figure \(\PageIndex{4}\)). What is the charge at the ligand? For the neutral atom method, the answer is trivial, the charge is always zero. In the oxidation state method both bonding electrons in the metal-ligand bond get assigned to the ligand. This gives the ligand a -1 charge. What is the number of electrons contributed? In the neutral atom method we need to think again how to cleave the metal-ligand bond to create a neutral ligand fragment. We need to recognize that we must cleave the bond homoleptically to produce that fragment. Cleaving the bond homolopetically means that the ligand has contributed one electron. In the oxidation state method, we cleave the bond always heteroleptically so that all bonding electrons are assigned to the ligand. Thus, the ligand contributes two electrons.

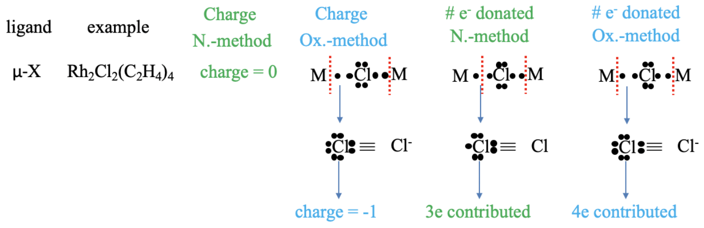


Figure \(\PageIndex{5}\): Counting electrons in a bridging halogenide as ligand

A halogenide anion as a ligand cannot only be terminal, but also bridging. An example is the μ-dichloro bis(tetraethylene rhodium(I)) complex in which two chloro-ligands bridge two rhodium atoms. What is the charge in the neutral atom method? Of course, it is zero. What is the charge in the oxidation state method? We can see that if we consider both metal-ligand bonds dative bonds, and cleave the bonds heteroleptically, that the Cl atom is surrounded by eight unshared electrons, which gives it a -1 charge. How, many electrons are contributed in the neutral atom method? To answer this question, we need to decide if we have to cleave the bonds homo- or heteroleptically to produce a neutral Cl atom. Can you see it? The answer is: We must cleave one bond homoleptically, and the other one heteroleptically. How many electrons are then contributed by the chloro ligand? It is the two electrons from the heteroleptically cleaved bond, and one electron from the homoleptically cleaved bond. So overall it is three electrons. What about the oxidation state method? In this case both bonds are cleaved heteroleptically, and this means that overall four electrons are contributed.

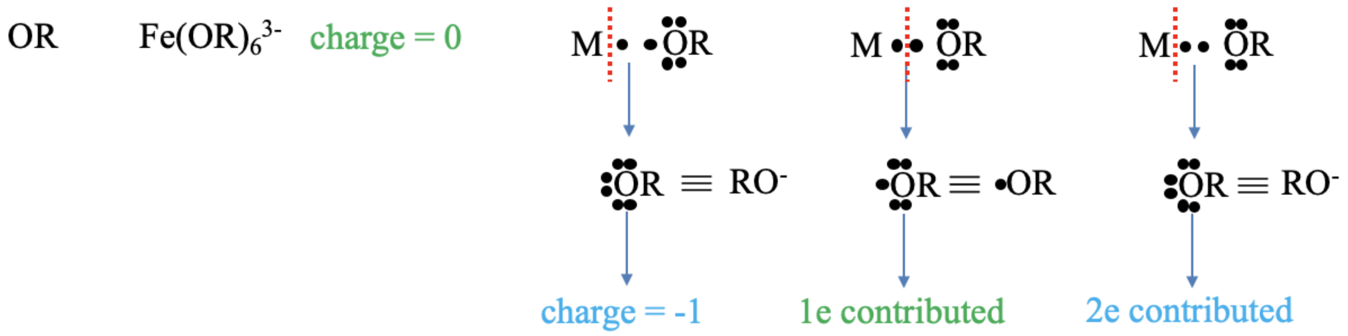


Figure \(\PageIndex{6}\): Counting electrons in an alkoxy ligand (OR)

What are the charges and electrons contributed by an alkoxy ligand (OR), Figure \(\PageIndex{6}\)? An example for a complex with such as ligand is hexaaphenoxy ferrate (3-). The charge according to the neutral atom method is zero. In the oxidation state method we cleave the bonds heteroleptically, and our ligand becomes an alkoxide anion. This anion has a 1- charge. How many electrons does the ligand contribute? To get a neutral fragment we must cleave the bond homoleptically. This actually produces an alkoxy radical. This radical contributes its radical electron, thus there is one contributed electron. In the oxidation state method we treat the bond as a dative bond and cleave the bond heteroleptically. Therefore two electrons are contributed according to the oxidation state method.

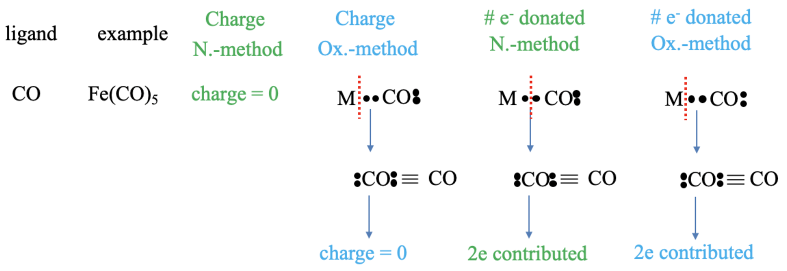


Figure \(\PageIndex{7}\): Counting electrons in a carbonyl ligand

Next, let us apply electron counting to the carbonyl ligand. For example, five carbon monoxide molecules form an iron pentacarbonyl complex with iron. The charge at the ligand in the neutral atom method is zero. In the oxidation state method, we assign both bonding electrons to the ligand, and that produces a neutral carbon monoxide molecule. Note that the carbon atom is formally negatively charged, because it is surrounded by 5 electrons, but the oxygen atom is positively charged because it is surrounded by five electrons. So overall, the molecule is neutral. What is the number of electrons contributed in the neutral atom method? To produce a neutral ligand we must cleave the bond heteroleptically. This produces a neutral carbon monoxide molecule. Because we cleaved the bond heteroleptically, the ligand contributes two electrons. In the oxidation state method we always cleave the bonds heteroleptically, and thus two electrons come from the ligand, too.

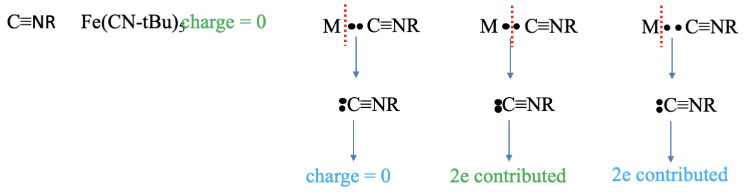


Figure \(\PageIndex{8}\): Counting electrons in an isonitrile ligand

The last ligand we discuss here is the isonitrile ligand. An example is the pentakis-(tert-butyl isonitrile) iron molecule. The charge of the ligand is zero in the neutral atom method, but what is it in the oxidation state method? Let us see what happens as we assign both bonding electrons to the ligand. We we see that the carbon is now surrounded by five electrons. Three are in the carbon-nitrogen triple bond and the other two come from the electron lone pair at the carbon atom. This means that the carbon atom has a -1 formal charge. Now, let us look at the N atom. We see that it is surrounded by four electrons, three coming from the C-N triple bond, and one from the C-R bond. That means that the N atom has a +1 charge. Overall, the molecule is neutral and does not carry a charge. What about the number of electrons contributed? We can see that we must cleave the bond heteroleptically to produce a neutral isonitrile, there are two electrons are contributed in the neutral atom method. The oxidation state method must cleave the bond heteroleptically, therefore, the number of electrons contributed is also two.

The 18 Electron Rule

Electron counting is important in the context of an important rule in coordination chemistry: The 18 electron rule. The 18 electron rule states that for d-block elements *normally* complexes with 18 electrons in the shell ($ns^2(n-1)d^{10}np^6$ configuration) are most stable. If this number is not reached, the species is **coordinatively unsaturated** and tends to add more ligands. It also tends to be reduced because adding electrons brings the complex to, or at least closer to 18 electrons. Coordinatively unsaturated complexes therefore tend to have a higher reactivity.

Definition: Coordinatively Unsaturated Complexes

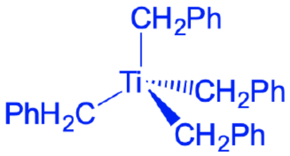
A complex is coordinatively unsaturated when the 18 electrons are not reached in the ($ns^2(n-1)d^{10}np^6$ configuration) shell. It tends to add more ligands, and tends to be reduced. It is associated with higher reactivity.

If a species has more than 18 electrons it is coordinatively oversaturated and tends to lose ligands. It is usually easily oxidized. Both loss of ligands and oxidation reduces to the number of electrons to or at least closer to 18.

Definition: Coordinatively Oversaturated Complexes

A complex is coordinatively oversaturated when it has more than 18 electrons in the shell ($ns^2(n-1)d^{10}np^6$ configuration). It tends to lose ligands and tends to get oxidized.

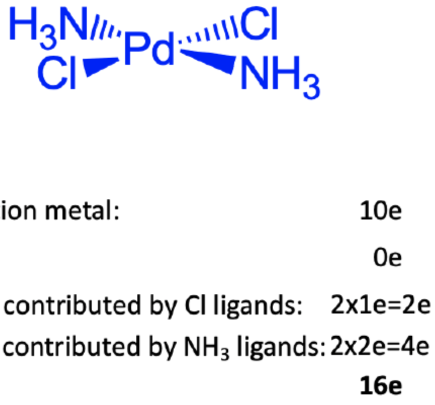
The 18 electron rule has many exceptions, and therefore needs to be applied with caution. In particular, group 3, 4, and 10 complexes deviate often from the 18 electron rule.



Contribution metal:	4e
Oxidation state: +4	-4e
Electrons contributed by ligands:	4x2e=8e
Sum:	**8e**

Figure \(\PageIndex{9}\): Example of counting electrons in the tetrahedral tetrabenzyltitanium(0) complex using the oxidation state method

For illustration purposes, let us count the number of electrons of the tetrahedral tetrabenzyltitanium(0) complex by the oxidation state method. We could also use the neutral atom method, which would give the same results. This complex is a group 4 complex because titanium is in group 4. How many electrons will the titanium contribute? Because the number of electrons is always the same as the group number, it will contribute four electrons. Next, what is oxidation state of Ti? To determine it we must determine the charge at the ligands. To do that we cleave the bonds heteroleptically. This will give benzylate anions with -1 charge. There are four of these ions, and therefore there will be four negative charges overall. The complex is charge-neutral, and thus the oxidation state is +4 because -4+4=0. Therefore, we need to subtract four electrons. Because we cleaved the bond heteroleptically, each ligand contributes two electrons, giving overall eight electrons coming from the four ligands. This means that we have overall eight electrons, or an 8-electron complex. This is far, far away from 18 electrons. Nonetheless, the complex is stable. How can we explain this? The answer is that in order to achieve 18 electrons it would need to add five additional ligands if each ligand is considered a 2-electron donor. This would increase the coordination number to 9 which is too high to produce a stable complex. In order to reduce the complex to an 18 electron complex, 10 electrons would need to be added. This would produce a complex with a -10 charge which is way to high to be stable. The arguments are generalizable for group 3 and group 4 complexes. Because these elements only have a few d electrons, the ligands would need to contribute a lot of electrons to produce an 18 electron complex. This would require just too many ligands to add. The coordination numbers would get too high. If electrons are added instead of ligands, the negative charge at the complex would be to high to be stable based on electron-electron repulsion arguments.



Contribution metal:	10e
Charge:	0e
Electrons contributed by Cl ligands:	2x1e=2e
Electrons contributed by NH_3 ligands:	2x2e=4e
Sum:	**16e**

Figure \(\PageIndex{10}\): Counting electrons in the diamminedichloro palladium complex using the neutral atom method.

These arguments cannot be applied for group 10 elements, because these elements have many d electrons. The explanation in this case is that these elements like to make square planar complexes when in the oxidation number is +2. Square planar complexes prefer 16 instead of 18 electrons. We will learn later, when we discuss bonding in coordination compounds, why this is. You can see that the square planar diamminedichloro palladium complex shown is square planar and has sixteen electrons. There are 10 electrons coming from Pd. If we use the neutral atom method, no electrons need to be added or subtracted due to the charge at the complex. The complex is charge-neutral. To assess how many electrons come from the ligands we need to cleave the bonds so that neutral ligands are produced. The Pd-Cl bonds need to be cleave homoleptically, the Pd-N bonds need to be cleave heteroleptically. Therefore, the two chloro ligands are 1e donors, and the two ammine ligands are 2e donors. This gives 10+4+2=16 electrons.

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Concept Review Questions Chapter 6

Concept Review Questions

Section 1

1. Describe the principles of the neutral atom method.

2. Describe the principles of the oxidation state method.

3. What does the 18 electron rule state?

4. What is a complex with 18 electrons called?

5. Why do group 3 and group 4 metal complexes often show deviations from the 18 electron rule?

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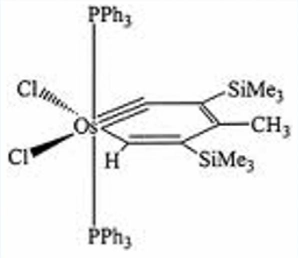
Homework Problems Chapter 6

Homework Problems

Section 1

Exercise 1

What is the number of valence electrons of the following complexes? Determine the number of valence electrons using both the neutral atom method as well as the oxidation state method:

a. $Ni(CO)_4$
b. $RhI_2(PPh_3)^-$ (Ph = phenyl)
c. $[Au(CN)_2]^-$
d. $PtCl_4$
e. $[Fe(CN)_6]^{3-}$
f. $[Fe(H_2O)_5(SCN)]^{2+}$
g. $CH_3Mg(THF)_2Cl$ (THF = tetrahydrofurane)
h. $VOCl_3$
i. 

Answer

a) 18

b) 14

c) 14

d) 14

e) 17

f) 17

g) 8

h) 10

i) 18

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CHAPTER OVERVIEW

7: Coordination Chemistry III - Bonding

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7.1: Bonding in Coordination Compounds

Bonding in Coordination Compounds

This chapter is devoted to bonding theories for coordination compounds. Let us first think about, what a good theory should be able to do in general. The answer is, that it should be able to make many correct explanations for experimental observations based on a few, sensible, assumptions. In addition, it should be able to predict experimental observations. The more the theory can explain and predict, and the fewer the necessary assumptions, the better the theory. What does this mean for a bonding theory? What would a good bonding theory for coordination compounds be able to do? It should certainly be able to explain and predict the number of bonds and the shape of a molecule. In addition, it should be able to explain the magnetism of molecules, in particular dia- and paramagnetism. Remember, a molecule is diamagnetic when it has no unpaired electrons. It is paramagnetic when there are unpaired electrons. A diamagnetic molecule is repelled by an external magnetic field. A paramagnetic molecule is attracted by an external magnetic field. It should further be able to explain the stability and reactivity of complexes, as well as the optical properties of complexes. Optical properties of compounds are linked to bonding because they are related to electronic states.

Valence Bond Theory

There are essentially three bonding concepts that are used to describe the bonding in coordination compounds. The first one is the valence bond theory. The valence bond concept was introduced by Linus Pauling in 1931 to explain covalent bonding in molecules of main group elements.

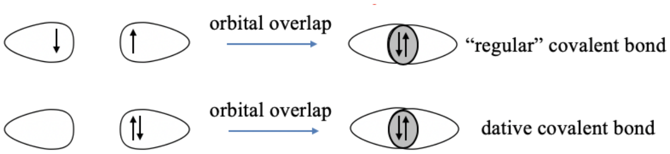


Figure 7.1.1 Electron sharing and valence bond theory

The basic idea is to overlap half-filled valence orbitals to form covalent bonds in which the two electrons are shared between the bonding partners (Fig. 7.1.1). These orbitals can either be atomic orbitals, or hybridized atomic orbitals. The concept works very well to explain the shapes of molecules of main group elements. The valence bond concept in its original form assumes that each bonding partner contributes one electron to the covalent bond. This is not consistent with the dative bonding in coordination compounds where it is assumed that one partner donates an electron pair and the other partner accepts it. To adapt valence bond theory to suit coordination compounds, Pauling suggested that a dative bond is formed via the overlap of a full valence orbital of the donor and an empty valence orbital of the acceptor. We will see that this concept can explain the shapes of coordination compounds in some cases, but overall it does not work very well. We will also see that valence bond theory can explain magnetism in some cases, but also here the valence bond theory has significant deficits. By its nature, valence bond theory cannot explain optical properties. Overall, valence bond theory is far more suitable for main group element molecules compared to transition metal complexes.

Crystal Field Theory

The second major theory is the crystal field theory. It is actually not a bonding theory because it is based on repulsive electrostatic interactions. It was originally developed to explain color in ionic crystals. Later, it was found that it can also explain colors in molecular coordination compounds, and is suitable to explain shapes and magnetism of complexes. However, because it is based on repulsive electrostatic interactions it cannot actually explain what holds the atoms in a molecule together. However, the crystal field theory is quite simple and convenient to use, and there is a lot of practicality to it.

Ligand Field Theory

The third theory is the ligand field theory. It is the most powerful theory, but also the most complicated one. Basically, it is molecular orbital theory applied to coordination compounds. It can make detailed statements about the number of bonds and shapes of molecules, and can explain the magnetism and optical properties of coordination compounds.

Valence Bond Theory for Coordination Compounds

Octahedral Complexes

Let us have a closer look at the valence bond theory, and assess valence bond theory for complexes by a number of examples.

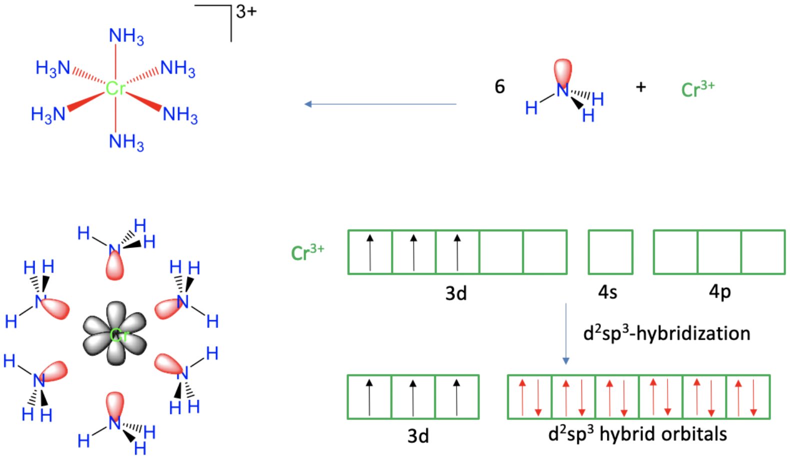


Figure 7.1.2 Valence bond theory applied to the hexaammine chromium (3+) cation

The first example is the hexaammine chromium (3+) cation (Fig. 7.1.2). From experiment we know that it has an octahedral shape, with six dative Cr-N bonds. Can valence bond theory explain the six bonds and the octahedral shape satisfactorily? In order to explain the six dative Cr-N bonds we would need to overlap six empty chromium valence orbitals with six filled valence orbitals of N. We can see that the six ammine ligands have one electron lone pair each that can serve as the valence orbitals. Does chromium have six empty valence orbitals? In order to assess this, we first need to know the oxidation state of the chromium. It is +3 because the ligands are all neutral when the bonds are cleaved heteroleptically, and the complex cation has a 3+ charge. Therefore, the chromium is a Cr^{3+} cation.

Next, we need to know the electron configuration of the Cr^{3+}. A neutral Cr atom has the electron configuration $4s^1 3d^5$. When a transition metal loses electrons to form a cation, it always loses its two valence electrons first, and then its d electrons. For chromium this means that we must remove the one 4s electron, and two of the five 3d-electrons. The three remaining 3d electrons are expected to be spin up in three different d orbitals according to Hund’s rule. How many empty valence orbitals remain? These would be two 3d and the 4s orbitals. In addition, it would also be justified to consider the three 4p orbitals as valence orbitals because the 4p orbitals are energetically only slightly higher than the 4s orbital. That means that we would have the six valence orbitals that we would need to explain the six bonds. There is, however, a complication. The six bonds in the complex are not distinguishable, but the six valance orbitals in the Cr^{3+} ion are distinguishable, for example, the 3d orbitals have different shape and energy than the 4s orbital, which is different from the 4p orbitals. Therefore, if we overlapped these orbitals with the electron lone pairs at N, the bonds would not be equivalent, or indistinguishable. We would have difficulty to explain the highly symmetric octahedral shape of the molecule. To go around this issue, valence bond theory uses the concept of hybridization. In this concept we mathematically mix the wave functions of the valence orbitals to form hybridized orbitals. In our example we would mix the two empty d-orbitals, the 4s orbital, and the three 4p orbitals to form six so-called d^2sp^3 hybridized orbitals. They have the same shape and size, and their lobes point toward the corners of an octahedron. Therefore, we can now create overlap between these six orbitals, and the six electron lone pairs at N to form six equivalent, indistinguishable Cr-N bonds. We conclude that we have now satisfactorily explained the bonding and the shape of the complex.

Can we also explain its magnetism? From experiment we know that the complex is paramagnetic, and that there are three unpaired electrons. Does valence bond theory predict the same? Yes, it does. There are three unpaired electrons in the three half-filled d-orbitals.

Tetrahedral Complexes

Our next is example is a tetrahedral complex, the tetrahydroxo zincate (2-) complex anion, Fig. 7.1.3.

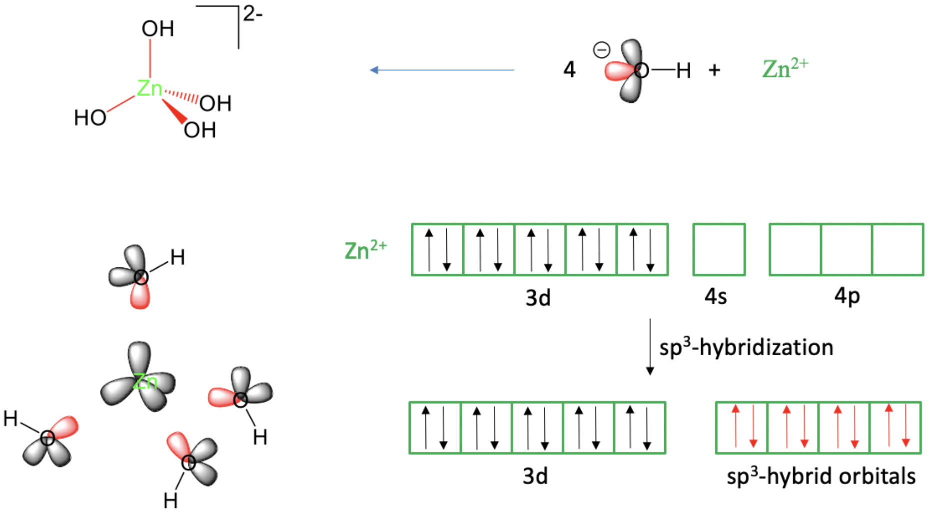


Figure 7.1.3 Valence bond theory applied to the tetrahydroxo zincate (2-) complex.

When viewing it as a Lewis-acid base complex with dative bonds it can be thought as an adduct of a Zn^{2+} and four hydroxide anions. One of the three electron lone pairs at the hydroxide ions would donate its electrons into empty Zn valence orbitals. That means we would need overall four empty Zn valence orbitals to explain the four Zn-O bonds. A neutral zinc atom has the electron configuration $4s^2$ $3d^{10}$. We can derive this from the fact that zinc is in group 12 of period 4 in the periodic table. A Zn^{2+} ion has two electrons less. Because we must remove s electrons before we remove d electrons, the Zn^{2+} has the electron configuration $3d^{10}$. Like in the previous example we can justifiably consider the 4p orbitals as additional valence orbitals. We can see that we have four empty orbitals available to make the four bonds, namely the 4s and the 4p orbitals, but these orbitals are not equivalent, and do not have the correct orientation to explain the tetrahedral shape of the complex. There is a 90° angle between the p-orbitals which is smaller than the 109.5° tetrahedral bond angle in the molecule. However, we can solve this problem by hybridizing the 4s and the three 4p orbitals to form four sp^3-hybridized orbitals. These hybrid orbitals have the property that their lobes point toward the corners of a tetrahedron. Thus, they are suitable to explain the tetrahedral shape of the molecule. We can place the ligands around the Zn^{2+} ion and approach the ligands on the bond axes to create orbital overlap between the empty sp^3-hybridized orbitals and one electron lone pair at the oxygen atom. This produces the tetrahedral tetrahydroxo zincate (2-) anion.

Can we also explain the magnetism of the molecule? What magnetism would valence bond theory predict? We can see that there are no unpaired electrons in any of the metal valence orbitals. Thus, the complex should be diamagnetic. This is also what we find experimentally. Thus, valence bond theory is able to explain the magnetism of this complex anion.

Square Planar Complex

Now let us see if the valence bond theory can also explain a square planar complex such as tetracyanonickelate (2-).

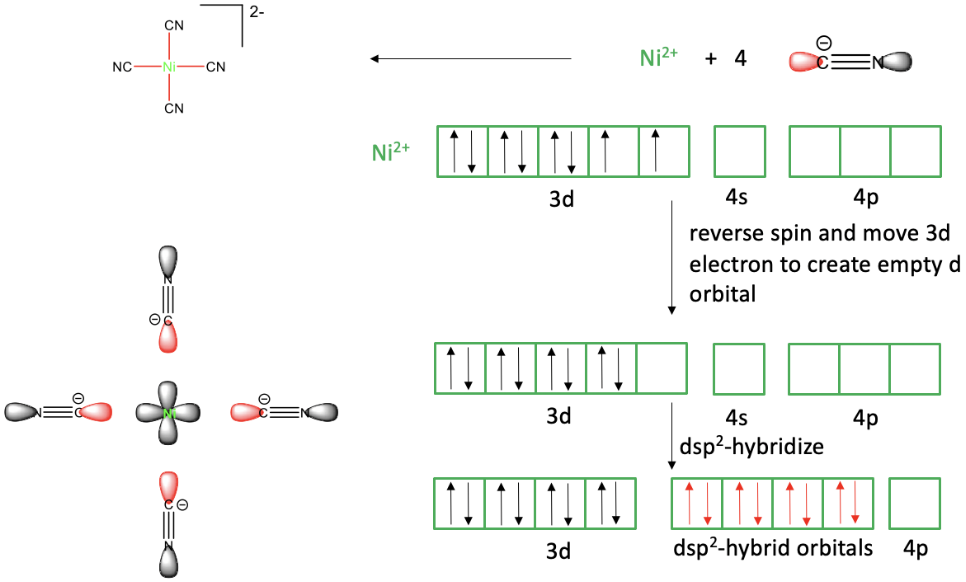


Figure 7.1.4 Valence bond theory applied to the tetracyanonickelate (2-) square planar complex

In the valence bond picture we view the Ni-CN bonds as dative bonds, and the complex is considered an adduct of Ni^{2+} and CN^-. To explain the four bonds, the Ni^{2+} ion would need to have four empty valence orbitals. Ni is a group 10 metal and a neutral Ni atom has the electron configuration $4s^2 3d^8$. To create a Ni^{2+} ion we must remove the two 4s electrons, and thus the Ni^{2+} has the electron configuration $3d^8$. Do we have four empty orbitals available? Yes, the 4s and the three 4p orbitals are empty but again they are not equivalent and thus not suitable to explain four equivalent Ni-C bonds. Can we hybridize these orbitals? Yes, we can, but the resulting four sp^3 hybridized orbitals would not be suitable to explain the square planar shape, only the tetrahedral shape. What valence bond theory suggests in this case is to reverse the spin of one of the unpaired d electrons and move it into the other half-filled d-orbital. This produces an empty d-orbital that we can now hybridize with the 4s and two of the 2p orbitals to four dsp^2-hybridized orbitals. These four orbitals have the property that their lobes point toward the vertices of a square, thus they are suitable to explain the square-planar shape. We can approach the ligands now on the bond axes to create orbital overlap between the empty dsp^2 Ni and the electron lone pairs of the ligands. We can also say that the ligands donate their electron lone pairs into the hybridized metal orbitals. This produces the four covalent bonds that we need and yields a molecule of a square planar shape.

We can see that the valence bond theory can still explain the square planar shape, but only with the help of the additional assumption that one of the d-electrons gets spin-reversed and moves into another d-orbital. An assumption a theory makes should always be reasonable, so let us critique how reasonable this assumption is. Firstly, is the spin-reversal reasonable? Spin-reversal is a quantum-mechanically forbidden process, and thus it is questionable to assume that it happens. Secondly, there is no good explanation for why the electron moves. The energy of two spin-paired electrons in the same orbital is actually higher than that of two spin-paired electrons in different orbitals. So overall, we see that valence bond theory has difficulties to explain the square planar shape. It must make assumptions that are not very plausible.

Octahedral d^5 High and Low Spin Orbital Complex

The valence bond theory has also difficulties to explain so-called high spin and low spin octahedral complexes. For example, it is known from magnetic measurements for $3d^5$ transition metal ions that they can make octahedral complexes with either one unpaired electron or five unpaired electrons, depending on the ligand. In the first case, the number of paired electrons in the d-orbitals is maximized, and we have a low-spin complex, in the other case the number of unpaired electrons is maximized, and we have a high spin complex. What approach does valence bond theory take to explain this phenomenon?

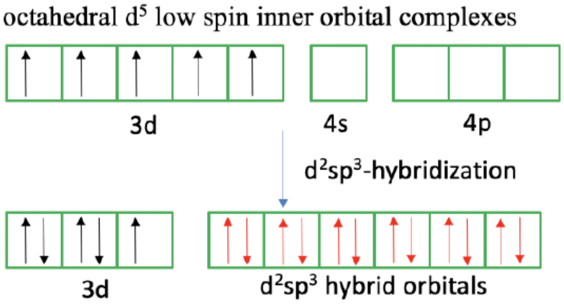


Figure 7.1.5 Valence bond theory applied to an octahedral d^5 low spin-complex

In the case of a low spin-complex, valence bond theory assumes a so-called inner orbital complex. Like in the square planar complex it is assumed that unpaired electrons reverse their spins and move into other half-filled d-orbitals so that spin-pairing is maximized. In the case of a d^5 ion, two electrons reverse their spin, and move into two other half-filled orbitals. This leaves one unpaired electron. We see that due to the movement of the two electrons two 3d-orbitals are empty now, and so are the 4s and the 4p orbitals. The six empty orbitals can now be combined to form d^2sp^3-hybridized orbitals that can explain the octahedral shapes. Approaching the ligands overlaps the electron lone pair at the ligand with the empty hybrid orbitals to form a dative, covalent bond. We can also say the ligands donate electron lone pairs to form six covalent bonds. We can again criticize that spin-reversal is forbidden and spin-pairing is energetically unfavorable making the approach valence bond theory takes to explain the low-spin complex unsatisfactory.

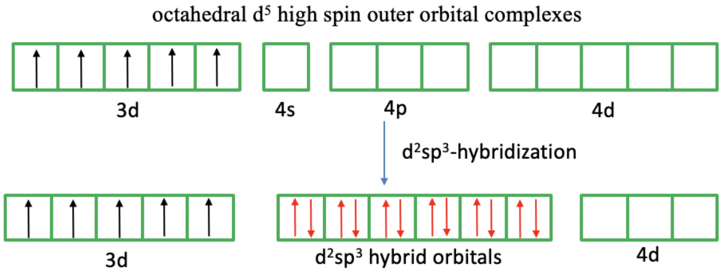


Figure 7.1.6 Valence bond theory applied to an octahedral d^5 high spin-complex

What about the $3d^5$ high spin complex (Fig. 7.1.6)? In this case we cannot pair spins to create empty d-orbitals because we need to explain five unpaired electrons. Now, valence bond theory makes another new assumption. It assumes that the outer 4d orbitals get involved in the bonding. These orbitals are empty and available for hybridization. We can therefore hybridize two 4d, the 4s, and the three 4p orbitals to form d^2sp^3 hybridized orbitals. In the last step we can approach the ligands, and the ligands can donate their electron lone pairs into the transition metal d-orbitals. Now we have explained the six bonds, the octahedral shape, and the five unpaired electrons.

We can again critique the valence bond approach. What justification is there to assume that the 4d orbitals are involved. The answer is: Very little. These orbitals are just too high in energy to be considered valence orbitals. It is not reasonable to assume that they are involved in the bonding. Therefore, again, we see that valence bond theory has difficulties to explain the properties of a complex. Valence bond theory also does not explain distortions of octahedral complexes due to the Jahn-Teller effect.

Octahedral d^7 High and Low Spin Orbital Complex

High-spin and low-spin complexes are not only observed for octahedral complexes of d^5-ions, but for example also for octahedral d^7 ion complexes. A low-spin complex has three unpaired electrons and a high-spin complex has one unpaired electron. We will see that valence bond theory has even greater troubles to explain these compounds.

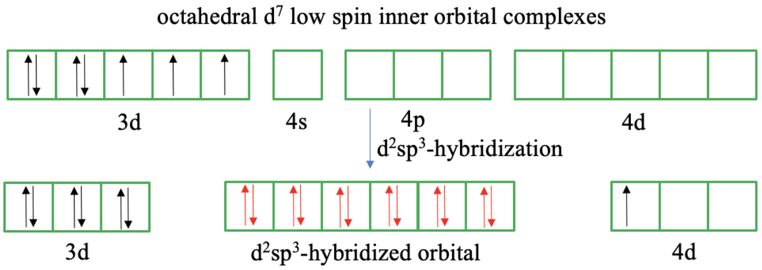


Figure 7.1.7 Valence bond theory applied to an octahedral d^7 low spin-complex

In a d^7 ion there are four paired and three unpaired electrons according to Hund's rule (Fig. 7.1.7). We can reverse the spin of one unpaired electron and pair it with an unpaired electron in another half-filled orbital to reduce the number of unpaired electrons to one. However, this gives us only one empty 3d orbital available for d^2sp^3-hybridization. In this case we cannot produce more empty 3d-orbitals by reversing the spin. Therefore, we must make again the questionable assumption that outer orbitals are involved in the bonding such as the 4d orbitals. Valence bond theory now suggests to move the unpaired electron from the 3d to the 4d orbital. This is simply done to create another empty 3d orbital that we need for d^2sp^3-hybridization. However, why would the 3d electron just go into another orbital of much higher energy? If we make this questionable assumption though, we have indeed six orbitals available for hybridization, and we can let the ligands donate an electron pair into the empty hybrid orbitals.

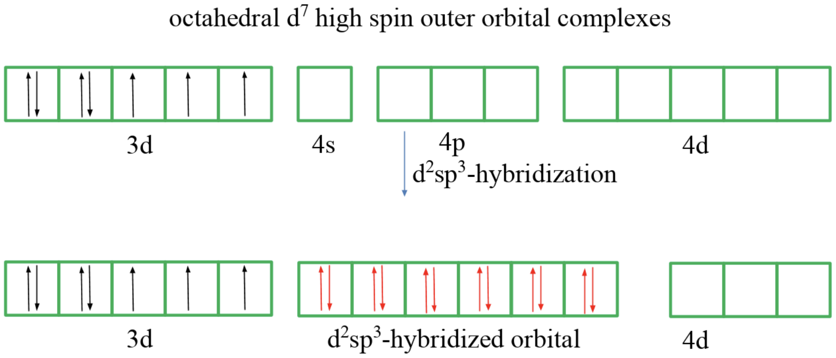


Figure 7.1.8 Valence bond theory applied to an octahedral d^7 high spin-complex

Finally, let us discuss an octahedral d^7 high-spin outer orbital complex (Fig. 7.1.8). In this case we cannot pair any spins in the 3d orbitals. Therefore we assume again that the 4d orbitals get involved in the bonding, and hybridize two of them with the 4s and the three 4p orbitals. The six ligands can then donate six electron pairs into the orbitals thereby creating six bonds and explaining the octahedral shape.

Overall, we see that in the valence bond theory we move around electrons as we please in order to explain shapes and magnetism of complexes without good justification. Therefore, the valence bond theory, while extremely valuable for main group compounds, is only of limited use for transition metal complexes.

Crystal Field Theory

Now let us discuss the second bonding theory for coordination compounds, the crystal field theory. It is actually not a bonding theory because it is based on repulsive electrostatic interactions. Nonetheless, it has many features of a bonding theory in the sense that it can explain many phenomena that a bonding can explain, in particular molecular shape, magnetism, and optical properties.

What are the principles of crystal field theory? Crystal field theory assumes that the electrons in the metal d-orbitals are surrounded by an electric field which is caused by the ligand electrons. This electric field is called the crystal field. The name crystal field comes from the fact that this principle was first applied to transition metal ions surrounded by anions in crystals, and was only later extended to transition metal ions surrounded by ligands in molecular coordination compounds. The assumption that ligands surrounding a transition metal ion produce an electric field makes sense because the ligands contain electrons that are associated with an electric field. It is further assumed that the crystal field raises the energy of the metal-d-orbitals because of electrostatic repulsion between the ligand electrons and the metal electrons.

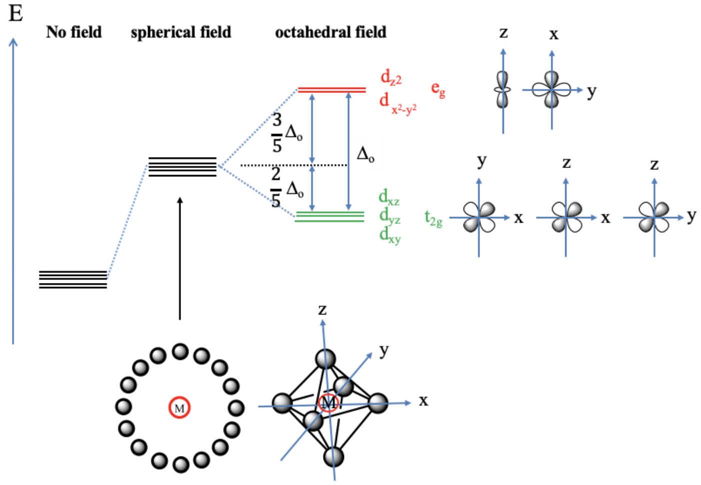


Figure 7.1.9 Crystal field theory demonstrated in the hypothetical spherical case, and the practical octahedral case

Let us first assume the hypothetical case that the ligand electrons surround the metal d-orbitals exactly spherically (Fig. 7.1.9, bottom left). In this case the electric field is completely isotropic, and this means that the energy of all five metal d-orbitals increases to the same extent. Now let us consider the practical case that the ligands surround the metal in octahedrally, which is the case in an octahedral complex. We can say we have an octahedral crystal field. The electric field will now not be spherical any more, it will be the strongest where the ligands are, namely on the vertices of the octahedron, and less strong elsewhere. The vertices of the octahedron lie on the x, y, and z axes of the coordinate system. Thus, the crystal field is the strongest on the axes, and less strong elsewhere. What consequence does this have on the metal d-orbital energies relative to the spherical crystal field? Orbitals that have their electron density mostly on the axes will experience a greater electrostatic repulsion from the crystal field, and therefore will be higher in energy. Orbitals that will have their electron density mostly elsewhere, meaning not on the axes, will experience smaller repulsion, and thus the energy will be smaller compared to the spherical crystal field. Which are the orbitals that have their electron density mostly on the axes? These are the d_{z^2} and the $d_{x^2-y^2}$ orbitals. The d_{z^2} orbital has its energy density mostly on the z-axis, the $d_{x^2-y^2}$ – orbital has its energy mostly on the x and the y axes. The energy of both orbitals is increased by exactly the same amount. This is not obvious given that the orbitals have very different shapes. To understand this, it helps to remember that when orbitals are symmetrically degenerate, they also must be energetically degenerate.

An octahedral complex belongs to the point group O_h and in the point group O_h the d_{z^2} and the $d_{x^2-y^2}$-orbitals are degenerate and have e_g symmetry. Therefore, the $d_{x^2-y^2}$ and the d_{z^2}-orbitals in an octahedral crystal field are also often just called the e_g-orbitals. The remaining d-orbitals, the d_{xy}, the d_{yz}, and the d_{xz} orbitals have their electron density mostly in between the axes, therefore their energy is lower compared to the spherical crystal field. The energy of all three orbitals is reduced by exactly the same amount. We can again understand this when considering that these orbitals are triple-degenerate in the point group O_h and have the symmetry type t_{2g}. For that reason the d_{xy}, the d_{yz}, and the d_{xz} in an octahedral crystal field are also often called the t_{2g}-orbitals. The energy difference between the t_{2g} and the e_g orbitals is called Δ_o. The energy of the t_{2g} orbitals is decreased by 2/5 Δ_o relative to the spherical crystal field, and the energy of the e_g-orbitals is increased by 3/5 Δ_o relative to the spherical crystal field. Where do the factors 2/5 and 3/5 come from? They are due to the law of the conservation of energy. The overall energy reduction due to the energy decrease of the t_{2g}-orbitals must be equal to the overall energy increase due to the energy increase of the e_g orbitals: $\Sigma E(t_{2g})=-\Sigma(E(e_g)$. Because there are three t_{2g} orbitals but only two e_g orbitals this equation only holds when the energy of the e_g orbitals is increased by 3/5 Δ_o and the energy of the t_{2g} orbitals is decreased by $2/5\Delta_o$, or 3 x 2/5 Δ_o = 2 x 3/5 Δ_o. Note that the energy of all orbitals will be greater in comparison to the case of no electrical field existing, but the energy is increased to a greater extent for the e_g-orbitals compared to the t_{2g} orbitals.

The Tetrahedral Crystal Field

What about a tetrahedral complex with a tetrahedral crystal field?

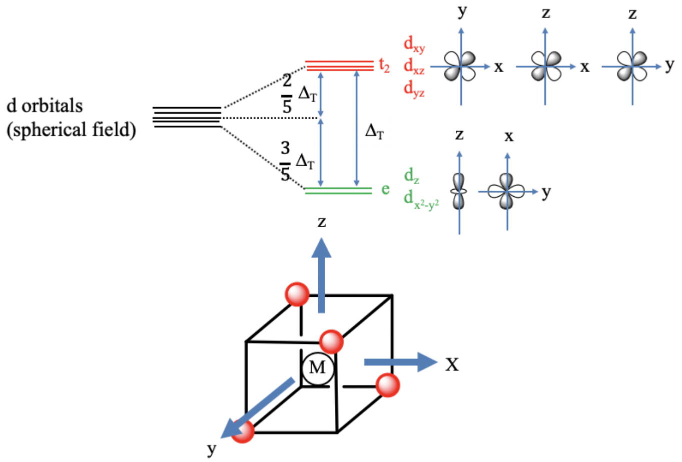


Figure 7.1.10 Crystal field theory for a tetrahedral complex

In this case, the ligands do not approach on the axes (Fig. 7.1.10). We can understand this when we consider that we can inscribe a tetrahedron in a cube. If we connect every other corner of a cube then we obtain a tetrahedron. We can define the coordinate system so that the three axes go through the centers of the square faces of the cube. We can see that the axes do not point toward the ligands, thus the ligands do not approach on the axes. Therefore, the orbitals that have their electron density mostly on the axes have a decreased energy relative to the spherical crystal field. These are the d_{z^2} and the $d_{x^2-y^2}$ orbitals. Their energy is the same despite the fact that they have quite different shape. We can explain this again with symmetry arguments. In the point group T_d the $d_{x^2-y^2}$ and the d_{z^2} – orbitals are double-degenerate and have the symmetry type *e*. Because they are symmetrically degenerate, they are also energetically degenerate. The energy of the d_{xy}, the d_{yz}, and the d_{xz} orbitals have most of their energy density in between the axes. Therefore, their energies are increased relative to the spherical crystal field. They are increased by the same amount because the orbitals are triply degenerated in the point group T_d and have the symmetry type t_2. The energy difference between the *e* and the t_2 orbitals is called Δ_t. The energy of the t_2 orbitals is decreased by 2/5 Δ_t. The energy of the e orbitals is increased by 3/5 Δ_t. This is again the due to the law of the conservation of energy. The total amount of decreased energy must equal the total amount of increased energy. The tetrahedral crystal field energy is smaller than that of the octahedral field because the octahedral field interacts more strongly with the d-orbitals compared to the tetrahedral field. One can calculate that it is actually just 4/9 of the octahedral field. This is mainly because the lobes of the t_2 orbitals to not point exactly toward the vertices of the tetrahedron, while the lobes of the e_g orbitals do point exactly toward the vertices of the octahedron.

Tetragonally Distorted Octahedral and Square Planar Crystal Fields

One nice feature of crystal field theory is that can can readily explain distortions such as the tetragonal distortion of octahedral complexes (Fig. 7.1.11).

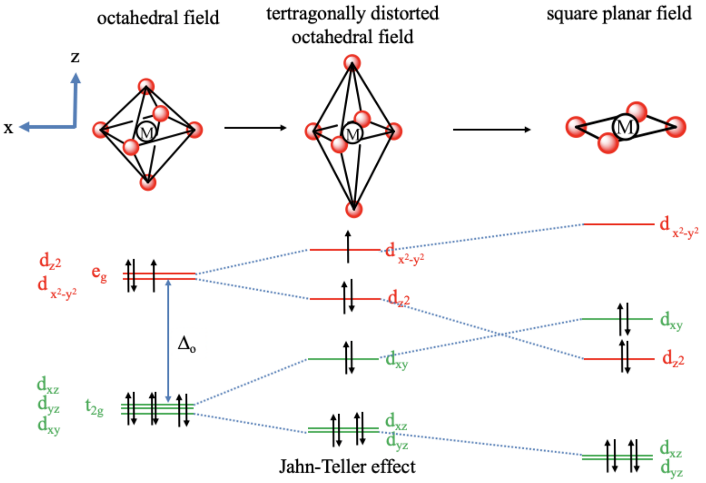


Figure 7.1.11 Tetragonal distortions in the octahedral crystal field leading to a square planar field.

In a tetragonally distorted complex there is a tetragonally distorted crystal field. In an elongated octahedron two ligands are further away from the metal than the four others. Let us assume these two ligands are on the z-axis. Then, the crystal field is weaker on the z-axis. To keep the overall crystal field constant we must bring the other four ligands closer to the metal center. That means that we compress along the x and the y-axis. What will happen to the energy of the orbitals as the octahedron distorts? Because we elongate in the z-direction, the d_{z^2} orbital, that has most electron density on the z-axis goes down in energy. Because we compress on the x and the y-axis, the energy of the $d_{x^2-y^2}$ orbital increases. What about the t_{2g} orbitals? The d_{xy} orbital goes up in energy because it has electron density in the xy plane, but not along the z-axis. The d_{xz} and d_{yz} decrease in energy because they have a significant electron density in z-direction, and the electron density in z-direction is the same for both orbitals. We can now also think about, if the crystal field theory can explain why tetragonal distortion occurs preferentially for certain electron configurations of the metal. For example, it is known that metal ions with d^9 electron configuration often make octahedral complexes with tetragonal distortions. For instance, the hexaaqua copper (2+) complex is an example of a tetragonally distorted complex with a Cu^{2+} ion that has a d^9 electron configuration. We can understand that the tetragonal distortion occurs when comparing the energy of the electrons in the undistorted vs the distorted octahedron. In the undistorted octahedron we have three electrons in the degenerated e_g orbitals. As we distort, we can move two electrons in the energetically lower d_{z^2}-orbital and fill the third one into the energetically higher $d_{x^2-y^2}$-orbital. Thus, overall the electrons have a lower energy explaining the distortion. This is an example of the Jahn-Teller effect. In general, the Jahn-Teller effect can occur when there are partially occupied degenerate orbitals. In this case a molecule can lower its energy through distortion. Note that not only partial occupation of the e_g-orbitals, but also partial occupation of the t_{2g}-orbitals can cause the Jahn-Teller effect, although the effect is typically smaller. For example in complexes with metal ions the d^4-electron configuration, all four electrons can be stabilized through Jahn-Teller distortion. It should also be noted that in addition to an elongation, there is also the possibility of compressing the octahedron along the z-axis. In this case the order of energy of the d_{z^2} and the $d_{x^2-y^2}$ orbital reverses, and the order of energy of the d_{xy}, as well as the d_{xz} and d_{yz} reverses as well.

Finally, let us look at the square planar crystal field in square planar complexes. To understand the square planar crystal field it helps to understand the square planar shape as an infinitely elongated octahedron. If we move the two ligands along the z-axis infinitely far away from the metal ion, then we have created a square planar structure. How will the orbital energies change compared to an elongated octahedron? The $d_{x^2-y^2}$ orbital will have an even higher energy due to the necessity to compensate for the decreased field associated with the ligands on the z-axis by further compressing along the x and the y-axis. The d_{z^2}-orbital is even further decreased in energy because the ligands along the z-axis are now completely gone. The d_{xy} orbital is increased in energy because of the enhanced field in the xy-plane. It is now higher than the d_{z^2}-orbital. The d_{xz} and the d_{yz} orbitals are further decreased in energy because they have significant electron density in z-direction.

Viewing the square planar shape as an extreme case of a tetragonally elongated octahedron also lets us understand why the square planar shape is so often adopted by d^8-metal complexes. We can see that the stabilization energy, and thus the tendency to distort is the greatest when two electrons are in the metal e_g orbitals. In this case two electrons lower their energy through distortion and no electron has an increased energy. Thus, we would understand that the distortion becomes so great, so that the octahedral complex eventually loses two ligands and adopts the square planar shape. This is a nice example how crystal field theory can explain shapes and the number of bonds in a complex without actually being a bonding theory.

High Spin and Low Spin Complexes

One of the greatest strength of crystal field theory is that it can explain high-spin and low spin octahedral complexes in a simple way. The basis for that is the assumption that different ligands produce crystal fields of different strengths and that the differently strong crystal fields produce different Δ_o values. This assumption is plausible because it can be expected that different ligands interact differently with a metal ion, for example, the bond length or the bond strength may be different. If the ligands produce a large crystal field then we would expect a large Δ_o, when the crystal field is small, then we would expect a small Δ_o. The size of the Δ_o determines if we get a high spin or a low spin complex. If the Δ_o is larger than the spin pairing energy, then a low spin complex is favored, if Δ_o is smaller than the spin-pairing energy, then the high spin complex is favored.

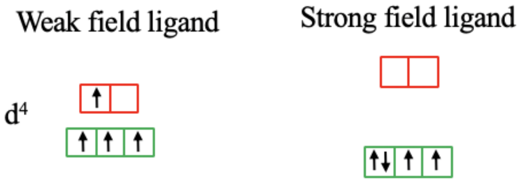


Figure 7.1.12 High and low spin d^4-metal complexes due to a weak and strong crystal field, respectively.

For example in a d^4-metal complex with small Δ_o all electrons are unpaired (Fig. 7.1.12, left). Three of them are in the t_{2g}-orbitals, and the fourth one is in the e_g-orbital. Now let us assume a different ligand that can produce a Δ_o that is large enough to overcome the spin pairing energy. In this case the fourth electron would pair the spin of one of the three electrons in the t_{2g}-orbitals (Fig. 7.1.12, right). We would obtain a low spin d^4-complex.

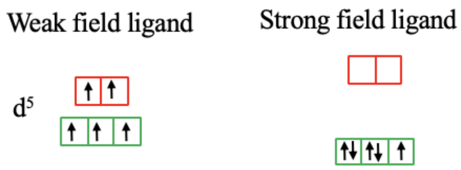


Figure 7.1.13 High and low spin d^5-metal complexes due to a weak and strong crystal field, respectively.

In the case of a d^5-metal high spin complex there are five unpaired electrons, and all orbitals are half-filled. If the the ligand produces a crystal field large enough, the spin pairing energy is overcome and there are two paired and one unpaired electron in the t_{2g} orbitals (Fig. 7.1.13).

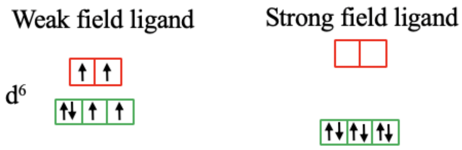


Figure 7.1.14 High and low spin d^6-metal complexes due to a weak and strong crystal field, respectively.

For a d^6-metal high spin complex with a weak crystal field there are two unpaired electrons in the t_{2g} and e_g orbitals respectively. In the case of a strong field ligand and a low spin complex all electrons are in the t_{2g} orbitals and all spins are paired (Fig. 7.1.14).

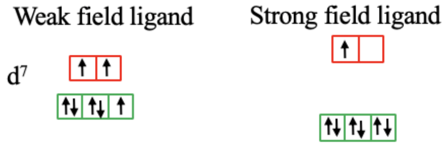


Figure 7.1.15 High and low spin d^7-metal complexes due to a weak and strong crystal field, respectively.

In the case of a d^7-high spin complex there are two electron pairs and one unpaired electron in the t_{2g} orbitals, and there are two unpaired electrons in the e_g orbitals. For the low-spin complex the spin pairing energy is overcome. However, one electron must remain unpaired in the e_g-orbitals because the t_{2g}-orbitals are fully occupied with six electrons. The number of unpaired electrons in high and low spin complexes predicted by crystal field theory is what is experimentally observed. Therefore we can state that crystal field theory can quite elegantly explain high and low spin complexes.

We can also understand why there are no d^1, d^2, d^3, d^8, d^9, and d^{10} low and high spin complexes. In the electron configurations d^1-d^3 all electrons are unpaired in the t_{2g} orbitals. Therefore, there is no electron that could be moved from an e_g to a t_{2g} orbital. For the configurations d^8-d^{10} all t_{2g} orbitals are necessarily full. Therefore, there is no possibility to move an electron from an e_g to a t_{2g} orbital regardless the crystal field strength.

Further, we can explain why there are no low spin tetrahedral complexes. We have learned previously that a tetrahedral crystal field has only 4/9 of the strength of an octahedral field. Because it is so much weaker, no ligand is able to produce a field strong enough to overcome the spin pairing energy. High spin and low spin complexes are possible though for square planar complexes.

Strong and Weak Field Ligands: The Spectrochemical Series

Crystal field theory cannot only explain magnetism well, it can also make statements about the optical properties of a coordination compound. A complex can absorb light when an electron is excited from a d orbital of lower energy to a d orbital of higher energy. The larger the Δ, the smaller the wavelength of the absorbed light. In the case of an octahedral complex, absorption of light would excite an electron from a t_{2g} to an e_g orbital.

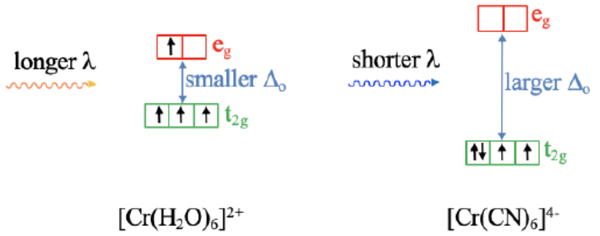


Figure 7.1.16 Octahedral $[Cr(H_2O)]_6^{2+}$ complex compared to an octahedral $[Cr(CN)_6]^{4-}$ complex

For example, an octahedral $[Cr(H_2O)]_6^{2+}$ complex has a smaller Δ_o compared to an octahedral $[Cr(CN)_6]^{4-}$ complex (Fig. 7.1.16), and thus the aqua complex absorbs light of longer wavelength compared to the cyano complex. Vice versa, measuring the absorption spectrum of the complexes, allows us to make statements about the relative crystal field strength of the ligands. By measuring the absorption spectrum of many complexes with a variety of ligands we can develop a so-called spectrochemical series that orders ligands according to their field strength.

$$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$$

Weaker field	Stronger Field
Smaller Δ	Larger Δ
Longer λ	Smaller λ

Figure 7.1.17 Spectrochemical series for selected ligands.

You can see such a series containing a non-exhaustive number of ligands in Fig. 7.1.17. You can see that the iodo ligands is on the very left side, and is the weakest field ligand, the carbonyl ligand is on the very right hand side, and is the strongest field ligand. All others are in between. We can see for example, that an aqua ligand is a stronger field ligand compared to a fluoro ligand, but a weaker ligand than an ammine ligand. Generally, ligands at the lower end of the series produce weaker fields, smaller Δs, and absorb light light with longer wavelengths. Ligands at the upper end of the series produce stronger fields, create larger Δs, and absorb light of shorter wavelengths. However, crystal filed theory cannot explain different ligand strength. Why does one ligand produce a stronger field than another? To answer this question, we need the ligand field theory.

Ligand Field Theory

Ligand field theory is the most powerful bonding theory for coordination compounds. It is essentially molecular orbital theory applied to coordination compounds. It can explain covalent bonding in coordination compounds, it can explain their shapes, it can explain their magnetism, and their electronic spectra. It can also explain the stability of coordination compounds, in particular the 18e rule and their exceptions. It is, however, more complicated than other bonding theories.

Just like in molecular orbital theory we can apply symmetry adapted linear combination of atomic orbitals to construct molecular orbitals. However, slightly modified rules apply to optimize molecular orbital theory for coordination compounds. These modifications are useful due to the greater complexity of coordination compounds. In the first step we determine the point group of the molecule and assign axes in a useful way. In the second step, we determine the valence orbitals, also called frontier orbitals of the metal. For example, for a transition metal of the 4th period we would consider the 4s, the 4p, and the 3d orbitals as the frontier orbitals. Next, we determine the symmetry of these orbitals. We can do this by just looking into the character table of the respective point group. In the following we select the highest-energy ligand orbitals that are suitable for σ-bonding. For ligands that are molecules or polyatomic ions, these orbitals are the HOMOs suitable for σ-bonding. For simple ions like chloro-ligands these are the highest occupied atomic orbitals. Next, we group the selected ligand orbitals to form ligand group orbitals (LGOs), and determine their symmetry types. To do so, we determine the reducible representation, and then the irreducible representations of the LGOs. This gives us the symmetry types of the ligand group orbitals. We then combine metal frontier orbitals and ligand group orbitals of the same symmetry type to form molecular orbitals. Now we have constructed all molecular orbitals suitable for σ-bonding, and can draw a molecular orbital diagram for the σ-bonding in the coordination compound.

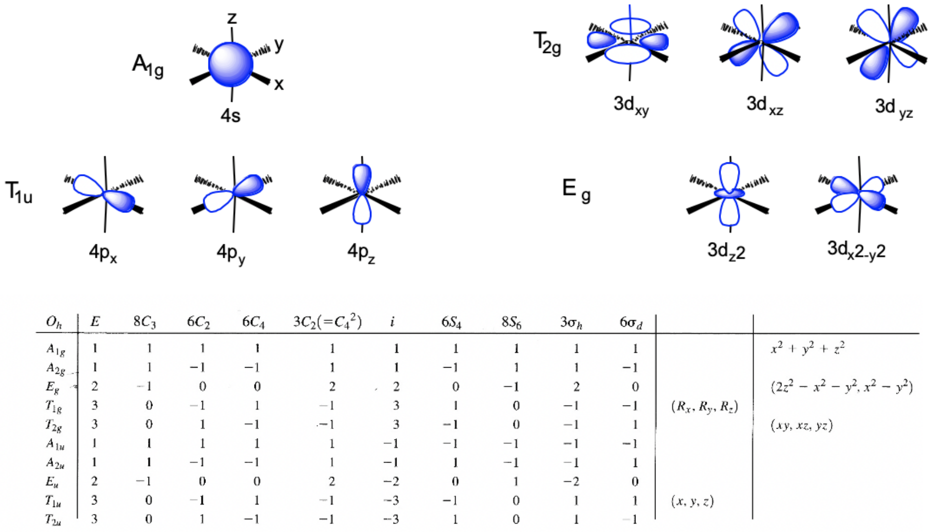
Next, we look for ligand orbitals that are suitable for π-bonding with the metal. We then determine the symmetry types of their ligand group orbitals. Ligand group orbitals and metal orbitals of the same symmetry will then be combined to form molecular orbitals. These MOs represent the π-bonding in the molecule. We add these molecular orbitals to the molecular orbital diagram. Finally, we check if there are ligand orbitals suitable for δ-bonding with the metal. If so, we also form ligands group orbitals for these, determine their symmetry types, and combine ligand group orbitals and metal orbitals of the same symmetry to form molecular orbitals. These orbitals will then also be added to the molecular orbital diagram.

Applicable rules for the construction of molecular orbital diagrams using ligand field theory

1. Determine point group of the complex and assign axes.
2. Determine which are the relevant metal frontier orbitals for bonding.
3. Determine symmetry types of these metal orbitals.
4. Select ligand HOMOs (suitable for σ-bonding) if the ligand is a molecule. If a simple ion, select the highest occupied atomic orbital.
5. Form ligand group orbitals (LGOs) from selected ligand orbitals and determine their symmetry types.
6. Combine metal orbitals and ligand group orbitals of appropriate symmetries to form molecular orbitals.
7. Select ligand orbitals for π and σ bonding if applicable, determine their symmetry and combine them with appropriate metal orbitals.

Ligand Field Theory for an Octahedral Complex of a 4th Period Transition Metal

Let us apply the ligand field theory to a 4th period octahedral transition metal complex first. According to the rules we must first determine the point group and define the coordinate system. The point group is obviously O_h.



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

Figure 7.1.18 Character table for the O_h point group and frontier metal orbitals

We can define the coordinate system so that the ligands approach on the x, y, and z axes, respectively. Next, we need to see what the frontier orbitals are. These would be the 4s, the 4p, and the 3d orbitals (Fig. 7.1.18). What symmetry types do they have? We can see this by looking into the character table for the point group O_h. An s orbital always has the totally symmetric symmetry type which is always listed first in the character table. In the point group O_h this is the symmetry type A_{1g}. What about the 4p orbitals? We can see that the letters x,y, and z are in parentheses in the irreducible representation of the symmetry type T_{1u}. This means that the three 4p orbitals are triply degenerate and have the symmetry type T_{1u}. Finally, we need to determine the symmetry types of the 3d orbitals. We find xy, xz, and yz in parentheses in the irreducible representation of the symmetry type T_{2g}. Thus, these orbitals have the symmetry type T_{2g}. We further find $2z^2$-x^2-y^2 and x^2-y^2 in the line for the symmetry type E_g , thus the d_{z^2} and the $d_{x^2-y^2}$ orbitals are degenerate and have the symmetry type E_g. Remember here from the chapter about atomic structure that $2z^2$-x^2-y^2 mathematically describes a cone, and that the d_{z^2} orbital has a conical node. We have now found all the symmetry types of the frontier orbitals.

Next, we need to direct our attention to the ligand and find the highest occupied molecular or atomic orbital suitable for σ-bonding. Of course, it depends now what the ligand is.

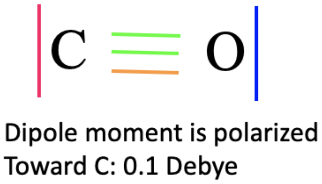
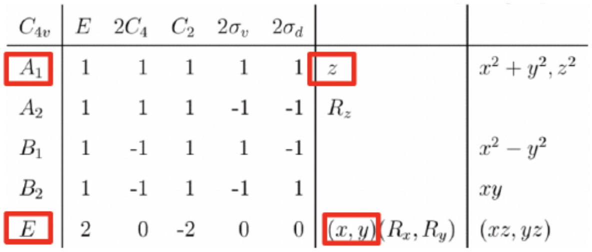


Figure 7.1.19 Lewis dot structure of carbon monoxide. σ-bond: orange. π-bonds: green. Electron lone pairs at C and O are red and blue respectively.

As an example let us choose the common and interesting carbonyl ligand (Fig. 7.1.19). To determine its HOMO suitable for σ-bonding with the metal, we will first need to know the molecular orbital diagram for the carbon monoxide molecule. The carbon monoxide molecule is a linear, polar molecule that belongs to the point group $C_{\infty v}$.



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x,y)(R_x,R_y)$	(xz,yz)

Figure 7.1.20 C_{4v} character table.

The character table of this point group is somewhat hard to work with because of the infinite order of the principal axis, and the infinite number of vertical mirror planes. We will therefore use the subgroup C_{4v} instead (Fig. 7.1.20). A subgroup of a group is a group that results when we remove certain symmetry elements from the original group. We should remove symmetry elements so that degeneracies in the molecular orbitals are not overlooked, which can happen when you reduce the symmetry too much. The point group C_{4v} is the point group with the lowest symmetry we can choose without overlooking degeneracies. Essentially, this is because the atomic orbitals of C and O are only 2s and 2p, and the 2p-orbitals perpendicular to the C-O bond axis can be rotated by 90° to make the orbitals interconvert. This requires a rotational axis of the order 4. If we chose the point group C_{2v}, which has even lower symmetry, we would still be able to construct a molecular orbital diagram, but we would overlook that the $2p_x$ and the $2p_y$ orbitals are degenerate. We see that in the case of a diatomic linear molecule there is no central atom and no ligands. Therefore, we cannot apply the SALC method exactly as we previously learned it. Therefore, we treat the C and O atoms like central atom orbitals that interact with each other. To determine their symmetry types we can just look into the character table for C_{4v}. We find that the 2s orbitals and the $2p_z$ orbitals have the symmetry type A_1 and the $2p_x$ and the $2p_y$ orbitals are double-degenerate and have the symmetry type E (Fig. 7.1.20). Now we can just combine the atomic orbitals to form molecular orbitals.

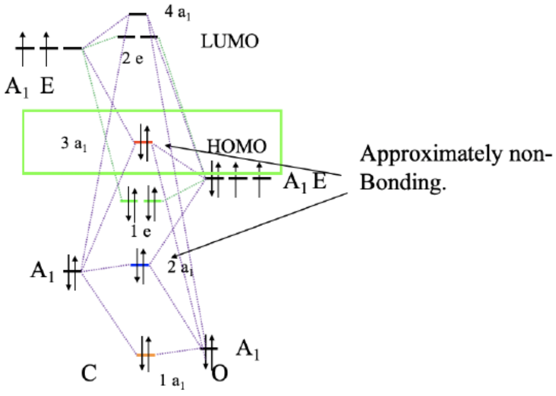


Figure 7.1.21 Molecular orbital diagram for the CO ligand. Orange, red, green and blue colors of MOs refer to the use of colors in the Lewis dot structure of Fig. 7.1.19

To construct a molecular orbital diagram we must consider that O is considerably more electronegative than C, and therefore, the 2s orbital of O is lower in energy compared to the 2s orbital of C. The 2p orbitals of O are lower in energy than those of C. Now we can label our orbitals with their symmetry types, and combine orbitals of the same symmetry type to form molecular orbitals (Fig. 7.1.21). We can start, for instance, with the orbitals of the A_1 symmetry type. There are two on each side, so we will have overall four. Our qualitative assumption would be that there should be a strongly bonding and a strongly anti-bonding orbital, and weakly bonding and a weakly anti-bonding orbital in addition. The strongly bonding one would have the lowest energy and be labeled 1a$_1$, the weakly bonding one would have higher energy and is labeled 2a$_1$, the weakly anti-bonding one has an even higher energy and is labeled 3a$_1$, and the strongly anti-bonding one would have the highest energy of all the four, and has the label 4a$_1$. The strongly anti-bonding orbital must be above the 2p$_z$ orbital of C, and the strongly bonding one must be below the 2s orbital of O. We can write the 2a$_1$ and the 3a$_1$ orbital at energy levels so that the energy differences between all four a$_1$ orbitals are about the same. We can now also connect the MOs and AOs of a$_1$ symmetry with dotted lines. Now we can turn our attention to the orbitals with E symmetry. There are overall four orbitals of E symmetry, therefore, we expect two bonding double–degenerate orbitals with e-symmetry, and two anti-bonding double-degenerate orbitals with e-symmetry. The bonding MOs must be below the energy level of the 2p orbitals of O, and the two anti-bonding orbitals must be written above the energy levels of the 2p orbitals of C. We can now connect the atomic and molecular orbitals with dotted lines. Finally, we still need to fill in the electrons. There are four electrons coming from the carbon and six electrons coming from the oxygen, which gives ten electrons overall. This means that the 1a$_1$, the 2a$_1$, the 1e$_1$ and the 3a$_1$ molecular orbitals are full. This makes the 3a$_1$ orbital the HOMO. It is suitable for σ-bonding with the metal because it has been created through σ-interactions between the 2p$_z$ and the 2s orbitals of O and P respectively.

It is again interesting to compare the MO picture of the bonding in CO with the Lewis-dot structure (Fig. 7.1.19). In the Lewis dot structure we have a triple bond with six bonding electrons. They correspond to the bonding 1a$_1$ and 1e electrons. In the Lewis dot structure all six electrons are energetically indistinguishable, but in the MO diagram we can clearly see that two electrons have a lower energy than the other four which are energetically degenerate. The 1a$_1$ MO is a σ-orbital while the other two are π-orbitals because the 2p$_x$ and the 2p$_y$ orbitals interaction in π-fashion. The 2a$_1$ and 3a$_1$ orbitals can be approximated as non-bonding MOs representing the two electron lone pairs at C and O respectively. Because the 3a$_1$ is slightly anti-bonding it has its electron density mostly at C, while the 2a$_1$ is slightly bonding and therefore its counterpart is the electron lone pair at O. Interestingly the dipole moment of CO is slightly polarized toward C by 0.1 Debye despite the fact that O is the more electronegative atom. This can be attributed to the fact that the HOMO as a weakly anti-bonding orbital is primarily located at C, In addition, the 2a$_1$ orbital is fairly close in energy to the 2s of C, therefore the 2s of C contributes significantly to this orbital. This leads to the fact that there is a significant amount of electron density located at C as well.

One a$_{1g}$ ligand group orbital
(no node)

Two e$_g$ orbitals
(two nodes)

Three t$_{1u}$ orbitals
(one node)

Figure 7.1.22 Ligand group orbital symmetry types

In the next step, we need to group the six HOMOs to form ligand group orbitals, and determine their symmetry types. This is being done by first determining the reducible representation of the orbitals using the orbital swapping method, and then determining the number of irreducible representations of a given type using the reduction formula from group theory. We will not go through the details of the calculations here, because there is nothing really new to learn, but just discuss the outcome. The outcome is that there is one ligand group orbital with the symmetry type a$_{1g}$, two doubly degenerated ligand group orbitals with the symmetry type e$_g$, and three triply degenerated ligand group orbitals having the symmetry type t$_{1u}$. The a$_{1g}$ orbital does not have a node because it is totally symmetric. The t$_{1u}$ orbitals have one node, and the e$_g$-orbitals have two nodes (Fig. 7.1.22). This is not a result of the reduction formula, but one could show that by actually computing the ligand group orbitals using a formula called the projection operator (which we will not discuss in detail here).

Because we now know our the symmetry types of our metal frontier orbitals and our ligand group orbitals we can construct a qualitative molecular orbital diagram (Fig. 7.1.23). To do so we can plot the frontier orbitals on the left side of the molecular orbital diagram, and the ligand group orbitals on the right side of the molecular orbital diagram.

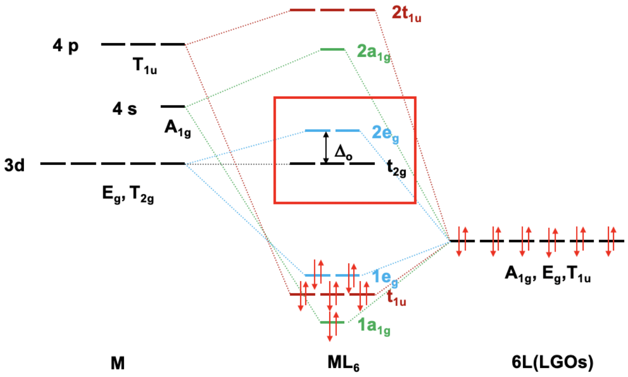


Figure 7.1.23 Qualitative molecular orbital diagram for an octahedral complex of a 4th period transition metal (σ-bonding only).

For a 4th row transition metal the sequence of energy is 3d<4s<4p. It makes sense to assume that the ligand group orbitals have about the same energy as the 3d orbitals of the metal, and we can plot them accordingly. Next, we can assign the orbitals their previously determined symmetry types. Then, we can start to combine orbitals of the same symmetry types to form molecular orbitals. We can start for instance with the orbitals having the symmetry type A_1. The 4s orbital has that symmetry type. Also one ligand group orbital is of this type. Therefore, we would expect one bonding and one anti-bonding molecular orbital. We can label them $1a_{1g}$ and $2a_{1g}$, respectively, and connect them with the A_{1g} atomic and ligand group orbitals by dotted lines. Next, for example, we can consider the E_g orbitals. There are two metal d orbitals and two ligand group orbitals of that symmetry. We therefore produce two doubly degenerate bonding, and two doubly degenerate anti-bonding molecular orbitals. We can label them $1e_g$ and $2e_g$ respectively. We can further see, that there are the three T_{1u} metal 4p orbitals that we can combine with the ligand T_{1u} orbitals. This gives three triple-degenerated bonding orbitals and three triple-degenerated anti-bonding orbitals with t_{1u} symmetry. Lastly, there are the metal T_{2g} orbitals. There are no ligand group orbitals with the same symmetry, and therefore the T_{2g} orbitals remain non-bonding. We have to write them with unchanged energy into the molecular orbital diagram.

Now we are finished with the construction of molecular orbitals, but still need to fill the electrons into them. We consider the metal-ligand bond a dative bond, with electron pairs being donated by the ligand's HOMO. Therefore, we consider all ligand group orbitals to be full with electrons. That means that we have overall 6x2=12 electrons to consider. What about the metal electrons? Well, it depends now which metal ion we have. Let us assume here that we have a d^0 metal ion with no d electrons. That means that we overall have 12 electrons that we need to fill into the molecular orbitals according to energy. This fills the $1a_{1g}$, three t_{1u}, and the two $1e_g$ orbitals. Now let us assume that we would not have a d^0 metal ion, but a metal ion with d electrons. There could be up to ten d electrons. Where would they go? They would go into the five orbitals with the next highest energies. Which ones are these? Well, these are the t_{2g} and the $2e_g$ orbitals. The t_{2g} orbitals are the non-bonding metal d_{xz}, d_{xy}, and d_{yz} orbitals, therefore these orbitals are located only at the metal. The $2e_g$ orbitals are anti-bonding molecular orbitals that have been constructed from the d_{z^2} and the $d_{x^2-y^2}$ orbitals, and are similar in energy to the $d_{x^2-y^2}$ and d_{z^2} orbitals. We can therefore say that the t_{2g} and the $2e_g$ orbitals are the d orbitals under the influence of an octahedral ligand field. Due to the presence of the ligand field the energies of the metal d-orbitals split and the difference in energy is the octahedral ligand field energy Δ_o. Now we can see that there is an interesting analogy to the crystal field theory. Like the d-orbitals split in energy under an octahedral crystal field into t_{2g} and e_g orbitals, the d-orbitals split in energy in an octahedral ligand field into t_{2g} and e_g orbitals. Like in crystal field theory the energy of the d_{z^2} and the $d_{x^2-y^2}$ is raised. The energy of the other three d-orbitals is unaffected similar, but not exactly the same as the d_{xy}, d_{yz}, and the d_{xz} orbitals in an octahedral crystal field.

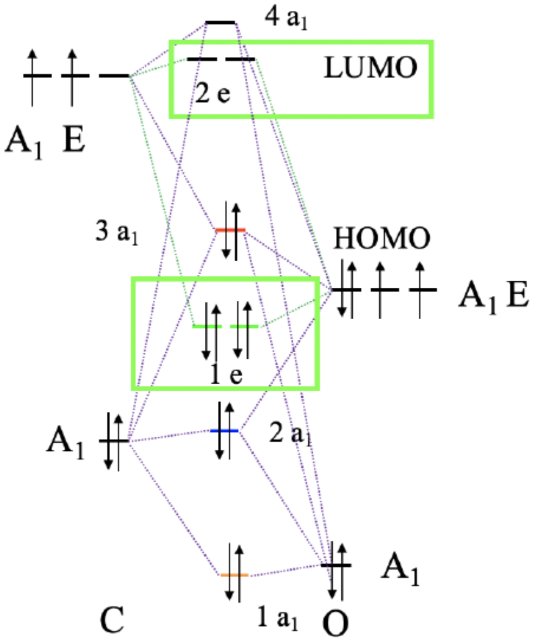


Figure 7.1.24 Molecular orbital diagram for CO ligand and relevant MOs for the π-bonding with the metal (green).

Now we have understood the σ-bonding in an octahedral complex, next let us consider the π-bonding. That means that we have to think about what orbitals of the ligand has the right symmetry for π-bonding with the metal. They should also have an energy similar to the metal orbitals so that significant covalent interaction can occur. We shall stick with our carbonyl ligand, thus we need to look into the molecular orbital diagram of the CO molecule again, and see if there are molecular orbitals suitable for π-bonding (Fig. 7.1.24). The CO molecule has the 1e and the 2e orbitals, that are bonding and anti-bonding π-orbitals, respectively. We can understand this when considering that they are constructed from the $2p_x$ and the $2p_y$ orbitals that overlap in π-fashion to make the π-bonding in the molecule. Each ligand has two 1e and two 2e orbitals which gives overall four orbitals. These orbitals are energetically similar to the HOMO, thus we can expect that they are energetically close enough to the energy of d-metal orbitals, and can get involved in bonding. We have six ligands meaning that we have 6x12=24 orbitals overall. The twelve 1e orbitals are bonding π-orbitals, and the twelve 2e orbitals are anti-bonding π*-orbitals.

Why are these orbitals suitable for π-bonding with metal d-orbitals? Let us look at their shape, and how they can overlap with a metal d-orbital (7.1.25).

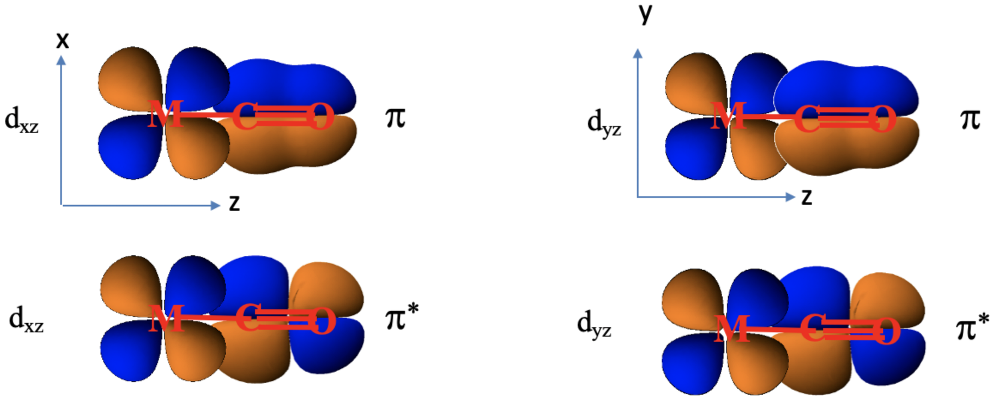


Figure 7.1.25 π-bonding in an octahedral carbonyl complex of a 4th period transition metal

Look for example at a 1e orbital constructed from two $2p_x$ orbitals, and how it is oriented relative to the metal-ligand bond axis which we shall define as the z-axis. Next, let us consider a metal d_{xz} orbital orbital. We can see that it is in plane with the 1e orbital, and that the overlap between the d_{xz} and the 1e orbital occurs in π-fashion. Now let us consider the analogous π*-orbital. We can see that it has an additional node, but it can also overlap with a d_{xz} orbital in π-fashion. The ligand does not only have π and π*-orbitals through overlap of two $2p_x$ orbitals, but also π and π*-orbitals that result from the overlap of two $2p_y$ orbitals. Those orbitals can overlap in π-fashion with a metal d_{yz} orbital. So far, we considered the interactions of a single ligand with the metal only. There are five other ligands, one also approaching from the z-axis, and the other four approaching from the x and y axes. They also have the π and π*-orbitals that interact with the d_{xz}, the d_{yz}, or the d_{xy} orbitals in π-fashion, depending on the direction of approach.

So what do we do with all these orbitals? We group the twelve bonding ones to form a set of ligand group orbitals, and group the twelve anti-bonding ones to form another set of ligand group orbitals. We determine the symmetry types of each set by first determining the reducible representation, and then the irreducible representations using the reduction formula. The result of this process is that the twelve bonding ligand group orbitals have T_{1g}, T_{2g}, T_{1u}, and T_{2u} symmetry. This means that there are three triple-degenerated ones that have T_{1g} symmetry, three other triple-degenerated ones that have T_{1u}, symmetry, three more triple-degenerated ones that have T_{1u} symmetry, and another three triple-degenerated ones that have T_{2u} symmetry. The twelve anti-bonding ligand group orbitals have the same symmetry types. Three have T_{1g} symmetry, three have T_{2g} symmetry, three have T_{1u} symmetry, and another three have T_{2u} symmetry.

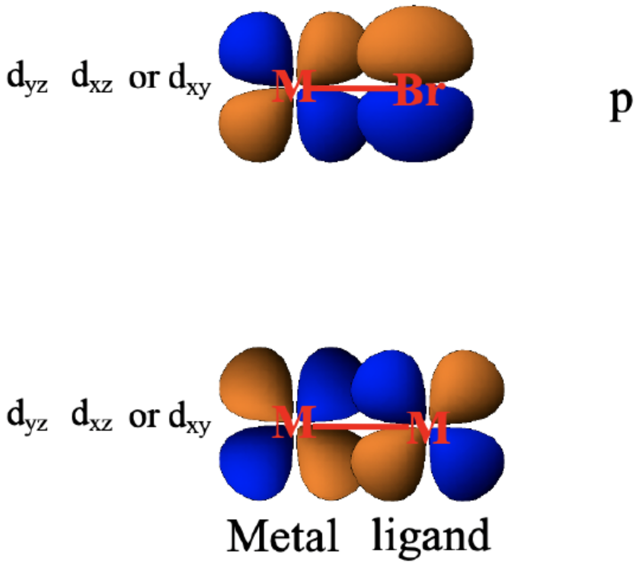


Figure 7.1.26 Other possibilities for π-interactions

It should be mentioned that there are a number of other orbitals that can make π-interactions when the ligand is not a CO ligand. For example halogenide ligands have p-orbitals that have suitable orientation to overlap with metal d-orbitals in π-fashion (Fig. 7.1.26). When there are complexes with metal-metal bonds then there is also the possibility of metal d-orbitals to overlap with other metal d-orbitals in π-fashion.

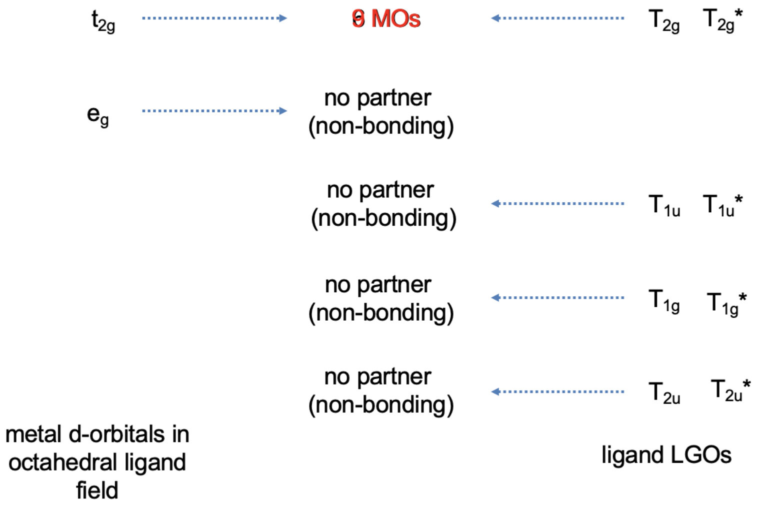


Figure 7.1.27 π-bonding MOs for the octahedral complex of a 4th period transition metal

Now that we have determined the symmetry types of the ligand group orbitals available for π-bonding, we need to select those ligand group orbitals that have suitable symmetry to form molecular orbitals with metal d-orbitals in the octahedral ligand field. These are the $2e_g$ and the t_{2g} MOs that resulted from the σ-interactions. For simplicity sake we will call the $2e_g$ molecular orbitals just the metal e_g orbitals. The t_{2g} MOs are identical to the metal T_{2g} atomic orbitals because the metal T_{2g} atomic orbitals remain exactly non-bonding with respect to σ-interactions. The ligand group orbitals have T_{1g}, T_{2g}, T_{1u}, and T_{2u} symmetry respectively. That means that we can combine the t_{2g} metal orbitals and the T_{2g} ligand group orbitals to form molecular orbitals. The metal e_g orbitals and the ligand T_{1g}, T_{1u}, and T_{2u} orbitals remain non-bonding because they do not find a partner (Fig. 7.1.27). The three bonding T_{2g} LGOs will form six MOs of the same symmetry type with the three metal t_{2g} orbitals. In addition, we need to consider that there are also three anti-bonding $T_{2g}{}^*$ LGOs that were formed from the anti-bonding π-orbitals. They can also interact with the metal t_{2g} d-orbitals. Because the number of MOs of a given symmetry type is always the sum of the atomic orbitals + the LGOs of that symmetry type this adds three MOs to the six MOs giving overall nine t_{2g} MOs. There are also the $T_{1u}{}^*$, the $T_{1g}{}^*$, and the $T_{2u}{}^*$ orbitals. They just remain non-bonding because they do not find a partner.

We can now think of two extreme cases for the combination of the metal t_{2g} with the ligand T_{2g} and $T_{2g}{}^*$ orbitals. In the first case the T_{2g} LGOs are much closer in energy to the metal t_{2g} orbitals, and the $T_{2g}*$ LGOs are energetically much higher than the metal t_{2g} orbitals. In this case we can neglect the covalent interactions between the $T_{2g}{}^*$ orbitals and the metal t_{2g} orbitals, and the $T_{2g}{}^*$ orbitals remain effectively non-bonding. We would consider only the interactions between the T_{2g} LGOs and the metal t_{2g} orbitals to form three bonding and three anti-bonding MOs of t_{2g} symmetry (Fig. 7.1.28). Now we need to consider the electrons. The bonding T_{2g} LGOs are full, and therefore there are overall six electrons to consider. These six electrons would go into the three bonding t_{2g} MOs. Now can also have up to ten metal d electrons. Six of them can be accommodated by the t_{2g} metal orbitals, the other four would be in the e_g orbitals. Upon the formation of the π-bond, the t_{2g} metal electrons will be in the anti-bonding t_{2g} orbitals. The e_g electrons will simply remain non-bonding. We can see that the π-interactions lower the energy of the ligand electrons, but increase the energy of the metal electrons. If we get a net stabilization of electron energies will depend on how many d electrons we have. As long as there are less than six d electrons we will see a stabilization, if there are more there will be an overall destabilization. We can also ask what impact the π-bonding has on the magnitude of the Δ_o. We can see that the π-bonding decreases the Δ_o. It is larger before the bonding compared to after the π-bonding.

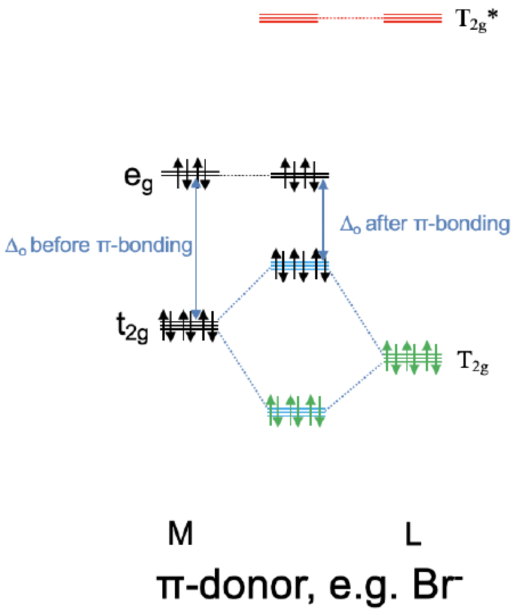


Figure 7.1.28 Influence of a π-donating ligand on Δ_o for the example of a d_{10} ion.

We call a ligand that has T_{2g} orbitals of similar energy to the metal t_{2g} orbitals, and $T_{2g}{}^*$ orbitals of much higher energy compared to the metal t_{2g} orbitals a π-donating ligand, or a π-donor (Fig. 7.1.28). This is because before the π-bonding the ligand electrons are localized exclusively at the ligand, and after the π-bonding they are in the bonding t_{2g} MOs which are shared between the metal and the ligand. Thus, a partial electron transfer has occurred from the ligand to the metal. An example for π-donating ligands are halogenide ligands such as a bromo ligand.

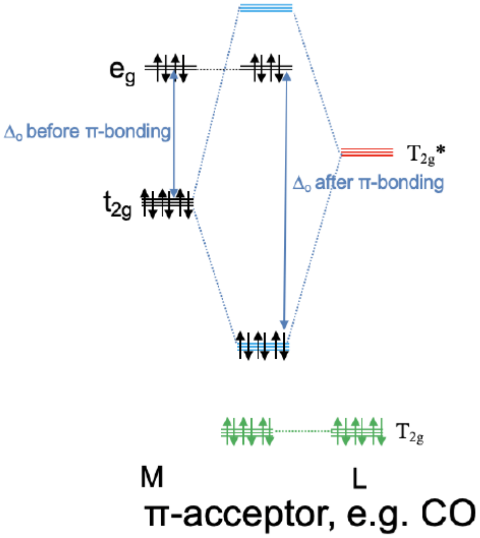


Figure 7.1.29 Influence of a π-acceptor ligand, e.g. CO, on Δ_o

Now let us consider the opposite case in which the anti-bonding T_{2g}^* ligand orbitals are energetically close to the metal t_{2g} orbitals and the bonding T_{2g} ligand orbitals are energetically too low in order to significantly interact with the metal t_{2g} orbitals. This means that the T_{2g}-orbitals remain practically non-bonding. The T_{2g}^* ligand group orbitals and the metal t_{2g} orbitals form three triply degenerated bonding molecular orbitals and three triply degenerated anti-bonding molecular orbitals. Because the T_{2g}^* ligand group orbitals are empty, no ligand electrons are filled into the new molecular orbitals. This means that up to six metal d electrons can be filled into the bonding molecular orbitals of t_{2g} symmetry. Any remaining d electrons in the e_g orbitals just remain in the e_g orbitals and do not change in energy. We can see that in contrast to the previous case, we can lower the energy of the metal d electrons through π-interactions. Because the bonding t_{2g} electrons are shared between the metal and the ligand, electron density has been transferred from the metal to the ligand. Therefore, a ligand that primarily utilizes its anti-bonding T_{2g}^*-orbitals for π-bonding is called a π-acceptor ligand, it accepts d-electron density from the metal. An example for a π-acceptor ligand is the carbonyl ligand (Fig. 7.1.29). It is also important to understand the influence of a π-acceptor ligand on the size of Δ_o. Because the anti-bonding t_{2g} MO is higher in energy than the non-bonding e_g orbitals, the Δ_o is now defined by the energy difference between the bonding t_{2g} MOs and the e_g orbitals (Fig. 7.1.29). We can see that Δ_o is increased when π-acceptor interactions are taken into account.

We have now discussed the two extreme cases, however there are many ligands that are actually in between these two extremes, and there is a continuous spectrum from strongly π-donating, to weakly π-donating, to weakly π-accepting, to strongly π-accepting ligands. It is also possible that π-donor and π-acceptor effects cancel out. This is the case when the the T_{2g} and T_{2g}^*-ligand group orbitals are energetically about equidistant to the metal t_{2g} orbitals. Some ligands also do not have orbitals suitable for π-bonding at all, and there are neither π-donating nor π-accepting effects.

The effect of π-bonding on Δ_o can nicely explain the spectrochemical series. Because π-accepting ligands increase Δ_o, these complexes absorb light of shorter wavelength and of higher energy. π-donating ligands decrease Δ_o and and thus lead to the absorption of light having longer wavelengths. We see here that the ligand field theory is more powerful than the crystal field theory. The latter was not able to explain why different ligands produce different Δ_o values.

Ligand field theory is also able to nicely explain the magnetism of coordination compounds, and high and low spin complexes in particular. It is also able to explain why certain ligands tend to produce low spin complexes, while others tend to form high spin complexes. According to ligand field theory π-acceptors tend to make low spin complexes, and π-donors tend to make high-spin complexes. This is in accordance with experimental observation.

Octahedral Complexes and The 18 Electron Rule

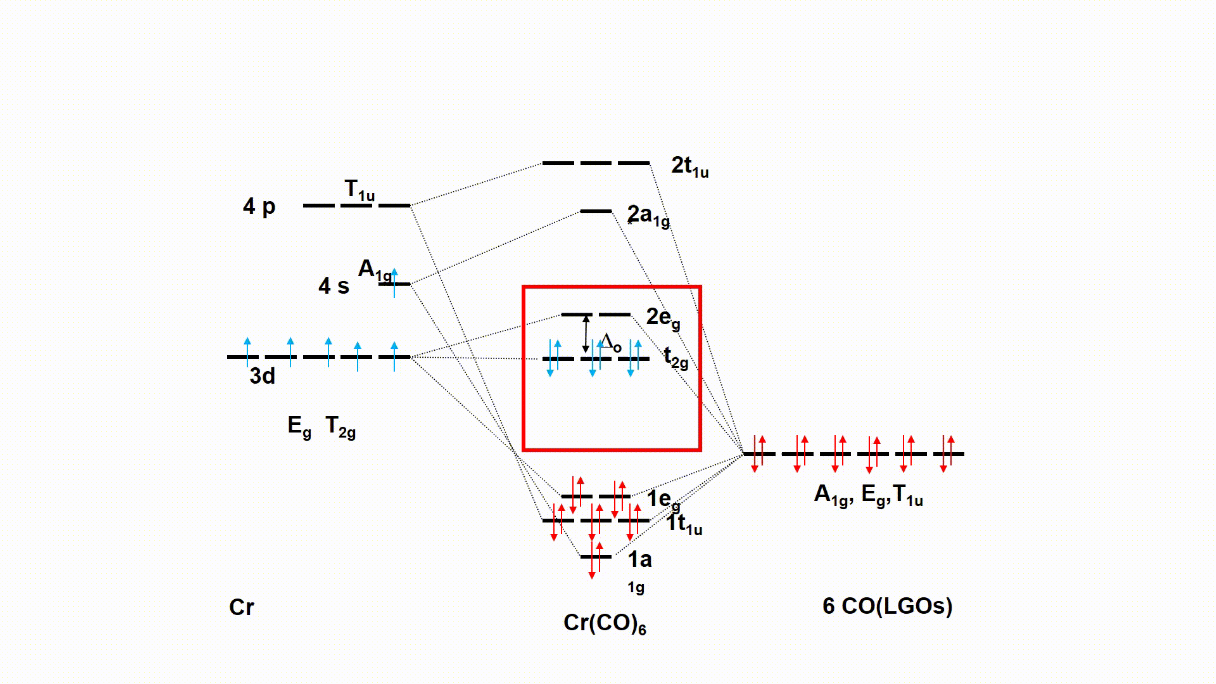


Figure 7.1.30 Qualitative MO diagram of the octahedral hexacarbonyl chromium complex under consideration of π-bonding.

Another great feature of ligand field theory is that it can explain the 18 electron rule, and exceptions from the 18 electron rule. For example, the octahedral hexacarbonyl chromium complex is an 18 electron complex. Let is construct a qualitative molecular orbital diagram and see if the MO diagram supports the stability of the complex. The MO diagram considering only the σ-interactions is shown in Fig. 7.1.30. We can see that all the twlelve ligand electrons are in the bonding molecular orbitals $1a_1$, $1t_u$, and $1e_g$. In addition the chromium has six valence electrons. These electrons remain non-bonding when considering σ-interactions only. However, this changes, when we consider π-interactions. The CO ligand is a strong π-acceptor ligand, therefore we consider only its $T_{2g}{}^*$ π-ligand group orbitals for bonding. They must be located energetically above the LGOs for σ-bonding. The interaction of the metal t_{2g} orbitals creates three bonding t_{2g} MOs and the three anti-bonding ones. Because we can fill metal d electrons into the bonding MOs the status of the d-electrons has changed from non-bonding to bonding. We can see now that all 18 electrons are in bonding MOs, and that no electron is in-non-bonding or anti-bonding MOs. When all electrons are in bonding MOs then this is the ideal situation for complex stability. This is explains why the 18 electron complex is stable. If we analyzed the MO diagrams of many other stable 18 electron complexes then we would also mostly find that all bonding MOs are filled, and all other MOs are empty. This explains the 18 electron rule.

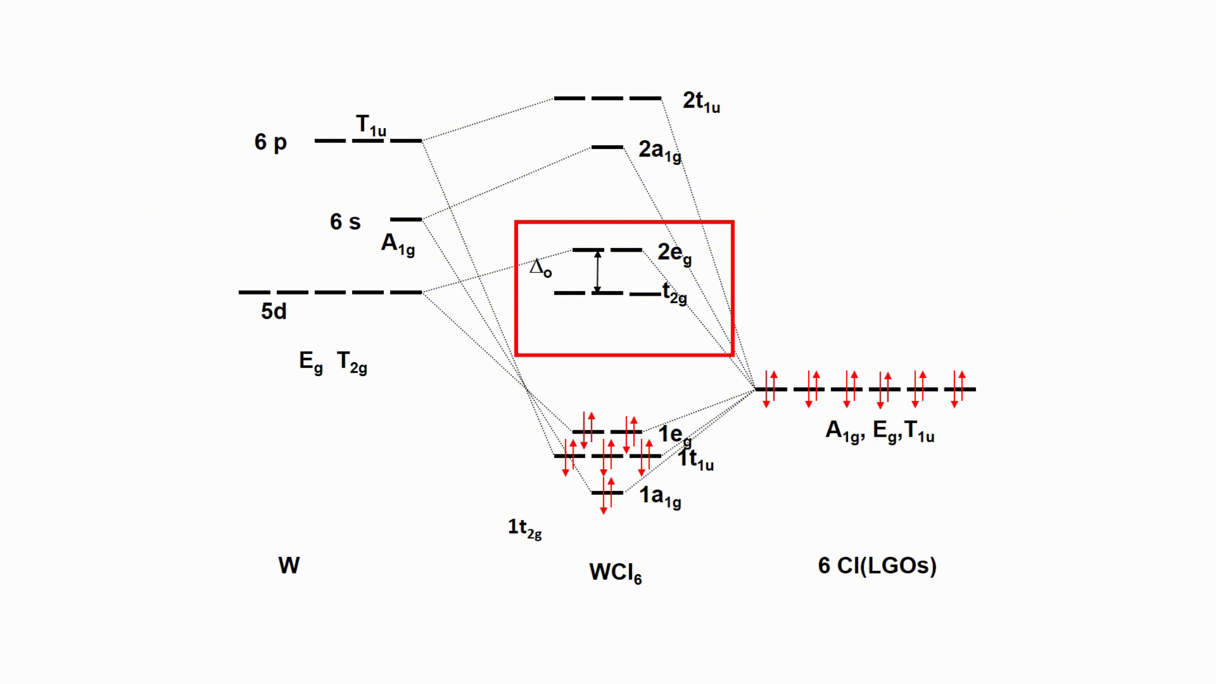
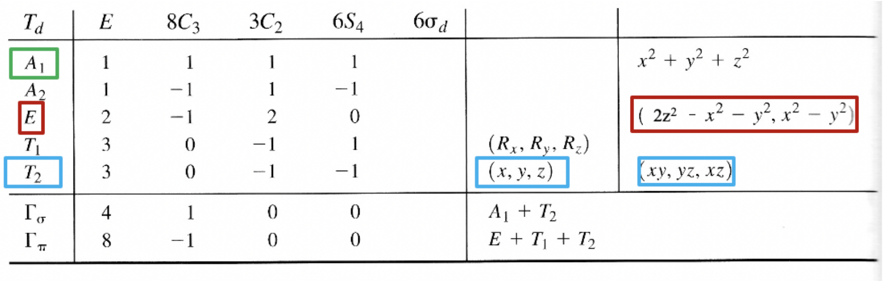


Figure 7.1.31 The qualitative molecular orbital diagram of WCl_6 under consideration of π-bonding.

Next, let us construct a qualitative molecular orbital diagram of WCl_6. This is not an 18 electron complex, it has only twelve electrons coming from the six chloro ligands. W is in the oxidation state +6 and is a d^0 species contributing no electons. Can ligand field theory explain this exception from the 18 electron rule? Let us again start with the MO diagram considering σ-bonding only. The twelve ligand electrons go into the bonding $1a_{1g}$, $1t_u$, and $1e_g$ orbitals. The non-bonding t_{2g} and the anti-bonding $2e_g$ orbitals remain empty due to the absence of metal d electrons. We can see that all bonding molecular orbitals are full and all others are empty, explaining the stability of the molecule, and thus the exception from the 18 electron rule. Now let us consider π-bonding in addition. A chloro ligand is a typical π-donor which uses its 3p electrons that are suitably oriented for π-bonding. Therefore, we only consider the T_{1g} ligand group orbitals for bonding here. These orbitals are full with electrons because a chloride anion has a full 3p subshell. The interaction of the T_{2g} LGOs with the metal t_{2g} orbitals creates a bonding t_{2g} MO and an anti-bonding t_{2g} MO. We can see that the ligand π-electrons now have a lower energy than without the π-interactions of the metal. Therefore, the π-bonding has further stabilized the complex. In a way, we can now even say that we have an 18 electron complex because when we add th 6 π electrons to the 12 σ electrons we get 18 bonding electrons overall. These additional 6 electrons are not accounted for in electron-counting because electron-counting treats the W-Cl bond as a single bond and only considers the σ-interactions between W and Cl.

Tetrahedral complex of a 4th period Transition Metal

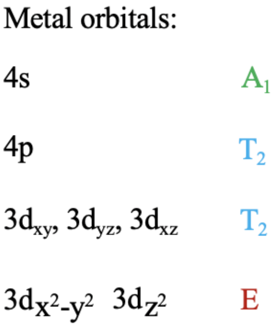
Next, let us consider a tetrahedral complex and see if ligand field theory can explain it well. The point group for a tetrahedron is T_d, and we will need the character table of this point group (Fig. 7.1.32)



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	−1	1	−1			
E	2	−1	2	0			$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1		(x, y, z)	(xy, yz, xz)
Γ_σ	4	1	0	0		$A_1 + T_2$	
Γ_π	8	−1	0	0		$E + T_1 + T_2$	

Figure 7.1.32 Character table for the point group T_d

We choose the coordinate system like in the crystal field theory. We inscribe the tetrahedron into a cube by occupying every other vertice of the cube with a ligand (Fig. 7.1.34). Then, we let the axes run perpendicular to the faces of the cube. Next, we need to think about the symmetry types of the metal frontier orbitals. For a fourth period transition metal these are the 3d, the 4s, and the 4p orbitals. Looking into the character table of the point group T_d gives us their symmetry types (Fig. 7.1.32 and Fig. 7.1.33). The 4s orbital has the totally symmetric symmetry type A_1, We find the letters x,y, and z in parentheses in the irreducible representation of the type T_2, and this means that the 4p orbitals are triply degenerated and have the symmetry type T_2. The $3d_{xy}$, the $3d_{yz}$, and the $3d_{xz}$ orbitals are found in the same irreducible representation, are also triple-degenerated, and have T_2 symmetry. The $3d_{x^2-y^2}$ and the $3d_{z^2}$ orbitals have the symmetry type E according to the character table for T_d.



Metal orbitals:

4s	A_1
4p	T_2
$3d_{xy}$, $3d_{yz}$, $3d_{xz}$	T_2
$3d_{x^2-y^2}$ $3d_{z^2}$	E

Figure 7.1.33 Metal orbitals

Now we need to think about the ligands. Because we need to consider σ-bonding first, we have to find the HOMO of the ligand suitable for σ-bonding. We can choose again a carbonyl ligand as an example ligand, and in this case the HOMOs of the CO ligands would be used for σ-bonding. This is actually not immediately obvious. If we chose the coordinate system of the metal and ligands to be same same, then then the CO bond axis, which we previously defined as the z-axis, would not point toward the metal, and no σ-overlap with a metal orbital would be possible. Therefore, we must give each ligand a different coordinate system with the z-axes pointing toward the metal (Fig. 7.1.34). Only then, the CO molecule would point toward the metal, and would be oriented to make σ-bonding with the metal. Generally, when constructing MOs, the ligands should always be oriented to that bonding is maximized. This is usually the case when orbital overlap for σ-bonding is maximized.

Figure 7.1.34 A tetrahedral complex inscribed in a cube with CO ligands each having its own coordinate system.

Because we have four ligands we will have four ligand HOMOs that we would group to form four ligand group orbitals. Which symmetry types do they have? In order to obtain the symmetry types we would need to determine the reducible representation first, and then the irreducible representations this reducible representation is composed of. We won't do this explicitly here and not go through the entire mathematical process, and only consider the results.

4 Ligand orbitals:

$$A_1 + T_2$$

Figure 7.1.35. Symmetry types for ligand group orbitals involved in σ-bonding

The result is that one ligand group orbital has the symmetry type A_1 and the other three have the symmetry type T_2 (Fig. 7.1.35).

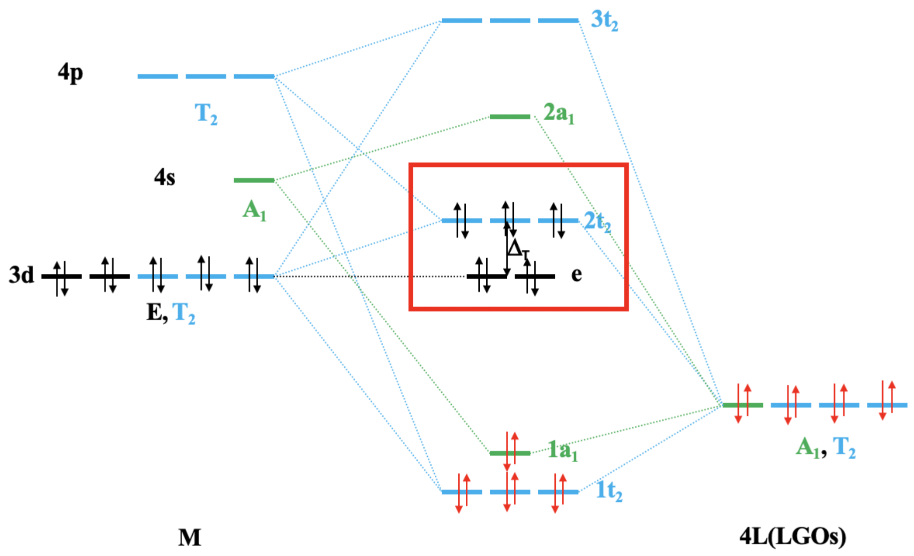


Figure 7.1.36 MO diagram reflecting the σ-bonding of a tetrahedral complex of a 4th period transition metal

We can now construct the molecular orbital diagram for σ-bonding (Fig. 7.1.36). First, we can plot the metal frontier orbitals according to the energy on the left side of the diagram, and label the orbitals according to their symmetry types. On the right side we plot the four ligand group orbitals, and label them according to their symmetry type. Their energy should be approximately that of the metal d-orbitals. Now we can construct molecular orbitals by combining atomic and ligand group orbitals of the same symmetry type. The 4s orbital and one LGO have A_1 symmetry, and therefore we can combine them to form a bonding $1a_1$ and an anti-bonding $2a_1$ orbital. Next, let us direct our attention to the t_2 symmetry type. The 4p and three metal d orbitals have that symmetry type, and so have three LGOs. That is overall nine orbitals, so we must get nine MOs with t_2 symmetry. Because of triple-degeneracy, there must be three sets of triple-degenerate MOs. We can estimate that one set will be bonding, one will be approximately non-bonding, and one will be anti-bonding. We can label them $1t_2$, $2t_2$, and $3t_2$ respectively. The $2t_2$ is actually somewhat anti-bonding in nature. Now only the metal e-orbitals are left. They do not find a partner and remain non-bonding.

We still need to fill the electrons into the MOs. The four ligand HOMOs are considered full, which gives 4×2=8 electrons. The electrons occupy the bonding $1t_2$ and the $1a_1$ orbitals explaining the four dative metal-ligand bonds. All metal d electrons, which could be up to ten, would need to go into the e and/or the t_2-orbitals. The e-orbitals are the non-bonding d_{z^2} and $d_{x^2\text{-}y^2}$ orbitals, and the $2t_2$ orbitals are only weakly anti-bonding and have strong d-metal orbital character because they are have been constructed from the d_{xy}, the d_{yz}, and the d_{xz} orbitals, and are fairly similar in energy to those orbitals. We can therefore say that the the e and the 2_{t2} orbitals are the metal t_2 and e_g orbitals in a tetrahedral ligand field. The energy difference between the e and the $2t_2$ orbitals is the tetrahedral ligand field energy Δ_T. You see here again the relationship between ligand and crystal field theory. You can also see that ligand field theory can explain why crystal field theory works as a bonding theory even though it is not an actually bonding theory.

π-bonding in a tetrahedral complex

What is the π-bonding in a tetrahedral complex?

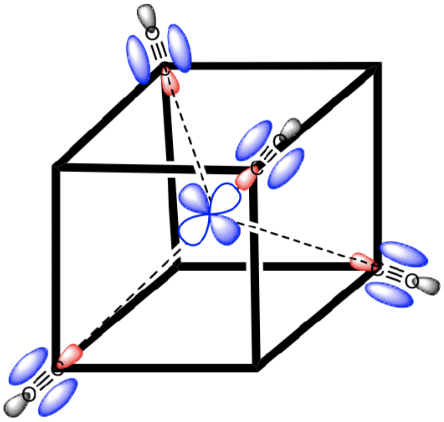


Figure 7.1.37 π-bonding in a tetrahedral complex

First, we need to decide if there are ligand orbitals that are suitably oriented to overlap with metal orbitals in π-fashion. We can see that no ligand orbital is overlapping with a metal d-orbital exactly in π-fashion, however, the e π and 2e π*-orbitals of the ligands still overlap so that at bonding interaction is created, and this orbital overall occurs similarly to π-overlap. Therefore, we can still approximate the bonding interactions as π-bonding. We need to consider though that because of smaller orbital overlap, the π-bonding in tetrahedral complexes is weaker than in octahedral complexes. How many ligand orbitals will we need to consider? Assuming that we will stick with CO as the ligand, there will be four per ligand, and thus there will be 4×4=16 overall. Of these, there will be eight bonding e π-orbitals and eight anti-bonding e π*-orbitals. We group the bonding ones to form a set of eight ligand group orbitals, and group the anti-bonding ones to form another set of eight anti-bonding ligand group orbitals. What will be their symmetry types? We can determine the reducible representations and irreducible representations to find this out. We are not going through the exact process here, but only look at the results. The result is that each set of ligand group orbitals has the two E-type orbitals, three T_1-type, and three T_2-type ligand group orbitals.

Figure 7.1.38 MO diagram of a tetrahedral complex of a 4th period transition metal (pi-bonding with pi-acceptor)

Since we now know the symmetry of the ligand group orbitals we can combine them with same-symmetry metal d-orbitals in the tetrahedral ligand field to form π-molecular orbitals. Let us do this for the example of nickel tetracarbonyl, a tetrahedral complex of Ni in the oxidation state 0 and four carbonyl ligand. We can use the MO diagram for σ-bonding which we constructed previously as a starting point, and modify it so that it accounts for π-bonding (Fig. 7.1.38).

First, we need to add the new ligand group orbitals to the MO diagram. We only need to consider the E and T_2 LGOs and not the T_1 LGOs because no metal orbital has t_1 symmetry. Next, we need to take into account that the CO ligand is a strong π-acceptor ligand. This means that we only need to consider the LGOs formed from the anti-bonding π*-orbitals. We must draw these orbitals above the LGOs for σ-bonding into the MO diagram because the LGOs for σ-bonding have been formed from the CO HOMOs while the anti-bonding LGOs for π-bonding have been formed from the CO LUMOs. We can now combine the π-LGOs and metal d-orbitals of the same symmetry to form π-MOs. We see that we can combine the e-type LGOs with the non-bonding e-type metal d_{z^2} and $d_{x^2-y^2}$ orbitals to form a pair of bonding MOs of e-symmetry, and an anti-bonding pair of e-symmetry, which we can label 1e and 2e, respectively. Now what is the effect on the T_2-type π-LGOs? We first need to realize that we have already three sets of triple-degenerated t_2-MOs generated through σ-interactions. The interaction of the T_2-LGOs with the σ-t_2-MOs must create another set of triply-degenerated orbitals so that the overall number of orbitals with t_2-symmetry remains the same. The interaction will occur mostly between the $2t_2$ MO and the T_2-LGOs because the $2t_2$ MOs have the most similar energy to the T_2-LGOs. This leads to the lowering of the energy of the $2t_2$ MOs, so that these formerly weakly anti-bonding orbitals become weakly bonding. The additionally created t_2-orbitals are weakly anti-bonding. We can label them $3t_2$. The former anti-bonding $3t_2$ –orbital will be re-labeled $4t_2$. We can double-check that we have constructed the t_2-MOs correctly by verifying that the number of T_2-LGOs, and that includes σ and π, plus the number of metal T_2 orbitals equals the number of t_2 molecular orbitals. We see that the number of metal T_2 orbitals + the number of T_2 LGOs is 6+6=12. The number of t_2 MOs is 4×3 which is also 12.

Finally, we still need to fill the electrons. As previously mentioned, the π-LGOs as empty and therefore the ligand does not contributed any electrons to the π-bonding. The Ni is in the oxidation state 0 and thus contributes 10 electrons because Ni is in the 10th group of the periodic table. Because a neutral Ni atom has the electron configuration $3d^84s^2$ we can draw eight electrons in to the 3d orbitals and two electrons into the 4s orbitals. The $1t_1$ and the $1a_1$ MOs are already full with ligand electrons due to σ-bonding. Thus, the metal electrons must go into the 2e and the $2t_2$ MOs. Both the e-orbitals and the $2t_2$-orbitals are bonding, and thus we can say that the metal d-electrons have been stabilized due to the π-acceptor nature of the ligand. We see here an analogy to the octahedral ligand field. Like in the octahedral ligand field π-acceptor ligands tend to lower the energy of the metal d-electrons. We can also ask: What is the effect of a π-acceptor ligand on Δ_T? The answer is: Like Δ_o gets larger in the octahedral ligand field, Δ_T gets larger in a tetrahedral ligand field. However, the increase is much smaller compared to the octahedral field. Why? this is because in the octahedral ligand field, the energy of the e_g orbitals is not affected through the π-acceptor interactions, and only the t_{2g} orbitals are lowered in energy. In the case of the tetrahedral ligand field both the energy of the e and the t_2 orbitals get lowered, and the energy of the e-orbitals gets only slightly more lowered than the energy of the t_2 –orbitals. Therefore, the Δ_T only slightly increases. This fact can also serve as an additional explanation why tetrahedral complexes never make low-spin complexes, even with strong π-accepting ligands. The effect of the ligand on Δ_T is simply still too small because both the energy of the e and the t_2 orbitals have been lowered.

Finally, let us discuss the results in the context of the 18 electron rule. We can see that the number of electrons involved in σ-bonding are in bonding molecular orbitals. Thus, it is justified to say that the ligand field theory is able to explain the 18 electrons rule.

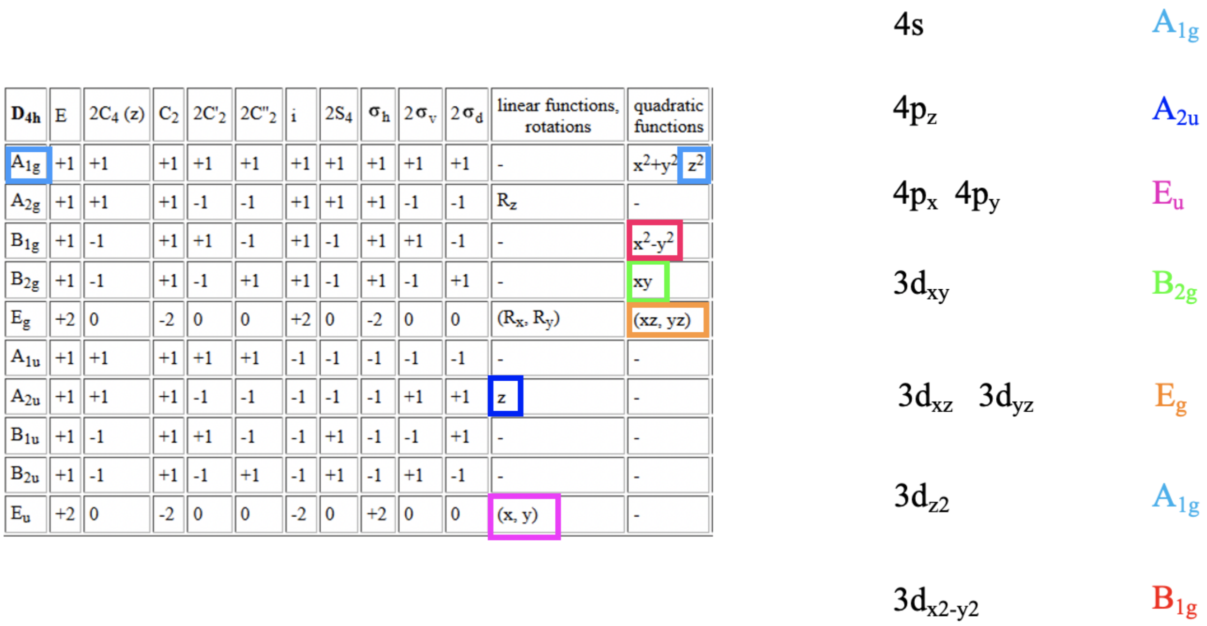
Figure 7.1.39 MO diagram of a tetrahedral complex of a 4th period transition metal (π-bonding with π-donor)

Now let us think about how a π-donating ligand influences the magnitude of Δ_T. In this case we only need to consider the bonding E and T_2 ligand orbitals if the ligand has π-bonds. Those orbitals will be energetically below the LGOs for σ-bonding. If the ligand is a simple ion like chloride, then we would consider LGOs from the filled p-orbitals that that have suitable symmetry for π-overlap. Those LGOs would have the essentially the same energy as the σ-LGOs. Let us construct a qualitative MO diagram of $TiCl_4$ which has chloro ligands which are typical π-donating ligands. When constructing the MO diagram for π-bonding we can again start with the MO-diagram for σ-bonding, and then modify this diagram. We can first plot the filled π-T_2 and E_g LGOs with similar energy as the σ-LGOs on the right side of the diagram. The E ligand group orbitals will now interact with the e-metal orbitals. That interaction leads to a pair of bonding MOs of e-symmetry, and a pair of anti-bonding MOs of e-symmetry. This means that effectively, the formerly non-bonding e-metal orbitals become anti-bonding MOs, and move up in energy. The bonding e-type MO is created in addition and must have lower energy than the E-type π-LGOs. The interaction of the T_2-LGOs with the metal t_2-orbitals creates an additional set of bonding t_2-orbitals. The $2t_2$ orbitals move up in energy, and become more anti-bonding, as a consequence of that. We can just renumber the t_2 and the e MOs. Now we still need to fill the electrons into the MOs. The π-LGOs have overall eight electrons. These electrons will go into the newly formed bonding 1e and $1t_2$ molecular orbitals. We see that this leads to a stabilization of these electrons. This is an analogy to the octahedral ligand field. When we have a π-donor ligand, then that the π-ligand electrons. What about the metal electrons. In $TiCl_4$ the Ti is in the oxidation state +4, therefore it is formally d^0, and it does not have any electrons. This explains the stability of the $TiCl_4$ as complex that does not obey the 18 electron rule. It has only 8 electrons, but the bonding situation is nonetheless ideal. All bonding MOs are full, and all others are empty. If the Ti had d electrons they would need to go into the 2e and the $3t_2$ orbitals which are both anti-bonding. This would destabilize the complex. In general π-donating ligands increase the energy of metal d-electrons, and this is another analogy to the octahedral ligand field. Now to the question, what is the effect of a π-donating ligand on Δ_T? Both the metal e and t_2 frontier orbitals have increased in energy but the e-orbitals more so than the t_2 orbitals. That means that the Δ_T has overall decreased. This is a further analogy to the octahedral ligand field. π-donating ligands lead to a smaller Δ_T.

Overall the ligand field theory can again provide an explanation for the spectrochemical series. π-donors lead to smaller Δ_T ligands, and thus the complex absorbs light of larger wavelengths, π-acceptors lead to larger Δ_T and those complexes absorb light of smaller wavelengths.

Square Planar Complex of a 4th Period Transition Metal

As a last example we will discuss now the molecular orbital diagram of a square planar complex. This will be the most complicated MO diagram we will discuss. The greater complexity stems from the lower symmetry in a square planar complex. It belongs to the point group D_{4h} whereas tetrahedral and octahedral complexes belong the high symmetry point groups T_d and O_h.



D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-

4s	A_{1g}
$4p_z$	A_{2u}
$4p_x$ $4p_y$	E_u
$3d_{xy}$	B_{2g}
$3d_{xz}$ $3d_{yz}$	E_g
$3d_{z2}$	A_{1g}
$3d_{x2-y2}$	B_{1g}

Figure 7.1.40 Character table for the D_{4h} point group and symmetry determination of the metal frontier orbitals.

The lower symmetry leads to a reduction in the degeneracy of the molecular orbitals. This creates more energy levels and hence a more complicated molecular orbital diagram. Let us think next about the definition of the axes. I would be sensible to define the xy plane as the plane of the molecule with the x and the y-coordinates going through the bonds. The z-axis would stand perpendicular to the plane of the molecule. What are the symmetry types of the metal frontier orbitals. Assuming a 4th period transition metal the 3d, the 4s, and the 4p orbitals would be the frontier orbitals. Looking into the character table of the point group D_{4h} (Fig. 7.1.10) shows that the symmetry of the 4s orbital is A_{1g}, the symmetry of the 4p orbitals is A_{2u} for the $4p_z$ orbital and e_u for the $4p_x$ and the $4p_y$ orbitals. The d orbitals have the symmetry types A_{1g}, B_{1g}, B_{2g}, and E_g for the $3d_{z^2}$, $d_{x^2-y^2}$, $3d_{xy}$, and $3d_{xz}/3d_{yz}$, respectively.

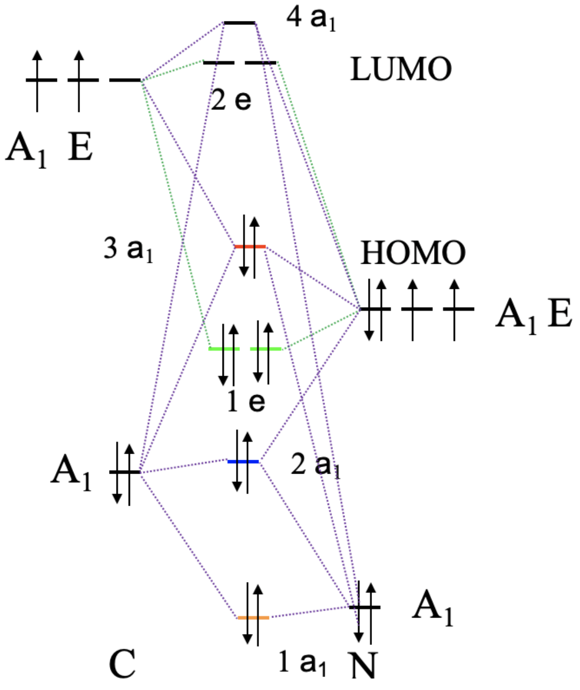


Figure 7.1.41 MO diagram of CN^-

Next, we to determine the ligand HOMOs suitable for σ-bonding. There are no square planar carbonyl complexes, therefore we will not choose the carbonyl ligand as a example ligand here. Instead we will use the related cyano ligand. The cyano ligand is isoelectronic with the carbonyl ligand. Formally, the O-atom in CO is replaced by N. Because N has one electron less than O, we must add one electron, giving the cyano ligand a 1- negative charge. Like in CO, the cyano ligand has a triple bond between C and N, and there is an electron lone pair at C, and one at N. The MO diagram is similar to that of CO, just the energy difference between C and N orbitals is somewhat smaller than that of the energy difference between C an O orbitals (Fig. 7.1.41). The number, symmetry, and energy order of the MOs of CN^- and CO is the same. Therefore, the CN^- has the same HOMOs suitable for σ-bonding, and we can select it for the construction of σ-MOs. Each ligand has one HOMO, therefore we have overall four HOMOs.

$$\Gamma_\sigma = A_{1g} + E_u + B_{1g}$$

Figure 7.1.42 LGOs for CN^-

We can group them to form LGOs and determine the symmetry types of the LGOs. The result is that there is on ligand group orbital with A_{1g} symmetry, there are two with E_u symmetry, and there is one with B_{1g} symmetry (Fig. 7.1.42).

Square Planar Complex: σ-bonding

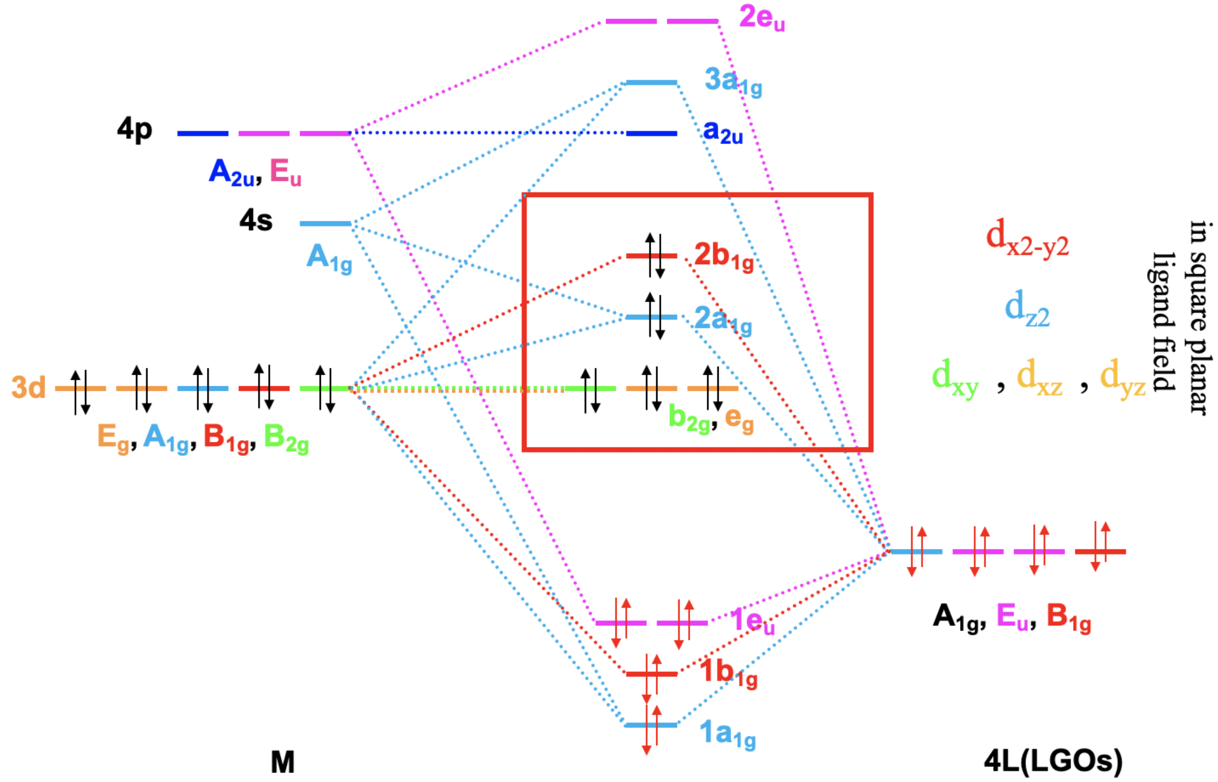


Figure 7.1.43 MO diagram for a square planar 4th period transition metal complex

We have now the all information necessary to construct a qualitative molecular orbital diagram for σ-bonding (Fig. 7.1.43). As usual we first plot the metal frontier orbitals on the left and the ligand group orbitals on the right side of the MO diagram, and label the symmetry types. Then, we need to combine metal frontier and ligand group orbitals of the same symmetry type to form molecular orbitals. We can for instance begin with the symmetry type A_{1g}. The 4s orbital and the $3d_{z^2}$ orbitals have this symmetry type, and so has one ligand group orbital. We will therefore get three molecular orbitals of that symmetry type, a bonding one, an approximately non-bonding one, and an anti-bonding molecular orbital. We plot them according to their expected energy into the MO diagram, and label the MOs $1a_{1g}$, $2a_{1g}$, and $3a_{1g}$, respectively. Next, we can look at the B_{1g} orbitals. The $3d_{x^2-y^2}$ orbital and one LGO of that symmetry type, and thus we can form a bonding and an anti-bonding MO from this combination. We can further see that we can combine the $4p_x$ and the $4p_y$ orbitals that have E_u symmetry with the remaining two LGOs of the same symmetry. This gives two double-degenerated bonding MOs of e_u symmetry, and two anti-bonding bonding ones of the same symmetry. Are there any orbitals with other symmetry types left? Yes, there are the metal d_{xy}, d_{xz}, and d_{yz} orbitals that have B_{2g}, and E_g symmetry, respectively, In addition, there is the p_z orbital that has a_{2u} symmetry. We can see that these metal orbitals do not find a partner. There is no LGO of these symmetry types. We therefore have to draw these orbitals as non-bonding orbitals into the MO diagram.

Now it is the time to fill the electrons into the molecular orbitals. The LGOs are occupied with electrons because they have been formed from the HOMOs of the ligand. Because we have four LGOs we have eight electrons to consider. These electron will therefore fill the $1a_1$, the $1b_{1g}$, and the $1e_u$ molecular orbitals. These orbitals are all bonding molecular orbitals. Thus, ligand field theory is able to explain the four bonds and the square planar shape of the molecule. Where would the metal d-electrons go? We could have up to ten d-electrons depending on the metal ion, and these ten electrons would go into the five MOs of the next higher energy. These are the non-bonding b_{2g} and e_g orbitals, the approximately-non-bonding $2a_{1g}$ orbital, and the anti-bonding $2b_{1g}$ orbital. We can consider these orbitals as the metal-d-orbitals in a square planar ligand field. The b_{2g} orbitals is the d_{z^2} orbital in the square planar ligand field, the e_g orbitals are d_{xz} and d_{yz} in a square planar ligand field, the $2a_{1g}$ orbital is the d_{z^2} orbital in a square planar ligand field and the $2b_{1g}$ orbital is the $d_{x^2-y^2}$ orbital in a square planar ligand field. We can see that these results are similar yet not completely analogous to those we obtained in the crystal field theory. Remember, that in the crystal field theory the $d_{x^2-y^2}$ orbital had also had the highest energy. However, the d_{z^2} was lower in energy than the d_{xy}, and the d_{xy} was not degenerate with the d_{xz} and the d_{yz} orbitals. The difference it due to the fact that in ligand field theory the d_{xy} orbital is considered non-bonding, not interacting with the ligands at all, whereas in crystal field theory a strong electrostatic repulsion between the d_{xy} and the ligands is assumed because the d_{xy} orbital is in the plane of the molecule.

Square Planar Complex π-bonding

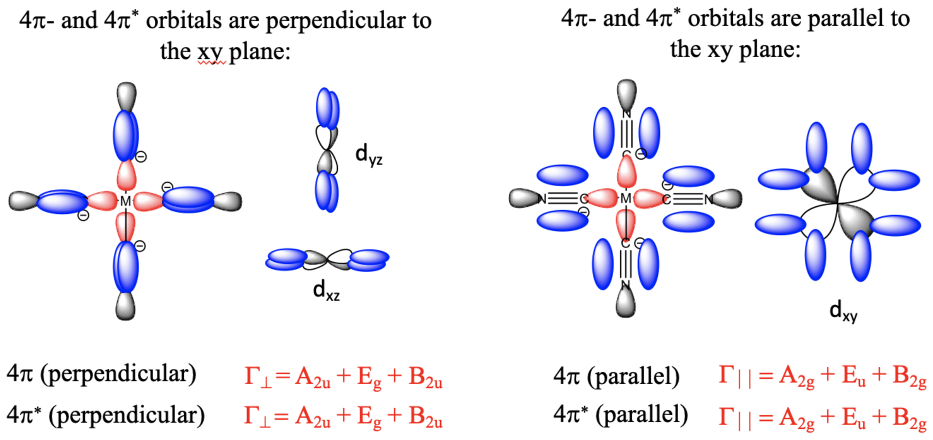


Figure 7.1.44 Square planar transition metal complexes: π-bonding

Now let us look at the π-bonding of a square planar transition metal complex (Fig. 7.1.44). If we assume a CN^- ligand, then the orbitals that have suitable symmetry to overlap with the metal frontier orbitals in π-fashion are the 1e and 2e π and π* orbitals from the MO diagram of CO. There are two π and two π* orbitals per ligand. Because we have four ligands there are overall eight π and eight π* orbitals. Now we need to consider that four of the π-orbitals are in the xy plane, while the other four are above and below the xy plane. We call the former the parallel orbitals, and the latter the perpendicular orbitals, because they are oriented parallel and perpendicular to the xy plane, respectively. We must distinguish them because they have a different symmetry and overlap differently with the metal d-orbitals. This is illustrated for the bonding π-orbitals in Fig. 7.1.44. The anti-bonding ones behave analogously. Therefore we group the orbitals to form four sets of ligand group orbitals $\pi_{\perp}$, $\pi_{||}$, $\pi^*_{\perp}$, and $\pi^*_{||}$. Our next task is to determine the symmetry types of these orbitals. We again omit the exact process, but only look at the results. Both the $\pi_{\perp}$ and the $\pi^*_{\perp}$ orbitals have one A_{2u}, two E_g and one B_{2u} ligand group orbitals. The $\pi_{||}$ and $\pi^*_{||}$ orbitals have one A_{2g}, two E_u, and one B_{2g} ligand group orbitals.

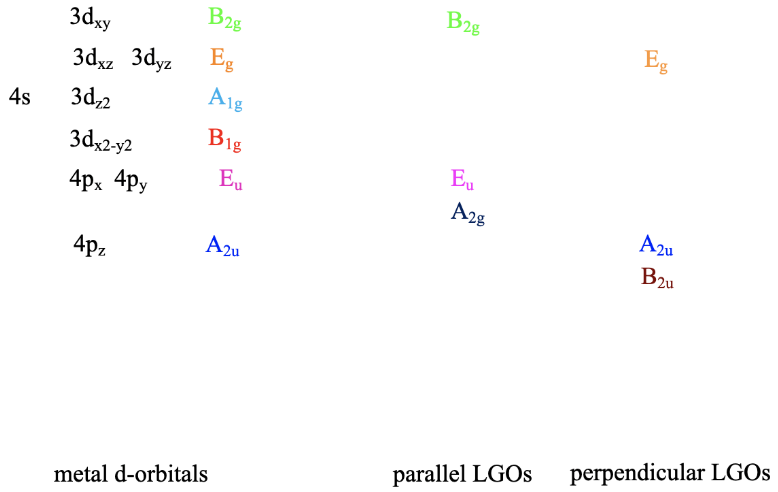


Figure 7.1.45 Symmetry types of metal frontier orbitals, parallel, and perpendicular LGOs for π-bonding

We now need to add the π-molecular orbitals to the molecular orbital diagram that we had constructed previously to account for σ-bonding. First, we need to consider which π-LGOs have the right symmetry to produce π-MOs with metal d-orbitals (Fig. 7.1.45). We can see that among the parallel LGOs the A_{1g} and the B_{1g} orbitals find partners, but not the E_u orbitals, For the perpendicular LGOs the E_g orbitals find partners, but not the A_{2u} and the B_{2u} orbitals. We therefore only need to consider the A_{1g}, the B_{1g} and the E_g LGOs. To make matters more complicated, to get a realistic MO diagram for a square planar complex with cyano ligands it is necessary to consider the interactions of the 4s and the 4p orbitals with the π-LGOs as well. The symmetry of the 4s was A_{1g} and the symmetry of the 4p orbitals was A_{2u} and E_u, respectively. The 4s still does not find a partner, but the 4p orbitals do.

MO Diagram of a Square Planar Complex With a Cyano Ligand

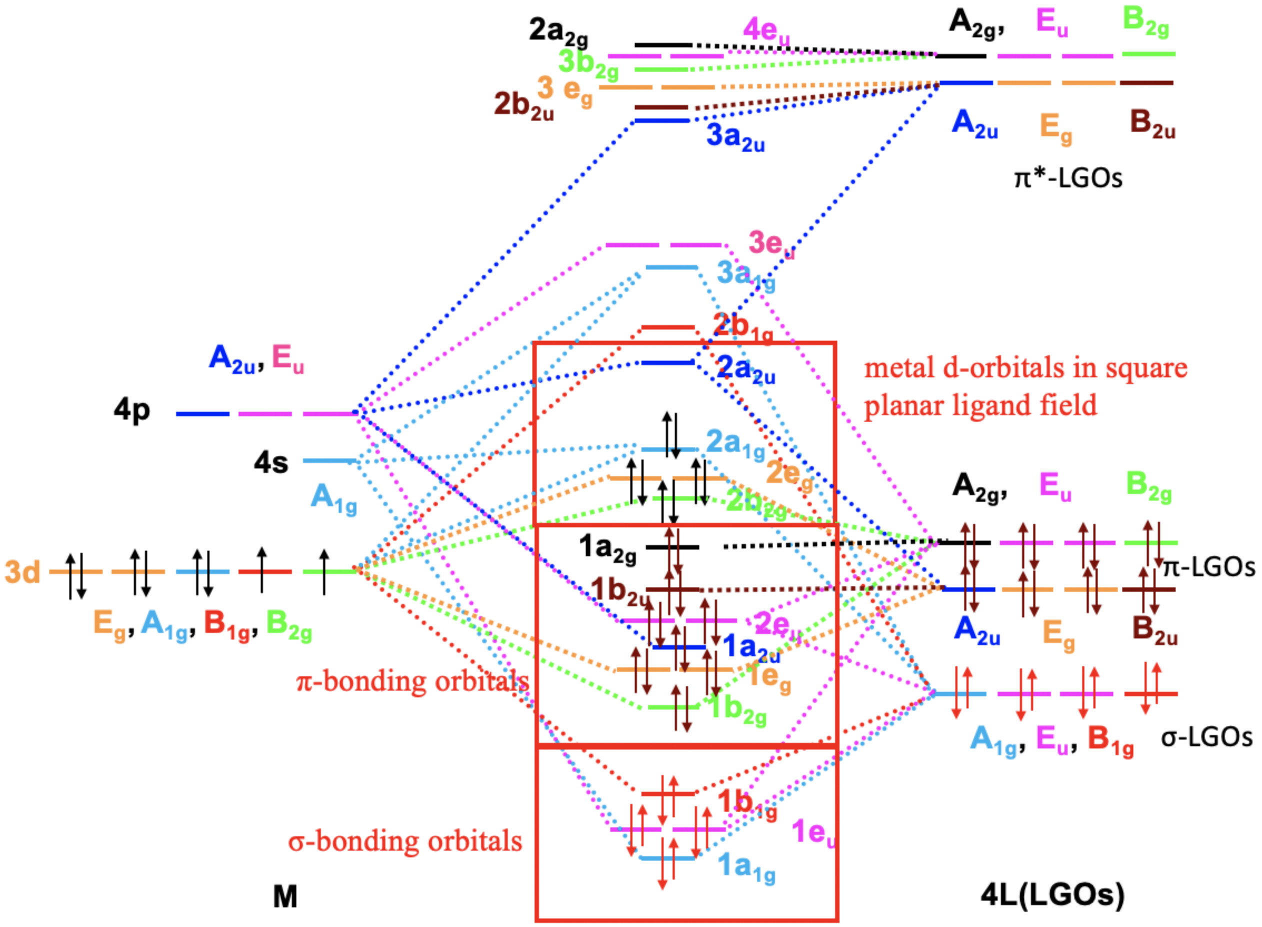


Figure 7.1.46 MO Diagram of a Square Planar Complex With a cyano Ligand under consideration of π-bonding.

Let us now construct the MO diagram of a square planar complex with a cyano ligand considering both σ and π-bonding for the example of the $Ni(CN)_4^{2-}$ complex anion. Because of the complexity of the diagram we will not modify the MO diagram for σ-bonding, like we did previously, but construct the complete MO diagram from scratch (Fig. 7.1.46). Like previously we can plot the metal 3d, 4s, and 4p orbitals on the left side of the diagram. On the right side of the diagram are now the LGOs for σ as well as π-bonding. For the $Ni(CN)_4^{2-}$ complex the σ-LGOs are energetically somewhat below the metal d-orbitals, the bonding π-LGOs have about the same energy as the metal d-orbitals, and the anti-bonding π*-LGOs have an energy significantly higher than the 4p orbitals. We can again construct MOs symmetry type by symmetry type until the MO diagram is complete. We can start with the symmetry type A_{1g}. We see there is only one σ-LGO that interacts with the 4s and the $3d_{z^2}$ which also have A_{1g} symmetry. That leads to a bonding, an approximately non-bonding, and anti-bonding a_{1g} MO which we can label $1a_{1g}$, $2a_{1g}$, and $3a_{1g}$, respectively. Next, we can for instance look at the B_{2g} orbitals. There is one d-orbital that has that symmetry, as well as two LGOs. The interaction is almost only with the bonding B_{2g} LGO because the energies are similar. This leads to a bonding and an anti-bonding π-MO with B_{2g} symmetry. The anti-bonding LGO is too high in energy and it does not significantly interact. Therefore we can draw it with the same energy into the MO-diagram. Now let us go to the B_{1g} orbitals. There is a metal d-orbital with B_{1g} symmetry, and a σ-LGO with B_{1g} symmetry. This produces a bonding and anti-bonding MO with B_{1g} symmetry. Now let us go to the E_g orbitals. There are two E_g metal d-orbitals, two E_g π-LGOs and two E_g π*-LGOs. Again, the π*-LGOs are too far off in energy, so that the bonding interaction is mostly between metal orbital the π-LGOs. This leads to a pair of bonding MOs and a pair of anti-bonding MOs. The π*-LGOs can be drawn with unchanged energy into the MO-diagram. The 4p orbitals of the metal have symmetry types, we have not considered yet: A_{2u} and E_u. Let us begin with the E_u orbitals. There are two σ-E_u LGOs, two π-E_u-LGOs and two π*-E_u LGOs. Overall we have four pairs of E_U-orbitals, and we would therefore expect four pairs of e_u-MOs. We can make the approximation that there will be a bonding one, a weakly bonding one, a weakly anti-bonding one, and a strongly anti-bonding one. We can label them $1e_u$, $2e_u$, $3e_u$, and $4e_u$, respectively. The $4e_u$ has almost only contributions from the anti-bonding π*-E_U LGOs due to energy arguments, therefore it is only connected to these via a dotted line, and not to the other E_u orbitals. Now to the A_{2u} orbitals: There is a π and a π*-orbital of A_{2u} symmetry that can be combined with the 4p A_{2u} orbitals. This leads to three A_{2u} MOs overall, one bonding, one approximately non-bonding, and one anti-bonding one. Now we have used all metal d-orbitals. We notice that there are still some LGOs that we have not used. These are the π and π* A_{2g} and the B_{2u} LGOs. They remain non-bonding can be drawn accordingly in the MO diagram.

We now need to fill the electrons into the MO-diagram. Firstly, there are the σ-electrons to consider. There are overall eight electrons stemming from the four occupied σ-LGOs. We can fill these eight electrons into the four MOs with the lowest energy. These are the $1a_1$, the $1e_u$ and the $1b_1$. These are all bonding MOs explaining the four σ-bonds within the complex. We can call these four orbitals the σ-bonding orbitals. Next we need to consider the electrons in the π-LGOs. There are overall eight of these orbitals containing 16 electrons. We must fill these electrons into the eight MOs of the next-higher energies. These are the $1b_{2g}$, the $1e_g$, the $1a_{2u}$, the $2e_u$, the $1b_{2u}$, and the $1a_{2g}$ orbitals. We see that these orbitals are either bonding or non-bonding, and thus overall the ligand π-electrons get stabilized due to the π-interactions with the ligand. We can call these orbitals the π-bonding molecular orbitals. Finally we need to look at the metal d-electrons. We assume Ni as the metal with Ni in the oxidation state +2 and d^8 electron configuration. We need to fill these eight electrons into the four next higher-energy MOs. This fills the $2b_{2g}$, the $2e_g$, and the $2a_{1g}$, orbitals which are either non-bonding or anti-bonding. This means that the metal electrons are overall destabilized. This behavior is consistent with the cyano-ligand acting as a π-donating ligand. We understand from this why square planar complexes prefer 16 over 18 electrons and disobey the 18 electron rule. If we had two more electrons then these would need to go into the energetically much higher $2a_{2u}$ orbitals. The energy gap between the $2a_{2u}$ and the $2a_{1g}$ orbital is significantly higher than that between the $1a_{1g}$, the $2b_{2g}$, and the $2e_g$ orbitals. Overall we can call the $2a_u$, the $2a_{1g}$, the $2e_g$, and the $2b_g$ orbitals the metal d-orbitals in a square planar ligand field. In a square planar ligand field we have three Δ_s. Δ_3 is the energy difference between the $2b_{2g}$ and the $2e_g$ orbitals, Δ_2 is the energy difference between the $2e_g$ and the $2a_{1g}$ orbitals, and Δ_1 is the energy between the $2a_{1g}$ and the $2a_{2u}$ orbitals. Δ_1 is much larger than the other two. It also almost always larger than the spin-pairing energy, therefore square planar complexes are almost always low-spin complexes.

Overall, we see that an MO diagram can become very complex even for a relatively simple molecule of relatively high symmetry. It should be noted that for MO diagrams as complex as this one, it is not possible any more determine the exact order of the energy levels just by qualitative inspection, and without exact computations. Nonetheless, you can see that it is possible to readily understand a complex MO diagram by following the symmetry-adapted linear combination of atomic orbitals approach. We just need to go through the symmetry types step by step and construct MOs by combining orbitals of the the same symmetry type until the process is completely. We have now reached the end of the chapter on ligand field theory.

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Concept Review Questions Chapter 7

Concept Review Questions

Section 1

1. What should a good theory be able to do?

2. What should a good bonding theory be able to do?

3. What is the major conceptual difference between valence bond theory of main group compounds with regular covalent bonds vs. coordination compounds with dative bonds?

4. Valence bond theory cannot explain optical properties of molecules. Explain why.

5. Explain the concept of crystal field theory.

6. Explain why the energy of the d_{z2} and the d_{x2-y2} orbitals in the octahedral crystal field is higher than that of the d_{xz}, the d_{yz}, and the d_{xy} orbitals.

7. Explain why the the d_{z2} and the d_{x2-y2} orbitals have the exactly the same energy in the octahedral crystal field.

8. Explain why the energy of the d_{xz}, the d_{yz}, and the d_{xy} orbitals are decreased by exactly 2/5 Δ_o.

9. Explain why the energy of the d_{xz}, the d_{xy}, and the d_{yz} orbitals are higher than the energy of d_{z2}, d_{x2-y2} orbitals in the tetrahedral crystal field.

10. Explain why the energies of the d_{xz}, the d_{xy}, and the d_{yz} orbitals are exactly the same in the tetrahedral crystal field.

11. Explain why the tetrahedral crystal field is smaller than the octahedral crystal field ($\Delta_T = 4/9\Delta_O$).

12. Which orbital energies increase and which ones decrease when an octahedral crystal field tetragonally distorts (elongated octahedra)? Explain why.

13. Explain why octahedral complexes of d^9 ions frequently distort tetragonally.

14. Explain the relationships between a tetragonally distorted octahedral crystal field and a square planar crystal field.

15. Explain why crystal field theory can explain why complexes with d^8 ions are often square planar.

16. Explain how crystal field theory explains high-spin and low-spin complexes.

17. Explain why crystal field theory can make statements about the electronic spectra of complexes.

18. What is meant by the spectrochemical series?

19. What is the relationship between molecular orbital theory and ligand field theory?

20. Describe the steps involved to construct a molecular orbital diagram in ligand field theory?

21. Why can ligand field theory explain the magnetic properties of coordination compounds?

22. Why is ligand field theory able to explain electronic spectra?

23. What are the relationships between crystal field theory and ligand field theory?

24. What is a π-donating ligand and what is a π-accepting ligand?

25. How do π-donating ligands change Δ_O in octahedral complexes? Explain briefly.

26. How do π-accepting ligands change Δ_O in octahedral complexes? Explain briefly.

27. How does ligand field theory explain the spectrochemical series?

28. How does ligand field theory explain that there are no low spin complexes for tetrahedral compounds?

29. What is the strength of π-bonding in tetrahedral complexes vs. octahedral complexes? Explain why.

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Homework Problems Chapter 7

Homework Problems

Section 1

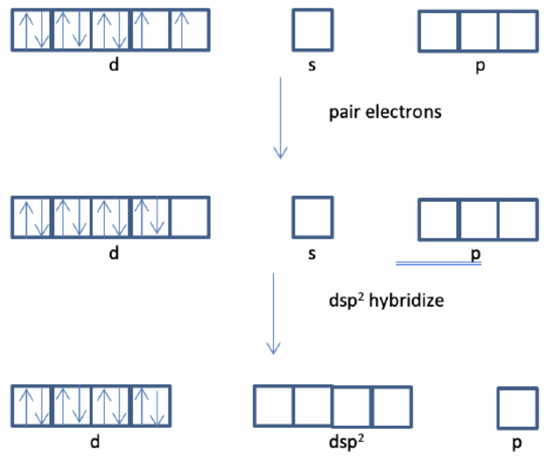
Exercise 1

Decide if valence bond theory is able to explain shapes of the following species. Explain your decision using appropriate electron box diagrams.

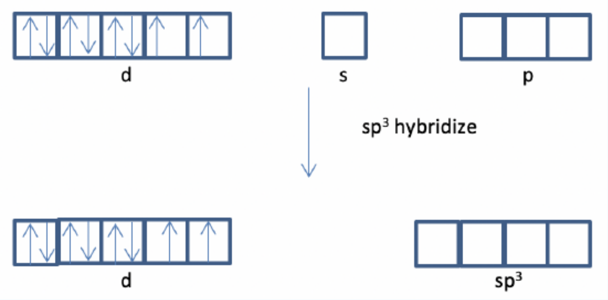
a. $PdCl_4^{2-}$ (square planar)
b. $NiCl_4^{2-}$ (tetrahedral)
c. $Cr(CO)_6$ (octahedral)
d. $ZnCl_4^{2-}$ (tetrahedral)
e. $Ag(NH_3)_2^+$ (linear)
f. $Au(PPh_3)_3^+$ (trigonal planar)
g. $Cu(NH_3)_4^{2+}$ (tetrahedral)

Answer

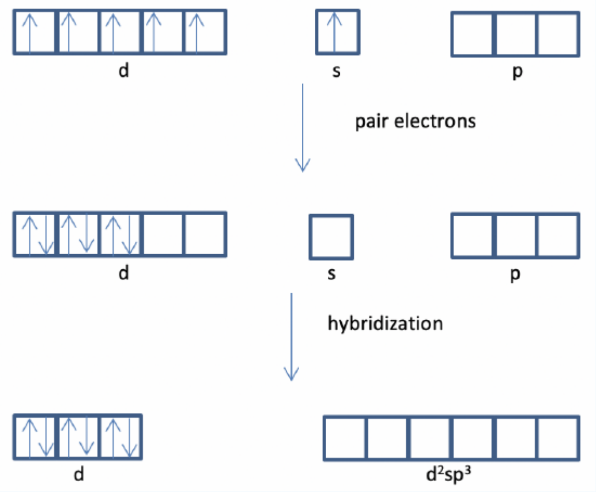
a) No. One would need to move an electron from one half-filled d-orbital into the other half-filled d-orbital. This would require to reverse the spin of the electron which is quantum-mechanically not allowed.



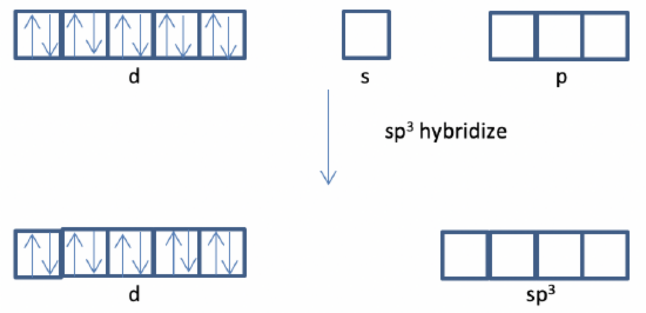
b) Yes, because s and p orbitals are empty and can be sp^3 hybridized:



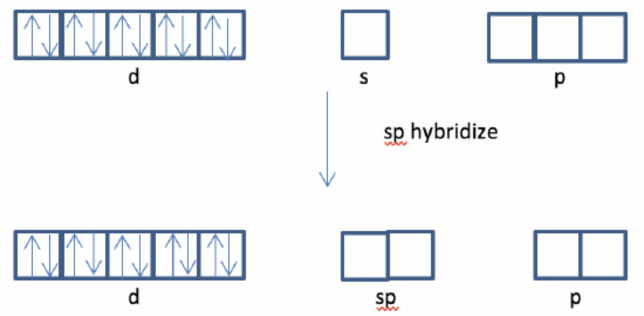
c) No, because one would need to move and spin-pair one s and two d electrons under spin-reversal.



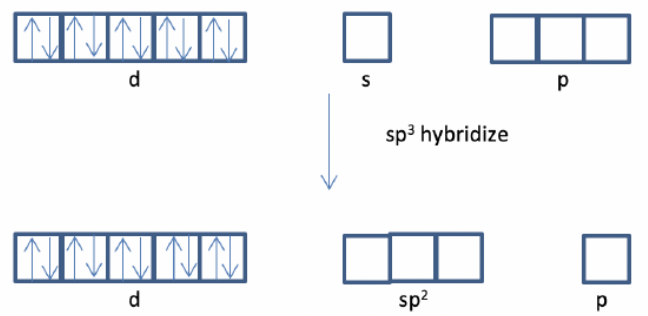
d) Yes, because empty s and p orbitals are available for hybridization



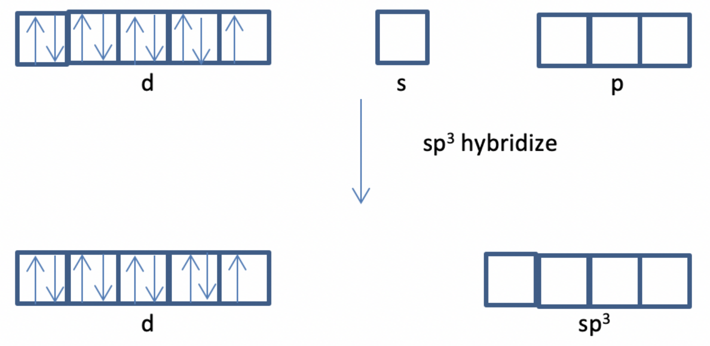
e) Yes, because empty s and p orbitals are available for sp hybridization which is able to explain linear shape.



f) Yes, because empty s and p orbitals are available for sp^2 hybridization which is able to explain trigonal planar shape.



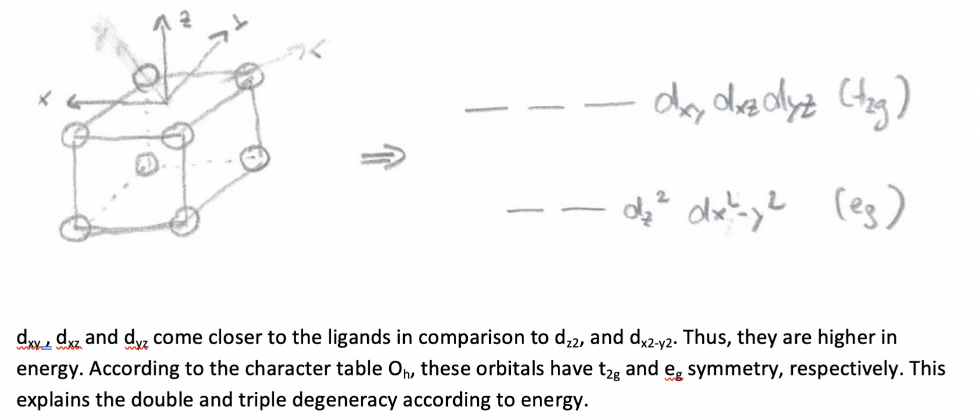
g) Yes, because empty s and p orbitals are available for sp^3 hybridization which is able to explain tetrahedral shape.



Exercise 2

We assume a hypothetical cubic crystal field. Predict how the energies of the metal d-orbitals split in this crystal field? Explain your decision briefly. What is the symmetry of these orbitals?

Answer



d_{xy}, d_{xz} and d_{yz} come closer to the ligands in comparison to d_{z2}, and d_{x2-y2}. Thus, they are higher in energy. According to the character table O_h, these orbitals have t_{2g} and e_g symmetry, respectively. This explains the double and triple degeneracy according to energy.

Exercise 3

The octahedral crystal field Δ_O for a d^4 metal complex is larger than the spin pairing energy. How many unpaired electrons would you expect in this complex?

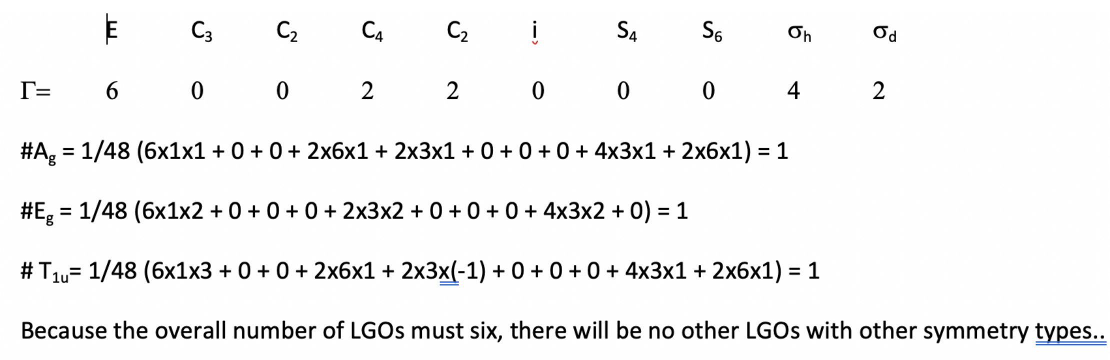
Answer

I would expect two unpaired electrons.

Exercise 4

Verify by applying the symmetry adapted linear combination of atomic orbitals (SALC) method that the ligand group orbitals suitable for sigma bonding have the symmetry types A_g, E_g, and T_{1u} for an octahedral complex.

Answer



	E	C_3	C_2	C_4	C_2	i	S_4	S_6	σ_h	σ_d
Γ=	6	0	0	2	2	0	0	0	4	2

$\#A_g$ = 1/48 (6x1x1 + 0 + 0 + 2x6x1 + 2x3x1 + 0 + 0 + 0 + 4x3x1 + 2x6x1) = 1

$\#E_g$ = 1/48 (6x1x2 + 0 + 0 + 0 + 2x3x2 + 0 + 0 + 0 + 4x3x2 + 0) = 1

T_{1u}= 1/48 (6x1x3 + 0 + 0 + 2x6x1 + 2x3x(-1) + 0 + 0 + 0 + 4x3x1 + 2x6x1) = 1

Because the overall number of LGOs must six, there will be no other LGOs with other symmetry types..

Exercise 5

Can the 4p orbitals of a period 4 transition metal also make pi-bonding with the ligands in an octahedral complex? Explain your decision briefly?

Answer

Yes, the 4p orbitals have T_{1u} symmetry which is suitable to make pi-bonding with the T_{1u} pi-ligand group orbitals.

Exercise 6

Which of the following ligands would you expect to be π-acceptors? Explain your decision briefly.

a) NO^+

b) H^-

c) Cl^-

d) CH_3^-

Answer

Only NO^+, because it is the only ligand that has π^*-orbitals.

Exercise 7

A general trigonal planar complex of the composition M(CN)3 is given. How many π- and π^* orbitals of the ligands will be involved in the π-bonding?

Answer

3*4=12 orbitals

Exercise 8

The energies of the metal d orbitals of the above complex are -24 eV. The energies of the π-orbitals of the ligand are -27 eV, the energies of the π*-orbitals are -10 eV. Would you expect the ligand to act as a π-donor or as a π-acceptor? Why?

Answer

It would act as a pi-donor, because the energy of the pi-orbitals is much closer to the energy of the metal d orbitals.

Exercise 9

Two octahedral complexes MX_6 and MY_6 are given. The energy of the ligand HOMOs suitable for sigma-bonding is about the same, but the orbital overlap between the metal and the ligand Y is significantly greater than the orbital overlap between the ligand X and the metal. For which complex would you expect a larger Δ_O?

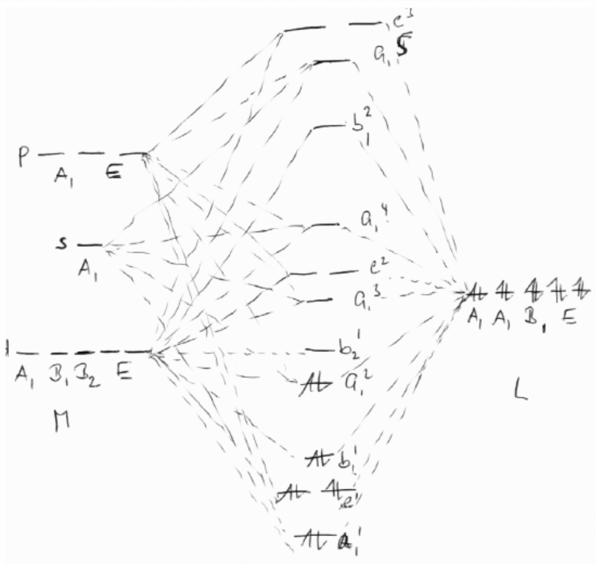
Answer

Δ_O will be greater for the orbitals with the ligand Y. This is because the stronger interactions raise the energy of the e_g^* orbitals, and thus the energy difference between these orbitals and the t_{2g} orbitals becomes larger.

Exercise 10

Construct a qualitative molecular orbital diagram of a square pyramidal complex using the symmetry adapted linear combination of atomic orbitals approach. Consider sigma-bonding only.

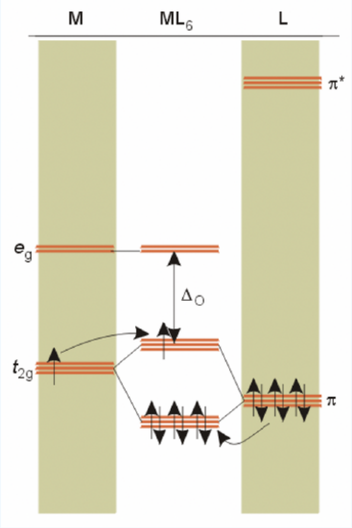
Answer



Exercise 11

Strong π-donating ligands lead to a decrease of the octahedral ligand field Δo. Illustrate this by sketching the relevant part of MO diagram.

Answer



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CHAPTER OVERVIEW

8: Coordination Chemistry IV - Electronic Spectra

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8.1: Microstates and Terms

A closer look at electronic spectra

Let us take a closer look at optical absorption spectra, also called electronic spectra of coordination compounds. We have previously argued that ligand field theory can predict and explain the electronic spectra. However, only in relatively few cases ligand field theory (LFT) is sufficient to explain the spectra. For example the hexaaqua nickel (2+) complex ion is an octahedral d^8-complex ion. According to ligand field theory the metal d-orbitals in an octahedral field are the t_{2g} and the e_g–orbitals (Fig. 8.1.1). Six electrons are in the t_{2g} orbitals, and two electrons are in the e_g orbitals. Ligand field theory would predict that there is one electron transition possible, namely the promotion of an electron from a t_{2g} into an e_g orbital. This process would be triggered by the absorption of light whereby the wavelength of the light would depend on the Δ_o between the t_{2g} and the e_g orbitals. Overall, this should lead to a single absorption band in the absorption spectrum of the complex. We can check this prediction by experimentally recording the absorption spectrum of the complex (Fig. 8.1.1).

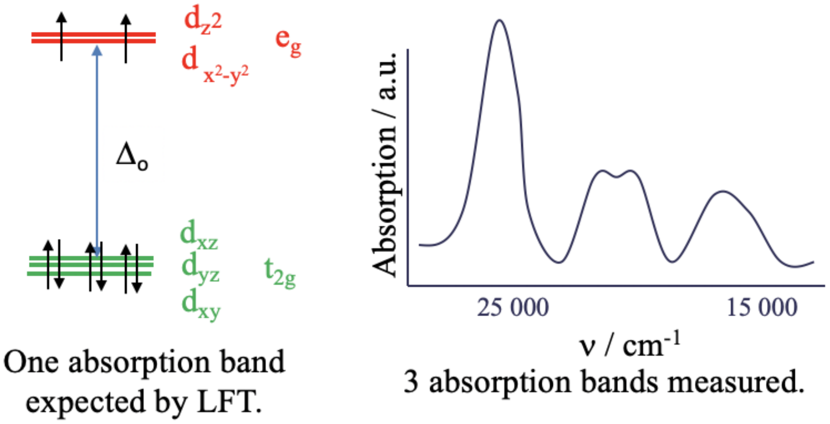


Figure 8.1.1 Electron transition according to LFT and actual absorption spectrum of the hexaaqua nickel (2+) complex ion. Attribution: E.R. Schofield.

What we find is that the absorption spectrum is far more complex than expected. Instead of just a single absorption band there are multiple ones. Obviously, ligand field theory is unable to explain this spectrum. The question is why? The answer is: LFT assumes that there are no electron-electron interactions. However, in reality there is repulsion between electron in d-orbitals and this has an effect on their energy.

Effect of Electron-Electron Interactions

Let us look closer at this. To simplify the problem let us consider a d^2 ion in an octahedral ligand field first (Fig. 8.1.2).

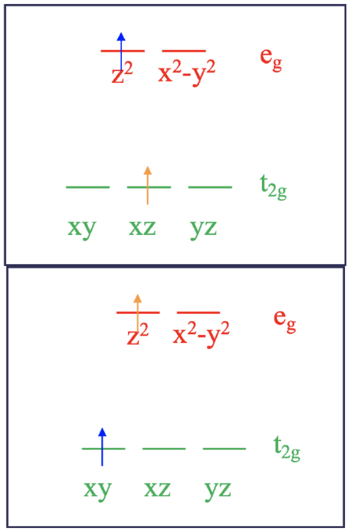


Figure 8.1.2 Two microstates with different energies for a d^2 ion in an octahedral ligand field

According to ligand field theory, the two electrons would be in the t_{2g} orbitals when in the ground state. For instance, they could be in the xy, and the xz orbitals. This is called a microstate. It is called a microstate of a state because there are other combinations of orbitals possible. For example, the ground state would also be realized if the two electrons were in the xz and the yz orbitals. This combination would be another microstate associated with the ground state electron configuration. Upon excitation using light the electron in the d_{xy} orbital could be promoted into an e_g orbital, which could be either the d_{z^2} or the $d_{x^2-y^2}$. Those two possibilities reflect to different microstates associated with the excited state (Fig. 8.1.2). Let us assume the electron goes into the d_{z^2} orbital. In this microstate one electron would be in the d_{xz} orbital and the other one in the d_{z^2} orbital. Now there us another possibility how to excite an electron. We could assume that not the d_{xy} electron is promoted into the d_{z^2} orbital, but the d_{xz} electron gets promoted. In this case, we would realize a microstate in which one electron in the d_{xy} orbital and the other one in the d_{z^2} orbital.

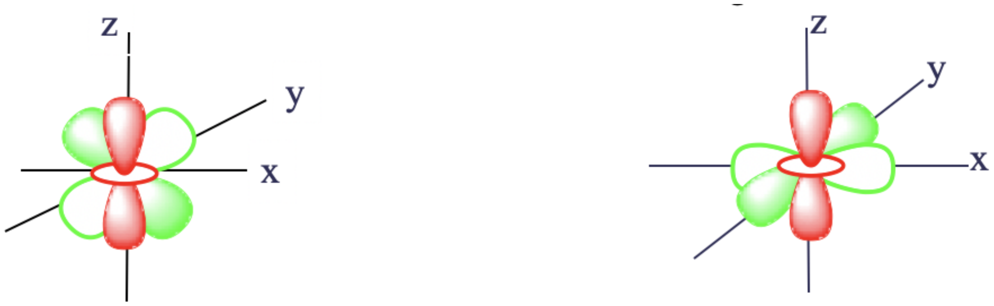
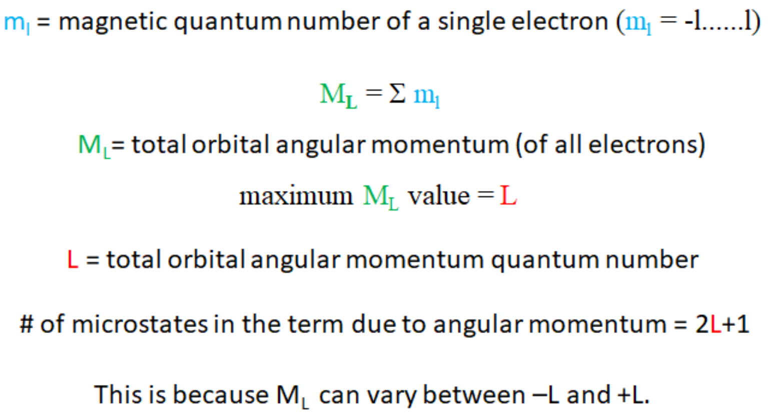


Figure 8.1.3 Orbitals associated with the two different microstates

Now let us compare the two cases. Ligand field theory would argue that both excited microstates have the same energy. However, in fact they do not. Why? That is because the electrons in the two excited microstates interact differently. This becomes plausible when considering the orbital shapes (Fig. 8.1.3). The d_{xz} orbital has electron density on the z-axis, while the d_{xy} orbital has not. Therefore, electrons in these orbitals would be expected to interact differently with an electron in a d_{z^2} orbital which has most of its electron density on the z-axis. As a result, the two excited microstates do not have the same energy. This means that in order to promote the electron into the two different microstates we need different amounts of energies. Thus, the complex would absorb light with more than just one wavelength. This is in contrast to what ligand field theory predicts. What will we need to do in order to correctly predict how many absorption bands we get? The answer is, we must find all possible microstates for the d^2 electron configuration and group those together which have the same energy. A group of microstates with the same energy is called a term. The number of electron transitions can then be predicted from the number of terms.

Russell Saunders Coupling of Electrons in Free Ions

Our task is now to find all the terms for the octahedral complex with d^2 electron configuration. To simplify matters let us first look at a free d^2 ion. A free ion is an ion which is not coordinated by any ligand.



m_l = magnetic quantum number of a single electron ($m_l = -l......l$)

$$M_L = \Sigma\, m_l$$

M_L = total orbital angular momentum (of all electrons)

maximum M_L value = L

L = total orbital angular momentum quantum number

# of microstates in the term due to angular momentum = $2L+1$

This is because M_L can vary between –L and +L.

Figure 8.1.4. Relationships between angular momentum, total orbitals angular momentum, total angular orbital quantum number, and associated number of microstates of a term

The energy of the microstates depends on the quantum numbers m_l and m_s of the electrons (Fig. 8.1.4 and Fig. 8.1.5). This is because these quantum numbers of determine how the electrons interact. This is also called the Russell-Saunders coupling of electrons. Let us first see how the quantum number m_l of the electrons influences the term symbol. The term is determined by the microstate with the highest quantum number M_L, whereby M_L is the sum of the quantum numbers m_l of the individual electrons. The maximum M_L value is also called the total orbital angular momentum quantum number L. The L value also tells you how many microstates belong to a term due to these magnetic interactions. The number of microstates is 2L+1. This is because M_L can vary between –L and +L. So for instance if L=2, M_L can adopt the values -2, -1, 0, +1, and +2, and that translates to 2L+1=5 microstates.

The quantum number L alone does not define the term yet. In addition, we must also consider the interaction of the spins of the electrons (Fig. 8.1.5).

$$m_s = \text{spin quantum number of a single electron}$$

$$M_S = \Sigma\, m_s \text{ (Total spin angular momentum)}$$

$$\text{maximum } M_s \text{ value} = S$$

$$S = \text{ total spin angular momentum quantum number}$$

$$\#\text{ of microstates in the term due to spin} = 2S+1$$

Figure 8.1.5 Relationships between the spin quantum number of the electron, the total spin angular quantum number, and the number of associated microstates.

The spin quantum number m_s of a single electron can be either +1/2 or -1/2. When the spins of the electrons interact, their spin quantum numbers add up, defining the total spin angular momentum M_s. The microstate with the maximum M_s value defines the total spin angular momentum quantum number S. The number of microstates due to the spin-spin interactions that belong to the term is 2S+1. This is also called the spin multiplicity (Fig. 8.1.6).

$$\#\text{ of overall microstates in the term} = (2L+1)\ 2S+1$$

Figure 8.1.6 Equation for the overall number of microstates from L and S.

Overall the term has (2L+1)(2S+1) microstates. The total orbital angular quantum number L and the total orbital spin quantum number S define the term symbol (Fig. 8.1.7).

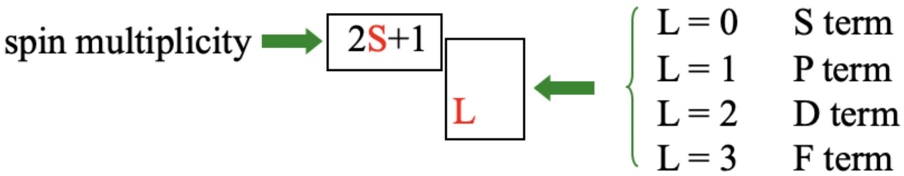
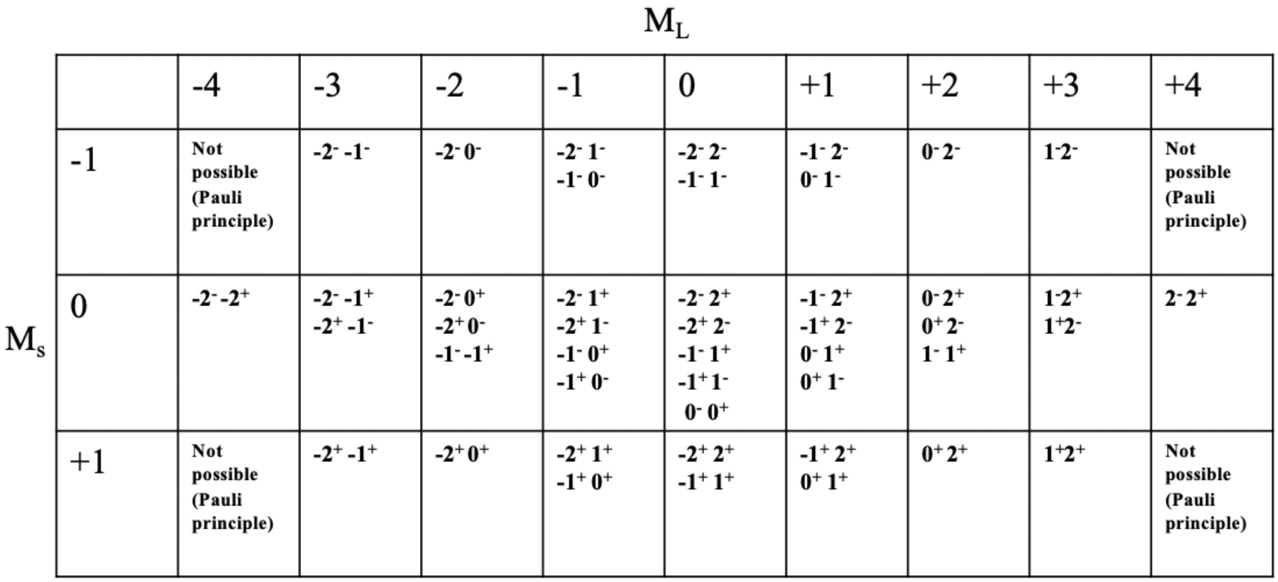


Figure 8.1.7 Term symbols. Attribution: E.R. Schofield.

When L=0 we have an S term, when L=1, we have a P term, when L=2, we call it a D term, and when L=3 we call it an F term. These symbols are chosen in analogy to the symbols s, p, d, and f for orbitals. The spin multiplicity 2S+1 is then written as a superscript in front of the letter defined by L. This gives the overall term symbol for a term. We call a term with a spin multiplicity of 1 a singlet term, when 2S+1=2, we call the term a doublet term. A term with a spin multiplicity of three is called a triplet term, one with a spin-multiplicity of 4 a quartet term, and so forth.

Microstates for a free d^2 ion

What are the possible microstates and the overall number of microstates for a free ion with d^2-electron configuration? We can express this in a so-called microstate table (Fig. 8.1.8).



M_L

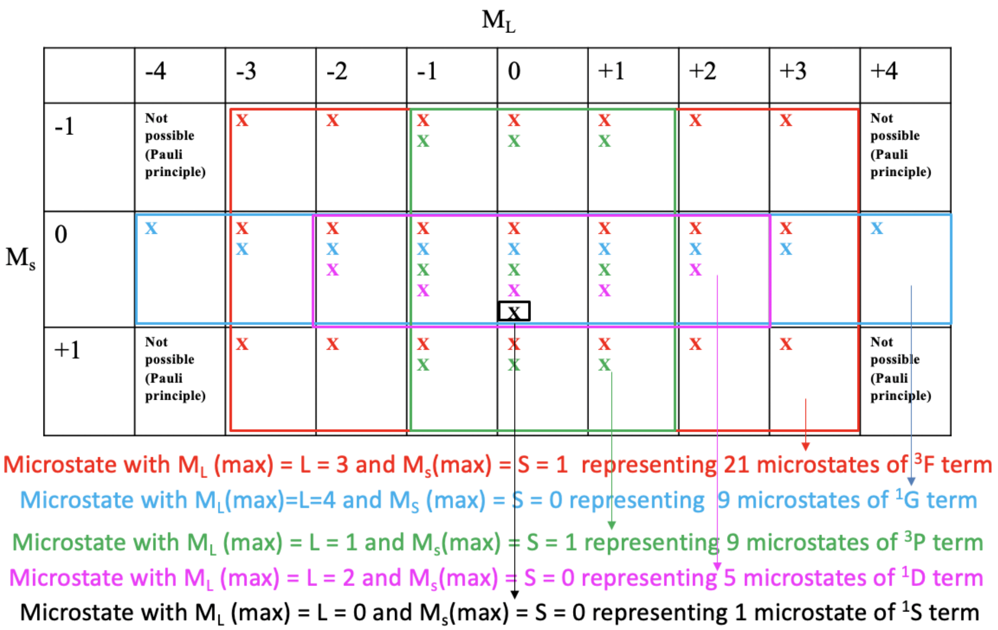
M_s

	-4	-3	-2	-1	0	+1	+2	+3	+4
-1	**Not possible (Pauli principle)**	$-2^{-}\,-1^{-}$	$-2^{-}\,0^{-}$	$-2^{-}\,1^{-}$ $-1^{-}\,0^{-}$	$-2^{-}\,2^{-}$ $-1^{-}\,1^{-}$	$-1^{-}\,2^{-}$ $0^{-}\,1^{-}$	$0^{-}\,2^{-}$	$1^{-}2^{-}$	**Not possible (Pauli principle)**
0	$-2^{-}\,-2^{+}$	$-2^{-}\,-1^{+}$ $-2^{+}\,-1^{-}$	$-2^{-}\,0^{+}$ $-2^{+}\,0^{-}$ $-1^{-}\,-1^{+}$	$-2^{-}\,1^{+}$ $-2^{+}\,1^{-}$ $-1^{-}\,0^{+}$ $-1^{+}\,0^{-}$	$-2^{-}\,2^{+}$ $-2^{+}\,2^{-}$ $-1^{-}\,1^{+}$ $-1^{+}\,1^{-}$ $0^{-}\,0^{+}$	$-1^{-}\,2^{+}$ $-1^{+}\,2^{-}$ $0^{-}\,1^{+}$ $0^{+}\,1^{-}$	$0^{-}\,2^{+}$ $0^{+}\,2^{-}$ $1^{-}\,1^{+}$	$1^{-}2^{+}$ $1^{+}2^{-}$	$2^{-}\,2^{+}$
+1	**Not possible (Pauli principle)**	$-2^{+}\,-1^{+}$	$-2^{+}\,0^{+}$	$-2^{+}\,1^{+}$ $-1^{+}\,0^{+}$	$-2^{+}\,2^{+}$ $-1^{+}\,1^{+}$	$-1^{+}\,2^{+}$ $0^{+}\,1^{+}$	$0^{+}\,2^{+}$	$1^{+}2^{+}$	**Not possible (Pauli principle)**

Figure 8.1.8 d^2 electron configuration microstate table

You can see the microstate table for the d^2 electron configuration depicted above. Each column represents a possible value M_L. For the d^2 configuration, M_L can adopt values from -4 to +4, hence there there are 9 columns. Each row represents possible M_s value. For the d^2 electron configuration, M_s can vary between +1 and -1. +1 means both electrons have the spin +1/2, 0 means one electron has the spin +1/2 and the other one has the spin -1/2. The M_s value of -1/2 is adopted when both electrons have the spin -1/2. Now we can combine each M_s value with each M_L value which defines a particular field in the table. You can see that some fields are empty due to the Pauli principle. For example, the field for M_L=-4 and M_s=-1 is not filled because in this case both electrons would have the same quantum numbers, namely m_l=-2, and m_s =-1/2. We can further see that for some fields only one combination of electrons is possible, while for others there are multiple. For example, for the field with M_L=4 and M_s=0 there is only one combination of electrons possible. You can see the symbol "2^-2^+" in this field. This means that the first electron has an m_l value of 2 and and a spin of -1/2 and the second electron also has an m_l value of 2 and an m_s value of +1/2. The most populated field is the field for M_L=0 and M_s=0. There are overall five microstates with that combination of M_L and M_s values. If we count the overall number of microstates in the table then we arrive at the number 45. This is consistent with what we would expect according to the formula #microstates = (2L+1)(2S+1). In our example L=4 and S = 1, and thus the number of microstates is ((2x4)+1) ((2x1)+1)=45. In general for a d^n electron configuration with *n* d-electrons the number of microstates is (10!)/((10-n)!n!).

One useful property of a microstate table is that we can derive the terms and term symbols for a particular electron configuration from it. For simplification sake, we indicate a possible microstate in the table just by an "x". Then we draw the largest possible rectangular box into the microstable that contains only fields with at least one possible electron combination (Fig. 8.1.9).



		M_L							
		-4	-3	-2	-1	0	+1	+2	+3	+4
M_s	-1	Not possible (Pauli principle)	X	X	X X	X X	X X	X	X	Not possible (Pauli principle)
	0	X	X X	X X X	X X X X	X X X X X	X X X X	X X X	X X	X
	+1	Not possible (Pauli principle)	X	X	X X	X X	X X	X	X	Not possible (Pauli principle)

Microstate with M_L (max) = L = 3 and M_s(max) = S = 1 representing 21 microstates of ^{3}F term

Microstate with M_L(max)=L=4 and M_S (max) = S = 0 representing 9 microstates of ^{1}G term

Microstate with M_L (max) = L = 1 and M_s(max) = S = 1 representing 9 microstates of ^{3}P term

Microstate with M_L (max) = L = 2 and M_s(max) = S = 0 representing 5 microstates of ^{1}D term

Microstate with M_L (max) = L = 0 and M_s(max) = S = 0 representing 1 microstate of ^{1}S term

Figure 8.1.9 Deriving the terms and term symbols for the d^2 electron configuration from the microstate table

You can see that the largest possible box is the red box drawn (Fig. 8.1.9). This box contains the microstates that belong to the first term of the electron configuration d^2. The number of microstates is equal to the number of fields within the red box. That makes 7x3=21 microstates. What is the term symbol for this term? In order to answer this question we need to find the microstate in the red box that has the highest M_L and the highest M_s value. You can see that it is the one with M_L=3 and M_s = 2. Thus, L=3 and S=1. This defines the term as a ^{3}F term because 2S+1 = 3, and L=3 corresponds to the term symbol F. This term is a triplet term. Note that a triplet term also includes microstates with paired spins. Overall seven of the 21 microstates have M_s=0.

Next, we look what is the next-largest rectangular box we can draw, and which contains microstates we did not consider yet. We can see that the blue box contains nine fields equaling nine microstates. The microstate within this box that has the highest M_L and M_s values is the one with M_L=4 and M_s=0. This defines a ^{1}G term. This is a singlet term. Note that a singlet term ONLY has microstates with paired spins (M_s=0).

There is another rectangular box which also contains nine microstates. It is the green one. The microstate with the highest M_L and M_s values is the one with M_L=1 and M_s=1. Thus, L =1, and 2S+1=3 which defines a ^{3}P term. Note that despite this being a triplet term, the term also contains three microstates with paired spins.

The next-largest box is the purple one containing five fields and five microstates. What is the term with the highest M_L and M_s values? It is the one with M_L=2 and M_s=0. This means that L=2 and S=0 which defined a ^{1}D term. This is a singlet term. A singlet term contains only microstates with paired spins. There is one microstate left we did not consider thus far. It is one with M_L=0 and M_s = 0. These are the highest M_L and M_s values because there is no other microstate. Thus, this term contains only one microstate and the term symbol is ^{1}S. Now we have found all terms and term symbols.

The Energy of Terms

What is the relative energy of the terms? First we need to consider Hund's rule which states that the higher the spin multiplicity, the lower the energy of a term.

Rule 1: The higher spin multiplicity the lowest energy (Hund's rule).

We therefore first need to rank the terms with regards to the spin multiplicity. Secondly, we need to consider the value of the total orbital angular momentum quantum number L. The higher the value the lower the energy for the term. This means that the energy of terms decreases from S, to P, to D, to F.

Rule 2: When the spin-multiplicity is the same then the energy increases with increasing L value.

Note that this is contrary to orbital energies which increase from s, to p, to d, to f. Therefore, what would be the expected energy sequence for the terms associated with a d^2 free ion? It should be: $^3F<^3P<^1D<^1S$. However, the actual energy sequence is $^3F<^1D<^3P<^1G<^1S$. This means that, unexpectedly, the ^1D term is energetically lower than the ^3P term. We can understand from this is why Hund's rule is a called a rule and not a law because there are exceptions. In most but not all cases a triplet term has a lower energy than a singlet term.

Free-Ion Terms of Other d Electron Configurations

What are the term of the other d-electron configurations (Fig. 8.1.10)?

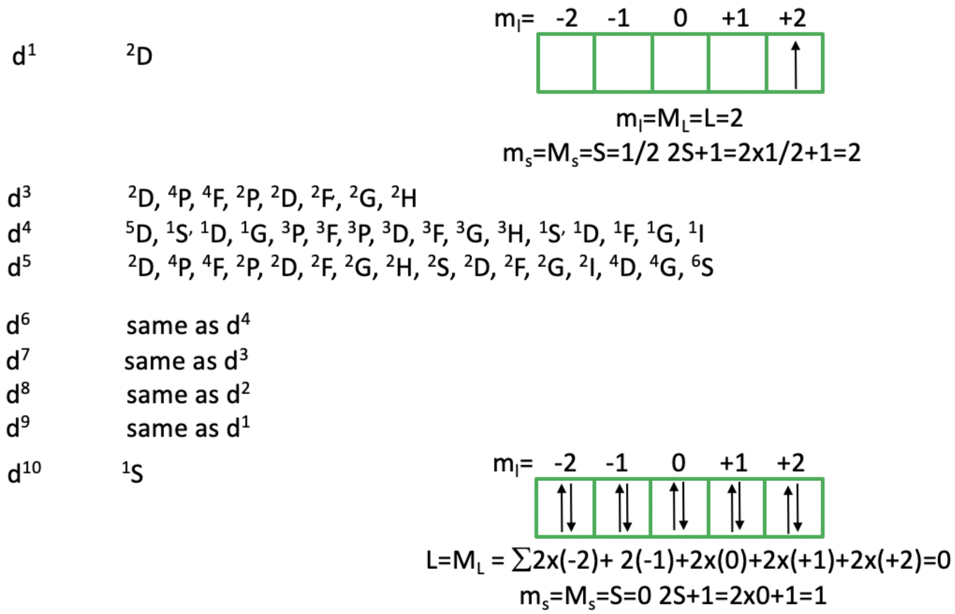


Figure 8.1.10 Terms for all d-electron configurations.

You can see above that there is only a single ^2D term for a d^1 free ion. How can we explain this term? Because there is no other electron, there are no electron-electron interactions, and thus every possible microstate has the same energy. This explains why there is only one term. Why is it ^2D? The term symbol is determined by the microstate with the highest M_L value and the highest M_s value. This is achieved when we fill the electron spin-up into the d-orbital with $m_l=2$ (Fig. 8.1.10). Because there is only one electron, $m_l=M_L=L=2$. This makes the term a D term. It is a doublet term because M_s is maximized when the electron is spin-up or $m_s=+1/2$. Thus, $m_s=M_s=S=1/2$. $2S+1=2\times1/2+1=2$, thus we have a doublet state. How many microstates are associated with this term? $(2L+1)(2S+1)=5\times2=10$. What does that mean? This means that we can fill the one electron that we have either spin-up or spin down in any of the five d-orbitals. All the 10 microstates are energetically equal.

When you go from d^2 to d^3 to d^4 to d^5 you can see that the number of the terms increases dramatically. This is because with increasing electron numbers the number of possible permutations increases, and thus the number of possible microstates. As a consequence, there are more terms. From d^6 to d^{10} the number of terms decreases again. The terms for d^6 are the same as the terms for d^4, the d^7-terms are identical to those for d^3, the d^8-terms are the same as the d^2 and the d^9-terms are the same as terms for the electron configuration d^1. Why is that? This is because unoccupied states in orbitals permute the same way as occupied ones do. For instance, in the d^3 electron configuration has three occupied states and seven unoccupied ones, while the d^7 electron configuration has seven occupied states and three unoccupied ones. The d^{10} electron configuration has also only one term with the term symbol ^1S (Fig. 8.1.10). Can we explain this? In the d^{10} electron configuration, there is no way to permute the electrons, hence there is only one microstate possible. In this microstate L=0. Why is that? When we sum up the individual m_l-values of the ten electrons, then this sum is $M_L = L = 2\times(-2)+2(-1)+2\times(0)+2\times(+1)+2\times(+2)=0$. The spin multiplicity of the term is 1 because all electrons are paired $(2S+1=(2\times0)+1=1)$. Hence, we have a singlet ^1S term.

Spin-Orbit Coupling

We have still not considered all electron-electron interactions. In addition to the interaction between the angular magnetic momenta, and the magnetic interactions between the spins, there are also magnetic interactions between the angular momenta and the spins. This is called the spin-orbit coupling. It is expressed by an additional quantum number J. J can run from L+S to L-S.

$$J = L+S \text{ ....} L-S$$

The quantum number J is added as a subscript behind letter describing the term. So a full term symbol is described as $^{2S+1}L_J$. Spin-orbit coupling may lead to additional terms depending on L and S (Fig. 8.1.11).

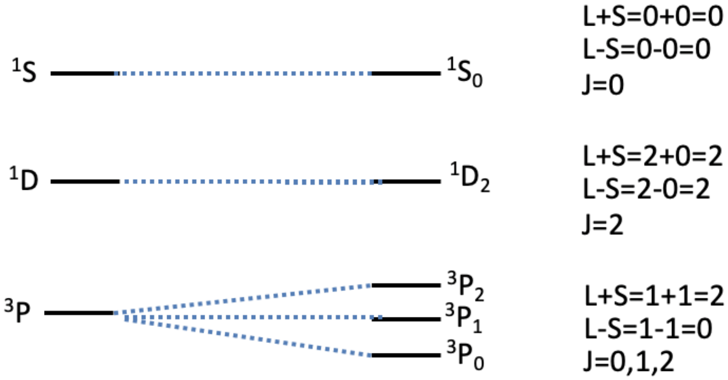


Figure 8.1.11. Spin-orbit coupling in ^1S, ^1D, and ^3P terms.

For instance, for a ^3P term, S=1, and L=1. Thus J can adopt values between L+S=1+1=2 and L-S=1-1=0. Thus, overall J can adopt the values, 0, 1, 2. This means a ^3P term splits into three terms due to the spin-orbit coupling. Their term symbols are $^3P_0$, $^3P_1$, and $^3P_2$. Their energy increases with increasing quantum number J. ^1S and ^1D terms on the other hand to do not split into additional terms. For a ^1S term L+S=0+0=0, and L-S=0-0=0. The full term symbol is $^1S_0$. For the ^1D term, L+S=2+0=2 and L-S=2-0=2, thus the full term symbol is $^1D_2$. Overall, the energy differences between terms due to J are very small, in the order of tens of wavenumbers, and orders of magnitudes smaller than energy differences due to RS-coupling, which are typically in the order of tens of thousands of wavenumbers. Thus, we usually ignore the effect of J when interpreting electronic spectra.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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8.2: Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions

Term Splitting of Terms in an Octahedral Field

Octahedral field

S-term → A_{1g}

P-term → T_{1g}

D-term → $E_g + T_{2g}$

F-term → $T_{1g}+T_{2g}+A_{2g}$

Figure 8.2.1: Octahedral field term splitting

Thus far we have only considered free ion terms, that means terms without the presence of a ligand field. Let us next think about the influence of an octahedral field on a term. Terms are wavefunctions, just like orbitals, and therefore they behave like orbitals in a ligand field. D-orbitals split into t_{2g} and e_g orbitals in an octahedral ligand field. A D-term behaves similarly. It splits into T_{2g} and E_g terms. P-orbitals are triple-degenerate having T_{1g} symmetry in the point group O_h and do not split in energy. P-terms have the same symmetry and also do not split. We can call a P-term in an octahedral ligand field a T_{1g} term. Following analogous arguments, S terms become A_{1g} terms. F terms do split in energy like f-orbitals and become T_{1g}, T_{2g}, and A_{2g} terms. Overall, the presence of the octahedral field increases the number of terms from four to seven (Fig. 8.2.1). It is easy to see that the ligand field leads to many states, and many potential electron transitions. Thus, we would expect quite complicated spectra. For other ligand fields, the terms also behave analogously to orbitals. For, instance in a tetrahedral field D-terms split into E and T_2 terms, and so forth.

Term Splitting for octahedral d^2 metal complexes

Now let us think about how the term energies of our free d^2-ion changes when placed in an octahedral ligand field, depending on the ligand field strength. We can express this by a correlation diagram (Fig. 8.2.2). In a correlation diagram, we plot the energies of the terms relative to the field strength.

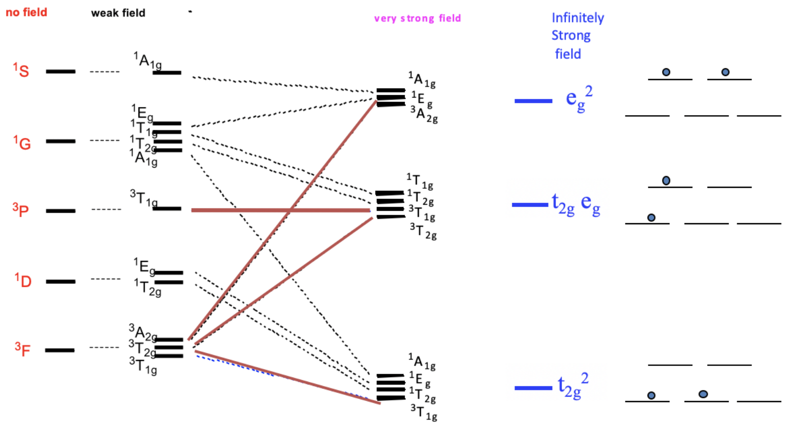


Figure 8.2.2 Correlation diagram

On the left side we plot the terms without any field according to their energies. In the case of a d^2 ion, the energies are $^3F<^1D<^3P<^1G<^1S$. Next, we plot the relative energies in a weak octahedral ligand field, and label the terms according to their symmetry. We can see that the D, F, and G terms split in energy, while the S and P terms do not. Because of the weak field, energy differences are very small. Now let us increase the ligand field strength continuously, until we have reached a very strong ligand field. We see that some of the terms move up in energy, while other terms move down as the ligand field increases. For example, two of the three terms resulting from the F-terms increase in energy while one decreases. It is also possible that a term does not change its energy. For example, the $^3T_{1g}$ term from the ^3P term does not change its energy. In very strong ligand field there are three groups of terms that have similar energy. In the hypothetical case of an infinitely strong ligand field, the terms that belong to a particular group become identical in energy. In this case, there are only three states for the electrons possible. The field is considered so strong so that the energy associated with electron-electron interactions become negligible compared to the energy of the field. The electrons behave as though there were no electron-electron interactions. Therefore, we can call the lowest energy state the t_{2g}^2 state. It is equivalent to the state of the two electrons being in the t_{2g} orbitals. The second state is called the $t_{2g}e_g$ state. It is equivalent to the state of one electron being in the t_{2g} and one electron being in the e_g orbitals. The third state is called the e_g^2 state, which is equivalent to the state with both electrons in the e_g^2-orbitals.

Selection Rules

In most cases, the ligand field strength is in between the very weak and very strong case, and thus, we could expect very complicated spectra. Fortunately, nature does not make things quite as complicated, because not all possible electron transitions are quantum-mechanically allowed. The allowed transitions are defined by two rules: The spin selection rule and the Laporte rule.

The **spin selection rule** states that transitions with $\Delta S = 0$ are allowed.

The spin selection rule states that only transitions are allowed in which the total spin quantum number S does not change. When S does not change also the spin multiplicity does not change. Thus, electron transitions are only allowed for transitions that do not involve a change in spin multiplicity. For example, it would be allowed to excite an electron from a triplet term to another triplet term, but not from a triplet term to a doublet or singlet term.

The **Laporte rule** states that the transitions with the change of parity, g → u or u → g are allowed.

The Laporte rule state that transitions are only allowed when there is a change of parity. This means a transition from a gerade (g) to an ungerade (u)-term and vice versa is possible, but not a transition from a g-term to another g-term, or the transition from a u-term to another u-term. For example, the transition from a T_{2g} to a T_{1u} term would be allowed, but not the transition from a T_{2g} to a T_{1g} term.

Tanabe-Sugano diagram of a d^2 octahedral complex

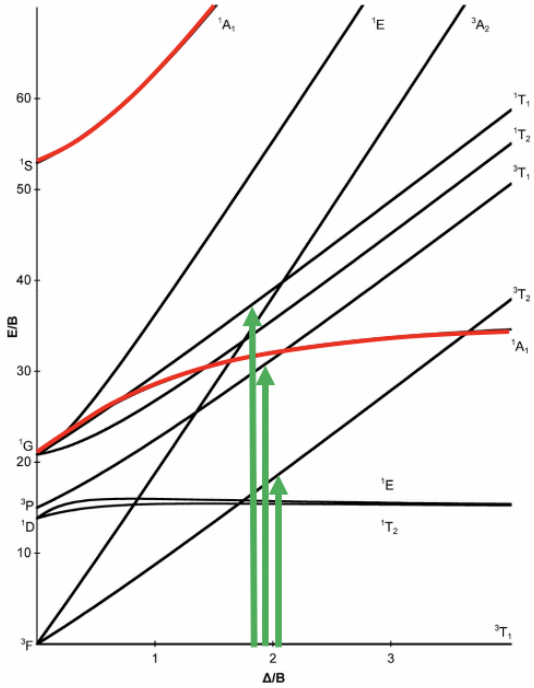


Figure 8.2.3 Tanabe-Sugano diagram of a d^2 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...o_diagrams.png)

A particular correlation diagram is the Tanabe-Sugano diagram (Fig. 8.2.3). It is illustrated here for an octahedral d^2 complex. The difference to the previously discussed correlation diagram is that the energy of the ground state is plotted horizontally, and the energy of all other terms are plotted relative to that. In the case of the d^2 electron configuration, the $^3T_{1g}$ term is the ground term and is plotted as a horizontal line. We can see that the ligand field strength on the x-axis is given in units of B, and the energy of the terms is also given in units of B. B is a so-called Racah parameter, that is a quantum-mechanical energy unit for the electromagnetic interactions between the electrons. It is chosen because it provides “handy” numbers.

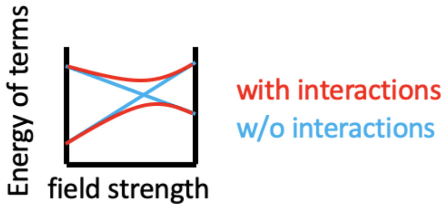


Figure 8.2.4 Origin of line-bending in Tanabe-Sugano diagrams.

You can see that some lines in the diagram are bent, and some are straight. Bending of lines occurs when two terms interact with each other because they are close in energy and have the same symmetry. This is again an analogy to orbitals. Like orbitals interact when they have the same symmetry type and similar energy, also terms interact when they have the same symmetry and the similar energy. Without taking their interactions into account, their energies can cross when the energy of term A declines and the energy of term B increases with increasing field strength (Fig. 8.2.4). The closer the terms come to the point where they cross, the stronger their interactions, because their energies become more and more similar. The interactions lead to the fact that the terms "bend away" from each other, leading to bent curves. This means that curves for two terms of the same symmetry type will bend away in a Tanabe-Sugano diagram and never cross. For example the terms for the two $^1A_{1g}$ terms bend away from each other and do not cross.

Next, let us think about which electron transitions would be allowed under the consideration of the spin selection and the Laporte rule. We notice that in the symmetry types the “g” for gerade has been omitted (Fig. 8.2.3). This is a common simplification made in the literature. We have to remind us that all the terms in the diagram are “g” terms. What does this mean for the allowance of electron transitions? It means that no electron transition would be allowed, and that would imply that the complex could not absorb light. The Laporte selection rule however does not hold strictly. It only says that the probability of the electron-transition is reduced, however, not forbidden. This means that an absorption band that disobeys the Laporte rule will have lower intensity compared to one that follows the Laporte rule, but it can still be observed. The spin-selection rule, however, holds strictly, and transitions between terms of different spin multiplicity are strictly forbidden, meaning that they have near zero probability to occur. Overall, we can therefore excite an electron from the $^3T_1$ ground state to other triplet terms, namely the $^3T_2$ term, and the $^3A_2$ term (Fig. 8.2.3).

Tanabe-Sugano diagram of d^3 octahedral complexes

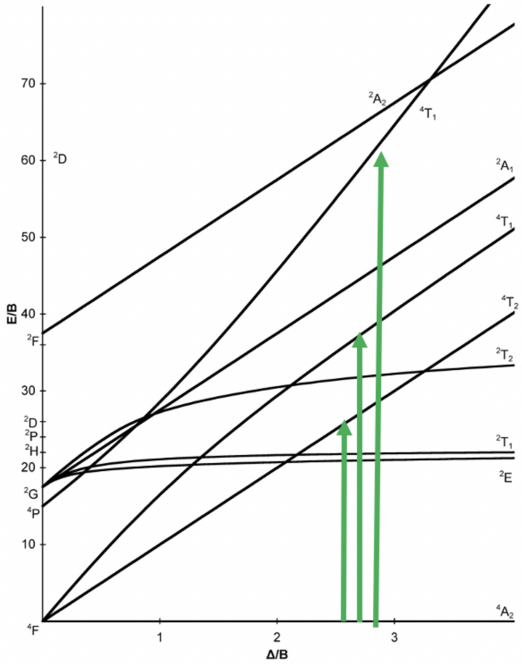


Figure 8.2.7 Tanabe-Sugano diagram of d^3 octahedral complexes (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Now, let us have a look at the Tanabe-Sugano diagram of a d^3 ion in an octahedral ligand field (Fig. 8.2.7). What is the ground term? We can see the term designation on the horizontal line reads "$^4A_2$", therefore this term is the ground term. How many electron transitions from the ground state should we expect? To answer this question we need to count the number of other quartet terms. There is the $^4T_2$, the $^4T_1$, and another $^4T_1$. Thus, there are overall three electron transitions possible. Can we understand why the ground state is a quartet term?

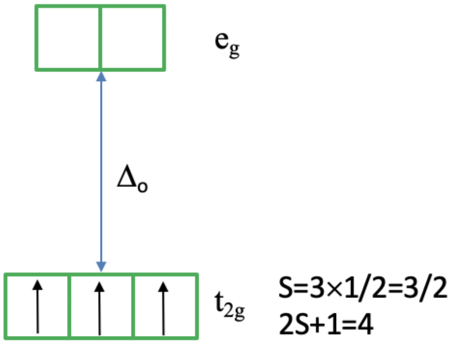


Figure 8.2.8 d-orbitals in an octahedral ligand field for the electron configuration d^3

It helps to consider how we would fill the electrons into the d-orbitals for the electron configuration d^3. All three electrons would be filled spin-up in the t_{2g} orbital following Hund's rule (Fig. 8.2.8). Because each electron has the spin +1/2 the total spin of all three electrons is 3x1/2=3/2. Thus, the spin multiplicity is ((3x3/2)+1)=4. Note that the microstate we have drawn is actually only one of the (2L+1)(2S+1) microstates. S=3x1/2=3/2, but what is L? You can see one the left side of the diagram that the $^4A_2$ term originated from a ^4F term. This means L=3, and (2L+1)((2S+1)=7x4=28. This means that there are actually 27 other microstates that have the same energy as the microstate that we drew. Why did we draw this microstate in favor of the others? This is because this microstate is the state with the maximum M_L (=L) and M_s (=S) values determining the term symbol.

Tanabe-Sugano diagram of d^4 octahedral complexes

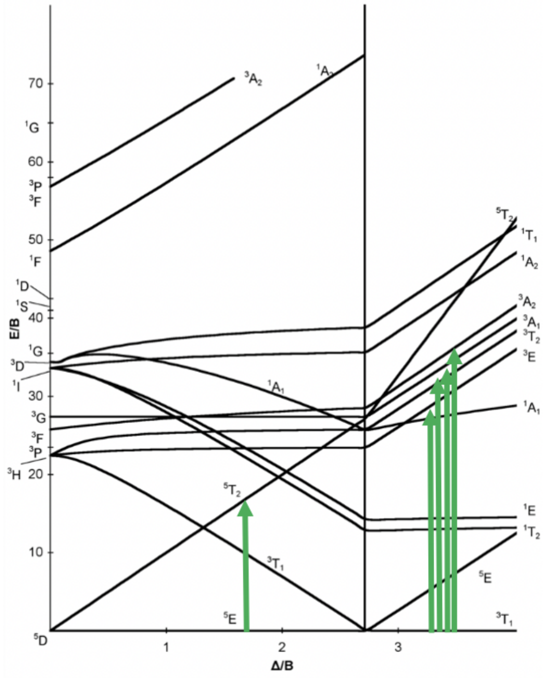


Figure 8.2.9 Tanabe-Sugano diagram of the d^4 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Now let us look at the Tanabe-Sugano diagram of a d^4 octahedral complex. You can see that this diagram is separated into two parts separated by a vertical line. The line indicates the ligand field strength at which the complex changes from a high spin complex. At lower ligand field strengths, the ground term is a ^5E term. At higher field strength the ground term is a ^3T term.

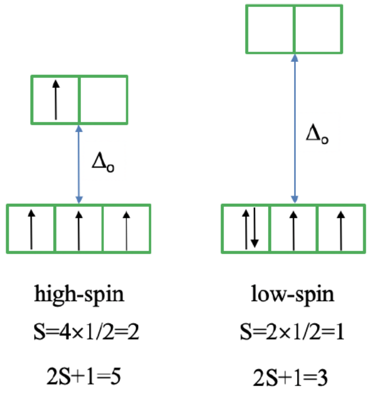


Figure 8.2.10 d-orbitals in the octahedral ligand field for the electron configuration d^4

We can rationalize this again by drawing the orbital box representation of the d-orbitals in the octahedral ligand field. In the high spin state, there are four unpaired electrons, thus S=4x1/2=2, and 2S+1=5. In the low spin state, there are two unpaired electrons, and thus S=2x1/2=1, and 2S+1=3. This explains the quintet and the triplet nature of the high and low spin ground terms. Note again, that the two microstates represented by the orbital box diagrams (Fig. 8.2.10) are not the only microstates that have the respective energy. They are only the "representative" microstates because the have the maximum M_L and M_S values.

How many electron transitions are possible from the ground term? For a high spin complex there is only one because the is only one other quintet term, namely the $^5T_2$ term. For the low spin complex, there are five transitions because there are five other triplet terms.

Tananbe-Sugano diagram of d^5 octahedral complexes

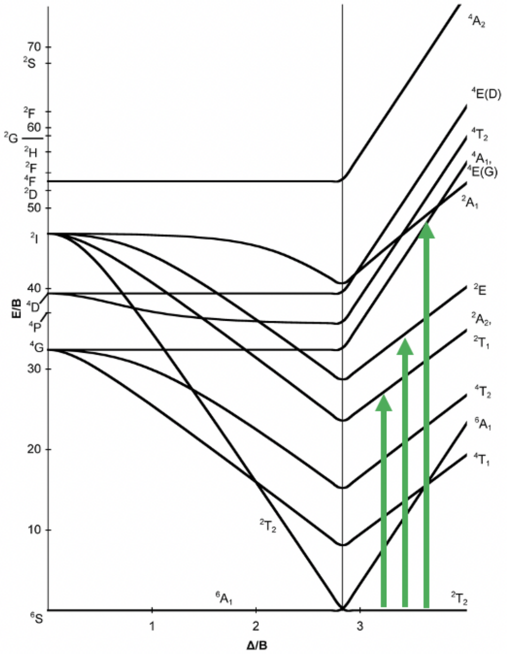


Figure 8.2.11 Tanabe-Sugano diagram of the d^5 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Also the Tanabe-Sugano diagram of a d^5 octahedral complex is divided into two parts separated by a vertical line (Fig. 8.2.11). The left part reflects the high spin and the right part the low spin complex.

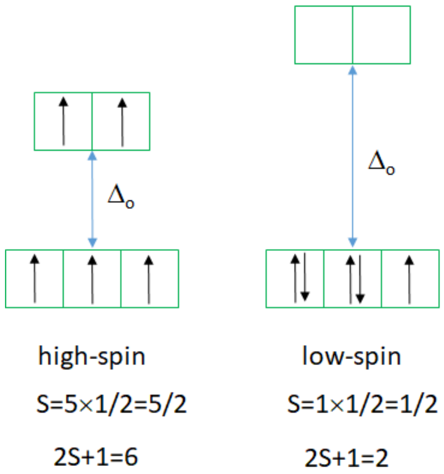


Figure 8.2.12 d-orbitals in the octahedral ligand field for the electron configuration d^5

The high spin ground state is a sextet term, and the low spin ground state is a doublet term. We can understand the sextet and doublet nature of the terms when considering that the associated electron box diagram have five and one unpaired electrons respectively. S=5x1/2=5/2 and 2S+1=6 for the high spin term, and S=1x1/2=1/2 and 2S+1=2 for the low spin term. What are the possible electron transitions from the ground state? For the high-spin complex there is no other sextet term, meaning that there is no electron transition possible. Hence, high-spin octahedral d^5-complexes are colorless. An example is the hexaaqua manganese (2+) complex. A solution of this complex is near colorless, only very slightly pinkish. The slight color is because also spin-forbidden transitions can occur, albeit at a very low probability. For a d^5-low spin complex there are three additional doublet states, and thus there are three electron transitions possible.

Tanabe-Sugano diagram of d^6 octahedral complexes

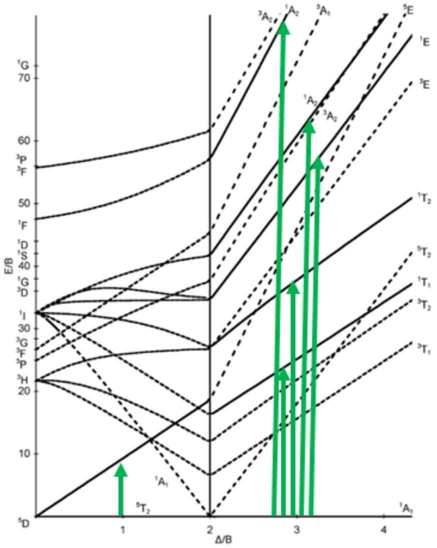


Figure 8.2.13 Tanabe-Sugano diagram of the d^6 octahedral complex (Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

The next diagram is the one for the d^6 electron configuration (Fig. 8.2.13). Again, the diagram is separated into parts for high and low spin complexes. You can see dotted lines in the diagram. They indicate the terms that have a different spin multiplicity than the ground term. This way we can more easily see how many electron transitions are allowed.

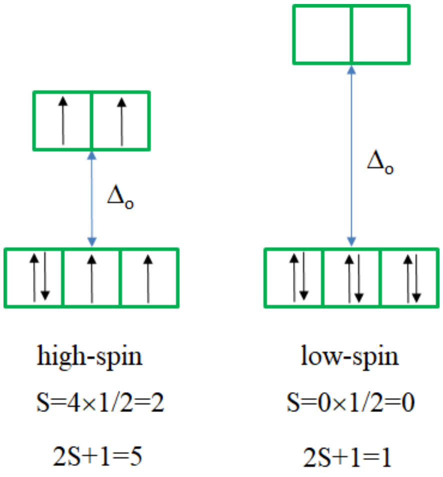


Figure 8.2.14 d-orbitals in the octahedral ligand field for the electron configuration d^6

The ground term for the high-spin complex is the quintet $^5T_2$ term. It is a quintet term because four electrons in the d-orbitals are unpaired, and two are paired. The value for S is thus 4x1/2=2, and the spin multiplicity is 2S+1=5. The ground term for the low spin complex is a $^1A_1$ term. It is a singlet term because all electrons are paired, and thus S=0, and 2S+1=1. How many electron transitions are there for the high-spin complex? There is only one because the ^5E term is the only other quintet term. There are five transitions possible for the low-spin case because there are five additional singlet terms.

Tanabe-Sugano diagram of d^7 octahedral complexes

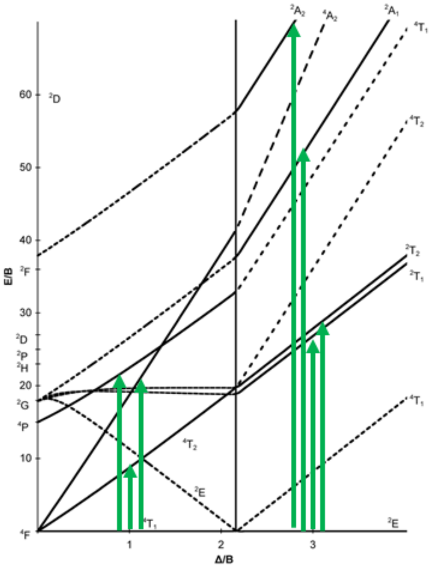


Figure 8.2.15 Tanabe-Sugano diagram of the d^7 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Next, let us look at the Tanabe-Sugano diagram of a d^7 octahedral complex (Fig. 8.2.15). In this case, the high spin complex has a $^4T_1$ ground term, and the low spin complex has a ^2E ground term.

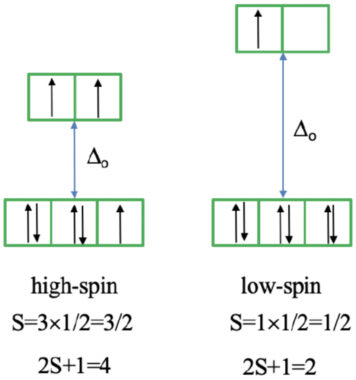


Figure 8.2.16 d-orbitals in the octahedral ligand field for the electron configuration d^7

The microstate that "represents" the high spin ground term has three unpaired electrons, hence the spin quantum number S=3/2 and the spin multiplicity is 2S+1=4. The microstate that represents the low spin ground term has one unpaired electron, an S value of ½, and a spin multiplicity of 2. There are three other quartet terms, and four other doublet terms, hence there are three electrons transitions for the high-spin complex, and four for the low spin complex.

Tanabe-Sugano diagram of d^8 octahedral complexes

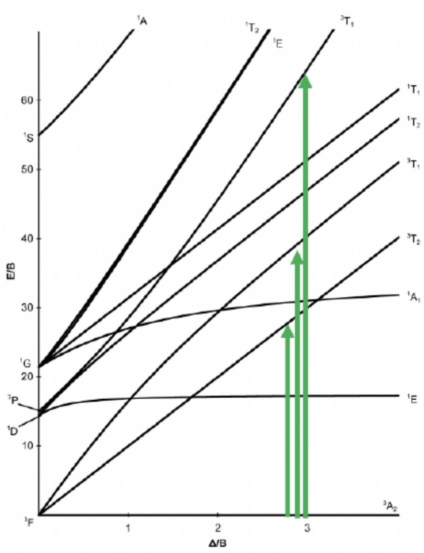


Figure 8.2.17 Tanabe-Sugano diagram of the d^8 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Now let us look at an octahedral complex with d^8 electron configuration. For this electron configuration, there are no high and low spin complexes possible, therefore, the Tanabe-Sugano diagram is no longer divided into two parts (Fig. 8.2.17).

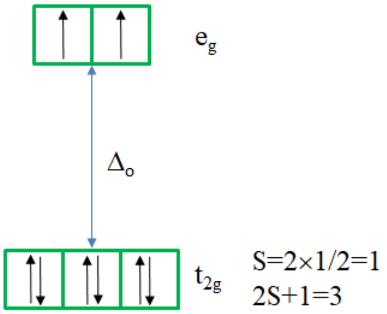


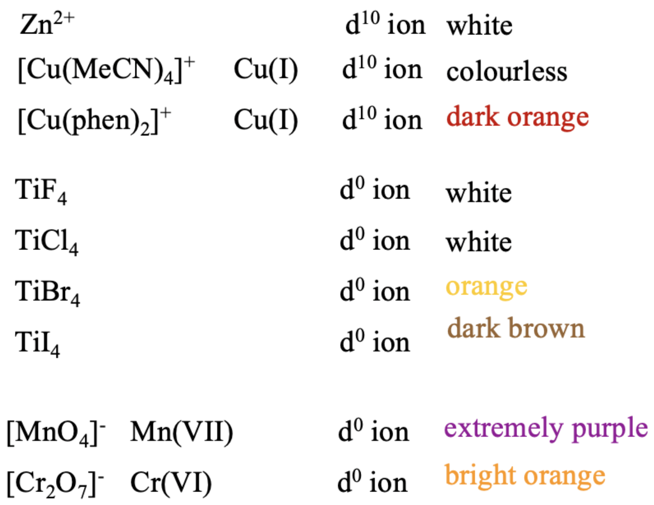
Figure 8.2.18 d-orbitals in the octahedral ligand field for the electron configuration d^8

There is a single ground term of the type ${}^3A_2$. It is a triplet state because the microstate representing the term has two unpaired electrons in the e_g orbitals (Fig. 8.2.18). Thus, S=2x1/2=1, and the spin multiplicity is 2S+1=2. How many electron transitions would you expect? There are three other triplet states, namely the ${}^3T_2$ and two ${}^3T_1$ terms. Therefore, there are three electron transitions possible.

We could also ask: Are there Tanabe-Sugano diagrams for d^1, d^9, and d^{10}? For, d^1 there are no electron-electron interactions, thus the simple orbital picture is sufficient. The ${}^2D$ term splits into T_{2g} and E_g terms, and there is only one electron transition possible. The d^9 electron configuration is the "hole-analog" of the d^1 electron configuration. It has also just one ${}^2D$ term which splits into a T_{2g} and an E_g term in the octahedral ligand field. Therefore, also in this case there is only one electron transition from the T_{2g} into the E_g term possible. In the case of d^{10} all microstates are filled with orbitals, and there is only the ${}^1S$ term which does not split in an octahedral ligand field. Therefore, there are no electron transitions in this case.

Finally, it should be mentioned that it is also possible to construct Tanabe-Sugano diagrams for other shapes such as the tetrahedral shape, but we will not discuss these further here.

Charge Transfer Transitions



Zn^{2+}		d^{10} ion	white
$[Cu(MeCN)_4]^+$	Cu(I)	d^{10} ion	colourless
$[Cu(phen)_2]^+$	Cu(I)	d^{10} ion	dark orange
TiF_4		d^0 ion	white
$TiCl_4$		d^0 ion	white
$TiBr_4$		d^0 ion	orange
TiI_4		d^0 ion	dark brown
$[MnO_4]^-$	Mn(VII)	d^0 ion	extremely purple
$[Cr_2O_7]^-$	Cr(VI)	d^0 ion	bright orange

Figure 8.2.19 Some examples of complexes with d^0 and d^{10} electron configurations, and their color. Attribution: E.R. Schofield.

We are still not done with our electronic spectra. Thus, far we have only considered transitions of d-electrons between d-orbitals, and their terms. They are called d-d transitions. However, there are also so-called charge transfer transitions possible, that are not d-d transitions. We can easily see that there must be other transitions but d-d transitions when we look at the color of d^{10} and d^0 ions. For those, the are no d-d transitions possible. Therefore, they all should be colorless. However, that is not always true. Some of these ions are indeed colorless, but some are not (Fig. 8.2.19). For example, Zn^{2+}, a d^{10} ion is colorless in complexes, but not Cu(I) which is also d^{10}. While tetrakis(acetonitrile)copper (+) is colorless, bis(phenanthrene) copper(+) is dark orange. Similar is true for d^0 ions. While TiF_4 and $TiCl_4$ are colorless, $TiBr_4$ is orange, and TiI_4 is brown. Some d^0 species are even extremely colorful, for example permanganate with Mn^{7+} which is extremely purple, and dichromate with Cr(VI) which is bright orange.

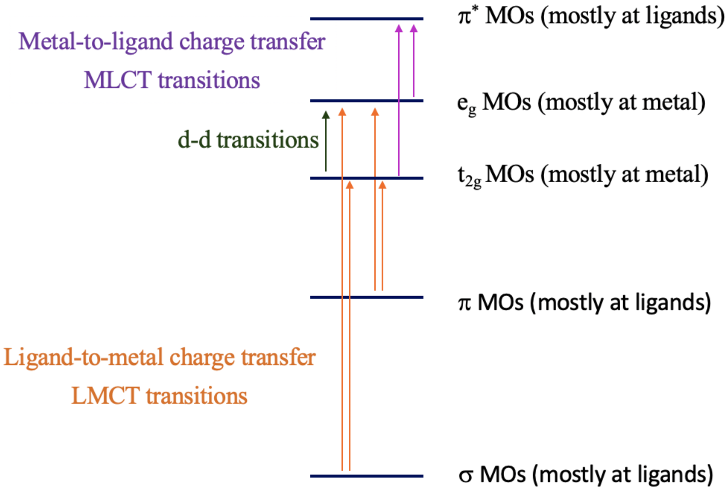


Figure 8.2.20 Charge-transfer transitions. Attribution: E.R. Schofield.

The explanation of these phenomena are charge-transfer transitions (Fig. 8.2.20). There are two types of charge-transfer transitions, the ligand-to-metal (LMCT) and the metal-to-ligand (MLCT) charge transfer transitions. For the ligand-to-metal transitions, electrons from bonding σ and π-orbitals get excited into metal d-orbitals in the ligand field, for example the t_{2g} and the e_g orbitals in an octahedral complex. If the energy difference between the σ/π-orbitals and the d-orbitals is small enough, then this electron-transition is associated with the absorption of visible light. The transition is called a ligand-to-metal transition because the ligand σ/π-orbitals are mostly located at the ligands, while the metal-d-orbitals in a ligand field are mostly located at the metal. Vice versa, the metal-to-ligand transition involves the transition of an electron from metal d-orbitals in a ligand field to ligand π*-orbitals. This essentially moves electron density from the metal to the ligand, hence the name ligand-to-metal-charge transfer transition. If the energy-difference between the ligand π* and the metal orbitals is small enough, then the absorption occurs in the visible range. Charge-transfer transitions are usually both spin- and Laporte allowed, hence if they occur the color is often very intense. How can we distinguish between d-d and charge transfer transitions? Charge transfer transitions often change in energy as the solvent polarity is varied (solvatochromic) as there is a change in polarity of the complex associated with the charge transfer transition. This can be used to distinguish between d-d transitions and charge-transfer bands.

LMCT Transitions

Can we predict when the energy windows between the bonding molecular orbitals and the metal d-orbitals are small enough so that LMCT transitions in the visible can take place? Generally, it would be desirable if the energy of the metal orbitals was as low as possible and the energy of the bonding ligand orbitals are as high as possible. The energy of metal d-orbitals decreases with increasing positive charge at the metal because the effective nuclear charge on the metal increases. This means that very high metal oxidation states favor an LMCT transition. The d-orbitals should have few or no electrons, so that electrons can be promoted into the orbitals, and orbital energy decreases because electron-electron repulsion is minimized. Examples are Mn(VII), Cr(VI), and Ti(IV). The energy of MOs from bonding ligand orbitals increases when the ligand orbitals have high energy this is typically the case for π-donor ligand with negative charge (Fig. 8.2.21).

Ligand properties	Metal ion properties
Ligand MOs: high energy	Valence orbitals: low energy
π-donor electrons	high positive charge
Negatively charged ligands	Few or no d electrons
O^{2-}, Cl^-, Br^-, I^-	Eg. Mn(VII), Cr(VI), Ti(IV)

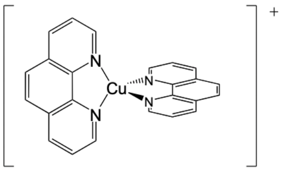
Figure 8.2.21 The properties of the metal ion and ligands suitable for LMCT transitions. MnO_4^- is deep purple due to LMCT transitions (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg) and (Attribution: Pradana Aumars / CC0 https://commons.wikimedia.org/wiki/F...entrations.jpg), respectively.

Examples of ligands are oxo- and halo ligands. This explains for example the LMCT transitions in permanganate. The Mn is in the very high oxidation state +7, and the ligands are are oxo-ligands wich are π-donors with a 2- negative charge. The transitions are both Laporte and spin-allowed leading to very high intensity of light absorption, and thus color (Fig. 8.2.21).

MLCT Transitions

What are favorable metal ion and ligand properties for a metal-to-ligand transition, then? In this case we would like to keep the energy of the metal orbitals as high as possible so that the energy difference between a metal d-orbital and a π*-orbital is minimized. This is accomplished when the positive charge at the metal ion is small, and there are many d-electrons that can repel each other, thereby increasing orbital energies, for examples Cu(I), Fig. 8.2.22.

Metal ion properties	Ligand properties
low metal ion charge	π-acceptor ligand with low-lying π* orbitals
many electrons	
Cu(I), d^{10} ion	1,10-phenanthroline, CN^-, CO, SCN^-



$[Cu(phen)_2]^+$, dark orange

Figure 8.2.22 bis(phenanthroline) copper(+). Attribution: E.R. Schofield.

The ligand should be a π-acceptor with low-lying π*-orbitals, for example phenanthroline, CN^-, SCN^-, and CO. For instance, the bis(phenanthroline) copper(+) is dark-orange and has a MLCT absorption band at 458 nm. Also, the MLCT transfer is both spin and Laporte-allowed.

It should be mentioned that some complexes allow for both metal-to-ligand and ligand to metal transitions. For example, in the $Cr(CO)_6$ complex the σ-orbitals are high enough and the π*-orbitals are low enough in energy to allow for light absorption in the visible range. Finally, also intraligand bands are possible when the ligand is a chromophore.

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Concept Review Questions Chapter 8

Concept Review Questions

Section 1

1. Explain the difference between a microstate and a state.

2. Explain what is meant by a term? Why do we need terms to explain electronic spectra?

3. What is meant by “Russell-Saunders coupling”?

3. What is the definition of the total angular momentum quantum number L?

4. What is the definition of the quantum number M_l?

5. What is the definition of the quantum number m_l?

6. What is definition of the total spin quantum number S?

7. What is the definition of the quantum number M_s?

8. What is the definition of the quantum number m_s?

9. How many microstates are associated with a term defined by a quantum number L and S respectively?

10. Which formula can be used to calculate the number of microstates with a specific d electron configuration?

11. What is meant by the spin-orbit coupling?

12. Why is the spin-orbit coupling usually neglected for electronic spectra?

13. What is the dependency between the quantum number L and the energy of a term?

14. What is the dependency between the quantum number S and the energy of a term?

15. What is meant by a “free ion term”?

Section 2

1. How do D, P, and S terms split in an octahedral and tetrahedral ligand field, respectively?

2. What is a correlation diagram?

3. What is meant by t_{2g}^2, $t_{2g}e_g$, and e_g^2 terms in octahedral complexes? Explain their relationship to molecular orbitals.

4. What is the major difference between a Tanabe-Sugano diagram and a correlation diagram?

5. Why do terms with the same symmetry never cross in Tanabe-Sugano diagrams?

6. When are lines in Tanabe diagrams straight and when are they bent?

7. What is a metal-to-ligand charge transfer (MLCT) transition?

8. What is a ligand-to-metal charge (LMCT) transfer transition?

9. Under which conditions does a MLCT transition occur in the visible range? Name one example of a complex that does MLCT.

10. Under which conditions does a LMCT transiton occur in the visible range? Name one example of a complex that does LMCT?

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Homework Problems Chapter 8

Homework Problems

Section 1

Exercise 1

How many microstates exist for the electron configurations

a) p^3

b) f^2

c) d^3

Answer

a) p^3 - 6!/((6-3)!3!) = 20

b) f^2 -14!/((14-2)!2!)=91

c) d^3 -10!/((10-3)!3!)=120

Exercise 2

What is the term symbol for the one term associated with the following electron configurations?

a) p^6

b) p^1

c) f^{14}

d) s^1

Answer

a) p^6 - ^1S

b) p^1 - ^2P

c) f^{14} - ^1S

d) s^1 - ^2S

Exercise 3

What is the number of microstates for a

a) ^5D term

b) ^4G term

c) ^2F term

Answer

a) (2L+1)(2S+1) = 5 x 5 = 25

b) (2L+1)(2S+1) = 9 x 4 = 36

c) (2L+1)(2S+1) = 7 x 2 = 14

Exercise 4

In a triplet term there are

a) only microstates with unpaired electrons.

b) only microstates with paired electrons.

c) microstates with paired and unpaired electrons.

Answer

c) microstates with paired and unpaired electrons.

Exercise 5

In a singlet term there are

a) only microstates with unpaired electrons.

b) only microstates with paired electrons.

c) microstates with paired and unpaired electrons.

Answer

b) only microstates with paired electrons.

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CHAPTER OVERVIEW

9: Coordination Chemistry V - Reactions and Mechanisms

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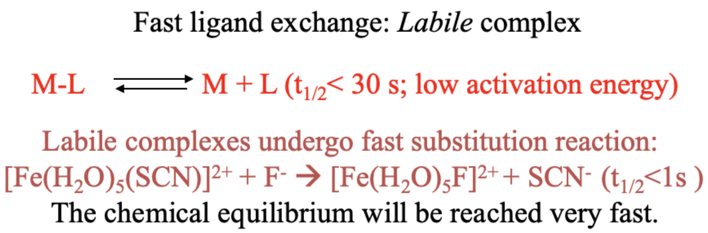
9.1: Substitution Reactions and their Mechanisms

Chemical Reactivity and Reactions of Complexes

In this chapter we will discuss the chemical reactivity and reactions of coordination compounds. First, let us briefly review what are the basic parameters that define if a reaction can be observed or not. The first parameter is the Gibbs free energy of reaction ΔG. The Gibbs free energy defines the thermodynamic driving force for the reaction. The more negative ΔG is, the greater the thermodynamic driving force. The Gibbs free energy of reaction is a measure for the difference in the stability of the reactants and products. The less stable the reactants, and the more stable the products, the more negative ΔG. The second parameter is the kinetics of a reaction. The kinetics is a measure of the speed at which a reaction occurs. The kinetics is independent from the thermodynamics. This means that even if there is a strong thermodynamic driving force for the reaction, the rate of the reaction may be extremely slow, and practically no reaction is observed. For example, graphite is thermodynamically more stable than diamond at ambient pressure and temperature, but the kinetics of the conversion at room temperature is so slow, so that practically no reaction is observed. The rate of the reaction is determined by the the activation energy that needs to be overcome to make the reaction happen. The lower the activation energy, the faster the reaction. In coordination chemistry the activation energy and the reaction rates are associated with the inertness and the lability of complexes. The more inert and the less labile a complex is the higher the activation barrier and the more slowly it reacts. The lability is the opposite of the inertness and is defined by the half-life time of a dative bond. The greater the half-life time, the more inert, and the less labile the complex.

Inert and Labile Complexes

The greater the half-life time of a dative bond, the more inert, and the less labile the complex. Where do we actually draw the borderline between a labile and an inert complex? A commonly accepted definition is that complexes with metal-ligand bond half life times of <30 s at standard conditions are considered labile complexes with a low activation energy. Those complexes undergo fast substitution reactions, and the chemical equilibrium is reached fast (Fig. 9.1.1).



Fast ligand exchange: *Labile* complex

M-L $\rightleftarrows$ M + L ($t_{1/2}$< 30 s; low activation energy)

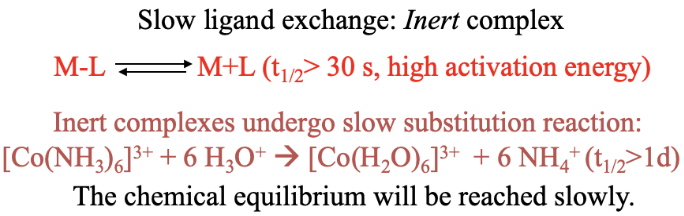
Labile complexes undergo fast substitution reaction:

$[Fe(H_2O)_5(SCN)]^{2+} + F^- \rightarrow [Fe(H_2O)_5F]^{2+} + SCN^-$ ($t_{1/2}$<1s)

The chemical equilibrium will be reached very fast.

Figure 9.1.1 Properties of labile complexes

An example is the substitution of a thiocyanato ligand in a pentaaquathiocyanato iron (2+) complex by a fluoro ligand. This substitution reaction is fast because the half-life time of the metal-ligand bond is smaller than a second.



Slow ligand exchange: *Inert* complex

M-L $\rightleftarrows$ M+L ($t_{1/2}$> 30 s, high activation energy)

Inert complexes undergo slow substitution reaction:

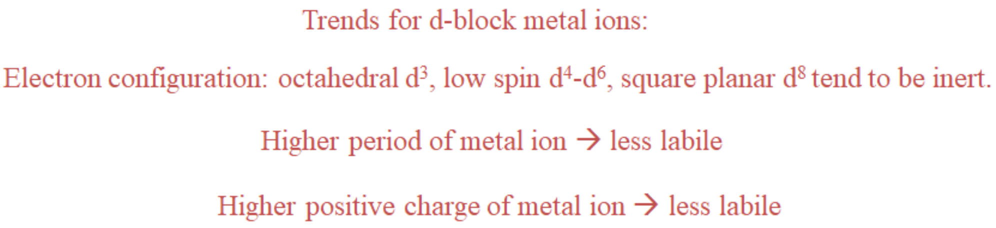
$[Co(NH_3)_6]^{3+} + 6\ H_3O^+ \rightarrow [Co(H_2O)_6]^{3+} + 6\ NH_4^+$ ($t_{1/2}$>1d)

The chemical equilibrium will be reached slowly.

Figure 9.1.2 Properties of inert complexes

If the half-life time is greater than 30s, then the complex is considered inert. For example, the hydrolysis of hexaammine cobalt (3+) is slow because the half-life time of the Co-N bond is larger than a day. The chemical equilibrium is reached only slowly (Fig. 9.1.2).

Can we predict which complexes are labile, and which ones are inert? Many factors determine this, but there are some trends we can keep in mind. For transition metals, octahedral d^3, low spin d^4-d^6, and square planar d^8 complexes tend to be inert. A second trend is that the lability decreases with the period within a group. For instance, we would expect that in group 10 the lability decreases from Ni to Pd to Pt. This is because covalency of the bonds tends to increase with increasing period due to the softer nature of higher period metals. A third trend is that higher positive charges at the metal ion lead to a decrease in liability. Metal ions with higher oxidation numbers also tend to make more covalent bonds because the high positive charge at the metal is stabilized by covalent interactions (Fig. 9.1.3).


Trends for d-block metal ions:

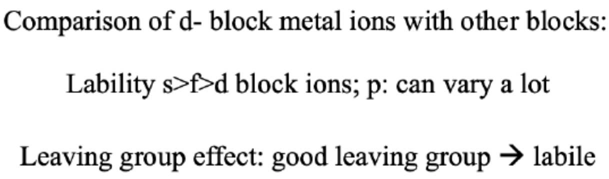
Electron configuration: octahedral d^3, low spin d^4-d^6, square planar d^8 tend to be inert.

Higher period of metal ion → less labile

Higher positive charge of metal ion → less labile

Figure 9.1.3 Trends for d-block metal ions

We can also compare the d-block metals with the other blocks. S-block metal complexes tend to have the greatest lability, followed by the f-block, followed by the d-block. P-block metal complexes can widely vary in lability (Fig. 9.1.4).


Comparison of d- block metal ions with other blocks:

Lability s>f>d block ions; p: can vary a lot

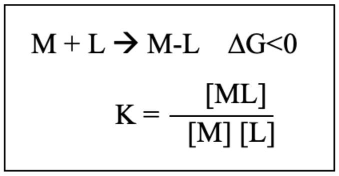
Leaving group effect: good leaving group → labile

Figure 9.1.4 Trends for the blocks and leaving groups

Also the nature of the ligand influences the lability. Generally, when the ligand is a good leaving group, then the bond tends to be labile. A ligand is usually a good leaving group when it is stable in the uncoordinated form. For instance, a chloro ligand is a good leaving group because chloride anions are quite stable in their non-coordinated form. An alkyl ligand on the other hand would not be considered as a good leaving group because the an alkylide anion is not a very stable species in the free form.

Stability of Complexes

Now let us have a closer look at the stability of complexes. The more negative the Gibbs free energy of formation, the greater the equilibrium constant of formation K. The larger the equilibrium constant K of formation, the more stable the complex. This can be expressed by the van’t Hoff equation ΔG = -RTlnK.


$$M + L \rightarrow M\text{-}L \qquad \Delta G<0$$

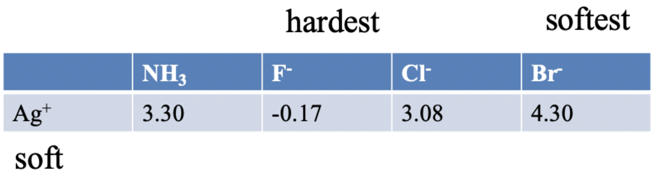
$$K = \frac{[ML]}{[M]\,[L]}$$

Figure 9.1.5 Equilibrium constant for a reaction that forms a single metal-ligand bond. Reaction proceeds to the right if ΔG<0.

For the formation of a single dative bond M-L the constant of formation is given by K=[ML]/[M][L] (Fig. 9.1.5). The greater K, the farther the equilibrium is on the side of the product. K is usually reported as logK because K can vary over 35 orders of magnitude.

Rationalizing the Different Stability of Complexes

How can we rationalize the different stabilities of coordination bonds, and coordination compounds? Here, the HSAB concept is very useful. Hard-hard and soft-soft interactions are typically strong and lead to high constants of formation and stable complexes. Hard-soft interactions lead to small constants of formation and less stable complexes.


hardest softest

	NH_3	F^-	Cl^-	Br^-
Ag^+	3.30	-0.17	3.08	4.30

soft

Figure 9.1.6 Formation constants log K for Ag^+ complexes

Let us understand this better by the example of the interaction of Ag^+ with different ligands (Fig. 9.1.6). You can see in the table the logK values for the different ligands. Br^- has the largest one, followed by NH_3 and Cl^-. F^- has the smallest one. Can we explain this with the HSAB concept? Ag^+ is a soft cation, thus it would be expected to make the strongest interactions with the softest ligand. Bromide is the softest of the four, and hence HSAB correctly predicts the stability. F^- is the hardest ligand and would be expected to make the weakest complex. This is in accordance with the small logK value for F^-. NH_3 and Cl^- have similar intermediate hardness, which is consistent with the similar, intermediate logK values.

Stabilities of Multi-ligand Complexes

Example ML_4

1. $M + L \rightarrow ML$ $\qquad K_1 = [ML] / [M] [L]$
2. $ML + L \rightarrow ML_2$ $\qquad K_2 = [ML_2] / [ML] [L]$
3. $ML_2 + L \rightarrow ML_3$ $\qquad K_3 = [ML_3] / [ML_2] [L]$
4. $ML_3 + L \rightarrow ML_4$ $\qquad K_4 = [ML_4] / [ML_3] [L]$

$$K_1>K_2>K_3>K_4$$

Figure 9.1.7 Equilibria associated with a complex of the composition ML_4

How does the stability of a complex change as more ligands are added? Let us take a look at the constants of formation to answer the question. The addition of an additional ligand is associated with an additional chemical equilibrium which relates to an additional constant of formation. The number of equilibrium constants is equal to the number of ligands. For instance, when we have a complex ML_4 with four ligands, then for the addition of the first ligand we get a constant $K_1= [ML] / [M] [L]$, for the second ligand we get a constant $K_2=[ML_2] / [ML] [L]$, for the third ligand there is a constant $K_3=[ML_3] / [ML_2] [L]$, and for the fourth ligand there is a constant $K_4=[ML_4] / [ML_3] [L]$. When we analyze the K-values, we notice that they decline from K_1 to K_4. For a general complex ML_n we find that the constants decline from K_1 to K_n. How can this be explained? The explanation is that the more ligands are getting added, the less many free ligands are available that could be further added. Thus, the probability that further ligands are added decreases, and this results in a smaller equilibrium constant. So it is a statistical effect that explains the phenomenon.

The stepwise and overall stability constants K are related as follows:

$$ML_4\text{: } K = K_1.K_2.K_3.K_4$$
$$ML_n\text{: } K = K_1.K_2\text{.........}K_n$$

Figure 9.1.8 Overall stability constants for a general complex ML_n

Then what is the overall stability constant K of the complex associated with the equation $M + 4\ L \rightarrow ML_4$ and more general $M + nL \rightarrow ML_n$? It is the product of the constants associated with each step. For the complex ML_4 it is $K=K_1K_2K_3K_4$. For the general complex ML_n it is $K=K_1K_2\text{.........}K_n$ (Fig. 9.1.8).

There are exceptions from the rule that the stability constants of complexes associated with the addition of one ligand decreases with the number of ligands. If there is an exception, then this is because the ligand addition causes a major change in the electronic structure of the complex. Here are a couple of examples.

$$[Fe(OH_2)_6]^{2+}(aq) + bipy(aq) \rightleftharpoons [Fe(OH_2)_4(bipy)]^{2+}(aq) + 2H_2O \qquad \log K_f = 4.2$$
$$[Fe(OH_2)_4(bipy)]^{2+}(aq) + bipy(aq) \rightleftharpoons [Fe(OH_2)_2(bipy)_2]^{2+}(aq) + 2H_2O \qquad \log K_2 = 3.7$$

High spin

$$[Fe(OH_2)_2(bipy)_2]^{2+}(aq) + bipy(aq) \rightleftharpoons [Fe(bipy)_3]^{2+}(aq) + 2H_2O \qquad \log K_3 = 9.3$$

Low spin

Figure 9.1.9 Example 1 for exceptions to the rule for stability constants

In the first example (Fig. 9.1.9) the aqua ligands of a hexaaqua iron (2+) complex are substituted by bipyridyl ligands. The bipyridyl ligand is a bidentate ligand, and so one bipydridyl ligand substitutes two aqua ligands. In the first substitution, the two aqua ligands get replaced by one bipyridyl ligand to form a tetraaqua(bipyridyl) iron (2+) complex. This step is associated with a $\log K_1$ value of 4.2.

In the second substitution step, two aqua ligands of the tetraaqua(bipyridyl) iron (2+) complex get replaced by another bipyridyl ligand to form a diaqua bis(bipyridyl) iron(2+) complex. As expected this step is associated with a smaller $\log K_2$ value of 3.7.

In the third step, the last two aqua ligands get substituted by another bipyridyl ligand forming a tris(bipyridyl) iron(2+) complex. What is the $\log K_3$ value? It is 9.3! This is much larger than $\log K_1$ and $\log K_2$, so this result is unexpected. A major change in electronic structure must have occurred. What is it? In this case it is a change from a high-spin to a low spin complex. The bipyridyl ligands are strong π-acceptors that increase Δ_o. Substitution of the first four aqua ligands increases Δ_O but the increase is not large enough yet so that it induces a switch from a high-spin to a low-spin complex. Only the third bipyridyl ligand does that. As a consequence, the formation constant $\log K_3$ is unusually large.

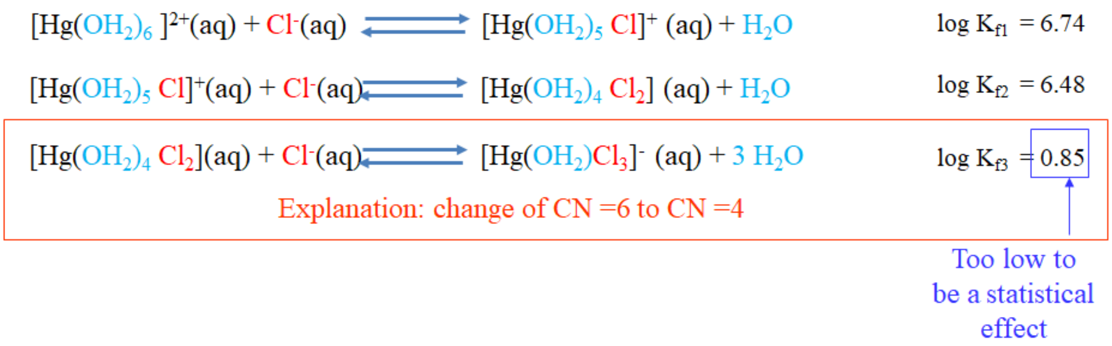


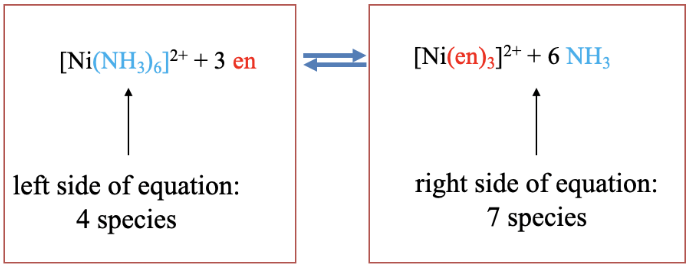
Figure 9.1.10 Example 2 for exceptions to the rule for stability constants

In the second example (Fig. 9.1.10) we subsequently substitute aqua ligands by chloroligands in a hexaaqua mercury(2+) complex. The first substitution leads to a pentaaquachloro mercury(+) complex. This reaction is associated with a $\log K_1$ value of 6.74. The second substitution leads to a tetraaquadichloro mercury(0) complex, and this reaction is associated with a smaller $\log K_2$ value of 6.48. The third substitution reaction leads to an aquatrichloro mercury(1-) complex. The $\log K_3$ value for this reaction is 0.85. We see that this value is smaller than $\log K_2$, and this is what we expected, but the difference between $\log K_3$ and $\log K_2$ is much larger than that between $\log K_1$ and $\log K_2$. The increased difference is too large to be just caused by a statistical effect, but must be induced by a change in electronic structure. In this case it is a change in coordination number. As the third chloro ligand is added, the complex does not lose only one but three aqua ligands. This reduces the coordination number from six to four.

Stability of Chelate Complexes

The Thermodynamic Chelate Effect

Chelating complexes tend to be more stable than complexes with monodentate ligands. This is called the "thermodynamic chelate effect". The effect deserves an explanation. The explanation is the increase of entropy that occurs when two or more monodentate ligands are replaced by a chelating ligand. The entropy increases because the overall number of particles increases as the substitution takes place.



$$\Delta S° = +88\ J\ K^{-1}\ mol^{-1}$$

Figure 9.1.11 Example of the thermodynamic chelate effect

For example, the substitution of six ammine ligands in the hexaammine nickel (2+) complex by three ethylenediamine chelating ligands increases the number of molecules from four to seven, and hence the entropy increases, in this case by 88 J K^{-1} and mol^{-1} (Fig. 9.1.11)

The Kinetic Chelate Effect

In addition to the thermodynamic chelate effect, there is the kinetic chelate effect. Chelate complexes are frequently more inert than complexes with monodentate ligands. Chelate complexes are more inert for two reasons (Fig. 9.1.12).

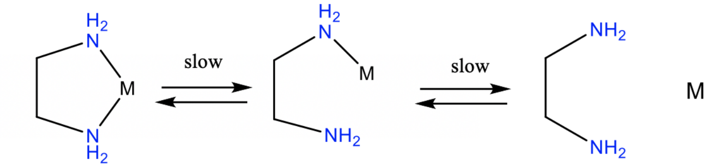


Figure 9.1.12 Illustration of the kinetic chelate effect

Firstly, the whole ligands needs to rotate and bend in order to cleave the first metal-ligand bond. This requires time and slows the kinetics of the bond cleavage. The second reason is that the detached donor atom cannot leave the proximity of the complex because the ligand is still attached via the other donor atom. This increases the probability of the re-formation of the metal-ligand bond which decreases the probability of both bonds being cleaved.

Mechanism of Ligand Substitution Reactions

Now let us talk about the mechanism of ligand substitution reactions. We know two basic mechanisms according to which a ligand substitution can occur. One is called the intimate mechanism, and the other one is called the stoichiometric mechanism.

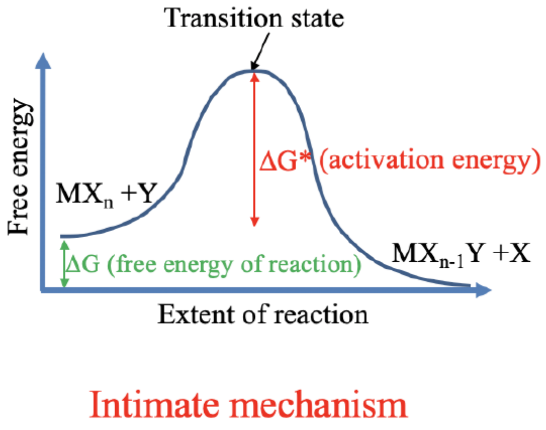


Figure 9.1.13 Intimate mechanism

The intimate mechanism goes through a single transition state as the reaction proceeds.

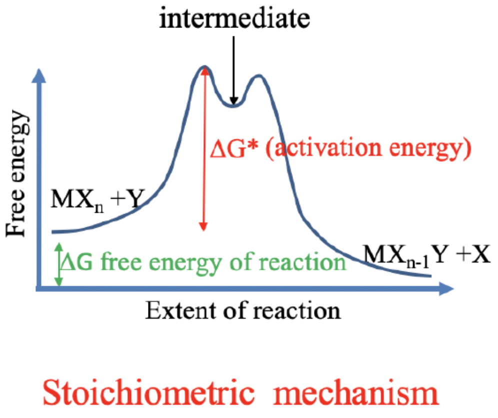


Figure 9.1.14 Stoichiometric mechanism

The stoichiometric mechanism goes through an intermediate. The intermediate is a shallow local minimum on the reaction coordinate. The transition state is the maximum on the reaction coordinate. For both mechanisms the principle of microscopic reversibility holds. This means that the reverse reaction follows the same free energy path as the forward reaction. For both mechanisms the free Gibbs energy of reaction is given by the difference between the free energy of the products and the free energy of the reactants. The reaction can only spontaneously occur if the free energy of the products is smaller than the free energy of the reactants. The activation energy is the free energy difference between the transition state and the reactants.

Classifications of Mechanisms

There are two forms of the stoichiometric mechanism: The dissociate mechanism D and the associative mechanism A. In the dissociative mechanism (Fig. 9.1.15), an old ligand X is lost first, and the intermediate has a lower coordination number. In the associative mechanism (Fig. 9.1.16), the new ligand Y is added first and the intermediate has a higher coordination number. The intermediates must be detectable, thus must be present in relatively high concentration to measurable with an analytical technique. This requires are relatively deep local thermodynamic minimum for the intermediate. In practice, many local minima are too shallow to allow for the clear detection of the intermediate. We call such a mechanism an Interchange mechanism. There are two forms of interchange mechanisms: I_a and I_d. I_a stands for associative interchange mechanism and I_D stands for dissociative interchange mechanism. Overall we can have a continuous range of mechanisms that range from A to I_a to intimate to I_d to D.

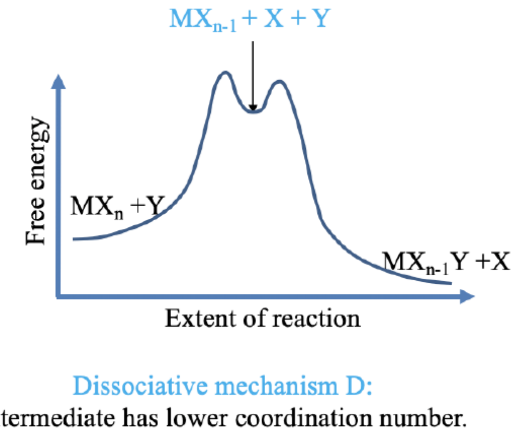


Figure 9.1.15 Dissociative mechanism

For a dissociative and the I_d mechanism the dissociation is the rate limiting step. This is because the activation energy is associated with the dissociative step. We need to go strongly uphill to achieve dissociation, and go into the local thermodynamic minimum. From, there we only need to go slightly uphill to add the new ligand.

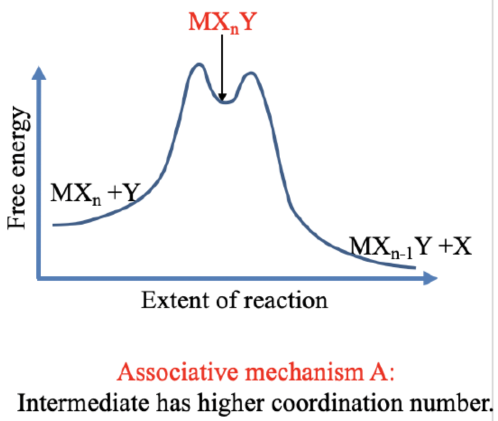


Figure 9.1.16 Associative mechanism

For the associative and the I_a mechanism (Fig. 9.1.16), the associative step is the rate limiting step because the activation energy is associated with the associative step. In this case we first need to go energetically strongly uphill to achieve association and reach the local thermodynamic minimum. We only need to go slightly uphill from the local thermodynamic minimum to lose the old ligand.

How to Distinguish Between D/I_d and A/A_d

We can use the relationships between the rate determining step and the mechanism to experimentally distinguish between associative A/I_a and dissociative D/I_d mechanisms. If the reaction rate strongly depends on the new ligand, then we likely have an associative or I_a mechanism. This is because the associative step is the rate determining step. If the reaction rate does not strongly depend on the new ligand, then the mechanism is likely dissociative D or I_d. This is because in the dissociate mechanism, the addition of the new ligand is not the rate-determining step.

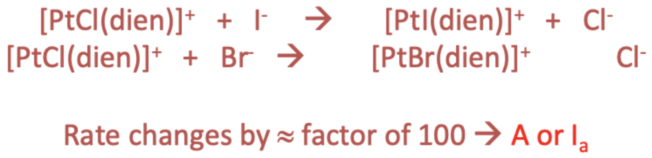


Figure 9.1.17 Distinguishing between D/I_d and A/A_d

For example, we can substitute a chloro ligand in a $[PtCl(dien)]^+$ complex by iodo and bromo ligands, respectively (Fig. 9.1.17). What we measure is that the reaction rates are by a factor of 100 different. This means that the reaction rates does depend on the new ligand and this indicates an associative or I_a mechanism.

Steric arguments can help to predict if a mechanism is associative or dissociative. Lower coordination numbers and little steric crowding tends to favor A and I_a mechanisms, while higher coordination numbers and greater steric crowding tend to favor the dissociative mechanism.

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Concept Review Questions Chapter 9

Concept Review Questions

Section 1

1. When in general does a chemical reaction occur?

2. What is meant by an inert and a labile complex?

3. For which d electron configuration would you expect inert complexes?

4. How does the leaving group effect influence the inertness of a coordination compound?

5. With which concept can the stability of coordination compounds be estimated?

6. What is the linear free energy relationship? Explain its origins qualitatively.

7. Explain why the constant of formation for multi-ligand complexes decreases with the addition of additional ligands? Under which circumstances are there exceptions?

8. What is the “thermodynamic chelate effect”?

9. What is the “kinetic chelate effect”?

10. What is meant by an “intimate” and a “stoichiometric” mechanism respectively?

11. What is the difference between a transition state and an intermediate?

12. What is the difference between an associate mechanism A and an interchange mechanism I_a?

13. What is the difference between a dissociative mechanism D and an interchange mechanism I_d?

14. How can one experimentally distinguish between an associative and a dissociative mechanism?

15. Which factors favor associative mechanisms and dissociative mechanisms respectively?

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Homework Problems Chapter 9

Homework Problems

Section 1

Exercise 1

An associative mechanism is favored when

a) the oxidation state of the metal is high

b) the coordination number of the metal is low

c) the complex has bulky ligands

d) the metal –ligand bonds are labile.

Answer

b) the coordination number of the metal is low

Exercise 2

Which of the following metal-ligand bonds would you expect to have the highest thermodynamic stability?

a) Hg-S

b) Hg-O

c) Hg-N

d) Hg-F

Answer

a) Hg-S

Exercise 3

Chelate complexes are thermodynamically particularly stable because

a) The substitution of a simple ligand by a chelating ligand is enthalpically particularly favorable.

b) The substitution of a simple ligand by a chelating ligand is entropically particularly favorable.

c) Chelating ligands are more inert than simple ligands.

Answer

b) The substitution of a simple ligand by a chelating ligand is entropically particularly favorable.

Exercise 4

What is true about intimate mechanisms?

a) The intimate mechanism involves an intermediate that is detectable

b) The intimate mechanism involves an intermediate that is not detectable.

c) The intimate mechanism involves a transition state.

Answer

c) The intimate mechanism involves a transition state.

Exercise 5

What is true about complexes that undergo metal to ligand charge transfer?

a) The metal ion has no or few d electrons

b) The ligands are good pi-acceptors

c) The metal ions have a high charge.

Answer

b) The ligands are good pi-acceptors

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CHAPTER OVERVIEW

10: Organometallic Chemistry

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10.1: Historical Background and Introduction into Metallocenes

Organometallic Chemistry

In this chapter you will get an introduction in a subfield of coordination chemistry: Organometallic chemistry. How is an orgamometallic complex defined?

> **Definition: Organometallic Complex**
>
> A complex with bonding interactions between one or more carbon atoms of an organic group or molecule and at least one metal atom is called an organometallic complex.

It is defined as a complex with bonding interactions between one or more carbon atoms of an organic group or molecule and at least one metal atom. It is important to understand that just the presence of an organic ligand is not sufficient to define an organometallic compound yet. There must be interactions between a carbon and a metal atom. If an organic ligand is present but no donor atom is a carbon atom, then we call this complex a metal-organic complex.

$SnMe_4$	$Sn(OMe)_4$
organometallic (Sn-C bonds)	metal-organic (Sn-O bonds)

Figure *[Math Processing Error]*: Example of organometallic vs metal-organic complexes

Let us practice this by one example: which of the following molecules are metal-organic and organometallic respectively: tetramethyl tin and tetramethoxy tin (Figure *[Math Processing Error]*). The former is organometallic while the latter is metal-organic. Why? This is because in tetramethyl tin there are Sn-C bonds, while in tetramethoxy tin there are Sn-O bonds.

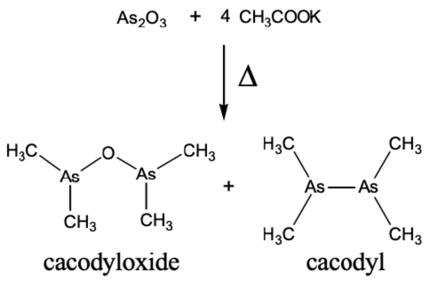
Industrial Importance of Organometallic Compounds

Organometallic compounds are an industrially very important class of compounds. For example, aluminum and tin alkyl compounds are produced at amounts in the order of tens of thousand of tons per year. Even more important however is the use of organometallic compounds as catalysts to produce other compounds. This ranges from commodity polymers like polypropylene and polyethylene to simple organic molecules like acetaldehyde and acetic acid. These compounds are produced at a scale in the order of millions of tons per year.

History of Organometallic Chemistry

Let us take a historical approach to organometallic chemistry and see how the field has evolved. The arguably first organometallic compound was kakodyl oxide, an organo-arsenic compound.

It was accidentally produced by the French chemist Louis Cadet in 1760 when he was working on inks. He heated arsenic oxide and potassium acetate and obtained a red-brown oily liquid, known as Cadet's fuming liquid.



gr. „kakodes“ = bad smell

Figure *[Math Processing Error]*: Cacodyl and cacodyl oxide

It consists mostly of cacodyl and cacodyl oxide (Figure *[Math Processing Error]*). In cacodyl, there is an As-As bond and two methyl groups attached to each As atom. In cacodyl oxide, there is an O atom in between the two As atoms, and each As is bound to two methyl groups. The names of these compounds come from the greek word “kakodes”=bad smell. Indeed, they have a very intense, garlic-like smell. The reaction can be used to identify arsenic in samples. For instance, if you suspected your food was poisoned with arsenic, you could heat a sample together with potassium acetate. If a bad, garlic-like smell evolved, then this would indicate that there is arsenic in your sample.

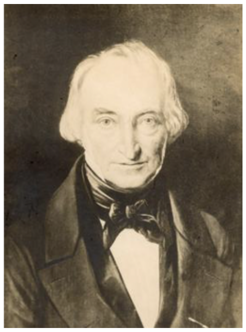


Figure *[Math Processing Error]*: Willam Zeise (Public domain)

Another important milestone in coordination chemistry was the discovery of Zeise’s salt by the Danish chemist William Zeise in 1827 (Figure *[Math Processing Error]*). Zeise’s salt was the first olefin complex in which an olefin was bound side-on to a metal using its π-electrons for σ-bonding. Zeise observed that when sodium hexachloroplatinate (2-) was heated in ethanol, a compound with the composition $Na[PtCl_3(C_2H_4)]$ could be isolated. The chemical composition of the compound suggested that there was a C_2H_4 organic fragment bonded to the platinum, but it was not clear how.

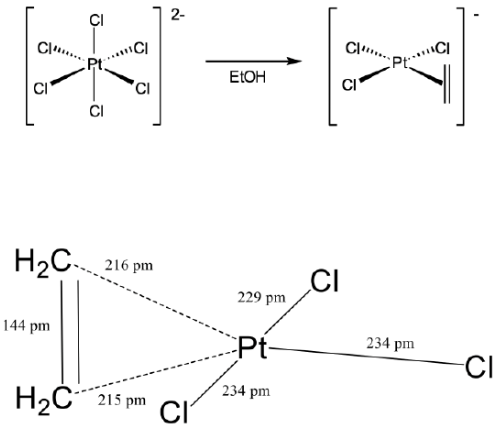


Figure *[Math Processing Error]*: Zeise's salt: Synthesis and crystal structure.

This question was only answered more than 100 years later in 1969 with the crystal structure analysis of Zeise’s salt. The crystal structure revealed that an ethylene molecule was bound side-on to the platinum (Figure *[Math Processing Error]*). The two carbon atoms had about the same distance to the Pt arguing that they were equally strongly involved in the bonding with Pt. The first C had a distance of 216 pm while the second carbon had a distance of 215 pm. The ethylene molecule was oriented perpendicular to the plane made of the three chloro ligands and the platinum atom. The Cl-Pt-Cl bond angles were near 90°. Overall, the structure could be described as a structure derived from a square planar structure with the ethylene as the fourth ligand that would stand perpendicular to the plane in order to minimize steric repulsion with the chloro ligands.

An important question was how to describe the bonding in the compound. It was noteworthy that the C-C bond length in Zeise’s salt was significantly longer (144 pm) than that in a free ethylene molecule (134 pm). Based on the bond-strength bond-length concept this argued that the bond was weaker than a regular C=C double bond, and that the bond order was smaller than 2. What could explain this lower bond order and the side-on coordination of the ethylene in Zeise’s salt?

Bonding in Zeise's Salt

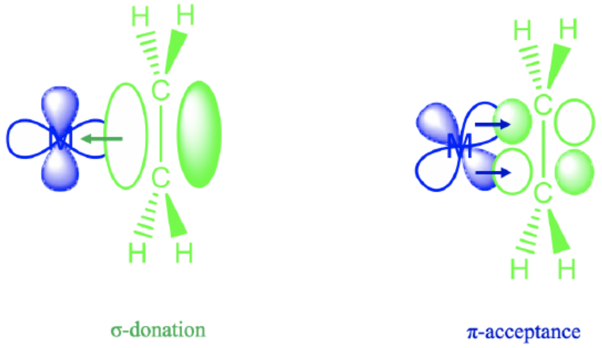


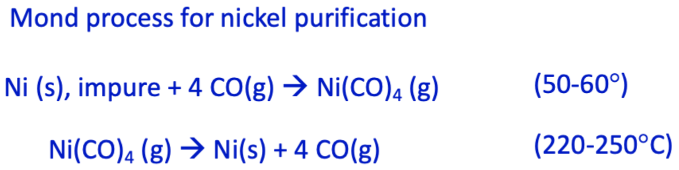
Figure *[Math Processing Error]*: Bonding in Zeise's salt

The answer is that the ethylene molecule uses its π-electrons for σ-bonding with a metal d-orbital (Figure *[Math Processing Error]*). You can see above that the lobe of a $d_{x^2-y^2}$ orbital has the correct orientation to overlap with the bonding π-orbitals of the ethylene ligand in a σ-fashion. Through this interaction electron density gets donated from the bonding ligand π-orbital into the metal-d-orbital. This results in a lower electron density for π-bonding within the ligand, and thus the bond order is decreased. In addition, there is another effect that lowers the bond order. A metal d-orbital can interact with the π*-orbitals in π-fashion. In this process, electron density can be donated from the metal d-orbital into the empty π-orbitals of the ligand. The increased electron density in the π-orbitals further decreases the bond order.

In 1890, a further milestone in organometallic chemistry was reached with the synthesis of the first carbonyl complex, the nickel tetracarbonyl. Nickel tetracarbonyl is a colorless liquid that boils at 43°C.

Figure *[Math Processing Error]*: Ludwig Mond (Public domain)

The compound was prepared by the German chemist Ludwig Mond (Figure *[Math Processing Error]*). Nickel tetracarbonyl forms spontaneously from nickel metal and carbon monoxide at room temperature.



Mond process for nickel purification

Ni (s), impure + 4 CO(g) → $Ni(CO)_4$ (g) (50-60°)

$Ni(CO)_4$ (g) → Ni(s) + 4 CO(g) (220-250°C)

Figure *[Math Processing Error]*: Reactions associated with the Mond process

The reaction is the basis of the Mond-process that is used up to date in order to purify nickel (Figure *[Math Processing Error]*). Carbon monoxide gas can be streamed over impure Ni metal at temperatures of 50-60°C to form $Ni(CO)_4$ in gaseous form. Impurities are left behind in solid form.

Figure *[Math Processing Error]*: $Ni(CO)_4$ spheres prepared through the Mond process (René Rausch, Nickel kugeln, CC BY-SA 3.0 DE)

Then, the nickel tetracarbonyl is thermally decomposed at ca. 220° to form nickel and carbon monoxide. The process can be varied to produce nickel in powder form, as spheres (Figure *[Math Processing Error]*), and as coatings. The Mond process is used up to date despite the very high toxicity of nickel tetracarbonyl.

Figure *[Math Processing Error]*: Victor Grignard (Public domain)

In 1900 the first Grignard reagents were discovered. Victor Grignard (Figure *[Math Processing Error]*) was an enthusiastic young French chemist who discovered how to make organomagnesium halides (RMgX) while working for his Ph.D.

$$\text{Mg(s)} + \text{R-X(ether)} \rightarrow \text{R-Mg-X(ether)}$$

Figure *[Math Processing Error]*: Grignard reaction

His supervisor, Sabatier, had been trying this chemistry for some time, but Victor was the genius who solved the problem. Organomagnesium halides form from magnesium and organic halides in ethers. This discovery in 1900 changed the course of organic chemistry and won Grignard and Sabatier the Nobel Prize in 1912.

Figure *[Math Processing Error]*: Wilhelm Schlenk (Public domain)

In 1917, the first lithium alkyls were prepared by Wilhelm Schlenk (Figure *[Math Processing Error]*). Like Grignard reagents, lithium alkyls are very valuable reactants in synthetic organic chemistry. Lithium alkyls are very air-sensitive compounds, and some do even self-ignite in air, for example tert-butyl lithium. Therefore, they need to be handled carefully under inert gas.

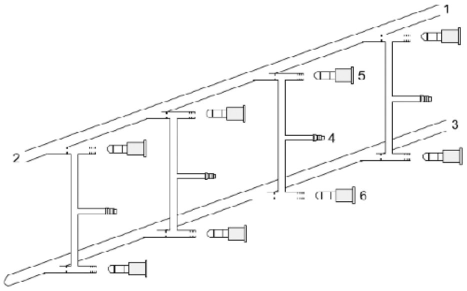


Figure *[Math Processing Error]*: The Schlenk-line (Pen1234567, Vacuum gas manifold with separate taps-diagram, CC BY 3.0)

In this regard, Wilhelm Schlenk made an important invention: The Schlenk-lines (Figure *[Math Processing Error]*). The Schlenk lines allow to evacuate reaction flasks and back-fill them with an inert gas. A Schlenk line has a dual manifold with several ports. One manifold is connected to a source of purified inert gas, while the other is connected to a vacuum pump. The inert-gas line is vented through an oil bubbler, while solvent vapors and gaseous reaction products are prevented from contaminating the vacuum pump by a liquid nitrogen or dry ice/acetone cold trap. Special stopcocks or Teflon taps allow vacuum or inert gas to be selected without the need for placing the sample on a separate line.

The discussed discoveries were important milestones in the development of organometallic chemistry, but the field expanded only rapidly with the discovery of the first metallocene: The ferrocene. Like often in science, ferrocene was discovered through an accident.

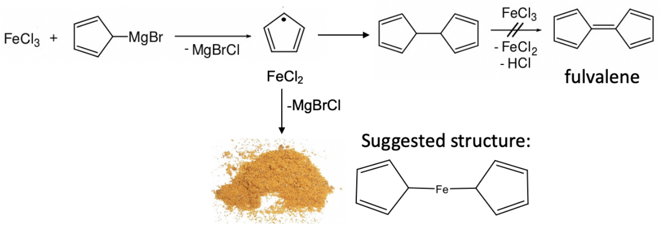
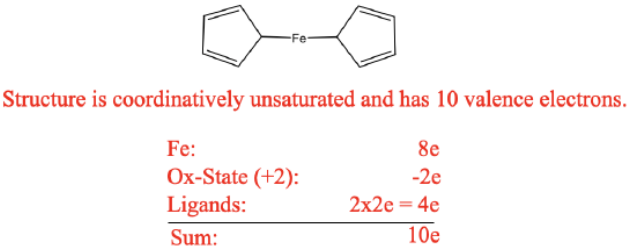


Figure *[Math Processing Error]*: Synthesis of ferrocene (Attribution: T.J. Kealy, P.L. Pauson, Nature 1951, 168, 1039.)

In 1951 Peter Pauson and Thomas Kealy attempted to synthesize the organic compound fulvalene through oxidative coupling of cyclopentadienyl magnesium chloride with iron (III) chloride. However, instead of obtaining fulvalene they observed the formation hydrofulvalene together with an orange powder with “remarkable stability”. Analysis of the powder showed that the chemical compound contained two cyclopentadienyl rings and one iron atom. According to the knowledge on bonding in organometallic compounds that was known at the time Kealy and Pauson suggested a structure for the molecule in which two cyclopentadienyl group were bound to a single Fe atom via two Fe-C bonds (Figure *[Math Processing Error]*).

However, the remarkable stability of the compound was in contradiction to this structure. The structure would be a 10 electron complex which would be highly coordinatively unsaturated. This would be inconsistent with the observed stability. We can briefly practice our electron counting skills again in order to prove that there are only 10 electrons (Figure *[Math Processing Error]*).



Structure is coordinatively unsaturated and has 10 valence electrons.

Fe:	8e
Ox-State (+2):	-2e
Ligands:	2x2e = 4e
Sum:	10e

Figure *[Math Processing Error]*: Electron counting in the wrong structure for Fe(Cp)$_2$

For example we can use the oxidation state method for electron counting. Fe in the neutral state has eight valence electrons. We would cleave the bonds heteroleptically which would create cyclopentadienyl anions with a 1- charge. This would mean that Fe is in the oxidation state +2, and thus we would subtract two electrons. The cyclopentadienyl anions would contribute two electrons each giving ten electrons overall. In contrast to expectations, the compound was stable in air, and could be sublimed without decomposition. Further the double-bonds in the cyclopentadienyl rings resisted hydrogenation. In addition, the structure was inconsistent with spectroscopic observations. Only one C-H stretch vibration was observed in the IR and only one signal was observed in the ^{1}H NMR. Kealy and Pauson's structure would have been consistent with three C-H stretch vibrations and three NMR resonances.

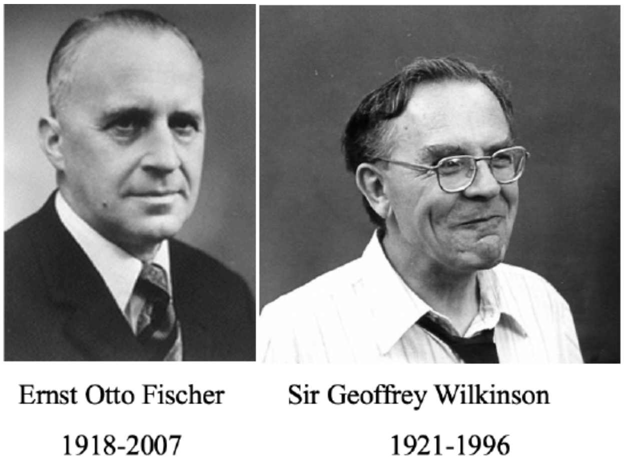
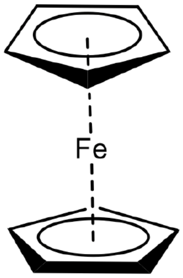


Figure *[Math Processing Error]*: Ernst Fischer (Attribution: Nobel Foundation https://www.nobelprize.org/prizes/chemistry/1973/fischer/biographical/) and Geoffrey Wilkinson (Smokefoot, Geoffrey Wilkinson ca. 1976, CC BY-SA 3.0)

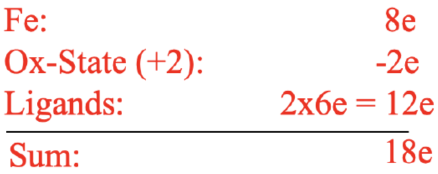
For these reasons, Kealy's and Pausons structure was soon questioned. Ernst Otto Fischer at University of Munich and Sir Geoffrey Wilkinson at Harvard University (Figure *[Math Processing Error]*) suggested an alternative structure that was very different from all known organometallic structures. The bonding in this structure was completely different from all bonding concepts considered thus far for organometallics.



Ferrocene

Figure *[Math Processing Error]*: The sandwich structure of ferrocene

What structure did they propose? They proposed a sandwich structure in which the two aromatic cyclopentadienyl anions would sandwich an Fe^{2+} ion. What would be the bonding in this structure? The cylopentadienyl anion would donate its six π-electrons into the valence orbitals of the metal. Thus, all five carbon atoms would be equally involved in the bonding, the ligand would act as a η^5-ligand. Because of the donation of π-electrons in the cycopentadiene unit, the structure was called "ferrocene". The ferrocene structure would explain the stability and low reactivity of the compound.



Fe:	8e
Ox-State (+2):	-2e
Ligands:	2x6e = 12e
Sum:	18e

Figure *[Math Processing Error]*: Electron counting in ferrocene using the oxidation state method

Electron-counting gives an 18 electron complex. Let us verify this using the oxidation state method. Fe would contribute eight electrons in the neutral state. The ligands would be considered as cyclopendienyl anions with a 1- charge. This would give an oxidation state of +2 for Fe reducing the number of electrons from eight to six. The two ligands would contribute six electrons each giving twelve electrons. 12+6=18. Hence, the structure fulfills the 18 electron rule. The structure is also consistent with the spectroscopic observation of one NMR resonance and one C-H stretch vibration. All these were excellent arguments to support the ferrocene sandwich structure, however they were not an absolute proof. The proof finally came with the X-ray crystal structure determination which unambiguously confirmed the sandwich structure.

Bonding in Ferrocene and MO Theory

Can the stability of the ferrocene structure also be explained by molecular orbital theory? Let us check! First, we need to decide on the point group. We will make the simplification that the two C_p cyclopentadienyl rings are in eclipsed formation, and then the point group is D_{5h}. Actually, the rings are in staggered confirmation and the point group is D_{5d}, but the energy difference is minimal, and there is a very small activation barrier between the two conformers.

[Math Processing Error]

We can define the z-axis standing perpendicular to the Cp rings, and the xy plane to be coplanar with the Cp rings.

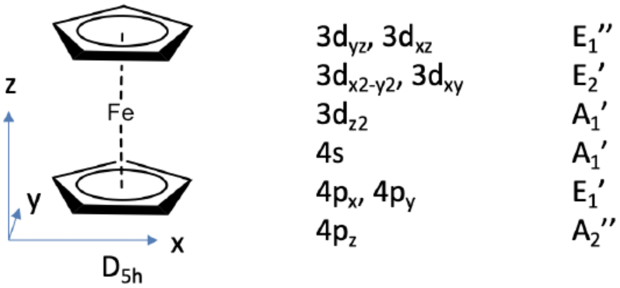


Figure *[Math Processing Error]*: The coordinate system for ferrocene, Fe valence orbitals, and their symmetry types.

The Fe 3d, 4s and 4p orbitals will be our frontier orbitals and we can read their symmetry types from the character table of D_{5h}. The $3d_{xz}$ and $3d_{yz}$ have E_1'' symmetry, the $3d_{x^2-y^2}$ and the $3d_{xy}$ have E_2' symmetry, the $3d_{z^2}$ has A_1' symmetry, the 4s has A_1' symmetry, and the $4p_x$ and the $4p_y$ orbitals have E_1' symmetry, and the $4p_z$ has A_2'' symmetry.

Next, we need to determine the ligand group orbitals. We know that the π-ligand molecular orbitals are the ones that donate the electrons into the metal-orbitals, thus we have to have a closer look at these orbitals. The π-MOs of the ligand are made from the five $2p_z$ orbitals of the carbon atoms that stand perpendicular to the ring. This means that there are 5 MOs to consider.

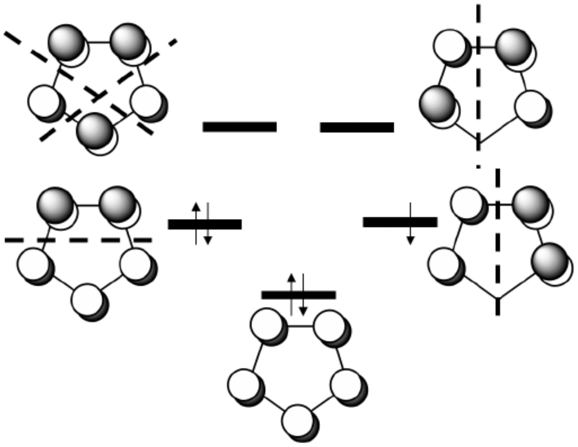


Figure *[Math Processing Error]*: MOs of the cyclopentadienyl ligand and their relative energy

You can see the five MOs and their relative energy above. One is strongly bonding and has no node. Then, there are two double-generate weakly bonding ones that have one node, and finally there are two anti-bonding ones that have two nodes. Because the cyclopentadienyl anion has six π electrons, the bonding MO and the two weakly bonding MOs are full, the anti-bonding MOs are empty.

Because we have two Cp^- anions to consider we have overall 10 MOs to combine. We would therefore expect ten ligand group orbitals (LGOs). We can determine their symmetry type by determining the reducible and irreducible representations. The results are shown below.

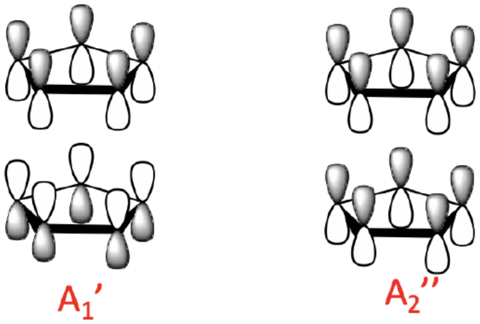


Figure *[Math Processing Error]*: 0-node LGOs

We can generally divide the LGOs into three groups with a different number of nodes. There are two 0-node LGOs with A_1’ and A_2’’ symmetry. They are made from the 0-node MOs of the ligand. There is a bonding an anti-bonding combination possible. In the bonding combination the 0–node ligand MOs have the lobes with the same algebraic sign pointing toward each other. The anti-bonding combination has the lobes with opposite algebraic sign pointing toward each other.

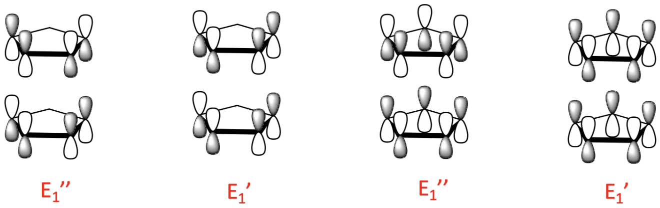


Figure *[Math Processing Error]*: 1-node LGOs

There are four 1-node LGOs with E_1’ and E_1’’ symmetry. They are constructed from the two 1-node ligand MOs. Like for the 0-node orbitals, there is a bonding and an anti-bonding combination possible.

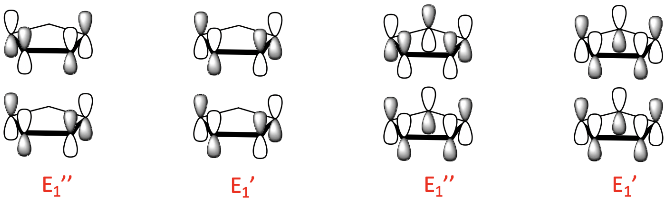


Figure *[Math Processing Error]*: 2-node LGOs

Finally, there are four 2-node LGOs with E_2’ and E_2’’ symmetry. They are made from the 2-node ligand MOs and there is also a bonding and an anti-bonding combination possible.

The Molecular Orbital Diagram of Ferrocene

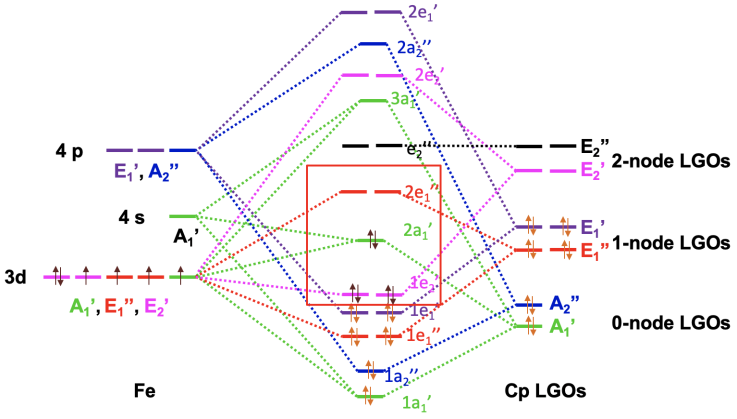


Figure *[Math Processing Error]*: MO diagram of ferrocene

Now we have all the information to draw the molecular orbital diagram of ferrocene. As usual we plot the metal frontier orbitals on the left and label their symmetry. We plot the Cp LGOs on the right and also label the symmetry. We can order the LGOs according to energy with the 0-node LGOs having the lowest energy and the 2-node LGOs having the highest energy. Then, we can start to combine orbitals of the same symmetry type to form MOs. There are two metal AOs of the A_1’ type and one A_1’ LGO giving three MOs of this symmetry type, one bonding, one approximately non-bonding, and third one anti-bonding. We can connect AOs, LGOs, and MOs with dotted lines. Next, we can combine the A_2’’ AO and the A_2’’ LGO to form a bonding and an anti-bonding MO. We again connect the AOs, LGOs, and MOs with dotted lines. Then, we can produce two bonding e_1’’ and two anti-bonding e_1’’ MOs from the E_1’’ metal AOs and the E_1’’ LGOs and connect the orbitals with dotted lines. There are two E_1’ LGOs and two E_1’ AOs that can be combined to two bonding 1e_1’ and two anti-bonding 2e_1’ MOs and we again connect the orbitals with dotted lines. The two E_2’ LGOs can be combined with the two E_2’ d-orbitals to form a pair of bonding 1e_2’ and anti-bonding 2e_2’ molecular orbitals. Lastly, we notice that the E_2’’ LGOs do not find a partner, and we have to write them as non-bonding with the same energy into the MO diagram.

Now we need to fill the electrons into the orbitals. The ligands have twelve electrons overall. They can be filled into the six orbitals of the lowest energy. This fills the 1a_1’, the 1a_2’’, the 1e_1’’, the and 1e_1’ orbitals. We notice that all MOs are bonding which supports the stability of the molecule. We still need to consider the metal d-orbitals. We have an Fe^{2+} ion and thus six metal d-electrons. They would go into the 1e_2’ orbital which is bonding and the 2a_1’ orbital which is weakly bonding. The 2a_1 is the HOMO, and the next higher 2e_1’’ is the LUMO. We can see that we can fill all metal electrons into bonding MOs. The LUMO is an anti-bonding orbital, and thus overall all bonding MOs are filled, and no non-bonding and anti-bonding orbitals need to be filled. This is the ideal situation for a stable molecule. We can also see that the MO diagram explains the 18 electron rule. All 18 electrons are in bonding MOs.

We can consider the 1e_2’, the 2a_1’, and the 2e_1’’ metal d-orbitals in the ligand field produced by the Cp-ligands as these 5 orbitals can hold the maximum possible number of 10 d-electrons, have similar energy then the d-orbitals, and have contributions from them.

Metallocenes with other cyclic π-ligands

Is it possible to make metallocenes with other π-conjugated rings but the cylopentadienyl anion?

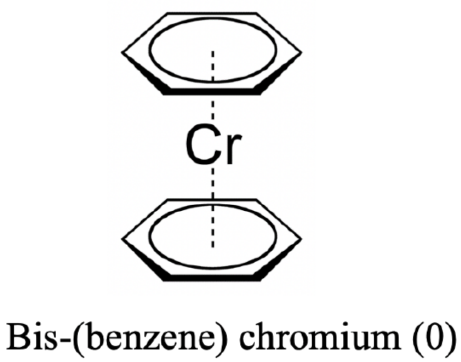


Figure *[Math Processing Error]*: Bis-(benzene) chromium

The answer is yes, for instance benzene is known to act as a ligand bis-(benzene) chromium (0). In this case the ligand acts as a η^6-ligand because all six carbon atoms are involved in the bonding. Why does chromium give stable metallocene complex with benzene? We can explain this again with the 18 electron rule. In bis-(benzene) chromium (0), chromium is in the oxidation state 0 because the benzene ligand has no charge. Thus, chromium contributes six electrons. Adding the 12 π-electrons from the two benzene ligands gives 18 electrons.

Other cyclic π-ligands

Also cyclobutadiene can act as a cylic π-ligand in complexes. The cyclobutadiene is is different from the cyclopentadienyl anion and the benzene ligand in two ways. Firstly, it has much more ring strain then the previous two, and secondly it is not an aromatic, but an anti-aromatic ligand. Remember, we have an aromatic ring when there are 4n+2 π-electrons, whereby n is an inter number. This means that rings with two (n=0), six (n=1), and ten (n=2) π-electrons are aromatic. Anti-aromatic rings are those that have 4n electrons, such as four (n=1), eight (n=2) and so forth. Cyclobutadiene has four electrons, and thus it is anti-aromatic. Anti-aromatic rings are less stable than aromatic ones because not all π-electrons are in bonding molecular orbitals. Let us illustrate this by constructing the MO diagram for the π-system of the cyclobutadiene molecule (Figure *[Math Processing Error]*)

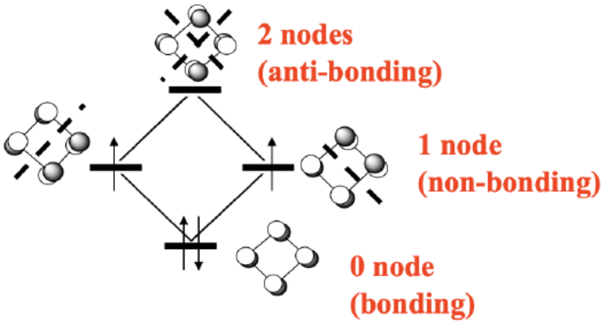


Figure *[Math Processing Error]*: MO diagram for the π-system of the cyclobutadiene molecule

The π-system is made of four carbon atoms contributing a half-filled $2p_z$ orbital each (if we define the plane of the molecule as the xy plane). That makes four p-orbitals with four electrons that give four molecular orbitals. There is a bonding MO with no node, two doubly-degenerate non-bonding ones with one node, and one anti-bonding one with two nodes (Figure *[Math Processing Error]*). There are four electrons. We can fill two electrons into the bonding MO, but the other two must go into the two non-bonding ones under obedience of Hund's rule.

Jahn-Teller distortion in cyclobutadiene

One may think that the cyclobutadiene is a square planar molecule because of complete delocalization of the π-electrons, but that is actually not the case. There are two shorter double-bonds and two longer single-bonds, and the shape of the molecules is a rectangle. This means that the two double bond are localized. We can view this effect as a Jahn-Teller distortion.

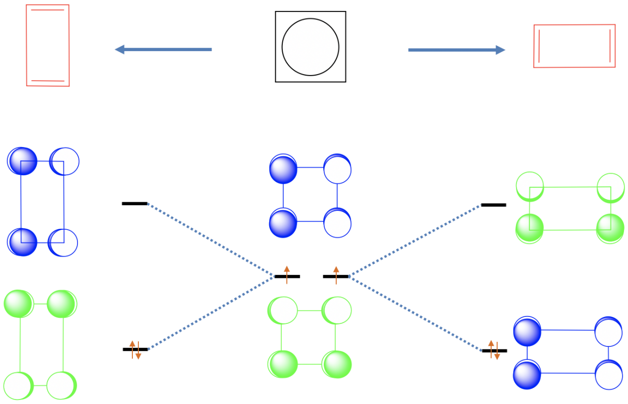


Figure *[Math Processing Error]*: Jahn-Teller distortion in cyclobutadiene

The distortion of the square to form a rectangle is energetically favorable because it lowers the energy of the two non-bonding electrons. Why? Let us look at the non-bonding orbital 1 first and elongate in x-direction, and squeeze in y-direction (Figure *[Math Processing Error]*). We can see that we bring the p-orbitals with bonding interactions further apart, and bring those with anti-bonding interactions closer together. This means that the energy of this orbital goes up and the orbital becomes anti-bonding. Let us do the same with non-bonding orbital 2. We see that the opposite happens. The bonding interactions are enhanced and the anti-bonding interactions are weakened. Therefore, this orbital becomes bonding and the energy goes down. We can now fill the two electrons into the bonding MO. We see that we have lowered the energy of the electrons through the distortion.

We could also have squeezed in x-direction and elongated in y-direction. In this case orbital 1 would have become bonding and orbital 2 anti-bonding. However, this distortion is symmetry-equivalent to the previous one, and does not produce a new molecule. Both molecules can be superposed by a simple 90° rotation.

Cyclobutadiene as η^4-ligand

Cyclobutadiene (Cb) in its free form is not stable because of the high ring strain and the anti-aromaticity, but complexes with cyclobutadiene as a ligand are stable. We would expect that 18 electron complexes are most stable.

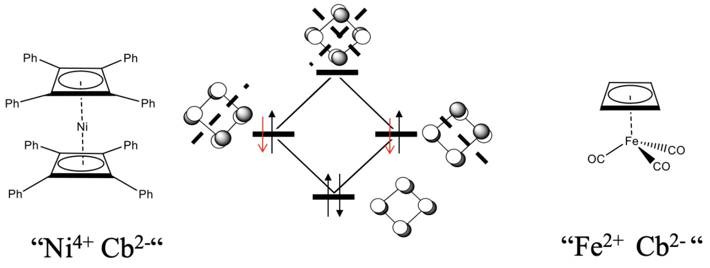


Figure *[Math Processing Error]*: Complexes with cyclobutadiene

What would be an 18 electron sandwich complex with two cyclobutadiene ligands? Because each cyclobutadiene contributes four electrons, ten electrons would need to come from the metal, and we would expect a nickel cyclobutadienyl complex $Ni(Cb)_2$. This complex is not known, but derivatives are. For example a Ni complex with two tetraphenyl butadiene ligands are known (Figure *[Math Processing Error]*). Another example is the butadienyl tricarbonyl iron (0) complex. Interestingly, when cyclobutadiene acts as a η^4-ligand, then it is not distorted, but square planar. An explanation is that we can formally treat the cyclobutadiene ligand as an Cb^{2-} ligand binding to a metal cation. For instance in $FeCb(CO)_3$ the Fe would be an Fe^{2+}, in the nickel complex, the nickel would be a Ni^{4+}. The Cb^{2-} anion would formally aromatic because it has 4n+2=6 electrons. The additional two electrons would be in the non-bonding orbitals. Because the two non-bonding orbitals are completely filled now, there would be no longer a driving force for the distortion. Note though that is is a formal view only, and there are arguments that speak against this view. One is that the addition of the two electrons to the ligand should further destabilize the ring because the added electrons are non-bonding. Aromaticity would rather be achieved by removing two electrons to form a Cb^{2+} cation that would have only two electrons in the bonding orbital.

Cyclooctetraene (cot) as a ligand

Also metallocenes with cyclooctatetraene (cot) acting as η^8-ligand is known. However, because of the large ring size only metals with large atomic radii, can make metallocenes with this ligand. For example uranium makes a uranocenes with two cyclooctatetraene ligands (Figure *[Math Processing Error]*).

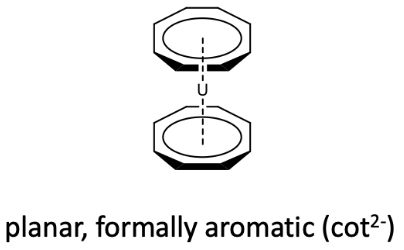


Figure *[Math Processing Error]*: Aromatic Cot^{2-} ligand

Like cyclobutadiene, cyclooctatetraene is an anti-aromatic ligand with 4n=8 π-electrons (n=2). In the free cyclooctatetraene molecule is non-planar and the π-electrons are localized (Figure *[Math Processing Error]*).

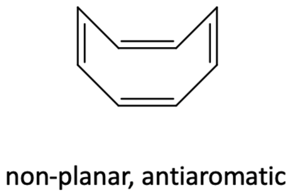


Figure *[Math Processing Error]*: Free cyclooctatraene is non-planar, thus *[Math Processing Error]* electrons are localized.

In metallocenes however, the ring becomes planar (Figure *[Math Processing Error]*). One can again formally explain that by assuming an aromatic *cot*$^{2-}$ ligand that binds to a metal 2+ cation, however one should keep in mind again that this is a formal view and not necessarily reflects the bonding situation in the compound.

Metals having smaller atomic radius can bind to *cot* in η^2, η^4, and less commonly in η^6-mode. The 18 electron rule holds in most cases. For instance, *cot* can make a η^4-complex in tricarbonyl cyclooctatetraene ruthenium (0) (Figure *[Math Processing Error]*).

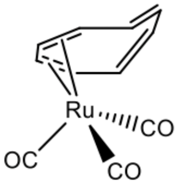


Figure *[Math Processing Error]*: tricarbonyl cyclooctatetraene ruthenium (0)

Also two metals can bind to a single *cot*-ligand. This is for instance realize in μ-cyclooctetraene bis(tricarbonyl ruthenium (0) (Figure *[Math Processing Error]*).

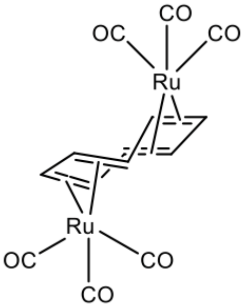


Figure *[Math Processing Error]*: bis(tricarbonyl) cyclooctetraene ruthenium (0)

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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10.2: Principles of carbonyl complexes

Introduction into Carbonyl Complexes

In this chapter we will look closer at carbonyl complexes, often just called carbonyls. Why? They are interesting for a number of reasons. Firstly, they are a quite extensive class of compounds with a diverse coordination chemistry. We will learn that the CO ligand can bind to a metal in various, sometimes non-obvious ways. Further, carbonyls are frequently used as starting materials for other coordination compounds. This is because the carbonyl ligand has no charge and carbon monoxide is a gas. Because of that a ligand substitution reaction can be easily driven to the right side by purging CO out of the reaction vessel. CO is a C_1 unit, and this is frequently used in catalysis with carbonyls. Carbonyls are often intermediates in reactions that add a single carbon atom to a hydrocarbon chain. A fascinating fundamental property of carbonyls is that its *[Math Processing Error]*-accepting properties stabilize metals in low, sometimes even negative oxidation numbers.

Bonding in CO

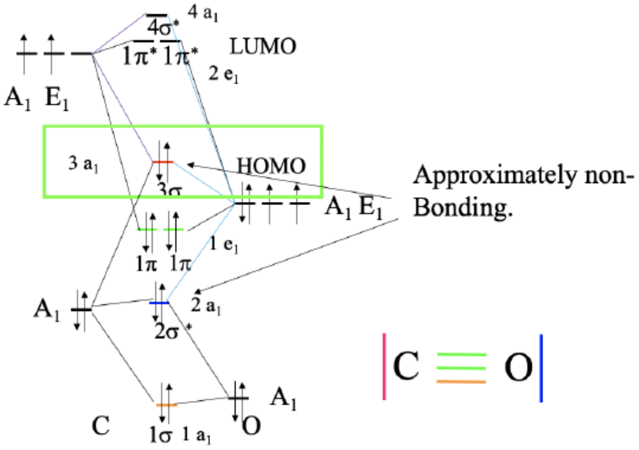


Figure *[Math Processing Error]*: Bonding in the CO molecule. MO diagram (left), and corresponding valence bond structure (right). For more explaination click here.

The carbon in the CO molecule is the more reactive end, and thus CO prefers to bind with the carbon to a metal, and not with oxygen. This is not obvious because the carbon is less electronegative than oxygen. The reason is that the HOMO of the CO molecule is an approximately non-bonding orbital which is primarily localized at the carbon (Figure *[Math Processing Error]*). In the valence bond picture it is resembled by the electron-lone pair at the carbon atom. The electron lone pair at the oxygen is resembled by the $2a_1$ molecular orbital which has a significantly lower energy, therefore it is rarely used in bonding. Both the *[Math Processing Error]* and *[Math Processing Error]**-orbitals are relatively close in energy to the HOMO, and thus these orbitals can also be used for bonding in carbonyls. This explains the diverse coordination chemistry of carbonyls.

σ-binding Modes of The Carbonyl Ligand

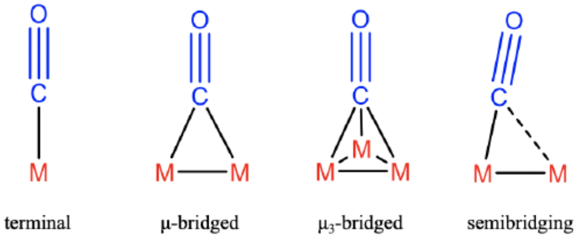


Figure *[Math Processing Error]*: σ-binding modes of the carbonyl ligand. Attribution: W. Petz

In the most simple case the CO uses its electron lone pair at the carbon to bind to single metal atom M (Figure *[Math Processing Error]*). In this case we call CO a terminal carbonyl ligand. In addition, it is possible that the electron lone pair is shared between two or even three metals that are interconnected via metal-metal bonds. In these cases, we say that the CO acts as a *[Math Processing Error]*-bridged, and *[Math Processing Error]*-brigded ligand, respectively. If two metals held together by a metal-metal bond are different, then the interaction of CO with one metal may be stronger than with the other. In this case the CO ligand acts as a semibridging ligand. In all these cases CO acts as a 2-electron donor because it donates its two electrons in the electron lone pair in the carbon atom.

In addition to the electron lone pair at the carbon the CO ligand can also use its binding [Math Processing Error]-orbitals for electron-donation into metal orbitals (Figure [Math Processing Error]). However, these electrons can only be used in conjunction with the electron lone pair at C because the electron pair has a higher energy than the [Math Processing Error]-electrons, and electrons of higher energy are always used first. For steric reasons the electron lone pair and the [Math Processing Error]-electrons are always donated to different metals that are held together by metal-metal bonds.

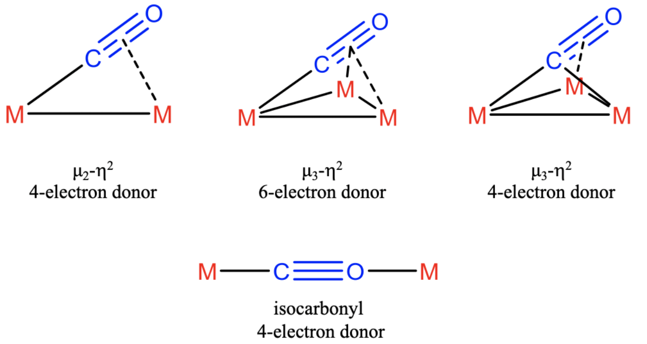


Figure [Math Processing Error]: Binding in [Math Processing Error]-orbitals for electron-donation into metal orbitals. Attribution: W. Petz

In the most simple case the CO ligand binds in [Math Processing Error]-[Math Processing Error]-mode which implies that the electron lone pair binds to one metal and two [Math Processing Error]-electrons bind to another. In this this case the CO ligand acts as a 4-electron donor. In addition, it is possible that all four [Math Processing Error]-electrons are involved involved in the bonding in addition to the electron lone pair. In this case three metal atoms are involved. The first one interacts with the electron-lone pair, the second one with the two [Math Processing Error]-electrons, and the third one with the other two [Math Processing Error]-electrons. Because three metals are bridged and both atoms of the ligand are involved in the bonding with the metal we can say that CO binds in [Math Processing Error]-[Math Processing Error]-fashion and acts as a 6-electron donor. It is also possible that the electron-lone pair is being shared between two metals, and two [Math Processing Error]-electrons are donated to the third metal. Also in this case the ligand binds in [Math Processing Error]-[Math Processing Error]-fashion, but acts as a 4-electron donor. Another way the CO ligand can act as 4-electron donor is when it acts as an isocarbonyl ligand. In this case it uses its electron pairs at both the C and the O-atoms. This is only possible when steric circumstances favor the utilization of the O-electron lone pair over the energetically higher [Math Processing Error]-electrons. This is rare.

[Math Processing Error]-binding Modes of The Carbonyl Ligand

The carbonyl ligand can use its [Math Processing Error]*-orbitals for bonding with metal d-orbitals in [Math Processing Error]-fashion. The ligand acts as a [Math Processing Error]-acceptor. There are two possibilities for the binding (Figure [Math Processing Error]).

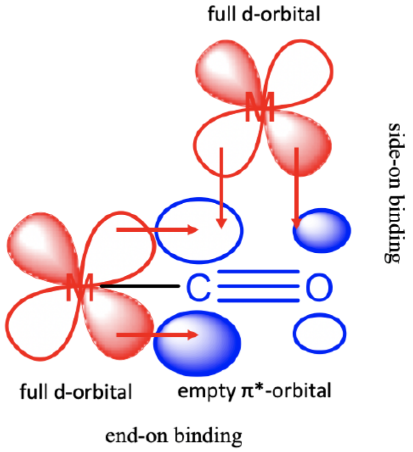


Figure *[Math Processing Error]*: *[Math Processing Error]*-binding modes of the carbonyl ligand

The first one occurs when the CO-ligand acts as a terminal ligand binding end-on. In this case the two lobes of the *[Math Processing Error]**-orbitals at the carbon interact with the the lobes of a metal d-orbital. Also the bonding *[Math Processing Error]*-orbitals have the right symmetry to overlap with the metal d-orbital in this mode, but their energies are much further away from those of the d-orbitals, so that these interactions can be neglected. The second possibility is that the CO binds side-on to the a metal-d-orbital. In this case one lobe at C and one lobe at O interacts with the metal d-orbital. These interactions are less strong compared to the end-on interactions because the orbital overlap is less efficient due to the unequal size of the lobes of the *[Math Processing Error]**-orbital. The *[Math Processing Error]**-orbital is mostly localized at the carbon-atom because the carbon atom is the more electropositive atom. Note that the bonding *[Math Processing Error]*-orbitals do not have the right symmetry to overlap with a metal-d orbital in *[Math Processing Error]*-fashion, they can only overlap in σ-fashion when the binding is side-on.

The Dewar-Chatt-Duncanson model

The σ-donor and the *[Math Processing Error]*-acceptor interactions in carbonyl complexes synergistically reinforce each other. This synergistic effect is called the Dewar-Chatt-Duncanson model for carbonyls. How can we understand the synergistic interactions. Let us consider a carbonyl ligand that binds end-on to a metal.

Figure *[Math Processing Error]*: σ-donor and the *[Math Processing Error]*-acceptor interactions in carbonyl complexes.

Let us first look at the σ-donor interactions. The electron lone pair at the carbon donates electron density into empty metal d-orbitals and a dative bond is formed between the metal and the carbon. The donated electron density enhances the energy of the metal d-electrons due to increased electron-electron repulsion. Because of their increased energy the d-electrons get more easily accepted by the carbonyl ligand through the *[Math Processing Error]*-acceptor interactions. The *[Math Processing Error]*-acceptor interactions increase the bond order between the metal and the carbon bond. At the same time the bond order between carbon and oxygen gets decreases because electron density has been transferred from the metal into the *[Math Processing Error]**-orbitals (Figure *[Math Processing Error]*).

The strength of the *[Math Processing Error]*-acceptor interactions can differ significantly in carbonyls. One can draw three different structures for weak, intermediate, and strong *[Math Processing Error]*-acceptor interactions (Figure *[Math Processing Error]* to *[Math Processing Error]*).

Figure *[Math Processing Error]*: Weak *[Math Processing Error]*-acceptor interactions

When only weak interactions are present we can represent the M-C bond as a single bond, and the C-O bond as a triple bond.

Figure *[Math Processing Error]*: Intermediate *[Math Processing Error]*-acceptor interactions

When the interactions have intermediate strength we can represent both the M-C bond and the C-O bond as a double-bonds.

Figure *[Math Processing Error]*: Strong *[Math Processing Error]*-acceptor interactions

When the *[Math Processing Error]*-acceptor interactions are strong then the M-C bond becomes a triple bond and the C-O bond becomes a single bond.

On what does the strength of the *[Math Processing Error]*-acceptor interactions depend? It depends mostly on the charge on the carbonyl. Carbonyl cations with a charge of +2 or higher tend to have weak *[Math Processing Error]*-acceptor interactions. Neutral carbonyls or carbonyls with a +1 or -1 charge have intermediate *[Math Processing Error]*-acceptor interactions. and those with a negative charge of 2- or higher have strong *[Math Processing Error]*-acceptor interactions. One can see from this that the smaller the positive charge and the higher the negative charge, the higher the metal-carbon bond-order, and the stronger the metal-carbon bond. As a consequence negative charges tend to stabilize carbonyls, while positive charges destabilize them. Therefore, carbonylate anions tend to be more stable compared to carbonyl cations. The stability of neutral carbonyls is intermediate.

Homoleptic Carbonyls of The Transition Metals

After having understood the principles of the bonding in carbonyls let us next think about what structures transition metal carbonyls make. The structures follow mostly the 18 electron rule. For the most simple homoleptic carbonyls, in which the carbonyl ligand binds end-on to the transition metal acting as a two-electron donor, we would just assemble as many ligands as needed until we have 18 electrons. This would give us the coordination number in the carbonyl from which we could deduct the structure. This works well for transition metals with an even number of valence electrons.

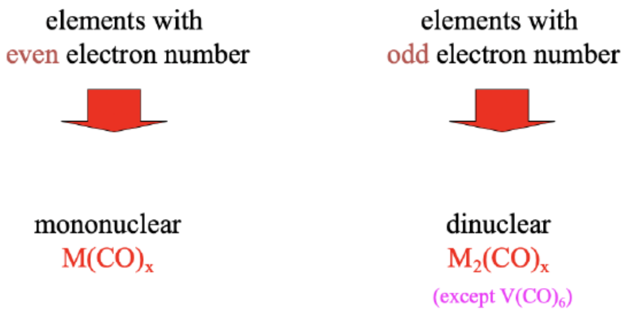
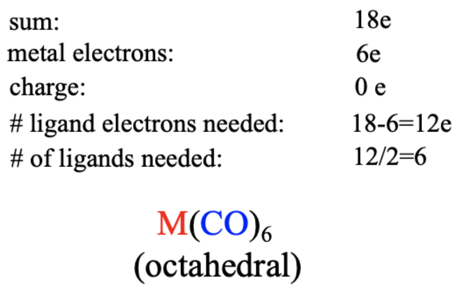


Figure *[Math Processing Error]*: Mononuclear carbonyls vs dinuclear carbonyls. Attribution: W. Petz

In this case the number of ligands x is just 18 minus the number of metal electrons divided by 2. We would therefore expect a mononuclear carbonyl of the type $M(CO)_x$ (Figure *[Math Processing Error]*). For metals with an odd number of electrons, the situation is more complicated because an odd number times two multiplied with an integer number never gives 18. In this case, as many ligands x as needed to make a 17 valence electron complex are added to the metal, and then the 17 valence electron complex dimerizes to form a dinuclear carbonyl of the composition $M_2(CO)_x$. An exception is the vanadium. It makes a 17 valence electron vanadium hexacarbonyl that does not dimerize because a coordination number of 7 is not favorable.

Homoleptic carbonyls of the 6th group (M = Cr, Mo, W)

Now let us look closer at the carbonyls with metals with an even number of electrons. We can start out with group 6 which contains the elements chromium, molybdenum, and tungsten. Our task is to determine the composition and structure of the carbonyls.



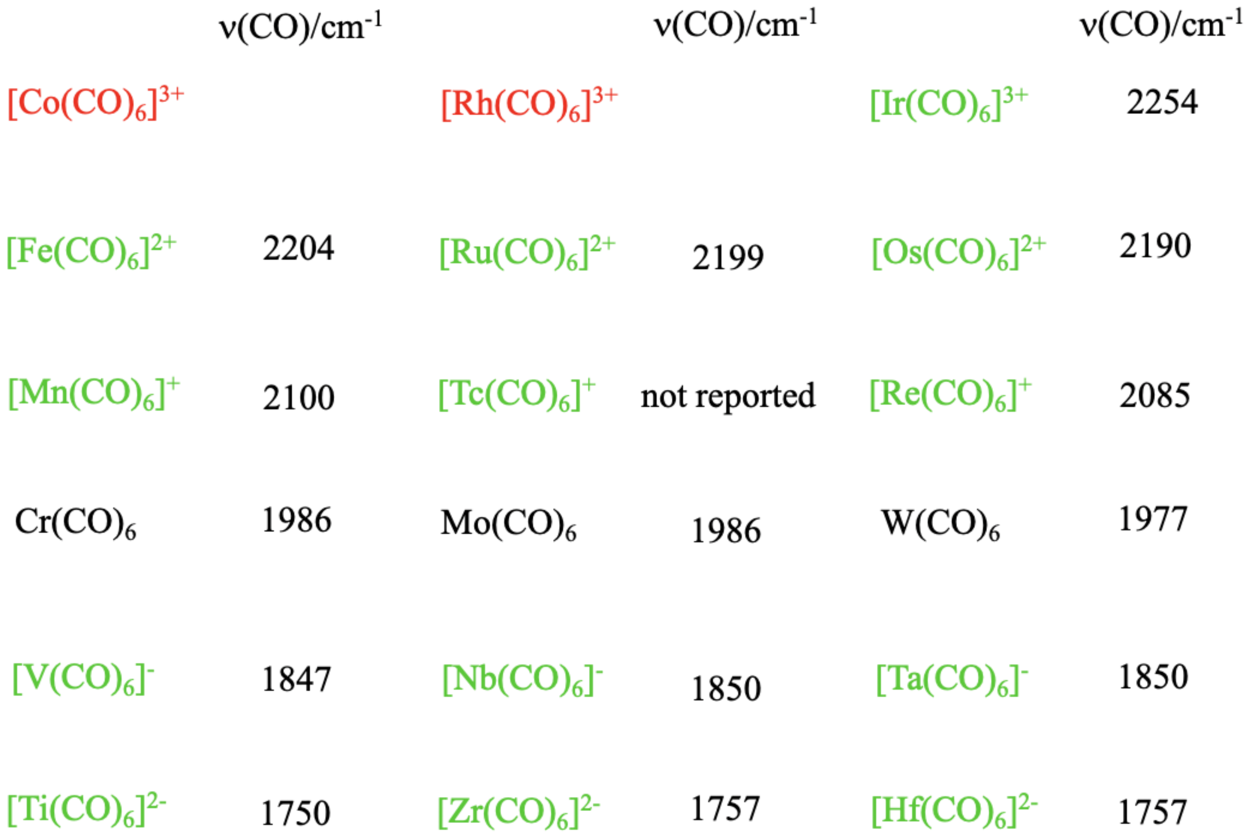
sum:	18e
metal electrons:	6e
charge:	0 e
# ligand electrons needed:	18-6=12e
# of ligands needed:	12/2=6

$M(CO)_6$
(octahedral)

Figure *[Math Processing Error]*: Determining the composition and structure of carbonyls via electron counting

According to the 18 electron rule we need 18 electrons overall. How many are contributed by the metal? Because the metals are in group 6, they all have six electrons. The carbonyls carry no charge, so there are no electrons to be subtracted or added. How many ligand electrons do we need to get to 18? Well, that is 18-6=12 electrons. How many carbonyl ligands are needed then? Because each ligand is considered a two electron donor, we need 12/2=6 ligands. The composition of the carbonyl will therefore be $M(CO)_6$. The carbonyl adopts octahedral shape in order to maximize the distance of the ligands from each other. The group 6 carbonyls are colorless, crystalline, and sublimable solids.

Charged Octahedral Carbonyls with 18 Electrons



	$\nu(CO)/cm^{-1}$		$\nu(CO)/cm^{-1}$		$\nu(CO)/cm^{-1}$
$[Co(CO)_6]^{3+}$		$[Rh(CO)_6]^{3+}$		$[Ir(CO)_6]^{3+}$	2254
$[Fe(CO)_6]^{2+}$	2204	$[Ru(CO)_6]^{2+}$	2199	$[Os(CO)_6]^{2+}$	2190
$[Mn(CO)_6]^{+}$	2100	$[Tc(CO)_6]^{+}$	not reported	$[Re(CO)_6]^{+}$	2085
$Cr(CO)_6$	1986	$Mo(CO)_6$	1986	$W(CO)_6$	1977
$[V(CO)_6]^{-}$	1847	$[Nb(CO)_6]^{-}$	1850	$[Ta(CO)_6]^{-}$	1850
$[Ti(CO)_6]^{2-}$	1750	$[Zr(CO)_6]^{2-}$	1757	$[Hf(CO)_6]^{2-}$	1757

Figure *[Math Processing Error]* Charged octahedral 18 electron carbonyls and the wave number of their C-O stretch vibrations. Green: Known charged carbonyls, Red: Unknown charged carbonyls.

Are there also other 18 e carbonyls of the type $M(CO)_6$ with other metals but group 6 metals? Yes, but the charge at the carbonyl needs to be adjusted so that the complex has 18 electrons. For instance, we can replace Cr by V, but then the we need a 1- charge which results in a carbonylate of the formula $V(CO)_6^-$. Why? The vanadium is in group 5 and has one electron less than chromium. For that reason, we must add an electron which gives the complex a 1- charge. Also the higher homologues $Nb(CO)_6^-$ and $Ta(CO)_6^-$ are known. What if we go further to the left in the periodic table? Titanium is left to the vanadium, and has four valence electrons. Therefore, the 18 valence electron hexacarbonyl of titanium has a 2- charge, and the formula is $Ti(CO)_6^{2-}$. Again, the higher homologues of $Ti(CO)_6^{2-}$, the $Zr(CO)_6^{2-}$ and the $Hf(CO)_6^{2-}$ are also known. Can we also go to the right in the periodic table? Manganese sits to the right of the chromium. The manganese has one electron more than the chromium, therefore the 18 electron hexacarbonyl of manganese must be a carbonyl cation with a 1+ charge, and the formula is $Mn(CO)_6^{2+}$. Of the higher homologues, both the $Tc(CO)_6^+$ and the $Re(CO)_6^+$ are known, too. To the right of the Mn, there is the Fe which has 8 valence electrons. Therefore the 18 electron iron hexacarbonyl must have a 2+ charge, and the formula is $Fe(CO)_6^{2+}$. The higher homologues $Ru(CO)_6^{2+}$ and $Os(CO)_6^{2+}$ are also known. Can we go even further to the left, to the Co? The expected formula for Co carbonyl would be $Co(CO)_6^{3+}$, but it is not known, and neither is the higher homologue, the $Rh(CO)_6^{3+}$. Only the $Ir(CO)_6^{3+}$ has been isolated. This reflects a general trend in carbonyl chemistry. Positive charges destabilize the carbonyl, and carbonyls with high positive charges are frequently not stable. On the other hand, negative charges stabilize a carbonyl and even carbonylates with high negative charges are stable. We can easily explain this by the fact that the bond order between the metal and the carbon decreases with increasing positive charge, and increases with increasing negative charge. Increasing bond order strengthens the stability of the carbonyl. We see from this that the *[Math Processing Error]*-acceptor properties are quite important for the stability of carbonyls. We also see that in carbonylates the oxidation numbers of the metals are negative. Negative oxidation numbers are quite unusual for metals. We conclude that the carbonyl ligand has the unusual property to stabilize the metal in negative oxidation states.

Is there a way to easily measure the bond order of an M-C bond? We can do this indirectly by measuring the IR-spectrum of the carbonyl. Because the bond order of the C-O bond decreases with increasing bond order for the M-C bond, the wavenumber for the C-O stretch vibration can be used as a measure for the M-C bond order. The lower the wavenumber, the lower the C-O bond order, and the higher the M-C bond order. When we look at the numbers for the different carbonyls within a period we see that as expected the wavenumbers increase with increasing group number indicating a decreasing bond order. We can also look down the groups. We see that in this case, the numbers hardly change, meaning that the bond order is hardly affected by the period of the metal.

Homoleptic Carbonyls of the 8th Group (Fe, Ru, Os)

What charge-neutral carbonyls would we expect for the group 8 elements Fe, Ru, and Os?

sum:	18e
metal electrons:	8e
charge:	0 e
# ligand electrons needed:	18-8=10e
# of ligands needed:	10/2=5

$M(CO)_5$
(trigonal-bibyramidal)

Figure *[Math Processing Error]*: Carbonyls for the group 8 elements

Overall, these carbonyl need to have 18 electrons. In this case the metals have 8 electrons. The charge is 0. This means that we would have 18-8=10 electrons that would need to come from the ligand. The number of ligands needed would therefore be 10/2=5. Thus, we would expect pentacarbonyls of the composition $M(CO)_5$ (Figure *[Math Processing Error]*). These carbonyls adopt the trigonal-bipyramidal shape. The group 8 carbonyls are all liquids. The iron pentacarbonyl has a light-orange color while the ruthenium and the osmium carbonyls are colorless.

Charged Trigonal-Bipyramidal Carbonyls with 18 electrons

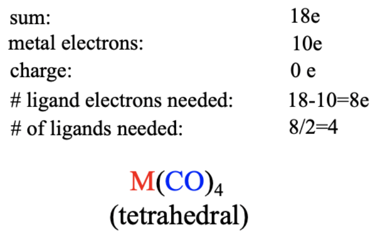
$[Ni(CO)_5]^{2+}$	$[Pd(CO)_5]^{2+}$	$[Pt(CO)_5]^{2+}$
$[Co(CO)_5]^{+}$	$[Rh(CO)_5]^{+}$	$[Ir(CO)_5]^{+}$
$Fe(CO)_5$	$Ru(CO)_5$	$Os(CO)_5$
$[Mn(CO)_5]^{-}$	$[Tc(CO)_5]^{-}$	$[Re(CO)_5]^{-}$
$[Cr(CO)_5]^{2-}$	$[Mo(CO)_5]^{2-}$	$[W(CO)_5]^{2-}$
$[V(CO)_5]^{3-}$	$[Nb(CO)_5]^{3-}$	$[Ta(CO)_5]^{3-}$

Figure *[Math Processing Error]*: 18 Charged trigonal-bipyramidal carbonyls with 18 electrons. Green: Known charged carbonyls, Red: unknown charged carbonyls.

We can again ask if there are charged isosteric pentacarbonyls with 18 e of metals other than group 8 metals. The answer is yes. The manganese is left to the iron in the periodic table and has one electron less. Therefore its pentacarbonyl needs to have a 1-charge and the composition is $Mn(CO)_5^-$. Also the higher homologues, the $Tc(CO)_5^-$ and the $Re(CO)_5^-$ exist. The Cr has one electron less than than the Mn, therefore its pentacarbonyl has a 2- charge and the formula is $Cr(CO)_5^{2-}$. $Mo(CO)_5^{2-}$ and $W(CO)_5^{2-}$ are also known. The vanadium has another electron less because it is in the 5th group, therefore its pentacarbonyl has a 3- charge, and the formula is $V(CO)_5^{3-}$. Again, the higher homologues, the $Nb(CO)_5^{3-}$ and the $Ta(CO)_5^{3-}$ are also stable. Also for the pentacarbonylates high negative charges are no problem for the stability of the complexes due to the stabilizing effect of the *[Math Processing Error]*-acceptor interactions. What about carbonyl cations with trigonal bipyramidal shape? As we go from Fe to Co, we need a 1+ charge at the carbonyl to achieve 18 electrons. The respective $Co(CO)_5^+$ cation is stable, and so are their higher homologues, the $Rh(CO)_5^+$ and the $Ir(CO)_5^+$. However, the group 10 pentacarbonyl cations $Ni(CO)_5^{2+}$, $Pd(CO)_5^{2+}$, and $Pt(CO)_5^{2+}$ are not stable. The 2+ positive charge weakens the metal-carbon bond too much. This behavior is consistent with the weakening of the M-C bond with increasing positive charge due to weaker *[Math Processing Error]*-acceptor effects.

Homoleptic carbonyls of group 10 (Ni, Pd, Pt)

What about the group 10 carbonyls?



sum:	18e
metal electrons:	10e
charge:	0 e
# ligand electrons needed:	18-10=8e
# of ligands needed:	8/2=4

$M(CO)_4$
(tetrahedral)

Figure *[Math Processing Error]*: Carbonyls for the group 10 elements

In this case the metals have 10 electrons. There is no charge. The number of ligand electrons needed is 18-10 = 8 electrons. Thus, the number of ligands is 8/2=4. Therefore, the composition is $M(CO)_4$ (Figure *[Math Processing Error]*). The shape is tetrahedral because we have an 18 and not a 16 valence electron complex. Nickel tetracarbonyl is a volatile, colorless liquid. The higher homologues, the $Pd(CO)_4$ and the $Pt(CO)_4$ are not stable. We can explain this when remembering that the *[Math Processing Error]*-orbital overlap in tetrahedral complexes is generally weak. Therefore, the M-C carbon bond is less effectively stabilized by the *[Math Processing Error]*-acceptor interactions compared to octahedral and trigonal-bipyramidal carbonyls. This effect is even more pronounced for the Pd and Pt carbonyls because they have larger orbitals that can overlap even less effectively with the relatively small *[Math Processing Error]**-orbitals of the CO ligand. In this case the *[Math Processing Error]*-acceptor interactions are so weak so that the entire molecule is no longer stable.

Charged Tetrahedral Carbonyls with 18 electrons

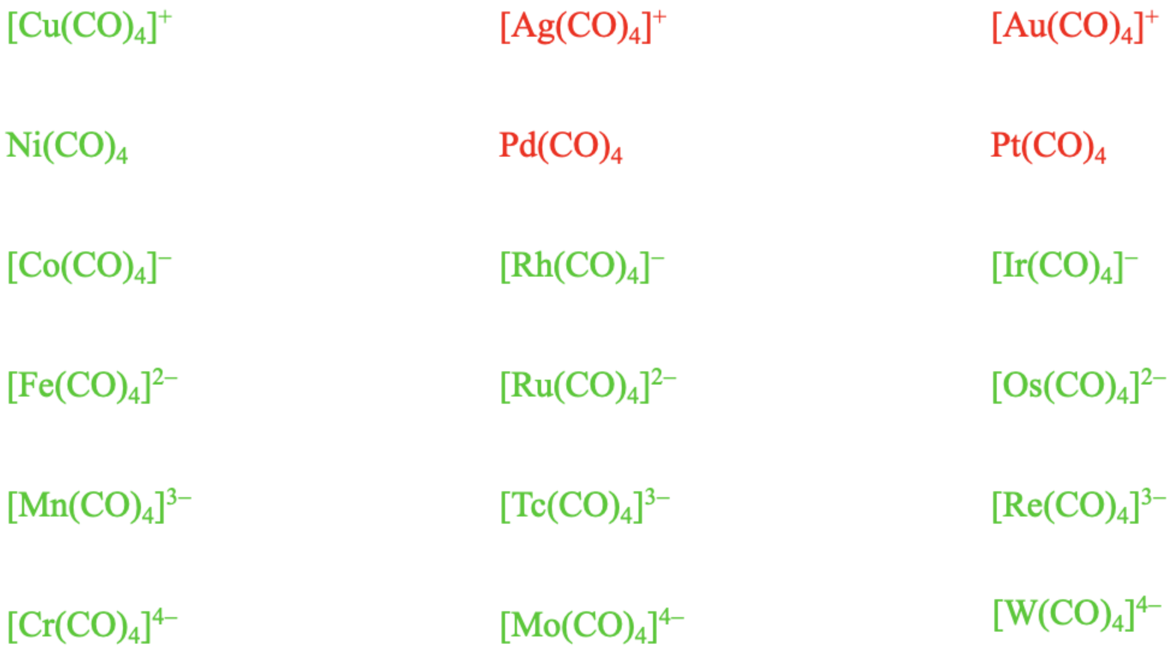


Figure *[Math Processing Error]*: Charged tetrahedral carbonyls with 18 electrons. Green: Known carbonyls. Red: Unknown carbonyls.

What about charged 18 electron tetrahedral carbonyls with other metals? Again, negatively charged carbonylates are stable, even with high negative charges. $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Mn(CO)_4^{3-}$, and $Cr(CO)_4^{4-}$ are all stable and so are their higher homologues. The $Cu(CO))_4^+$ which has a 1+ positive charge is also known, but its higher homologues, the $Ag(CO)_4^+$ and the $Au(CO)_4^+$ are not.

Overall Stability Trends

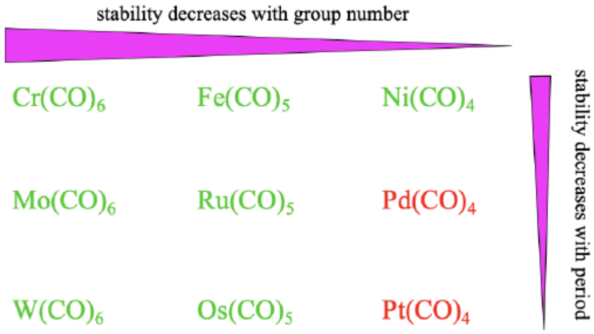


Figure *[Math Processing Error]*: Stability trends. Attribution: W. Petz

Overall the stability of carbonyls tends to decrease from group 6 to group 8 to group 10 (Figure *[Math Processing Error]*). This trend is because the octahedral shape allows for the best orbital overlap for *[Math Processing Error]*-acceptor interactions, followed by the trigonal bipyramidal, followed by the tetrahedral shape. The stability also tends to decline from the 4th to the 6th period. This trend can be explained by less efficient orbital overlap due to increasingly different orbital size between the ligand and the metal orbitals. These effects are sufficiently large for $Pd(CO)_4$ and $Pt(CO)_4$ to make them instable.

Group 4 and Group 12 Carbonyls (non-existing)

We have discussed group 6, 8, and 10 carbonyls, but not group 4 and group 12. Why? Because no carbonyls of these groups are stable. What is the reason? For group 4 carbonyls, we would need seven carbonyl ligands. This would lead to a coordination number of seven which is unacceptably high for carbonyls. For group 12 carbonyls, we would only need three carbonyl ligands. This would lead to an unacceptably low coordination number of 3.

Homoleptic carbonyls of the 7th group (M = Mn, Tc, Re)

Now let us think about what structures the homoleptic carbonyls with metals having an odd number of electrons form. Let us start with the 7th group which consists of the metals Mn, Tc, and Re. Our approach is to see how many ligands we need to produce a 17 valence electron fragment, and then dimerize that fragment.

sum:	17e
metal electrons:	7e
charge:	0 e
# ligand electrons needed:	17-7=10e
# of ligands needed:	10/2=5

$(CO)_5M\text{-}M(CO)_5 = M_2(CO)_{10}$

(derived from octahedral $M(CO)_5L$ ($L=M(CO)_5$))

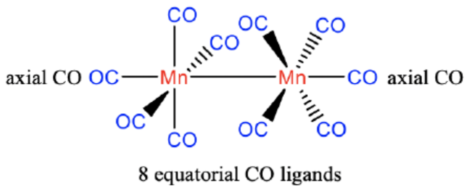


Figure *[Math Processing Error]*: Homoleptic carbonyls with group 7 metals. Attribution: W. Petz.

The group 7 metals have seven valence electrons. Again, we will assume that there is no charge on the carbonyl. The number of ligand electrons to produce the 17 valence electrons fragment will therefore be 17-7 = 10. The number of ligands needed is therefore 10/2=5 assuming that the carbonyl ligand is a 2-electron donor binding end-on to the metal. This gives an $M(CO)_5$ fragment that dimerizes to form an $M_2(CO)_{10}$ carbonyl with a metal-metal bond. The structure can be thought to be derived from an octahedral structure in which each metal is surrounded octahedrally by five CO ligands and an $M(CO)_5$ fragment acting as the sixth ligand. Each $M(CO)_5$ unit has one axial ligand and four equatorial ligands, whereby the axial ligand is co-directional with the metal-metal bond. The four equatorial ligands of the first metal are in staggered conformation relative to the four equatorial ligands of the second metal due to steric repulsion arguments.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_{10}$

Can we make charged isoelectronic carbonyls of the type $M_2(CO)_{10}$ with other metals? The answer is yes, but only carbonylate anions with low negative charge, and no carbonyl cations. The formation of carbonyl cations is prohibited because of the weakening of the *[Math Processing Error]*-acceptor interactions that result from the positive charge. High negative charges are not possible because too many negative charges on the metal atoms lead to electrostatic repulsion and the destabilization of the metal-metal bonds.

$Mn_2(CO)_{10}$	$Tc_2(CO)_{10}$	$Re_2(CO)_{10}$
$[Cr_2(CO)_{10}]^{2-}$	$[Mo_2(CO)_{10}]^{2-}$	$[W_2(CO)_{10}]^{2-}$

Figure *[Math Processing Error]*: Charged isoelectronic carbonyls of the type $M_2(CO)_{10}$

There are therefore only $Cr_2(CO)_{10}{}^{2-}$, and the higher homologues $Mo_2(CO)_{10}{}^{2-}$ and $W_2(CO)_{10}{}^{2-}$, but no other M_2CO_{10} type carbonyl ions.

Homoleptic carbonyls of the 9th group (M = Co, Rh, Ir)

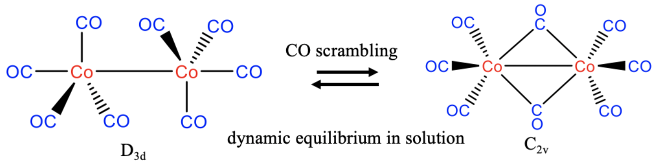
What are the expected structures for the homoleptic carbonyls of group 9?

sum:	17e
metal electrons:	9e
charge:	0 e
# ligand electrons needed:	17-9=8e
# of ligands needed:	8/2=4

$(CO)_4M\text{-}M(CO)_4 = M_2(CO)_8$

(derived from trigonal-bipyramidal M$(CO)_4$L (L=M$(CO)_4$))

Only $Co_2(CO)_8$ is stable ($Rh_2(CO)_8$ and $Ir_2(CO)_8$ are unstable)



C_{2v} structure is present in solid exclusively.

Figure *[Math Processing Error]*: Homoleptic carbonyls of the group 9 metals. Attribution: W. Petz.

In this case, the metal contributes 9 electrons, and this means that 17-9=8 electrons need to come from the carbonyl ligand. We therefore need 8/2=4 CO molecules to produce an $M(CO)_4$ 17 valence electron fragment. Two of the fragments then dimerize to form a dinuclear carbonyl of the composition M_2CO_8. In nature, however, only the Co-carbonyl is realized, the Rh and the Ir analogs are unstable. The structure of the $Co_2(CO)_8$ carbonyl can be derived from an $M(CO)_4$L trigonal-pyramid, whereby L is the second $M(CO)_4$ unit (Fig. 10.2.19). According to that, the coordination number is 5. There are two axial and six equatorial ligands whereby the equatorial ligands are oriented in a staggered conformation. In solution this structure is in dynamic equilibrium with a second structure with C_{2v} symmetry in which two CO ligands are bridging. Due to this equilibrium there is constant ligand scrambling, meaning that the CO ligands constantly move from axial to equatorial positions, and migrate from one metal atom to the other. In solid state the C_{2v}-type structure is present exclusively indicating that it is slightly more stable.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_8$

The charged, isoelectronic carbonyls of the type $M_2(CO)_8$ behave similarly to that of the type $M_2(CO)_{10}$. There are no highly charged binuclear carbonylate anions, and no carbonyl cations.

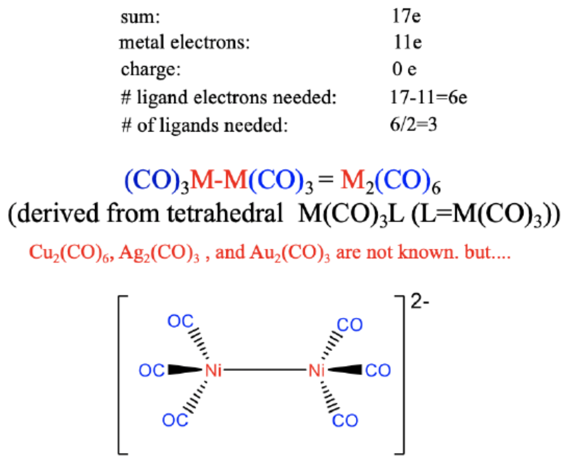
$Co_2(CO)_8$	$Rh_2(CO)_8$	$Ir_2(CO)_8$
$[Fe_2(CO)_8]^{2-}$	$[Ru_2(CO)_8]^{2-}$	$[Os_2(CO)_8]^{2-}$

Figure *[Math Processing Error]*: Charged isoelectronic carbonyls of the type $M_2(CO)_8$ (green: stable carbonyl. red: unstable carbonyl)

There are only the weakly negatively charged $[Fe_2(CO)_8]^{2-}$, $[Ru_2(CO)_8]^{2-}$, and $[Os_2(CO)_8]^{2-}$. The weakly negative charge stabilizes the metal-carbon bond without destabilizing the metal-metal bond too much. We can further see from this that a weakly negative charge is better for the stability of the species than no charge at all.

Homoleptic Carbonyls of the 11th Group (M = Cu, Ag, Au)

The group 11 metals Cu, Ag, and Au have eleven valence electrons.



sum:	17e
metal electrons:	11e
charge:	0 e
# ligand electrons needed:	17-11=6e
# of ligands needed:	6/2=3

$(CO)_3M\text{-}M(CO)_3 = M_2(CO)_6$

(derived from tetrahedral $M(CO)_3L$ ($L=M(CO)_3$))

$Cu_2(CO)_6$, $Ag_2(CO)_3$, and $Au_2(CO)_3$ are not known. but....

Figure *[Math Processing Error]*: Homoleptic carbonyls of the 11th group metals (Attribution: W. Petz)

Therefore, six ligand electrons are needed to achieve 17 electrons (Figure *[Math Processing Error]*). This means that 6/2=3 CO ligands are required to produce the 17 valence electron fragment. The dimer of it has the composition $M_2(CO)_6$ and its structure can be derived from a tetrahedral $M(CO)_3L$ structure in which L is the second $M(CO)_3$ fragment. Neither the Cu, nor the Ag, nor the Au carbonyl are known due to the weak *[Math Processing Error]*-overlap in tetrahedral coordination. However, the weakly negatively $[Ni_2(CO)_6]^{2-}$ ion is known which may be explained by the stabilizing effect of one negative charge on the M-C bond.

Overall Stability Trends

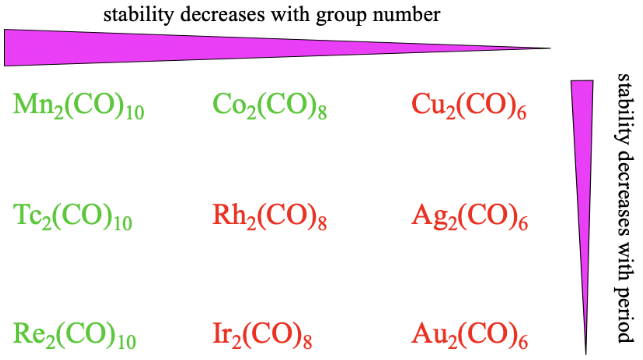


Figure *[Math Processing Error]*: Overall stability trends for dinuclear carbonyls. Green: stable. Red: Unstable.

Overall, we see the same stability trends for the dinuclear carbonyls as compared to the mononuclear ones. The stability decreases with the group number because *[Math Processing Error]*-overlap becomes smaller with smaller coordination numbers. Also, we see that the stability decreases with the period because of decreasing match of orbital sizes.

Homoleptic carbonyls of the 5th group (M = V, Nb, Ta)

The 17 valence electron fragment of the carbonyl of vanadium has the composition $V(CO)_6$. It does not dimerize because the coordination number of 6 is much more favorable compared to the coordination number 7. $V(CO)_6$ is a dark violet radical of octahedral shape. The radical electron is sterically inactive. $V(CO)_6$ can be used as an oxidant because it can be reduced easily to the 18 valence electron species $V(CO)_6^-$. The higher homologues $Nb(CO)_6$ and $Ta(CO)_6$ are not known. This may be explained by the weaker orbital overlap between the relatively small *[Math Processing Error]**-orbitals of the carbonyl ligand and the large metal d-orbitals of Nb and Ta.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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10.3: The Concept of Isolobality, Carbonyl Clusters, and Ligands Related to CO

Isolobality

In the previous chapter we discussed the most simple homoleptic carbonyls. We still need to discuss more complex carbonyls, but before we do this, we will learn about the concept of isolobality. This isolobality concept greatly helps to understand and rationalize complex carbonyls, but its applications are not limited to carbonyl chemistry. It is generally very useful to predict the stability of organic and inorganic compounds. This makes it helpful in synthesis, because in synthesis it is important to be able to estimate if the target molecule is stable or not.

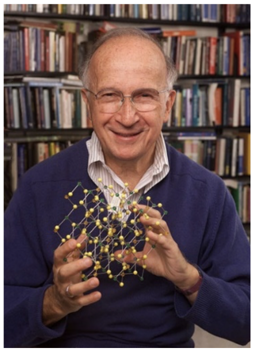


Figure 10.3.1 Roald Hoffman (Attribution: .The original uploader was Xtreambar at English Wikipedia. / Public domain https://commons.wikimedia.org/wiki/F...d_Hoffmann.jpg)

The concept of isolobality was developed by Roald Hoffmann, who won the Nobel prize in chemistry in 1981. It comes from the greek words "isos" meaning "similar" and "lobos" meaning lobe. Hence, "isolobal" means "similar lobes". In his Nobel speech he defined isolobality as follows: "Molecular fragments are isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar - not identical, but similar. " When molecular fragments are isolobal then they can likely be combined to form a stable molecule. Thus, isolobal fragments are compatible building blocks for the construction of stable molecules. We can also say that the concept of isolobality helps us to predict when a stable bond forms. Whenever two molecular fragments are isolobal, then they will likely form stable bonds between them.

The Concept of Isolobality

Are there simple means how to estimate if two molecular fragments are isolobal? In main group chemistry the octet rule is a very helpful guide, especially for the period 2 elements for which the octet rule holds fairly strictly. The difference between the number "8" and the number of valence electrons (VE) of the molecular fragment is equal to the number of frontier orbitals and the number of electrons in it: # frontier orbitals = number of electrons in the frontier orbitals = 8 – VE(fragment). Thus, when two fragments have the same number of valence electrons, they can be considered isolobal.

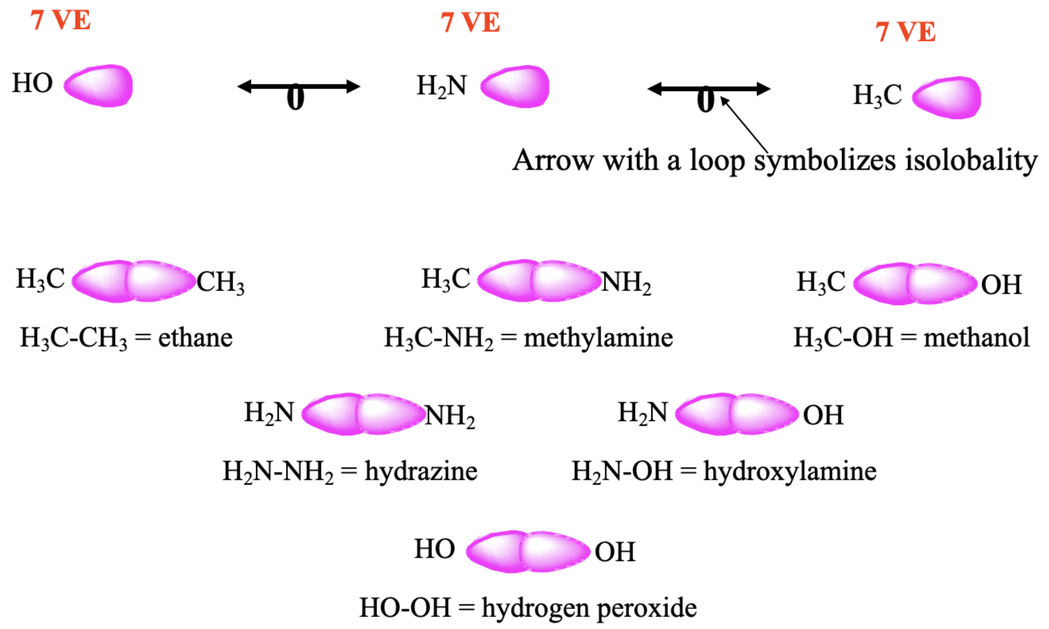


Figure 10.3.2 Isolobal 7 VE fragments (Attribution: W. Petz)

For example, the CH_3 fragment has 7 VE, therefore it has one frontier orbital with one electron it (Fig. 10.3.2). The same is true for the NH_2 and the OH fragments. The NH_2 fragment has 5+2=7 VE, and the OH fragment has 6+1=7 VE. Therefore, these three fragments are isolobal. Isolobality between two fragments is symbolized by an arrow with a loop, and therefore we can write two such arrows between the three isolobal fragments. It should be possible to combine these isolobal fragments to form stable molecules. Let us test this. Two CH_3 fragments can be combined to form an ethane molecule which is known to be stable. The combination of CH_3 and NH_2 gives methylamine which is stable, and the combination of CH_3 and OH gives methanol, which is also stable. Two NH_2 fragments give hydrazine, $H_2N\text{-}NH_2$ which exists, the combination of NH_2 and OH gives the known hydroxylamine molecule NH_2OH. The combination of two OH fragments gives hydrogen peroxide H_2O_2.

The Concept of Isolobality

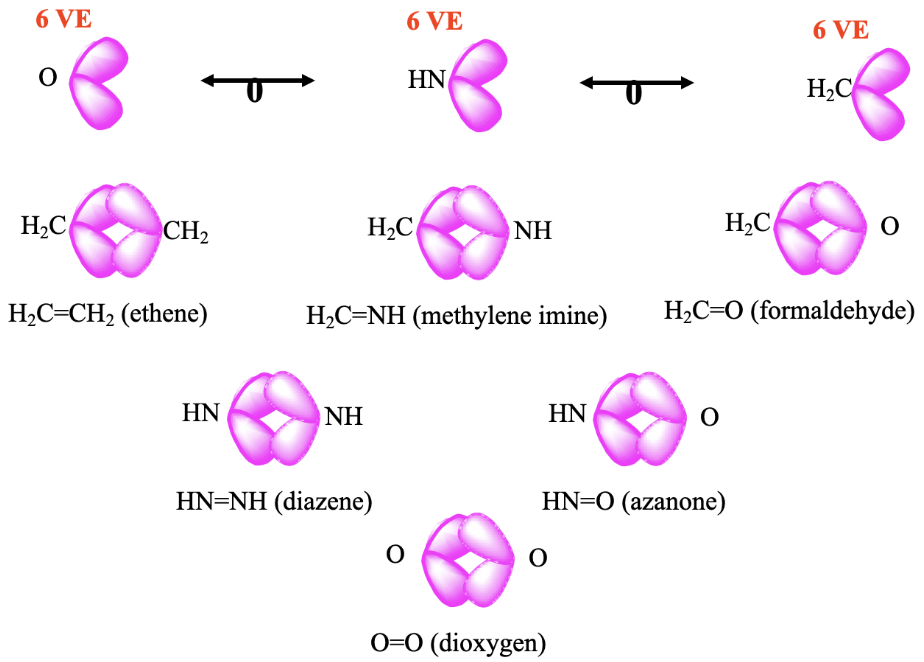
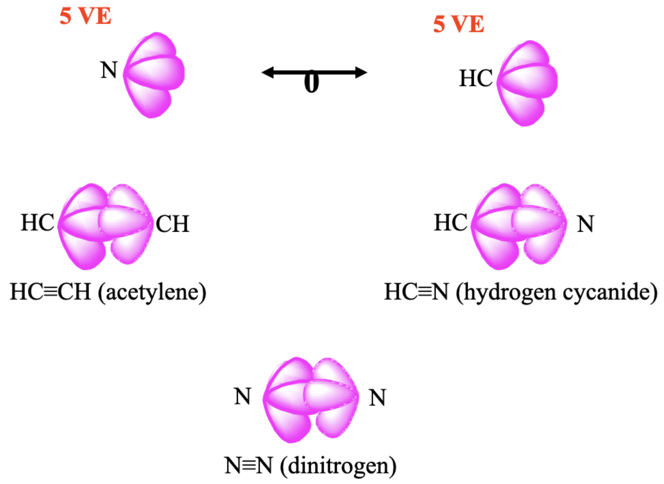


Figure 10.3.3 Examples of isolobal 6 VE fragments (Attribution: W. Petz)

As another example, the CH_2 fragment is a 6 VE fragment, thus there are 8-6=2 frontier orbitals with overall two electrons in them (Fig. 10.3.3). An NH-fragment and an O-atom also have 6 VE, and are therefore isolobal to CH_2. In NH there are 5+1=6 valence electrons, and an oxygen atom has 6 valence electrons. We can combine two CH_2 fragments to form ethene $H_2C{=}CH_2$. Combining CH_2 with NH and O, respectively gives methylene imine H_2CNH, and formaldehyde $H_2C{=}O$, respectively. Methylene imine is stable in the gas phase, and oligomerizes in higher concentrations to form a hexamer, called urotropine. Other oligomers and polymers are also known. The combination of two NH fragments gives the known molecule diazene HN=NH, and the combination with an O atom gives H-N=O, which is known as nitroxyl or azanone, and is stable in the gas phase. The combination of two oxygen atoms gives the well known O_2 molecule.



HC≡CH (acetylene)

HC≡N (hydrogen cycanide)

N≡N (dinitrogen)

Figure 10.3.4 Examples of isolobal 5VE fragments (Attribution: W. Petz)

Lastly, let us look at a few 5 VE fragments (Fig. 10.3.4). The CH fragment has 4+1=5 VE, and an N-atom has 5 VE as well, thus they can be considered isolobal. Two CH fragments give acetylene C_2H_2, and two N atoms give the dinitrogen molecule N_2. The combination of a CH fragment with an N fragment gives H-CN, well known as hydrogen cyanide.

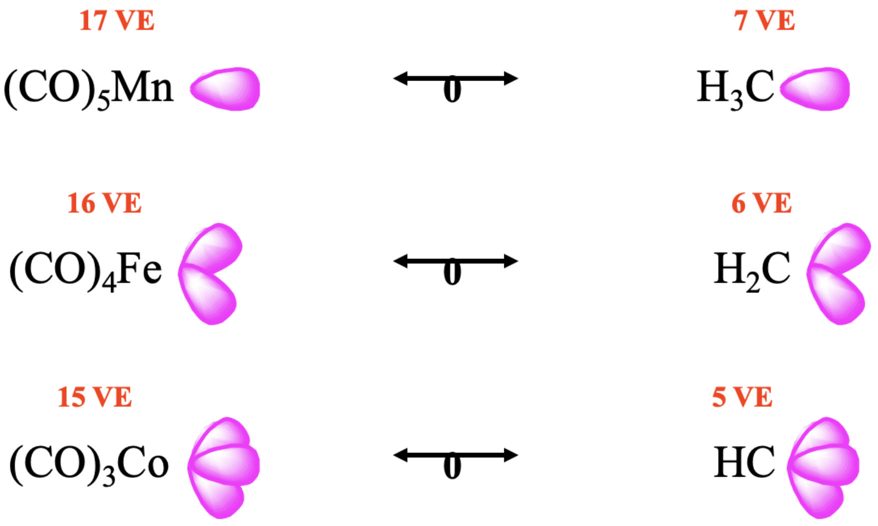


Figure 10.3.5 Examples for isolobal carbonyl and organic fragments (Attribution: W. Petz)

In the way the octet rule can help to predict the number of frontier orbitals and the electrons in them for main group element fragments, the 18 electron rule can be used to predict the number of frontier orbitals and electrons for organometallic fragments, including carbonyl fragments. The number of frontier orbitals and the number of electrons in them is 18 minus the number of valence electrons the organometallic fragment has: # frontier orbitals = number of electrons in them = 18-VE. For instance for a 17 VE fragment such as $Mn(CO)_5$ there is one frontier orbital with one electron, for a 16 VE fragment such as $Fe(CO)_4$ there are two frontier orbitals with one electron in each of them, and for a 15 VE fragment such as $(CO)_3Co$ there are three frontier orbitals with overall three valence electrons (Fig. 10.3.5). This implies that a 17 VE carbonyl fragment is isolobal to a 7 VE organic fragment such as CH_3. Similarly, a 16 VE carbonyl fragment is isolobal to a 6 VE fragment such as CH_2, and a 15 VE fragment is isolobal to a 5 VE fragment such as CH (Fig. 10.3.5).

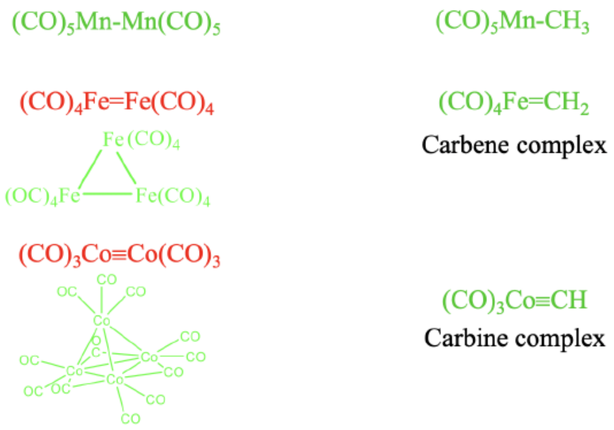


Figure 10.3.6 Green: Stable molecules formed from isolobal fragments. Unknown forms are denoted in red (Attribution: W. Petz).

It should be possible to combine the isolobal fragments to form stable molecules. Let us check how well this works (Fig. 10.3.6). It should be possible to combine the two 17 VE electron fragments such as $Mn(CO)_5$ to form $(CO)_5Mn\text{-}Mn(CO)_5$. This is a known molecule. Remember we encountered it previously when we discussed the homoleptic carbonyls of metals with an odd number of electrons. Combining this fragment with a 7 VE CH_3 fragment leads to $(CO)_5Mn\text{-}CH_3$ which is also stable. Can we also combine two 16 VE electron fragments to form $(CO)_4Fe{=}Fe(CO)_4$ with an Fe=Fe double bond? The answer is no. Metal-metal double bonds, and also metal-metal triple bonds in carbonyl complexes are not formed. Instead clusters with single bonds are realized. The number of single bonds a metal makes is equal to the number of its frontier orbitals. In the case of 16 VE fragments trimeric clusters with single bonds are formed. In this cluster the two frontier orbitals of each fragment make two single bonds to two other fragments. In contrast, a 16 VE carbonyl fragment such as $(CO)_4Fe$ can be combined with a 6 VE fragment to form a compound with a Fe=C double bond. A compound with a metal-carbon double bond is called a carbene complex. Similarly, the combination of 15 VE fragments of the type $Co(CO)_3$ does not lead to a stable $(CO)_3Co{\equiv}Co(CO)_3$ molecule with a Co≡Co triple bond. Instead, nature realizes a tetrameric tetrahedral cluster in which the three frontier orbitals of each 15 VE fragment make three single bonds to the other three 15 VE fragments. In clusters the CO ligands may not only be terminal, they can also be bridging. In the tetrameric Co-cluster, there are are nine terminal and three bridging CO-ligands. The three bridging CO ligands are connecting the three Co atoms at the base triangular face of the tetrahedron. What about the combination of a 15 VE fragment with an organic 5 VE fragment? The combination of a 15 VE fragment such as $Co(CO)_3$ with a 5 VE organic fragment such as CH to does yield stable complexes such as the $(CO)_3Co{\equiv}CH$ complex with a Co≡C triple bond. Complexes with metal-carbon triple bonds are called carbine complexes.

Synthesis of Terameric Cluster Carbonyls

How can we make a carbonyl cluster like $((Co(CO)_3)_4$?

$$2\ Co_2(CO)_8 \xrightarrow{\text{above } 54°C} Co_4(CO)_{12} + 4\ CO$$

Figure 10.3.7 Thermal reaction of $Co_2(CO)_8$ leading to $Co_4(CO)_{12}$ (Attribution: W. Petz)

It can be prepared by heating the $Co_2(CO)_8$ to a temperature above 54°C. Above this temperature the reactant loses four CO ligands and rearranges to form the cluster (Fig. 10.3.7). Interestingly, the higher homologues of the Co-cluster, the $Rh_4(CO)_{12}$ and the $Ir_4(CO)_{12}$ form spontaneously from the elements. Remember, that we previously determined that the $Rh_2(CO)_8$ and the $Ir_2(CO)_8$ are not stable. Rh and Ir favor the tetrameric clusters with 12 COs over the dimer with 8 CO ligands.

Structures of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$

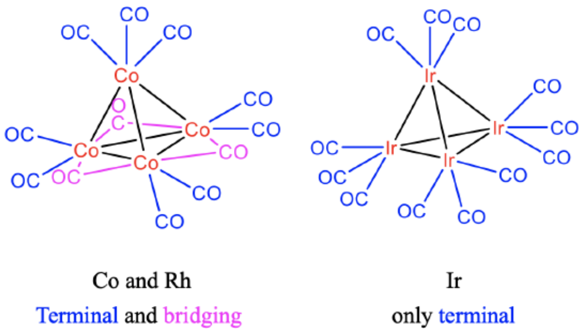


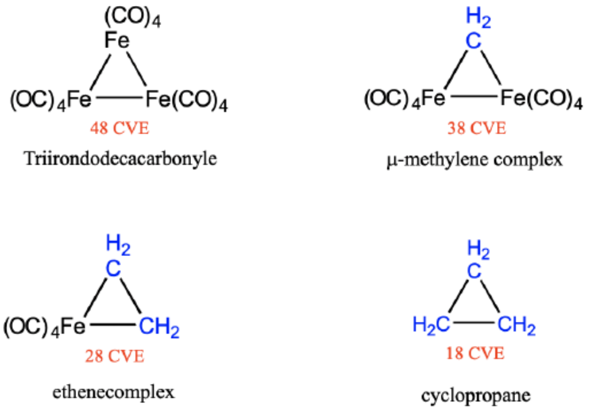
Figure 10.3.8 Structures of tetrameric group 9 carbonyl clusters (Attribution: W. Petz)

Like in the Co-cluster, there are 9 terminal and three bridging CO ligands in the $Rh_4(CO)_{12}$ cluster. By contrast, there are only terminal CO ligands in the iridium cluster (Fig.10.3.8) . This may be explained by the larger Ir-Ir bond length in comparison to the Co-Co and Rh-Rh bond lengths. The observation reflects the general rule that only 3d and 4d elements have bridging CO ligands, while only terminal ligands are observed in metals with 5d electrons.

Isoelectronic Charged Carbonyl Clusters

The previously discussed clusters were charge-neutral. Can we construct charged isoelectronic ones with different metals, and what is their stability? Let us start with the tetrameric Co-cluster made of four 15 VE fragments. The element left to the Co is the Fe. It has one electron less, therefore $Fe(CO)_3^-$ is the 15 VE electron fragment which is isoelectronic to the neutral $Co(CO)_3$ fragment. Its tetramer would be a $Fe_4(CO)_{12}^{4-}$ cluster. This cluster is not known. The cluster already carries a 4- charge which is too high to support stable Fe-Fe bonds. Each Fe carries formally a 1- negative charge and there is too much electrostatic repulsion between the Fe atoms. Another possibility to realize a 15 VE fragment with Fe is a $(CO)_4Fe^+$ fragment. Here an additional ligand is added contributing two electrons, and one electron is removed resulting in a fragment with a 1+ charge. The fragment could be combined to form an $Fe_4(CO)_{16}^{4+}$ cluster. However, such a cluster is also not stable. This is because the coordination number would be 7, which is too high for a carbonyl. In addition, there is the destabilizing effect of the positive charge on the Fe-C bond. Similarly, tetramers of the 15 VE fragments $Mn(CO)_4$, $Cr(CO)_4^-$ and $(CO)_5Cr^+$ are also not known. Also in these cases, the coordination numbers would be too high. The $Mn(CO)_4$ and the $Cr(CO)_4^-$ would lead to a coordination number of 7, in the case of the $Cr(CO)_5^+$ fragment the coordination number would be even 8. We see here the limitations of the concept of isolobality. The presence of isolobality is not always sufficient to make a stable molecule, also other factors like coordination numbers and charge needs to be considered.What about charged isoelectronic clusters made from 16 VE? We saw previously that the neutral 16 VE $Fe(CO)_4$ fragment gave a $Fe_3(CO)_{12}$ trimer. If we go from the Fe to the Mn, the isoelectronic 16 VE fragment would be a $Mn(CO)_4^-$ fragment because Mn has one electron less than Fe. This fragment can indeed be trimerized to give a stable $Mn_3(CO)_{12}^{3-}$ cluster with a 3- charge. This charge is not too high yet to destabilize the Mn-Mn bond and the coordination number of 6 is ideal for the stability of carbonyls. We could add a ligand and remove two electrons to produce a 15 VE $Mn(CO)_5^+$ fragment. However, in this case the coordination number would become 7 upon trimerization, which is too high to produce a stable cluster. In addition, the positive charge destabilizes the Mn-C bond. Replacing Mn by Cr in $Mn(CO)_5^+$ would give a neutral 16 VE $Cr(CO)_5$ fragment, but its trimer is not stable because also in this case the coordination number becomes too high. Replacing Fe in $Fe(CO)_4$ by Co would require a 1+ charge giving a $Co(CO)_4^+$ 16 VE fragment. Its trimer would have the coordination number 6, but it would carry a 4+ charge which is too high. A $Co(CO)_3^-$ fragment would also have 16 VE, but its trimer is also not known, possibly because the relatively small coordination number of 5, which is less favorable than a coordination number of 6. Overall we can say as a rule for the stability for carbonyl clusters that there should not be positive charges, and no high negative charges. There should not be high coordination numbers.

Clusters with 16 VE and 6 VE Fragments



48 CVE
Triirondodecacarbonyle

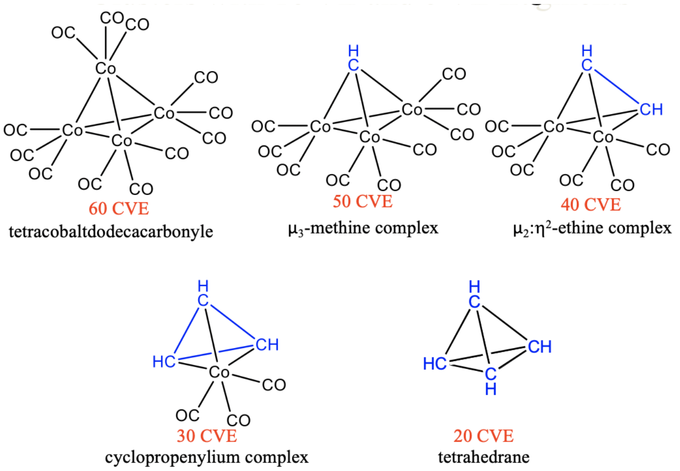
38 CVE
μ-methylene complex

28 CVE
ethenecomplex

18 CVE
cyclopropane

Figure 10.3.9 Clusters with 16 VE and 6 VE fragments (Attribution: W. Petz)

The cluster chemistry of carbonyls is even more versatile due to the possibility to substitute 16 and 15 VE fragments by 6 and 5 VE fragments, respectively. For instance, we can replace one 16 VE Fe(CO)$_4$ fragment by a 6 VE CH$_2$ fragment in the trimeric triiron dodecacarbonyl Fe$_3$(CO)$_{12}$ cluster (Fig. 10.3.9). In the resulting cluster a methylene group bridges two Fe atoms, therefore the complex can be regarded a μ-methylene complex. The substitution reduces the number of cluster valence electrons (CVE) from 48 to 38. A second substitution of another 16 VE tetracarbonyl iron fragment by another 6 VE methylene fragment gives a cluster with two Fe-C bonds and one carbon-carbon bond having 28 cluster valence electrons. This complex can be regarded as a ethene complex in which an ethene molecule binds side-on to a 15 VE Fe(CO)$_4$ fragment. Upon binding, the two Fe-C bonds are formed at the expense of the C-C π-bond and the bond order in the C-C bond is reduced from 2 to 1. If we substitute the last tetracarbonyl iron fragment by a third CH$_2$ unit, then a completely organic molecule, cyclopropane, results. All the molecules are known to be stable molecules, and their stability can be nicely understood by using the concept of isolobality.



60 CVE
tetracobaltdodecacarbonyle

50 CVE
μ$_3$-methine complex

40 CVE
μ$_2$:η^2-ethine complex

30 CVE
cyclopropenylium complex

20 CVE
tetrahedrane

Figure 10.3.10 Clusters with 15 VE and 5 VE fragments (Attribution: W. Petz)

Similarly, we can substitute 15 VE tricarbonyl cobalt units by 5 VE CH fragments in tetracobaltdodecacarbonyl Co$_4$(CO)$_{12}$. A first substitution gives a 50 VE cluster with one CH fragment that makes three bonds to three Co(CO)$_4$ fragments (Fig. 10.3.10). Because the CH group bridges three metal atoms it is regarded a μ$_3$-methine complex. A second substitution produces a 40 VE cluster with an organic CH-CH unit that makes four bonds to two Co atoms of two 15 VE Co(CO)$_3$ fragments. The CH-CH fragment can be considered an ethine molecule binding side-on to a dicobalthexacarbonyl fragment, whereby the two π-bonds in ethine are expended to form four Co-C single bonds. The cluster can be considered a μ$_2$:η$_2$-ethine complex because the ethine bridges two Co atoms and both carbons are involved in the bonding with Co. A third substitution leads to a 30 CVE cluster with three CH units binding to one Co(CO)$_3$ fragment. There are three C-C single bonds and three Co-C bonds in the cluster. The three CH units form a cyclopropenylium complex that binds side-on to a Co(CO)$_4$ fragment. A free cyclopropenylium molecule is a 3-ring with three π-electrons that are delocalized in the ring. Therefore, the bond order in a free cyclopropenylium molecule is 1.5. In the complex the three π-electrons are being used to make the three single bonds with the cobalt atoms. The bond order in cyclopropenylium is thereby reduced from 1.5 to 1. Finally, the fourth substitution of a tricarbonyl cobalt fragment by a methine fragment yields the completely organic tetrahedrane molecule. This molecule and the others discussed before are stable. The isolobality concept lets us rationalize these complex structures easily and understand their stability.

Synthesis of Cluster Complexes From Alkynes

The view that the 40 VE clusters are alkyne clusters is not just a formal view. They can be synthesized from alkynes. For instance alkyne-dicobalt clusters are accessible from dicobalt octacarbonyl and alkynes (Fig. 10.3.11).

$$Co_2(CO)_8 + RC{\equiv}CR \rightarrow (\mu\text{-}RC{\equiv}CR)Co_2(CO)_6 + 2\ CO$$

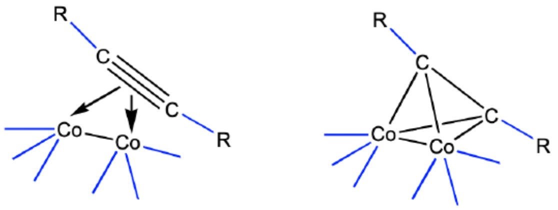
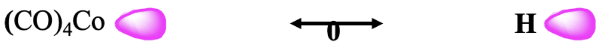


Figure 10.3.11 Synthesis of cluster complexes from alkynes (Attribution: W. Petz)

The cluster forms via the donation of the four π electrons of the alkynes into the metal d-orbitals of the dimeric cobalt carbonyl. This leads to a loss of of two CO ligands, and the formation of four Co-C bonds. Under harsher conditions the C-C triple bond can also cleave and this can give access to methine complexes.

Carbonyl Hydrides

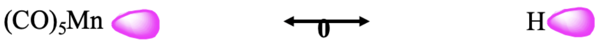
Now let us leave the carbonyl cluster compounds and talk about another interesting class of carbonyls: carbonyl hydrides. They can be rationalized by the concept of isolobality as well. A hydrogen atom can be conceived as a species with one frontier orbital containing one electron. In this case the frontier orbital is simply the 1s orbital of the hydrogen. Thus, it should be possible to combine an H atom with a 17 VE carbonyl fragment like tetracarbonyl cobalt.



$$Co_2(CO)_8 + H_2 \rightarrow 2\ HCo(CO)_4$$

Figure 10.3.12 Example for the formation of a cobalt carbonyl hydride (Attribution: W. Petz)

Indeed, one can combine such fragments to form stable carbonyl hydrides such as tetracarbonylhydrido cobalt (0). This molecule can be synthesized by reduction of bis(tetracarbonyl cobalt) (0) with dihydrogen (Fig. 10.3.12). Counter-intuitively, this molecule is a strong acid, it has an acidity similar to sulfuric acid. One would think that the Co-H bond would be polarized toward H based on electronegativity arguments. However, this is not the case. The carbonyl fragment has a frontier orbital which is energetically higher than that of H, and thus the bond is polarized toward H. In another view we can explain the high acidity be the fact that the loss of the proton leads to the very stable 18 VE tetrahedral $Co(CO)_4^-$ anion. Thus, loss of the proton occurs easily.



$$Mn_2(CO)_{10} + H_2 \xrightarrow{200\ \text{bar},\ 150°\ C} 2\ (CO)_5MnH$$

Figure 10.3.13 Example for the formation of a manganese carbonyl hydride (Attribution: W. Petz)

Another 17 VE electron fragment is the $Mn(CO)_5$ fragment. Also this fragment can be combined with an isolobal H fragment to form a stable molecule, which has the composition $HMn(CO)_5$ (Fig. 10.3.13). It can be prepared from bis(pentacarbonyl manganese) and dihydrogen at 200 bar and 150°C. This carbonyl hydride is a weak acid, it has a similar acidity as H_2S. We could argue that this lower acidity may be because the loss of the proton reduces its coordination number from 6 to 5. The coordination number of 6 is the preferred coordination number for carbonyls and thus the tendency to lose the proton is relatively small. The different metal and the number of carbonyl ligands will likely lead to a different energy of the frontier orbital compared to the previous example, which leads to a different polarity.

Overall, one can tune the properties in carbonyl hydrides from highly acidic to hydridic by choice of the metal the coordination number, and also by the choice of additional ligands L other than carbonyl. The electronic and steric properties of the ligands have an influence on the energy of the HOMO of the fragment, and thus on the polarity of the metal-hydrogen bond, and the acidity.

Ligands related to CO

The cyano ligand (CN^-)

Now let us leave the CO ligand, consider a number of related ligands, and discuss similarities and differences compared to the CO ligand. Let us start with the cyano ligand CN^-. This ligand is isoelectronic to the CO ligand. The N atom has one electron less than O, but the negative charge at the cyanide ligand compensates for that. One question we can ask is: What is the reactive end? The answer is: In analogy to the carbonyl ligand the reactive end is the carbon atom. We can explain this by the fact that the MO diagram is similar to that of CO, only the differences in atomic orbital energies are smaller due to the smaller electronegativity difference between C and N compared to C and O. Therefore, like in CO, the HOMO is represented by the electron lone pair at the C, which makes C the more reactive end. Due to the smaller electronegativity difference, the difference in energy between the lone pair at C and the lone pair at N is smaller, therefore, in contrast to CO, the cyano ligand acts far more often as a bridging ligand between two metals using both of its electron lone pairs.

Would we expect the cyano ligand to be a stronger or weaker σ-donor compared to the CO ligand? Think about it for a moment. The answer is: It is a stronger σ-donor because of its negative charge. The negative charge at the ligand increases electrostatic repulsion between the electrons, and this increases the orbital energies. Therefore, there is a stronger tendency to donate the electrons. Our next question is: Is the CN^- ligand a stronger or weaker π-acceptor than CO? The energy of the π*-orbitals is higher compared to CO because of the negative charge at the ligand. Because of that, electrons from the metal cannot be as easily accepted by the ligand. Therefore, the cyano ligand is a weaker π-acceptor than the carbonyl ligand. Our last question is: Are cyano complexes more stable with metals in high or low oxidation states. Because of electrostatic arguments a cyanide anion interacts more strongly with a metal cation rather than a metal in a zero or negative oxidation state. Therefore, unlike CO, CN^- does not stabilize metals in low oxidation states. It prefers to make complexes with metal in high, positive oxidation numbers.

The Nitrosyl Ligand NO

The nitrosyl ligand NO is another ligand similar to CO. It has one more electron that CO because N has one more electron than C. The additional electron makes NO an "odd" molecule with a radical electron. Like in CO and CN^-, the more electropositive element is the reactive end. In the case of NO it is the N atom. The radical electron is the most reactive electron that can be most easily donated, however the electron lone pair at N may be donated in addition. In the former case, the NO is a 1-electron donor, in the latter it is a 3-electron donor. How can we tell if one or three electrons have been donated? When only one electron is donated, the electron lone pair at the nitrogen is sterically active and leads to a bent structure (Fig. 10.3.14).

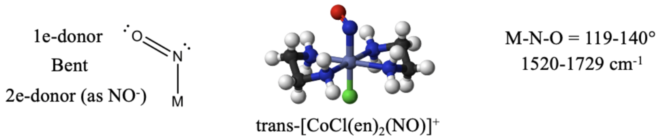


Figure 10.3.14 The Trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation as an example of an NO complex with NO as 1e donor.

An example is the trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation. Generally, the O-N-M bond angle in nitrosyl complexes with NO as a 1e-donor can vary between 119 and 140°. We can also identify a bent nitrosyl ligand in the IR spectrum. Typical wave numbers are 1520-1729 cm^{-1}.

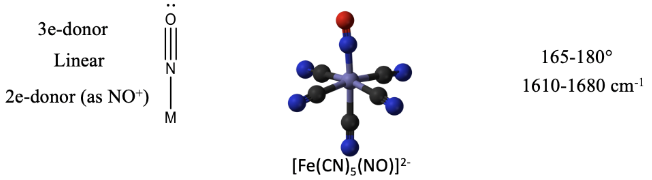


Figure 10.3.15 THe Nitroprusside anion as an example of a complex with NO as a 3e donor. (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...l-3D-balls.png)

When the nitrosyl ligand donates all three electrons, then it binds to the metal in a linear fashion (Fig. 10.3.15). The electron lone pair is no longer sterically active because it is involved in the bonding. An example is the nitroprusside anion $[Fe(CN)_5(NO)]^{2-}$. It is used as a medication for the treatment of high blood pressure. The bond angles in complexes with NO as the 3-electron donor are often not exactly 180°, but vary between 165 and 180°. It can also be identified in the IR because it has a characteristic band between 1610-1680 cm^{-1}.

There is a also a different view on nitrosyl complexes with linear and bent structures. In bent structures we can also consider the ligand as an NO^- anion that donates two electrons. The NO^- anion has two electron lone pairs at N. When it donates two electrons then one sterically active electron lone pair remains at the nitrogen atom. In linear structures we can regard the ligand also as an NO^+ cation that donates two electrons. An NO^+ cation has one electron lone pair at N, and when it donates that lone pair then there is no sterically active electron at the nitrogen left, and thus the ligand binds in a linear fashion.

We could also ask: What can neutral NO not be a 2-electron donor with the radical electron left at N? The answer is: The radical electron is the highest energy electron, and is always used first in interactions with a metal.

Phosphine Ligands

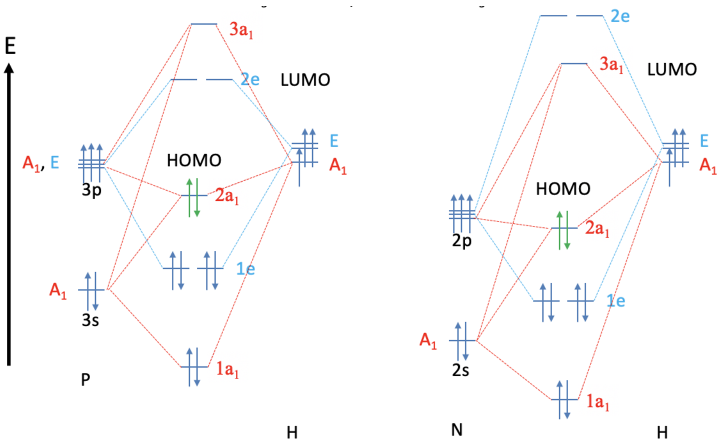


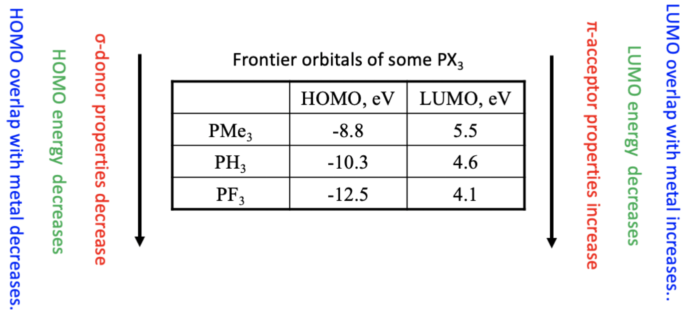
Figure 10.3.16 MO diagrams of PH_3 and NH_3

Phosphines are another class of important ligands in coordination chemistry. To approach the coordination chemistry of phosphines let us have a look at the MO diagram of the PH_3 molecule and compare it with the NH_3 molecule. As one would expect, the MOs are overall similar, but there is one important difference. While the LUMO in NH_3 is the anti-bonding $3a_1$ orbital, the LUMOs in the PH_3 molecule are the anti-bonding 2e orbitals. The relative energies of the $3a_1$ and 2e orbitals in the PH_3 and NH_3 molecules are swapped up. This can be attributed to the fact that the the P atom uses the 3s and the 3p orbitals as valence orbitals, while N uses the 2s and 2p orbitals. The 3s and the 3p orbitals are larger and overlap less effectively with the small 1s orbitals of the hydrogen. They also have a higher energy making the P-H bonds less polar than the N-H bonds. The energy of the PH_3 HOMO is higher than that of the NH_3 HOMO. Both the HOMO and the LUMO of PH_3 are more diffuse and polarizable than the respective orbitals in NH_3.

The higher energy of the HOMO in PH_3 makes it a better donor than NH_3. In addition, the PH_3 has π-acceptor properties because the 2e LUMO are relatively low-lying anti-bonding 2e orbitals and have suitable shape for π-overlap with metal d-orbitals. NH_3 does not have these π-acceptor properties because its LUMO is the $3a_1$ orbital, and not the 2e orbitals. The 2e orbitals in NH_3 are energetically too high in order to allow for significant π-acceptor interactions.

Bonding in Phosphine Complexes

The σ-donor and π-acceptor properties of the phosphine ligand can be modified by substituting H by other groups. Generally, more electron donating groups increase the energy of the HOMO and the LUMO. This strengthens the σ-donor and reduces the π-acceptor properties. Vice versa, more electron withdrawing groups decrease the energy of the HOMO and the LUMO. As a consequence, the ligand becomes a weaker σ-donor and a stronger π-acceptor (Fig. 10.3.17).



Frontier orbitals of some PX_3

	HOMO, eV	LUMO, eV
PMe_3	-8.8	5.5
PH_3	-10.3	4.6
PF_3	-12.5	4.1

PF_3 forms stable complexes with Pd^0 and Pt^0, ML_4, while CO does not

Figure 10.3.17 HOMO and LUMO energies of three phosphines

The table above shows the HOMO and LUMO energies of three phosphines. As expected the HOMO and LUMO energies decrease from PMe_3 to PH_3 to PF_3 due to the increasingly electron-withdrawing nature of the substituent. As a consequence, the σ-donor properties weaken and the π-acceptor properties strengthen from to PMe_3 to PH_3 to PF_3.

Not only the energies, but also the orbital overlap is important for the strength of the π-acceptor properties of the phosphine ligands. The more strongly electron-withdrawing the group is the more the anti-bonding e-type LUMO orbitals are located at the P atom. The more these orbitals are localized at P, the better they can overlap with the ligand. Vice versa the localization of the HOMO shifts toward the group as the group becomes more electron-withdrawing, thereby weakening the σ-donor properties.

Phosphine ligands with strongly electron withdrawing groups such as PF_3 have π-acceptor properties strong enough to stabilize metals in low oxidation numbers, similar to CO. For example, the PF_3 ligand forms stable complexes with Pd and Pt atoms in the oxidation number 0, while the respective Pd and Pt carbonyls are not known.

Dihydrogen Complexes

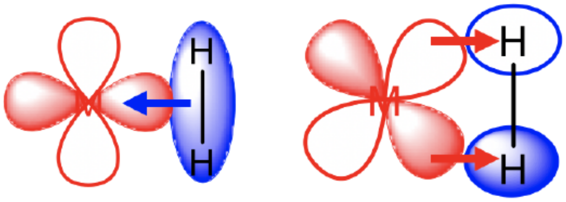


Figure 10.3.18 Bonding in dihydrogen complexes

Even a simple dihydrogen molecule can serve as a ligand. We call the respective complexes dihydrogen complexes. When dihydrogen acts as a ligand, it binds side-on to the metal (Fig. 10.3.18). It uses its bonding σ-orbital for σ-donation. In addition, it uses its σ*-orbital as π-acceptor. The combination of the σ-donor and π-acceptor interactions leads to the lowering of the bond order and the lengthening of the H-H bond in the dihydrogen molecule. When these interactions are strong enough, then the H-H bond can cleave and two, separate hydrido-ligands bind to the metal via two metal-hydrogen single bonds. The π-acceptor interactions tend to be strong enough to cleave the H-H bond when the metal is relatively electron-rich. Dihydrogen complexes are therefore usually observed when the metal has a high oxidation number and/or when it has other strongly π-accepting ligands such as CO. For instance, the $Mo(PMe)_5H_2$ complex is a dihydride while the $Mo(PR_3)(CO)_3(H_2)$ complex is a dihydrogen complex because the latter contains three strongly π-accepting CO ligands, while the former does not.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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Concept Review Questions Chapter 10

Concept Review Questions

Section 1

1. What is the difference between an organometallic compound and a metal-organic compound?

2. What is kakodyloxide?

3. What is Zeise's salt and what is unusual about its structure and bonding?

4. What is the Mond process?

5. Explain why the physical and chemical properties of ferrocene are inconsistent with the monohapto coordination of Fe by cyclopentadienyl ligands.

6. Describe qualitatively how the cyclopentadienyl ligands are bonded to Fe in ferrocene.

7. Explain why the cyclobutadiene is not square planar in free state but is square planar when coordinated to transition metals in η^4 fashion?

8. Explain briefly why cyclooctatetraene makes sandwich complexes (metallocenes) only with very large metal ions?

Section 2

1. Explain why carbonyls are interesting and important.

2. Which molecular orbitals of CO can be involved in bonding with transition metals? Explain why these orbitals can be involved.

3. Which types of binding do you know for carbonyls in which CO acts as 2-electron donor?

4. Which types of binding do you know for carbonyls in which CO acts as 4- and 6- electron donor?

5. Which types of binding do you know for carbonyls in which CO acts as an electron acceptor? Which of these binding types leads to a stronger interaction? Explain this.

6. What is the Chatt-Dewar-Duncanson model for carbonyls?

7. What is meant by pi-backbonding in carbonyls?

8. Explain what the strength of the pi-backbonding in carbonyls depends on?

9. Explain how one can derive the structure of the most simple carbonyls?

10. How can one experimentally measure the strength of the pi-backbonding in carbonyls?

11. What is unusual about the structure of $Co_2(CO)_8$? Explain.

12. What is unusual about the structure of $V(CO)_6$? Explain.

13. Why do the most simple group 4 and group 12 carbonyls not exist?

14. Why don't highly positively charged carbonyls exist?

15. Why don't highly negatively charged dimeric carbonyls exist?

Section 3

1. What is meant by the concept of isolobality?

2. Explain how the concept of isolobality is helpful for the prediction of stable structures?

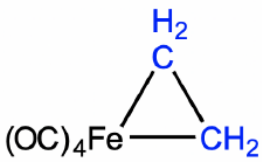
3. Explain how one can explain the structure of $Co_4(CO)_{12}$ using the concept of isolobality.

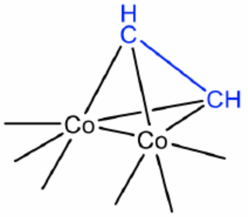
4. What is the structural difference between $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$. Explain this difference.

5. The stability of the most simple monomeric carbonyls decreases from group 6 to group 10. Explain.

6. The stability of the most simple monomeric carbonyls decreases from period 4 to period 6. Explain.

7. Explain why the following complexes are considered ethene and ethine complexes, respectively.





8. What is a carbonyl hydride?

9. Explain why $HCo(CO)_4$ is more acidic than $HMn(CO)_5$?

10. Why is the CN^- ligand a stronger sigma-donor and a weaker pi-acceptor compared to the CO ligand?

11. Explain why the CN^- ligand tends to make complex cations, while the CO ligand prefers to make complex anions?

12. Explain why the carbon atom is the reactive end in cyanide complexes?

13. What are the two binding modes in nitrosyl (NO) complexes?

14. Why is a neutral NO ligand never a two electron donating ligand?

15. How can one explain the two different binding modes in NO complexes?

16. Why is phosphine a pi-accepting ligand while ammonia is not?

17. Why is PF_3 a stronger pi-acceptor than PH_3?

18. Why is PMe_3 is stronger sigma-donor than PH_3?

19. Why is H_2 a pi-accepting ligand?

20. Explain how the pi-accepting properties lead to the dissociation of the H-H bond in the H_2 molecule when H_2 acts as a ligand.

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Homework Problems Chapter 10

Homework Problems

Section 1

Exercise 1

Predict the charge *n* of cobaltocene $(Co(Cp)_2)^n$. Cp=cyclopentadienyl. Explain briefly.

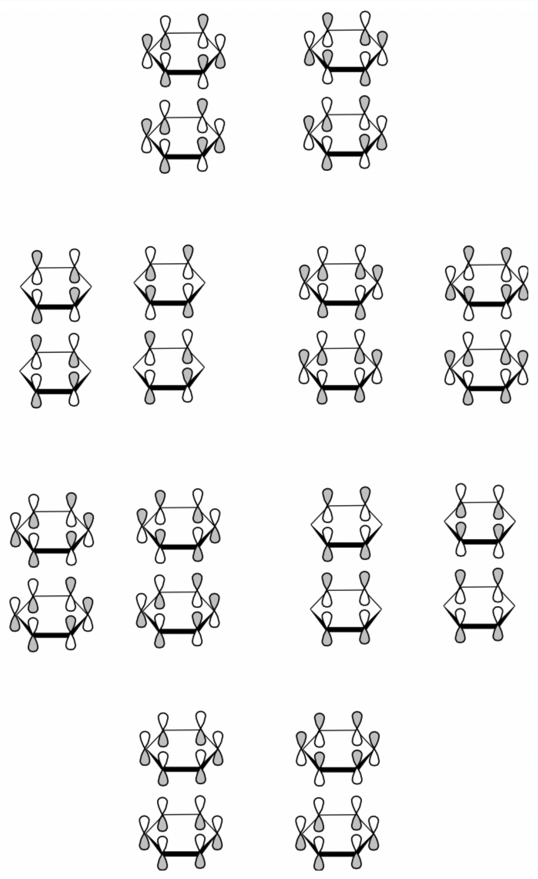
Answer

+1, because the 18 electron rule is fulfilled.

Exercise 2

Bis-benzene chromium $(\eta^4\text{-}C_6H_6)Cr$ is a sandwich compound having two parallel benzene rings in an eclipsed conformation. Sketch the ligand group orbitals for this molecule.

Answer



Section 2

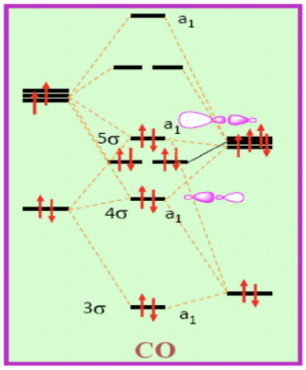
Exercise 1

The MO diagram of the CO molecule is given below. Identify the molecular orbitals that can act

a) As sigma-donors

b) Pi-acceptors in carbonyls.

Review of the MO diagram of CO



Dipolmoment: 0.11 D
negative end at C

Answer

a) 5 σ, 4 σ, bonding π orbitals

b) anti-bonding π orbitals

Exercise 2

Which carbonyl will most likely exhibit the highest frequency for the C-O stretch vibration? Give a brief explanation for your decision.

a) $V(CO)_6^-$

b) $Cr(CO)_6$

c) $Mn(CO)_6^+$

Answer

c) $Mn(CO)_6^+$

Carbonyl cations have the weakest pi-backbonding, therefore the bond order for the C-O bond is the highest and thus the frequency of the C-O stretch vibration is the highest.

Exercise 3

Predict the right charge of the most stable pentacarbonyl of

a) Iron

b) Mn

c) Cr

Answer

a) 0

b) 1-

c) 2-

Section 3

Exercise 1

What structure would you expect for a carbonyl made of the following fragments according to the concept of isolobality? Predict if the structure would likely be stable.

a) $Cr(CO)_5^+$

b) $Cr(CO)_4^-$

c) $Mn(CO)_4^-$

Answer

a) 15VE -> tetrahedral cluster (not stable b/c CN too high)

b) 15 VE -> tetrahedral cluster (not stable b/c CN too high)

c) 16 VE -> trimer (stable b/c CN = 6, charge not too high).

Exercise 2

Which of the following fragments are isolobal to the CH_2 fragment?

a) NH_2

b) NH

c) OH

d) $Fe(CO)_3$

e) $Co(CO)_4^+$

Answer

b) NH

Exercise 3

Which of the following fragments are isolobal to the $Mn(CO)_5$ fragment?

a) CH_3

b) CH_2CH_3

c) OH

d) F

e) NH

Answer

a) CH_3

b) CH_2CH_3

c) OH

d) F

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CHAPTER OVERVIEW

11: Complexes with Metal-Metal Bonds

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11.1: Complexes with Multiple Metal-Metal Bonds

Molecular orbital considerations in Dinuclear Metal Complexes with Multiple M-M Bonds

Let us begin a new chapter and think about dinuclear transition metal complexes with multiple metal-metal bonds. What is the maximum bond order that we could expect? The transition metals have five d-orbitals available, and in order to determine the maximum possible bond order we need to see how they overlap to form molecular orbitals (Fig. 11.1.1).

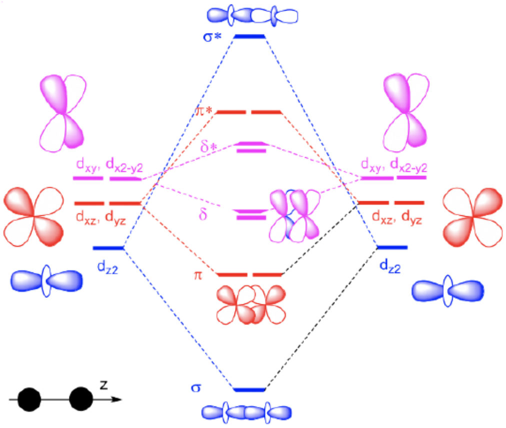


Figure 11.1.1 Molecular orbital overlap of metal d-orbitals forming M-M bonds

If we define the M-M bond axis as the z-axis, then two d_{z^2}-orbitals can overlap in σ-fashion to form a bonding and an anti-bonding σ-molecular orbital. A d_{xz}, and a d_{yz} can overlap with another d_{xz} and another d_{yz} in π-fashion to form two degenerated bonding π and two degenerated anti-bonding π*-orbitals. π-overlap is smaller than σ-overlap, therefore the split in energy between the bonding and the anti-bonding π-orbitals is smaller than the split between the bonding and the anti-bonding σ-orbitals. The d_{xy} orbital can overlap with another d_{xy} orbital in δ-fashion, and so can the $d_{x^2-y^2}$ with another $d_{x^2-y^2}$. This gives two bonding δ-orbitals and two anti-bonding δ-orbitals. The δ-overlap is even smaller than the π-overlap, therefore the energy split between the bonding and the anti-bonding δ-orbitals is even smaller than those for the π and π*-orbitals. So what would be the maximum bond order that could be achieved? The maximum bond order would be achieved when all bonding MOs were full, and all anti-bonding MOs were empty. We have overall five bonding MOs that we could fill with ten electrons from two metal atoms with d^5-electron configuration. The maximum bond order BO would therefore be BO=5. However, in practice only bond orders up to 4 are well known. This is because the $d_{x^2-y^2}$ orbital is usually too involved in the bonding with the ligands thereby becoming unavailable for metal-metal interactions. The $d_{x^2-y^2}$ orbital makes the strongest interactions with the ligands because most ligands approach on or near the x and the y-axes.

Electron Configurations and Multiple M-M Bonds

We can easily predict now which electron configuration leads to which metal-metal bond order. The bond order increases from 1 to 4 with the electron configuration changing from d^1 to d^4. At d^4 all bonding MOs are full with eight electrons.

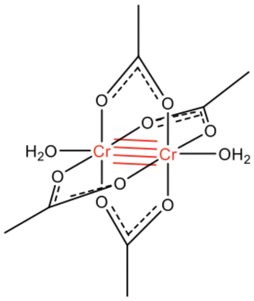
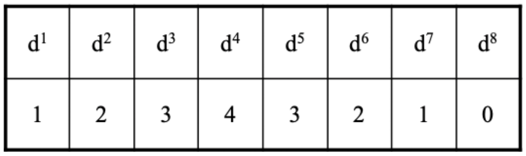


Figure 11.1.2 Tetraacetatodiaquadichromium complex

An example of a complex with a bond order of 4 is the tetraacetatodiaquadichromium complex shown (Fig. 11.1.2). Cr is in the oxidation state +2, which makes the chromium a d^4 species. We can quickly show this by counting the valence electrons. A neutral Cr atom has 6 VE, and an electron configuration $3d^5 4s^1$. There are four acetate ligands having a 1- charge each which gives four negative charges overall. The complex is overall neutral which means that each Cr must have formally a 2+ charge, and the electron configuration is $3d^4$.



d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
1	2	3	4	3	2	1	0

Figure 11.1.3 Relationship between metal-metal bond order and electron configuration

With even more electrons in the metal d-orbitals the bond order begins to decrease again as anti-bonding MOs need to be filled (Fig. 11.1.3). The combination of two metals with d^5 electron configuration leads to a triple bond, two d^6-metals give a double bond, and two d^7 metals give a single bond. A metal-metal bond should not exist for two d^8-metals because then the bond order is zero.

Evidence for M-M Multiple Bonds

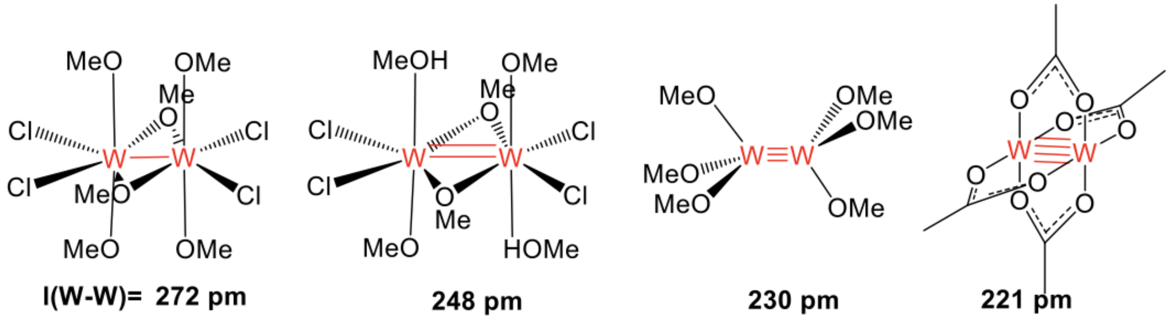


Figure 11.1.4 M-M bond length in four tungsten complexes

What experimental evidence can support the existence of a particular bond order (Fig. 11.1.4)? One argument is the bond length which can be obtained through the crystal structure determination of the complex. The shorter the bond, the higher the bond order. For instance, in the four tungsten complexes shown the bond lengths decrease from 272 pm, to 248 pm, to 230 pm to 221 pm corresponding to a single, double, triple, and quadruple bond, respectively.

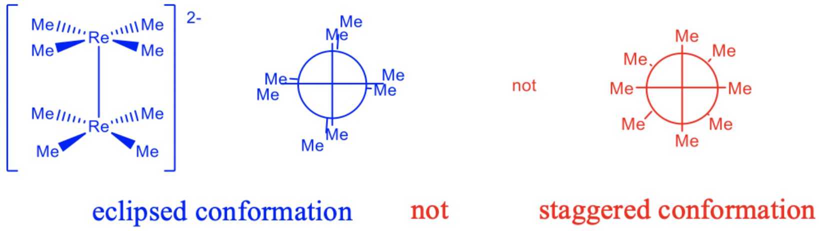


Figure 11.1.5 $ReMe_4$ confirmations

Another hint can be the conformation of a molecule (Fig. 11.1.5). For instance, the two square-planar units of the $Re_2Me_8^{2-}$ complex anion show eclipsed conformation. Steric repulsion arguments would favor the staggered conformation, so there must be a reason why the two $ReMe_4$ units are eclipsed. The rhenium is in the oxidation state +3, thus it is a d^4 species, and we would argue that there may be a Re-Re quadruple bond. This quadruple bond can only form when the d_{xy} orbitals are in eclipsed conformation, and this is only possible when the two $ReMe_4$ fragments are in eclipsed conformation. The very short bond length of 218 pm further supports the existence of the quadruple bond.

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Concept Review Questions Chapter 11

Concept Review Questions

Section 1

1. What experimental evidence exists for the presence of metal-metal multiple bonds?

2. Why is the bond order in metal-metal bonds limited to four?

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Homework Problems Chapter 11

Homework Problems

Section 1

Exercise 1

Which bond order would you expect for metal-metal bond when the metals have

a) d^1

b) d^4

c) d^5

d) d^7

electron configurations?

Answer

a) d^1 --> single bond

b) d^4 --> quadruple bond

c) d^5 --> triple bond

d) d^7 --> single bond

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CHAPTER OVERVIEW

12: Organometallic Reactions and Catalysis

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12.1: Organometallic reactions

Introduction

In this chapter we will discuss common reactions and catalysis of organometallic compounds. We can classify reactions into two main categories. The first one includes reactions with gain or loss of ligands. You will hear about four reactions that belong to this category: ligand substitution reactions, oxidative additions, reductive eliminations, and nucleophilic displacement. The latter three can involve a change in coordination number while ligand substitution reactions do not.

The second main category are reactions that involve the modification of ligands. There are two reactions you will learn about: The migratory insertion and the β-hydride elimination.

Oxidative Addition Reactions

Let us start with the oxidative addition. How is it defined? An oxidative addition is a reaction in which one or more ligands add to the metal center of a complex and oxidize it. This addition can occur in a cis- or trans-fashion. A cis-addition means that two ligands are added so that they have cis-orientation to each other after the reaction is complete. A trans-addition implies that two new ligands are in opposite, trans-position after they have been added. We can further distinguish between mononuclear and dinuclear additions. Mononuclear addition involves a complex with a single metal. Dinuclear additions are additions to a metal-metal bond. The addition cleaves the metal-metal bond and adds one ligand to each fragment.

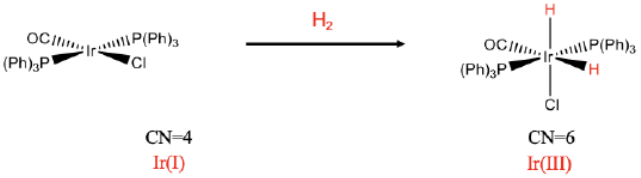

Figure 12.1.1: Mononuclear oxidative cis-addition (Attribution: A. Vedernikov, U Maryland (modified))

Here are a few of examples. The first example is a mononuclear cis-addition (Fig. 12.1.1). In the reaction we add dihydrogen to a square planar iridium complex. After the reaction there are two additional hydrido ligands, and the coordination number has increased from 4 to 6. We can see that the two hydrido ligands are oriented in cis-fashion relative to each other. We can verify that the addition of the hydrido ligands oxidized the metal by determining the oxidation number of the metal before and after the reaction. There are three neutral ligands and one negatively charged chloro ligand. There is no overall charge at the complex. This means that the oxidation number of Ir is +1. After the reaction, there are the two hydrido ligands that have both a -1 charge. Remember, we get the charge at a ligand by cleaving the metal-ligand bond so that all electrons in the bond get assigned to the ligand. This means the oxidation number must be increased by +2, and is +3 after the reaction.

We can rationalize why the addition occurs in cis-fashion and not in trans-fashion. The two hydrido ligands are the smallest ligands, therefore, steric repulsion is minimized in the complex is minimized when the two hydrido ligands are in cis-position.

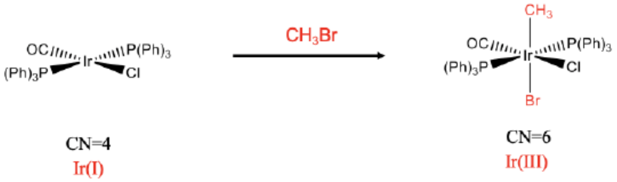

Fig. 12.1.2: Mononuclear oxidative trans-addition (Attribution: A. Vedernikov, U Maryland (modified))

The second example is a mononuclear trans-addition (Fig. 12.1.2). In this reaction CH_3Br is added to the iridium complex. In this case the two new ligands, a CH_3 and the Br group are in opposite position. Again, the coordination number increases from four to six. We can again verify that an oxidation has occurred by analyzing the oxidation number of Ir. As previously determined, the oxidation number of iridium in the reactant complex is +1. Let us analyze the product complex. The chloro ligand and the bromo ligand have a 1- charge. In addition to that also the CH_3 ligand has a 1- charge assuming that we treat the Ir-C bond as a dative bond. Thus, the oxidation number of Ir must be +3 to give a neutral complex.

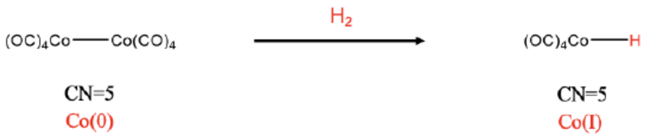

Figure 12.1.3: Dinuclear addition (Attribution: A. Vedernikov, U Maryland (modified))

The third example is a dinuclear addition (Fig. 12.1.3). This addition is neither cis nor trans because it cleaves a metal-metal bond, and the one new ligand is added to each fragment. In the example the Co-Co bond of the dicobalt octacarbonyl gets cleaved upon the reaction with dihydrogen, and two $HCo(CO)_4$ complexes with Co-H bonds form. In this case the coordination number does not increase. Both the reactant and the products have the coordination number 5. We can see that an oxidation of Co has occurred by comparing the oxidation numbers. In the reactant the oxidation number of Co is zero because all CO ligands are neutral and the complex is overall neutral. In the carbonyl hydride product, Co has the oxidation number +1, because the hydrido ligand has a 1- charge.

Oxidative Additions with Intact Ligands

In the previous examples, the ligands that reacted with the complexes lost their integrity. The H-H bond in the H_2 molecule cleaved to form the hydrido ligands, and the C-Br bond in CH_3Br was cleaved to form separate Br and methyl ligands. Not all ligands lose their integrity upon their addition, in particular when they contain multiple bonds. These ligands are called intact ligands. In these cases the bond order within the ligand is reduced, but the number is still greater than zero.

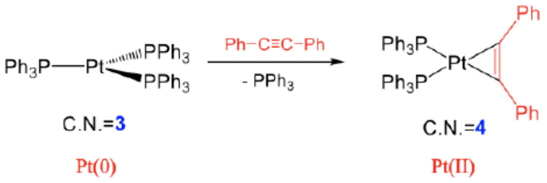

Figure 12.1.4: Oxidative addition with intact ligands (Attribution: A. Vedernikov, U Maryland (modified))

Examples for intact ligands are are alkenes, alkynes, O_2, etc. In an oxidative addition with an alkyne for example, the alkyne binds side-on to the transition metal under the formation of two metal-C single bonds, and the reduction of the bond order within the alkyne from 3 to 2 (Fig. 12.1.4). In the shown reaction, a diphenyl ethine molecule adds to tris(triphenyl phosphine) platinum under the formation of two Pt-C single bonds. The C-C triple bond in the ligand becomes a double bond. This reaction occurs under loss of one of the three triphenyl phosphine ligands. The coordination number at the metal increases from 3 to 4. We can again show that the reaction is oxidative by comparing the oxidation numbers of the metal. In the reactant, Pt has the oxidation number 0 because the three triphenyl phosphine ligands have no charge and the complex has overall no charge. After the reaction, the oxidation number of Pt is +2. This is because when we assign the four electrons of the two Pt-C single bonds to the ligand, the ligand becomes a $(Ph\text{-}C{=}C\text{-}Ph)^{2-}$ ligand with each C atom carrying a 1- charge. Because the product complex is overall neutral, the oxidation number of Pt is +2.

Reductive Elimination Reactions

The reductive elimination reaction is the reverse of the oxidative addition. The reductive elimination can only occur when the two ligands to be eliminated are in cis-position.

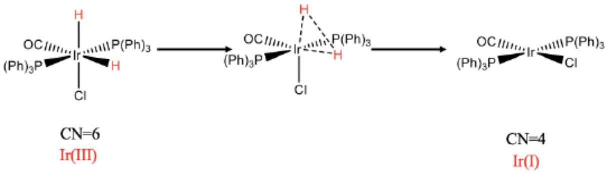

Figure 12.1.5: Reductive elimination (Attribution: A. Vedernikov, U Maryland.)

For instance the previously discussed oxidative cis-addition of H_2 to the iridium complex is reversible, and the reverse is called the reductive elimination (Fig. 12.1.5). The cis-orientation of the two hydrido ligands is necessary to form an H-H bond. The reaction can be thought of going along a reaction path in which the Ir-H bonds become gradually larger and and the H-H distance gradually smaller until the H_2 molecule is eliminated from the complex.

Catalytic Deuteration of Benzene

Combinations of oxidative additions and reductive eliminations have many applications in the synthesis of organic molecules using an organometallic reactant.

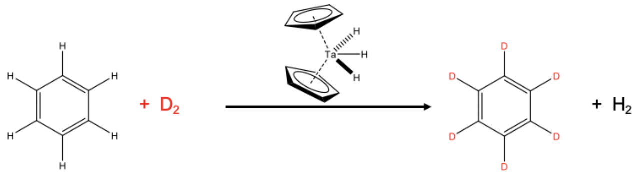

Figure 12.1.6: Deuteration of benzene

An example is the deuteration of benzene (Fig. 12.1.6). Deuterated benzene is an important solvent in NMR spectroscopy. Industrially, the deuteration is done using a dicyclopentadienyltrihydridotantalum(V) catalyst starting out from benzene and D_2. The D_2 is provided in excess to drive the chemical equilibrium to the right side.

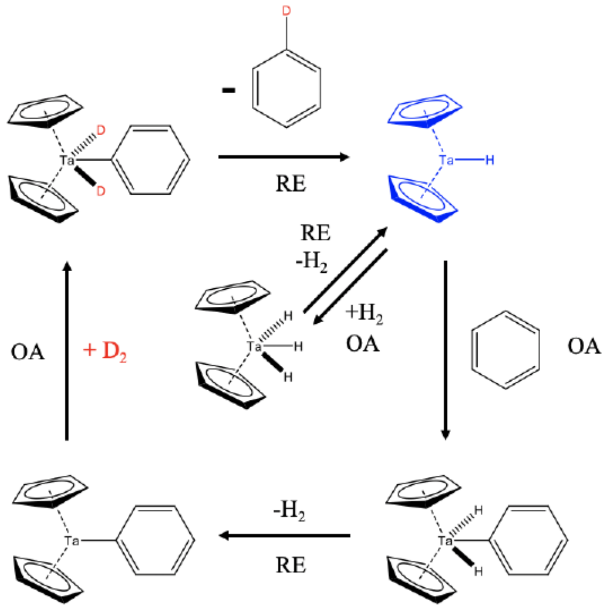

Figure 12.1.7: Mechanism of the catalytic deuteration of benzene

How does this reaction work mechanistically? This 18e Cp_2TaH_3 is actually a precatalyst that is in chemical equilibrium with H_2 and the 16e dicyclopentadienylhydrido tantalum(III) which is the actual catalyst (Fig. 12.1.7). Elimination of H_2 from the Ta(V) catalyst is a reductive elimination (RE) and the re-addition of H_2 to the Ta(III) species an oxidative addition (OA). In the presence of benzene, the Ta(III) species can oxidatively add benzene to form an 18e Ta(V) complex. This complex can reductively eliminate H_2 to form a 16e Cp_2Ta(III)-Ph complex. In the presence of deuterium this complex can add D_2 oxidatively to form an 18e Cp_2D_2Ta(V)-Ph complex. This species can then reductively eliminate a monodeuterated benzene molecule under formation of Cp_2Ta(III)-D. In the presence of enough D_2 this monodeuterated benzene can be further deuterated in subsequent catalytic cycles.

Nucleophilic Displacement Reactions

Another important reaction is the nucleophilic displacement reaction. In these reactions a complex, typically an anion, acts as a nucleophile. The ligand is added, but no electrons are added to the complex. The reactions can be extremely useful for the synthesis of organic compounds. The utility results mostly from the fact that an organic electrophile is turned into a nucleophile.

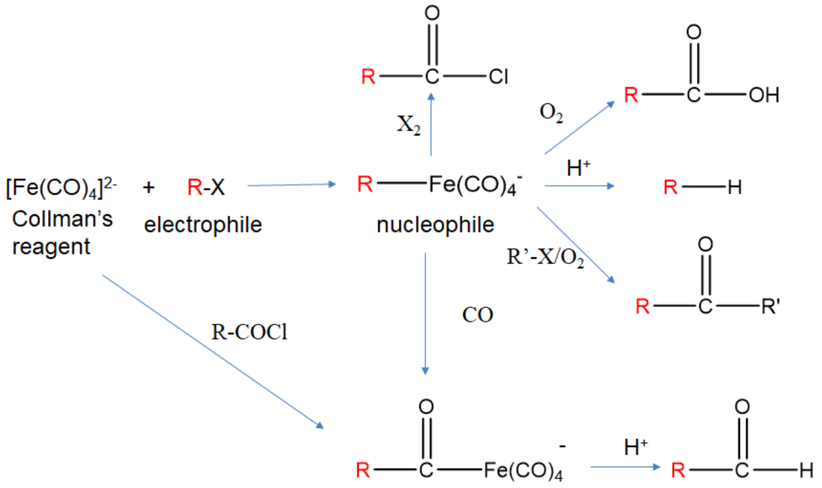

Figure 12.1.8: Examples of nucleophilic displacement reactions

For example, tetracarbonyl ferrate (2-), also known as Collman's reagent reacts with alkyl halides to form alkyl tetracarbonyl ferrate (-) (Fig. 12.1.8). We can check that the addition of the alkyl group did not add any electrons by counting the electrons before and after the reaction. The $Fe(CO)_4^{2-}$ anion is an 18e complex. Applying the neutral atom method to the electron counting in $[R\text{-}Fe(CO)_4]^-$ means that Fe contributes 8e, the 1- charge adds 1e, the CO ligands 4x2=8 electrons and the alkyl ligand 1e. This gives 8+1+8+1=18 electrons. Also the oxidation number of Fe has not changed upon the addition of the ligand. It is -2 before and after the reaction.

In the alkyltetracarbonyl ferrate (1-) anion, the group R which was formerly an electrophile in R-X, can now act as a nucleophile due to the fact that the Fe-C bond is polarized toward the C-atom. As a nucleophile it can for instance react with protons to form an alkane. It can also react with oxygen to form a carboxylic acid. In the presence of another alkyl halide R'-X it can form a ketone R-C(O)-R'. It can also insert CO into the Fe-C bonding in a so-called migratory insertion reaction, and the reaction product can react with acid to form an aldehyde. With dihalogens X_2 it can form acyl chloride. Collman's reagent cannot only add alkyl halides by also acyl halides to form acyl tetracarbonyl ferrates (-).

Migratory Insertion and Deinsertion (Elimination) Reactions

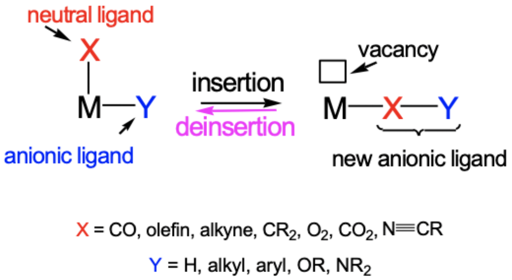

Figure 12.1.9: Migratory insertion (Attribution: A. Vedernikov, U Maryland.)

Our next reaction is the migratory insertion. In a migratory insertion reaction, there is an anionic ligand X and a neutral unsaturated ligand Y in cis-position, and the two ligands couple to form another anionic ligand XY that is attached to the same metal (Fig. 12.1.9). This produces a vacancy at the metal, meaning a coordination site at the metal which is not occupied by a ligand. In an insertion reaction it is more common that the anionic ligand moves. The reaction is reversible and there is typically a chemical equilibrium. The reverse reaction is called a deinsertion. To drive the chemical equilibrium to the right side one can add the neutral ligand in excess or add a different neutral ligand. The neutral ligand then adds to the vacancy and prevents the reverse reaction. Typical neutral, unsaturated ligands are CO, olefins, alkynes, carbenes, dioxygen, carbon dioxide, and nitriles. Typical anionic ligands are hydrido, alkyl, aryl, alkoxy, and amido-ligands.

Carbonyl Migratory Insertions

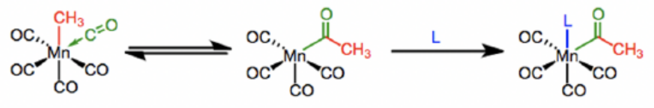

Figure 12.1.10: Carbonyl migratory insertions (Attribution: Michael Evans http://organometallicchem.files.word...8-pm.png?w=700)

One of the most common insertions are carbonyl insertions into alkyl groups like methyl groups (Fig. 12.1.10). The carbonyl insertion produces an acyl group. To drive the reaction, the reaction can be carried out in the presence of a neutral ligand L like free CO, which occupies the vacant site.

Olefin Insertion and β-Hydride Elimination

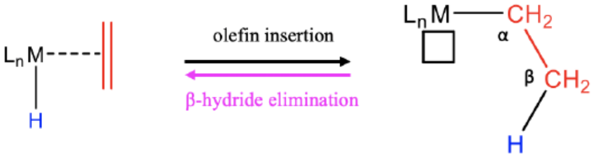

Figure 12.1.11: Olefin insertion and β-hydride elimination

Another very common migratory insertion is the olefin migratory insertion into hydrides (Fig. 12.1.11). This produces an alkyl group. When the reaction is carried out in the presence of CO which binds to the vacant site, then the reaction is driven to the right side. The reverse of this reaction is the β-hydride elimination. It is called “β”-elimination because of the H-atoms that are attached to the carbon atom in the alkyl chain that is second-closest to the metal are called “β”-hydrogens. The hydrogen atoms that are attached to the carbon which is bound to the carbon bonded to the metal via a metal-carbon bond are called “α”-hydrogens.

Instability of Transition Metal Complexes Caused by β-Hydride Elimination

The β-hydride elimination is responsible for the frequent instability of transition metal alkyl complexes that possess β-hydrogen atoms.

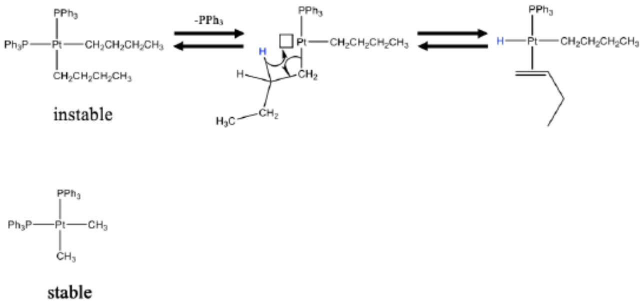

Figure 12.1.12: Instability of transition metal complexes caused by β-hydride elimination (Attribution: A. Vedernikov, U Maryland (modified).)

For example, the depicted dialkyldiphosphine platinum complex is unstable because it has β-hydrogen atoms (Fig. 12.1.12). Statistically, the complex can lose a phospine complex at a certain rate due to the lability of the Pt-P bond leading to a complex with a vacant site. This complex can then undergo a β-elimination to form an olefin complex. In this case the olefin is a volatile butene molecule which can detach from the metal and leave the system unless the system is hermetically closed. In contrast, the respective methyl complex is stable because it only has α-hydrogens, but not β-hydrogens.

Carbene Migratory Insertion

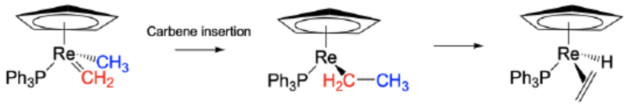

Figure 12.1.13: Carbene migratory insertion (Attribution: A. Vedernikov, U Maryland.)

Migratory insertions are also possible for carbenes. In this case, a CH_2 group bonded to the metal via a M=C double bond plays the role of the neutral, unsaturated ligand. In the shown Re complex the carbene inserts into a Re-CH_3 bond to form an ethyl group. This ethyl group is unstable because it can undergo β-hydride elimination to form an alkene complex with a hydride ligand.

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12.2: Organometallic Catalysts

Organometallic Compounds as Hydrogenation Catalysts

Migratory insertions play an important role in catalysis.

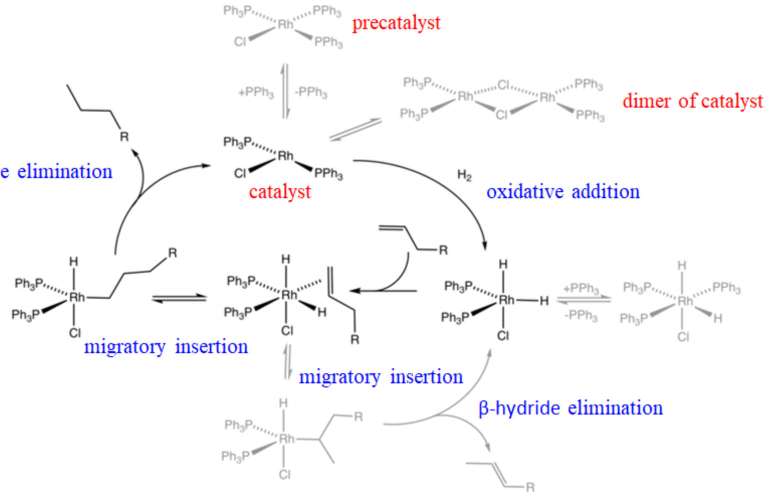

Figure 12.2.2 Mechanism of the Wilkinson hydrogenation catalyst (Attribution: Smokefoot / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0) https://commons.wikimedia.org/wiki/F...cleJMBrown.png)

For example a Rh-catalyst called the Wilkinson catalyst is an effective hydrogenation catalyst for olefins. The mechanism of the hydrogenation involves a combination of oxidative additions, olefin migratory insertions, and reductive eliminations (Fig. 12.2.2). Wilkinson's catalyst is the square planar chloro tris(triphenylphosphine) rhodium(I) complex. This molecule is actually a precatalyst that becomes the actual catalyst when it statistically loses a triphenylphosphine ligand producing chloro bis(triphenylphosphine) rhodium(I). The loss of this ligand is a reversible reaction, and thus the catalyst is in chemical equilibrium with the precatalyst. The actually catalyst is in a second chemical equilibrium with its dimer. The chloro bis(triphenylphosphine) rhodium(I) catalyst can undergo an oxidative addition in the presence of hydrogen to form a trigonal bipyramidal chlorodihydrido bis(triphenylphosphine) (III) rhodium complex. This species is in chemical equilibrium with an octahedral chlorodihydrido tris(triphenyl phosphine) rhodium(III) species that can form due to the presence of free triphenylphosphine ligands in the system. The trigonal bipyramidal species can then add an olefin that binds side-on to the Rh. Because the olefin is in cis-position to the hydride ligand it can undergo an olefin insertion. The Rh-C bond can either form with the first or the second carbon in the carbon chain of the olefin, giving a linear and a branched alkyl complex, respectively. The branched complex can undergo a β-hydride elimination thereby reforming the trigonal bipyramidal Rh-complex, and an olefin. This reaction is a side-reaction because the branched alkyl complex is sterically more crowded than the linear complex. The linear alkyl Rh complex can undergo a reductive elimination to form the linear alkane and the $RhCl(PPh_3)_2$ catalyst. This completes the catalytic cycle, and a new cycle can start.

Ziegler-Natta Polymerization

Another example of an organometallic catalytic reaction is the Ziegler-Natta olefin polymerization. This reaction is of high industrial importance for the production of olefins like polyethylene. There are both heterogeneous and homogeneous Ziegler-Natta catalysts. The mechanism for the homogeneous catalysts is generally well understood. Homogeneous catalysts are typically metallocene catalysts.

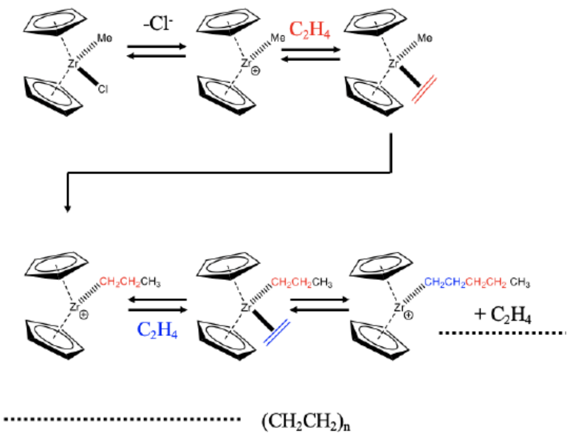

Figure 12.2.3 Zirconium-based Ziegler-Natta catalyst (Attribution: A. Vedernikov, U Maryland (modified).)

An example of a zirconium-based catalyst is shown (Fig. 12.2.3). The catalyst is a coordinatively unsaturated complex cation with two cyclopentadienyl rings and a methyl group. The catalyst is formed from its precatalyst, a neutral molecule with an additional chloro ligand. The catalyst oxidatively adds an olefin like an ethylene molecule to the coordinatively unsaturated site. This step is followed an olefin insertion step that produces a propyl group. The migratory insertion leads to the formation of a vacant site, that can be re-oocupied by another ethylene molecule. This molecule can insert into the propyl chain thereby prolonging the propyl chain to a pentyl chain. The olefin insertion step generates another vacant site that can be reoccupied by a new ethylene molecule. Repeating the catalytic cycle many times eventually leads to polyethylene.

Catalytic Olefin Hydroformylation

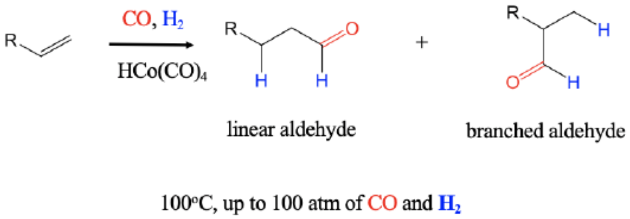

Figure 12.2.4 Catalytic olefin hydroformylation

A further important industrial reaction is the catalytic hydroformylation reaction, also known as oxo-process. It was discovered in 1938 by Otto Roelen at BASF. In the hydroformylation reaction an H atom and a formyl group are added to an alkene to form aldehydes. The reaction can produce both branched an linear aldehydes from terminal alkenes, CO, and H_2 using a carbonyl hydrides such as $HCo(CO)_4$ as a catalyst. The reaction is performed at about 100°C at a pressure of up to 100 atm.

Mechanism of the Catalytic Olefin Hydroformylation by $HCo(CO)_4$

How does the hydroformylation work mechanistically?

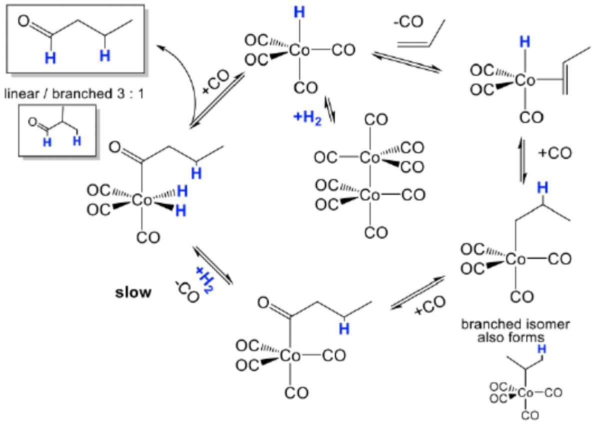

Figure 12.2.5 Mechanism of the catalytic olefin hydroformylation by $HCo(CO)_4$ (Attribution: A. Vedernikov, U Maryland (modified).)

The mechanism is illustrated for the hydroformylation of propene (Fig. 12.2.5). The actual catalyst $HCo(CO)_4$ is first formed from its precatalyst $Co_2(CO)_8$ in the presence of H_2 in a dinuclear oxidative addition reaction. The catalyst can undergo a substitution reaction in which a CO ligand is replaced by the olefin that binds side-on to the cobalt. This species can then undergo a migratory olefin insertion reaction. This leads to a mixture of linear and branched alkyl groups attached to the Co. A new CO ligand can add to the vacant site. The alkyl group can then insert into a carbonyl group in another migratory insert step, and the vacant site can be reoccupied by a new CO molecule. Then, H_2 is added in an oxidative addition. This is the slowest and rate-limiting step in the catalytic cycle. From the addition product the aldehyde can then be eliminated in a reductive elimination reaction. Addition of CO regenerates the catalyst, and the catalytic cycle can begin again.

Hydrocarbonylations

After the hydroformylation, a number of other hydrocarbonylations were developed, and industrially deployed.

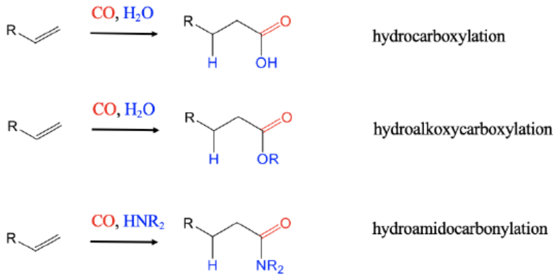

Figure 12.2.6 Hydrocarbonylation reactions

When hydrogen is replaced by H_2O hydrocarboxylations of alkenes lead to carboxylic acids (Fig. 12.2.6). With an alcohol instead of H_2 hydroalkoxycarbonylcations lead to esters. The employment of amines instead of H_2 leads to amides in hydroamidocarbonylation reactions.

The Monsanto Acetic Acid Process

Another carbonylation reaction involving an organometallic catalyst is the Monsanto acetic acid process. It has been introduced by Monsanto in the 1970s for the industrial production of acetic acid from methanol. The reaction involves dual catalysis with HI and $[RhI_2(CO)_2]^-$ as a co-catalysts. How does this reaction work?

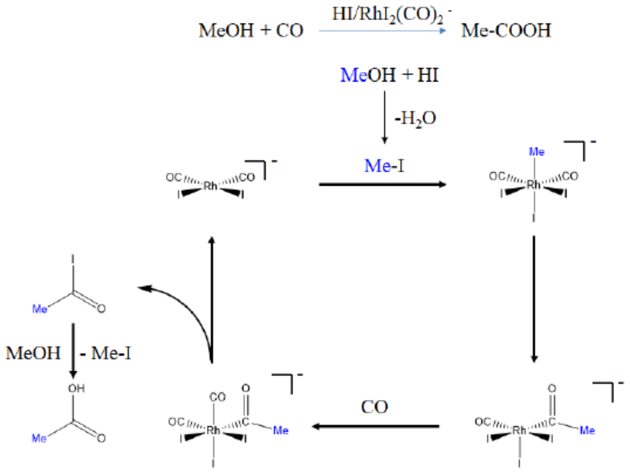

Figure 12.2.7 The catalytic cycle in the Monsanto acetic acid process

In the first step methanol reacts with HI to form methyl iodide. The methyl iodide then reacts with the Rh-catalyst in an oxidative addition reaction in which a methyl and an iodo group are added in trans-fashion to the square-planar Rh-complex to give an octahedral complex. The octahedral complex then undergoes a migratory insertion reaction with CO producing an acyl group and a vacant site. A CO molecule can then add to the vacant site. The acetyl iodide can then be eliminated in a reductive elimination to reform the Rh-catalyst thereby closing the catalytic cycle. The acetyl iodide can then react with methanol to form new methyl iodide and acetic acid. The methyl iodide can start a new catalytic cycle with the Rh-catalyst.

Olefin Metathesis

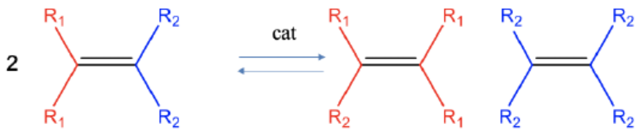

Figure 12.2.8 Olefin metathesis

Olefin metathesis is a reaction which allows to cut and rearrange C=C double bonds in olefins to make new olefins (Fig. 12.2.8). Formally, the carbon-carbon bond of the reactant is cleaved homoleptically and the two carbene fragments are combined in a different way. This reaction is typically an equilibrium reaction, and neither the reactants nor the products are clearly favored. This reaction is catalyzed by molybdenum arylamido carbene complexes or ruthenium carbene complexes.

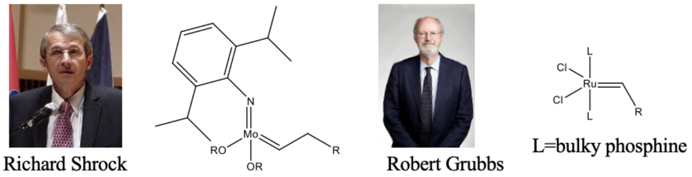

Figure 12.2.9 Shrock catalyst (Attribution: R._Schrock_-_IChO_2012_Opening_Ceremony.JPG: A.mela93derivative work: Materialscientist / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...hrock_2012.jpg) and (Attribution: The Royal Society / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...al_Society.jpg)

The former are called Shrock catalysts, and the latter Grubbs catalysts named after their discoverers Richard Shrock and Robert Grubbs who received the Nobel prize for Chemistry in 2005 (Fig. 12.2.9). The Schrock catalysts are more active, but also very sensitive to air and water. The Grubbs catalysts, while less active, are less sensitive to air and water.

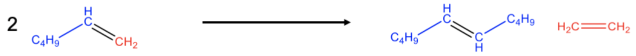

Figure 12.2.10 Regular metathesis

Olefin metathesis often allows for simpler preparation of olefins compared to other methods. Olefin metathesis is particularly powerful when one olefin product is gaseous because then it can be quite easily removed from the chemical equilibrium by purging. This drives the chemical equilibrium to the right side. An example is the preparation of 5-decene from 1-hexene. Cleavage of the C=C double bond in the hexene leads to C_5 and C_1 carbene fragments (Fig. 12.2.10). The two C_1 fragments can combine to form ethylene and the two C_5 fragments combine to 5-decene. The ethylene is volatile and can be purged from the reaction system thereby driving the chemical reaction to the right side.

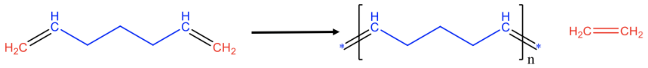

Figure 12.2.11 Acylic diene metathesis (ADMET)

The same principles can also be applied to produce polymers from dienes with two terminal C=C double bonds at the chain ends. This is called acylic diene metathesis (ADMET), Fig. 12.2.11. For instance the cleavage of the two terminal double bonds in a diene with seven C atoms leads to C_1 and C_5 fragments. The C_1 fragments can combine to form ethylene, and the C_5 fragments can combine to make an unsaturated polymer of the type $[CH(CH_2)_3CH]_n$. Again, the reaction can be driven to the right side by removing the gaseous ethylene from the reaction mixture through purging.

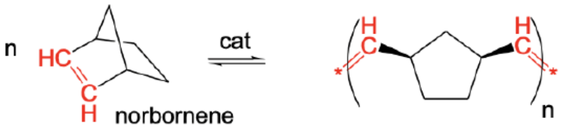

Figure 12.2.12 Ring-opening metathesis polymerization (ROMP)

Another variation of olefin metathesis is ring-opening metathesis polymerization (ROMP). It allows to make polymers from strained cycloolefins, for example norbornene. The reaction driving force is the relief of the strain. Because the strain is removed in the polymer, the chemical equilibrium lies far on the right side. The reaction product in norbornene is a polymer with 5-membered rings that are interconnected by ethylene -CH=CH- units (Fig. 12.2.12).

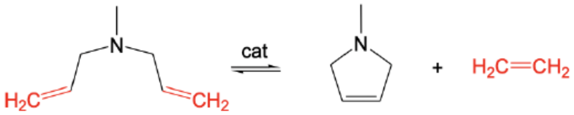

Figure 12.2.13 Ring-closing metathesis (RCM)

The opposite of ROMP is ring-closure metathesis (RCM). RCM allows for the preparation of unstrained rings with C=C double bonds from dienes with C=C double bonds that are five or six carbon atoms apart. This distance is suitable to produce unstrained rings. In the shown example a five-membered ring with a C=C double bond is formed from a diene with terminal C=C double bonds that are five atoms apart.

The Mechanism of Olefin Metathesis

What is the mechanism of olefin metathesis?

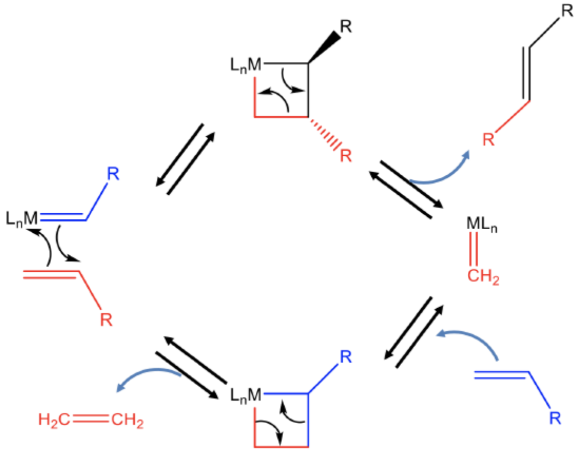

Figure 12.2.14 The mechanism of olefin metathesis

In the first step, the alkene adds to the the carbene fragment of the catalyst in a 2+2 cycloaddition reaction to produce an unstable intermediate with a highly strained four-membered ring (Fig. 12.2.14). This four membered ring can open to produce the first new alkene product R-CH=CH-R and a metal carbene species. This metal carbene can react with another reactant olefin to form another highly stained 4-ring intermediate via a 2+2 cycloaddition reaction. This ring can then reopen again to produce the second alkene metathesis product, in this case ethylene, and the original catalyst. The regenerated catalyst can then start a new catalytic cycle.

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Concept Review Questions Chapter 12

Concept Review Questions

Section 1

1) What is an oxidative addition?

2) What is a reductive elimination?

3) What is a cis and a trans addition, respectively?

4) Does the coordination number in oxidative additions always increase? Explain.

5) What is the reverse reaction of an oxidative addition?

6) What is a migratory insertion?

7) Are migratory insertions reversible reactions?

Section 2

1) Why are transition metal alkyl complexes that have alkyl groups longer than 1 carbon atom often unstable?

2) What is meant by beta-hydride elimination?

3) What is alpha-abstraction?

4) What is a nucleophilic displacement reaction?

5) What is meant by an oxidative addition of an intact ligand?

6) Write the catalytic cyclic for the deuteration of benzene with Cp_2TaH_3 as a catalyst. Name each reaction step.

7) What is Collman’s reagent and how is it being used?

8) What is Wilkinson’s catalyst, and what reactions can it be used for. Write the catalytic cycle.

9) Write done the reaction mechanism for the Ziegler-Natta olefin polymerization.

10) What is carbene migratory insertion?

11) Write down the catalytic cycle for the hydroformylation of olefins.

12) Name three hydrocarbonylation reactions. What are the reactants?

13) Write down the mechanism for the Monsanto acetic acid process.

14) What is olefin metathesis?

15) What is ring-opening olefin polymerization (ROMP)?

16) What is acyclic diene metathesis?

17) Why are olefins with terminal C=C double bonds particularly useful in olefin metathesis?

18) What is ring-closing metathesis?

19) What are the characteristics of Schrock and Grubbs catalysts, respectively?

20) Write down the catalytic cycle for olefin metathesis.

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Homework Problems Chapter 12

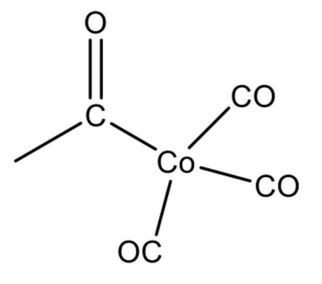
Homework Problems

Section 1

Exercise 1

The coordination compound $CH_3Co(CO)_4$ undegoes a migratory insertion. What is the reaction product?

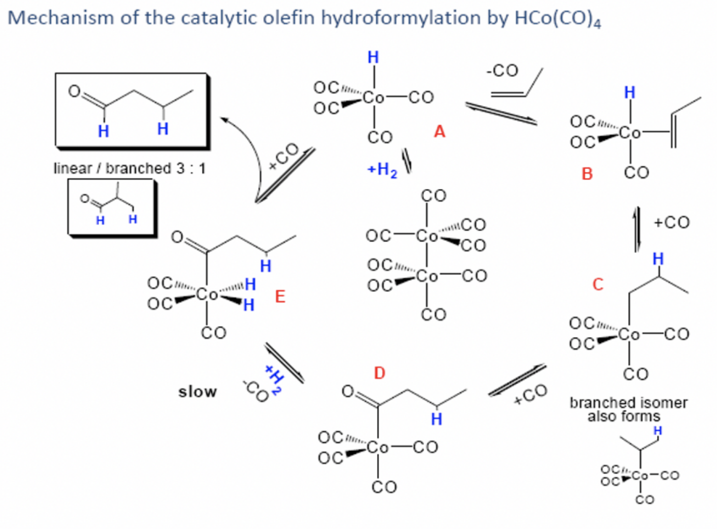
Answer



Section 2

Exercise 1

Identify all oxidative additions in the catalytic cycle of olefin hydroformylation:


Mechanism of the catalytic olefin hydroformylation by $HCo(CO)_4$

Answer

Step D --> E is an oxidative addition

Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is also an oxidative addition.

Exercise 2

1. What are the reaction products of the following olefin metathesis reactions?

a) 2 CH_2=CH-Ph -->

b) n CH_2=CH-CH=CH_2 -->

Answer

a) CH_2=CH_2 and Ph-CH=CH-Ph

b) CH_2=CH_2 and $(CH=CH)_n$

Exercise 3

What reaction product would you expect would you expect from the following reaction:

$Fe(CO)_4^{2-}$ + CH_3CH_2I -->

Name the reaction.

Answer

$Fe(CO)_4CH_2CH_3^-$ + I^- Nucleophilic displacement

Exercise 4

Which of the following phosphines would you expect to be most suitable to stabilize metals in low oxidation states:

a) $P(CF_3)_3$

b) $P(CH_3)_3$

c) PH_3

Answer

a) $P(CF_3)_3$

Exercise 5

What reaction product would you expect from the following reaction?

$Pt(PPh_3)_4$ + 4 NPh_3 -->

Answer

There would be no reaction.

Exercise 6

Which of the following complexes would likely be unstable:

a) $[PtCl_3(C_2H_5)]^{2-}$

b) $[PtCl_3(CH_3)]^{2-}$

c) $PtCl_4^{2-}$

Answer

a) $[PtCl_3(C_2H_5)]^{2-}$

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