2.3: Electronic factors which govern bonding and structure

The bonding and structure of a compound are determined by electronic properties such as the power of constituent atoms to attract or repel electrons, the molecular orbitals occupied by valence electrons, etc. Geometrical arrangements of atoms are also influenced by the electronic interactions between non-bonding electrons. Here, some fundamental concepts are described.

(a) Effective nuclear charge

Since the positive nuclear charge is generally offset by the negative charge of the internal electrons in the electron shell inside the valence electrons, the nuclear charge that valence electrons feel is smaller than the integer charge, Ze for an atomic number Z. This reduction is expressed by the **shielding constant** σ, and the net nuclear charge is called the **effective nuclear charge**, Z_{eff} e.

$$Z_{eff} = Z - \sigma$$

The effective nuclear charge varies with different electron orbitals and distances from the nucleus.

(b) Ionization energy

Ionization energy is defined as the minimum energy required to remove an electron from the atom in a gaseous phase (g), as shown in the following equation. Ionization energy is expressed in units of electron volt (eV), where 1 eV = 96.49 kJ mol^{-1}.

$$A(g) \rightarrow A^{+}(g) + e^{-}(g)$$
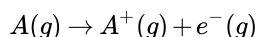
The 1st ionization energy, which removes the outermost electron, is the smallest, and the 2nd and 3rd ionization energies, which further ionize cations, increase rapidly. The ionization enthalpy, which is the standard enthalpy change of the ionization process and is used in thermodynamic calculations, is the ionization energy multiplied by RT (R is the universal gas constant 8.31451 J K^{-1} mol^{-1} and T is temperature, 2.479 kJ (0.026 eV), at room temperature). The difference between these two parameters is small. The 1st ionization energy varies periodically with atomic number across the periodic table, with the lower left (cesium, Cs) being the smallest and the upper right (helium, He) the largest.

It is understandable that alkali metals generally have the lowest ionization energies because they are stabilized by removal of an s electron to attain the rare gas configuration. Rare gas elements have stable electronic structures, and their ionization energies are the largest. Although the ionization energy increases almost monotonically from alkali metals to rare gases in each period, there are reversals at several places, such as nitrogen N and oxygen O, and phosphorus P and sulfur S. The 1st ionization energies are given in Table 2.3.5.

Table 2.3.5 Electronic parameters of atoms (eV). I: 1st ionization energy, A$_e$: electron affinity, χ_M: electronegativity (Mulliken)

Atom	I	A	χ_M
H	13.60	0.75	7.18
He	24.59		
Li	5.39	0.62	3.01
Be	9.32		
B	8.30	0.28	4.29
C	11.26	1.27	6.27
N	14.53		
O	13.62	1.46	7.54
F	17.42	3.40	10.41
Ne	21.56		
Na	5.14	0.55	2.85
Mg	7.65		
Al	55.99	0.44	3.22

Atom	I	A	χ_M
Si	8.15	1.39	4.77
P	10.49	0.75	5.62
S	10.36	2.08	6.22
Cl	12.97	3.61	8.29
Ar	15.76		
K	4.34	0.50	2.42
Ca	6.11	0.02	3.07
Sc	6.56	0.19	3.38
Ti	6.83	0.08	3.45
V	6.75	0.53	3.64
Cr	6.77	0.67	3.72
Mn	7.44		
Fe	7.90	0.15	4.03
Co	7.88	0.66	4.27
Ni	7.64	1.16	4.40
Cu	7.73	1.24	4.48
Zn	9.99		
Ga	6.00	0.30	3.20
Ge	7.90	1.23	4.61
As	9.82	0.81	5.31
Se	9.75	2.02	5.89
Br	11.81	3.36	7.59
Kr	14.00		
Rb	4.18	0.49	2.34
Sr	5.69	0.11	2.90
Y	622	0.31	3.27
Zr	6.63	0.43	3.53
Nb	6.76	0.89	3.83
Mo	7.09	0.75	3.92
Ru	7.36	1.05	4.26
Rh	7.46	1.14	4.30
Pd	8.34	0.56	4.45
Ag	7.58	1.30	4.44
Cd	8.99		

Atom	I	A	χ_M
In	5.79	0.30	3.10
Sn	7.34	1.11	4.23
Sb	8.64	1.07	4.86
Te	9.01	1.97	5.49
I	10.45	3.06	6.76
Xe	12.13		
Cs	3.89	0.47	2.18
Ba	5.21	0.15	2.68
La	5.58	0.50	3.09
Hf	6.83	0.00	3.42
Ta	7.89	0.32	4.11
W	7.98	0.82	4.40
Re	7.88	0.15	0.40
Os	8.70	1.10	4.90
Ir	9.10	1.60	5.40
Pt	9.00	2.13	5.61
Au	9.23	2.31	5.77
Hg	10.44		
Tl	6.11	0.20	3.16
Pb	7.42	0.36	3.89
Bi	7.29	0.95	4.12

(c) Electron affinity

Electron affinity is the negative of the electron-gain enthalpy ΔH_{eg} of an atom in a gas phase, as shown in the following equation and denoted by A_e (= -ΔH_{eg}) (Table 2.3.5).

$$A(g) + e^-(g) \rightarrow A^-(g)$$
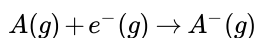
It may be regarded as the ionization enthalpy of an anion. Since halogen atoms achieve rare gas electron configurations if an electron is added to them, their electron affinities are large.

(d) Electronegativity

Electronegativity is one of the most fundamental atomic parameters which expresses numerically the tendency to attract electrons to atoms in a molecule. It is very useful in explaining differences in bonding, structure, and reaction from the standpoint of atomic properties. Various schemes have been proposed to explain the theoretical basis of the power of electron attraction, and studies are still actively seeking new numerical values of electronegativity. The Pauling scale, introduced first in 1932, is still the most frequently used , and subsequent new numerical values have been justified if they are close to those of Pauling.

L. Pauling defined electronegativity as the quantitative ionic character of bonds. Originally, the following equation was proposed as a formula to define the ionic character of the bond between atoms A and B.

$$\Delta D(AB) - \frac{1}{2}[D(AA) + D(BB)]$$

where D is the bond energy of a covalent bond. However, it turned out that Δ is not necessarily positive, and Pauling modified the definition

$$\Delta = D(AB) - \sqrt{D(AA) \times D(BB)}$$

and redefined it as the ionic character of the A-B bond. Furthermore, electronegativity χ was defined in such a way that the difference of the electronegativities of atoms A and B is proportional to the square root of the ionic character. Here, the coefficient

$$|\chi_A - \chi_B| = 0.208\sqrt{\Delta}$$

0.208 is so determined that the electronegativity of hydrogen H becomes 2.1 when bond energies are expressed in kcal mol^{-1}. Since Pauling electronegativities increase the higher the oxidization states of an atom, these values correspond to the highest oxidization number of each element. The electronegativities calculated using recent values of bond energies are shown in Table 2.3.6.

	1	2	3	4	5	6	7	8	9
1	H 2.2								
2	Li 0.98	Be 1.57							
3	Na 0.93	Mg 1.31							
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
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28
6	Cs 0.79	Ba 0.89	Lanthanoid	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20
7	Fr 0.7	Ra 0.9	Actinoid						

10	11	12	13	14	15	16	17	18
								He
			B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
			Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
Ni 1.91	Cu 2.0	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.0
Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.6
Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn

A. L. Allred and E. G.. Rochow defined electronegativity as the electric field Z_{eff}/r^2 on the atomic surface. They added a constant in order to make the electronegativity χ_{AR} as near as possible to the Pauling values by using r for the covalent bond radius of atoms.

$$\chi_{AR} = 0.74 + 0.36 \frac{Z_{eff}}{r^2}$$

It turns out that elements with small covalent radii and large effective nuclear charges have large electronegativities (Table $2.3.6$).

R. Mulliken defined electronegativity χ_M as the average of the ionization energy I and electron affinity A_e as follows (Figure $2.3.14$).

$$\chi_M = \frac{1}{2}(I + A_e)$$

As ionization energy is the energy of electronic excitation from the HOMO and electron affinity the energy of electron addition to the LUMO (refer to Section 2.3 (e)), in this definition electronegativity can also be called the average value of the energy levels of the HOMO and LUMO. Those elements which are hard to ionize and easy to attract electrons have large values. Although the electronegativity is defined for the atoms in a valence state in a molecule and has the dimensions of energy, it is treated as a dimensionless number (Table $2.3.5$).
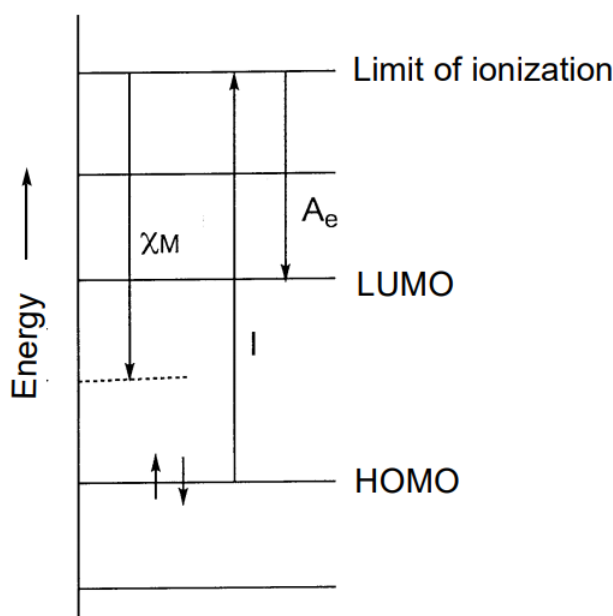
Figure 2.3.14: - Mulliken electronegativity.

Although the definition of Mulliken is intelligible since it is directly related to atomic orbitals, generally the values of Pauling or Allred-Rochow are used. As these values are not much different, the Pauling electronegativity is appropriate when choosing only one. Electronegativity values change not only by definition, but are also considerably affected by the bonding state of atoms, and they should be used with considerable caution. The electronegativities of the constituent atoms are fundamental to explaining the differences in bonding, structure, and reactions of compounds. Therefore theoretical chemists continue in their efforts firmly to extend the foundations of this parameter.

> **? Exercise 2.3.4**
>
> Describe the numerical tendency of electronegativities of the elements in the periodic table.
>
> **Answer**
>
> They increase toward the right and decrease down the table. Namely, the electronegativity of alkali metal Cs is the smallest and that of fluorine F is the largest.

(e) Molecular orbitals

The wave functions of electrons in an atom are called **atomic orbitals**. Since the probability of finding electrons in a molecular orbital is proportional to the square of a wave function, the electron map looks like a wave function. A wave function has domains

of positive and negative amplitude called lobes. The overlapping positive lobes or negative lobes of the wave functions of atoms in a molecule amplify each other to form a bond, but the positive and negative lobes cancel each other forming no bond. The extent of this interference effect corresponds to the magnitude of the overlap integral in quantum chemistry.

In the formation of a molecule, atomic orbitals overlap to generate a **molecular orbital** which is the wave function of the electrons in the molecule. The number of molecular orbitals is the sum of the atomic orbitals and these molecular orbitals are classified into **bonding, nonbonding,** or **antibonding molecular orbitals** by the extent of their participation in the bond between atoms. The conditions of the formation of a bonding molecular orbital are as follows.

[Conditions of the formation of bonding molecular orbitals]
1. The lobes of the atomic orbitals of the constituent atoms are suitable for an overlap.
2. The positive or negative sign of the overlapping lobes is the same.
3. The energy levels of atomic orbitals are close.

The simplest case where a molecular orbital is constructed from atomic orbitals A and B is explained here. A bonding molecular orbital is formed between A and B if the above mentioned conditions (1), (2), and (3) are satisfied, but if the sign of one of the atomic orbitals is reversed, condition (2) is not satisfied and an antibonding molecular orbital, in which the signs of the overlapping lobes are different (Figure $2.3.15$) results. The energy level of a bonding orbital is lower and the level of an antibonding orbital is higher than those of the constituent atomic orbitals. The larger the energy difference of a bonding and an antibonding orbital, the stronger the bond. When there is no bonding or antibonding interaction between A and B, the resultant molecular orbital is a nonbonding orbital. Electrons occupy the molecular orbitals in order of lowest to highest energy levels. The highest occupied molecular orbital is called the **HOMO** and the lowest unoccupied one the **LUMO**. Ken'ichi Fukui (1981 Nobel prize) named these orbitals **frontier orbitals**.

Two or more molecular orbitals of equal energy are called **degenerate orbitals**. The symbol of a nondegenerate orbital is a or b, a doubly degenerate orbital e, and triply degenerate orbital t. The symbol g (gerade) is attached as a suffix to the centrosymmetric orbital and u (ungerade) to the orbital which changes sign under inversion around an inversion center. The number before the symmetry symbol is used in order of energy to distinguish orbitals of the same degeneracy. Additionally, they are named **sigma (** $sigma$**)** or **pi (π)** orbitals according to the orbital character. A sigma orbital has rotation symmetry around the bond axis, and a pi orbital has a nodal plane. Therefore, sigma bonds are formed by the overlap of s-s, p-p, s-d, p-d, and d-d orbitals (Figure $2.3.16$) and pi bonds the overlap of p-p, p-d, and d-d orbitals (Figure $2.3.17$).
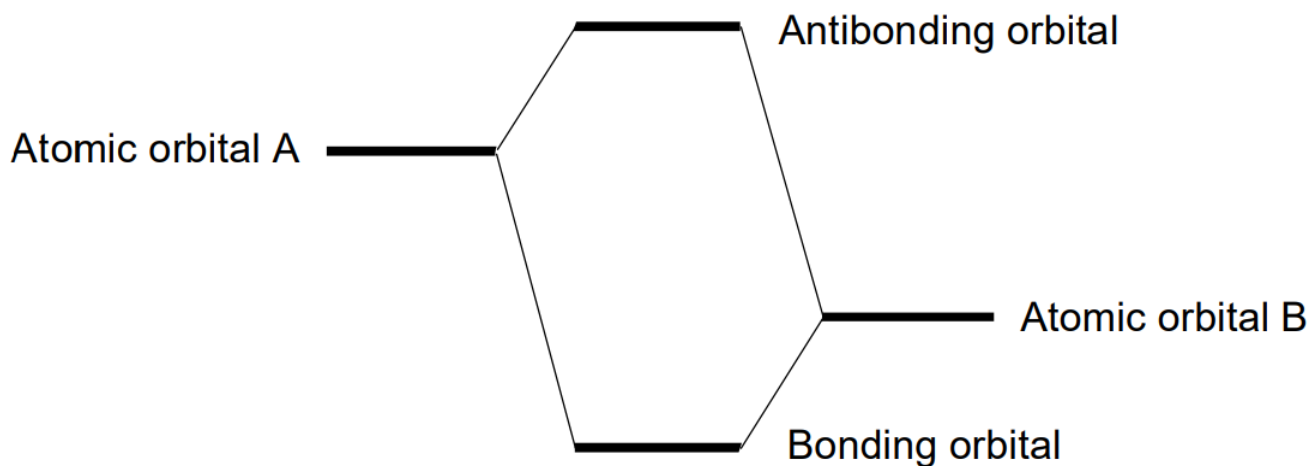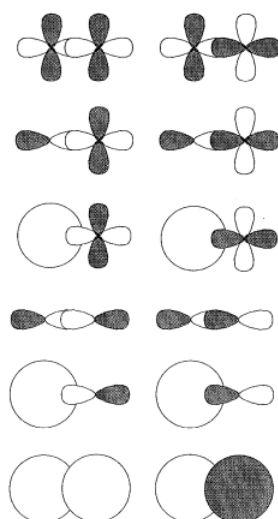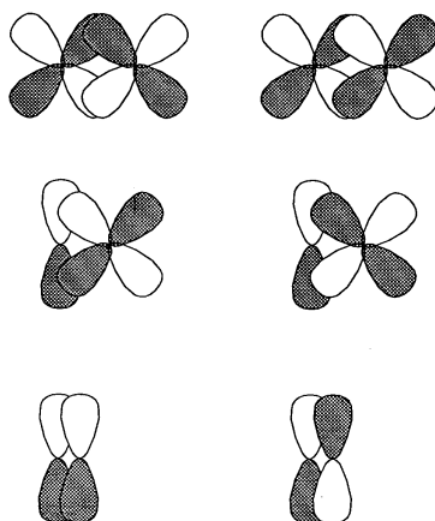

Figure 2.3.15: - Construction of molecular orbitals.

Bonding σ orbital   Antibonding σ* orbital

Figure 2.3.16: - The σ molecular orbitals

Bonding π orbitals   Antibonding π^* orbitals

Figure 2.3.17: - The π molecular orbitals.

When the wave functions of two atoms are set to ϕ_A and ϕ_B, a molecular orbital is a linear combination of the atomic orbitals (LCAO) expressed as

$$\psi = C_A\phi_A + C_B\phi_B$$

Only the atomic orbitals of the valence electron shell are used in the simplest molecular orbital method. Construction of a molecular orbital is illustrated below for the simplest case of the two-atom molecules. All the levels below the HOMO are occupied by electrons and the levels above the LUMO are empty.

In a hydrogen molecule, H_2, the overlap of the 1s orbital of each hydrogen atom forms a bonding orbital σ_g if the lobes have equal sign and an antibonding orbital σ_u if they have opposite signs, and two electrons occupy the bonding orbital σ_g (Figure 2.3.18).
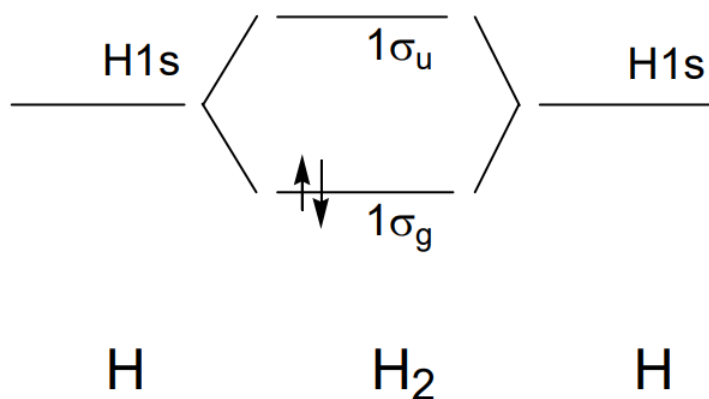
Figure 2.3.18: - The molecular orbitals of H_2. The arrows indicate the electron spins.

In the two-atom molecules of the 2nd period, from lithium Li_2 to fluorine F_2, if the z axis is set as a bond axis, $1\sigma_g$ and $1\sigma_u$ are formed by the overlap of 2s orbital of each atom and $2\sigma_g$ and $2\sigma_u$ from $2p_z$ orbitals and $1\pi_u$ and $1\pi_g$ from $2p_x$, and $2p_y$. The orbital energy levels for the molecules from Li_2 to N_2 are ordered as $1\sigma_g < 1\sigma_u < 1\pi_u < 2\sigma_g < 1\pi_g < 2\sigma_u$ and electrons occupy the levels sequentially from the bottom. The example of an N_2 molecule with ten valence electrons is shown in Figure 2.3.19. Since the ordering of orbitals is somewhat different in O_2 and F_2, in which the $2\sigma_g$ orbital comes under that of $1\pi_u$, the molecular orbital of the oxygen molecule, O_2, is illustrated in Figure 2.3.20. The 11th and 12th electrons among the 12 valence electrons occupy the doubly degenerate $1\sigma_g$ orbital in the ground state and they have parallel spins under **Hund's rule** and hence an oxygen molecule has two unpaired electrons.
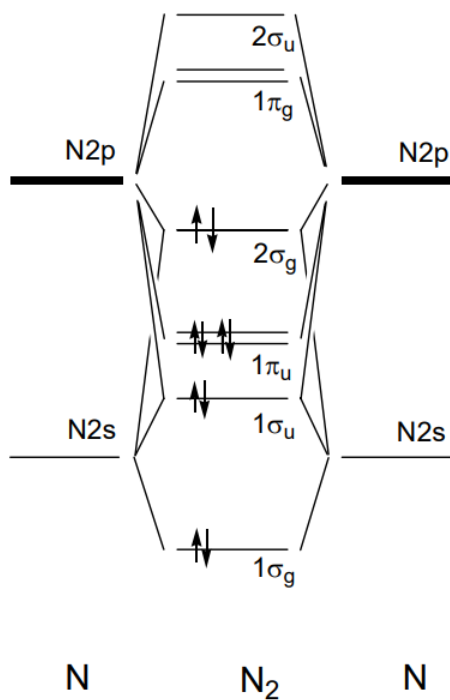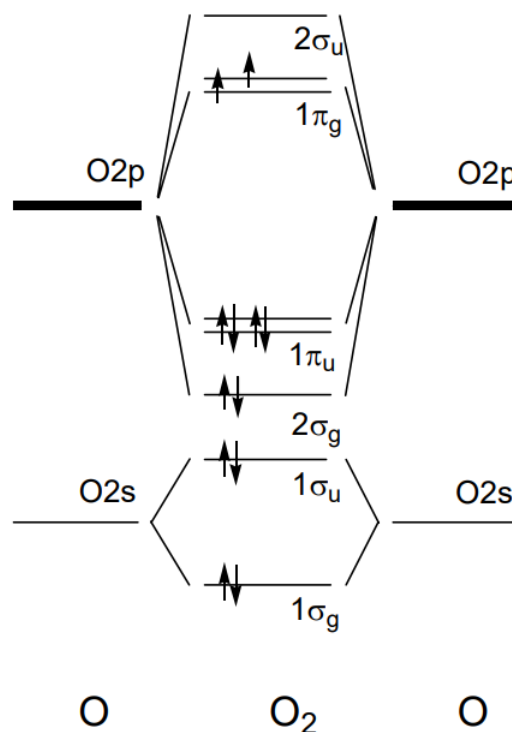

Figure 2.3.19: - Molecular orbitals of N_2.

Figure 2.3.20: - Molecular orbitals of O_2.

The molecular orbitals of two different atoms are formed by the overlap of atomic orbitals with different energy levels. The energy level of the orbital of the atom with larger electronegativity generally is lower, and the molecular orbitals are more characteristic of the atomic orbital with the nearer energy level. Therefore, the bonding orbitals have the character of the atom with the larger electronegativity, and the antibonding orbitals that of the atom with the smaller electronegativity.

For example, five molecular orbitals in hydrogen fluoride, HF, are formed from the 1s orbital of hydrogen and the 2s and 2p orbitals of fluorine, as shown in Figure 2.3.21. The bonding 1σ orbital has the 2s character of fluorine, and the antibonding 3σ orbital the 1s character of hydrogen. Since hydrogen has only one 1s orbital, the overlap with the 2p orbital of fluorine with πcharacter is not effective, and the fluorine 2p orbital becomes a nonbonding orbital. Since HF has eight valence electrons, this nonbonding orbital is the HOMO.
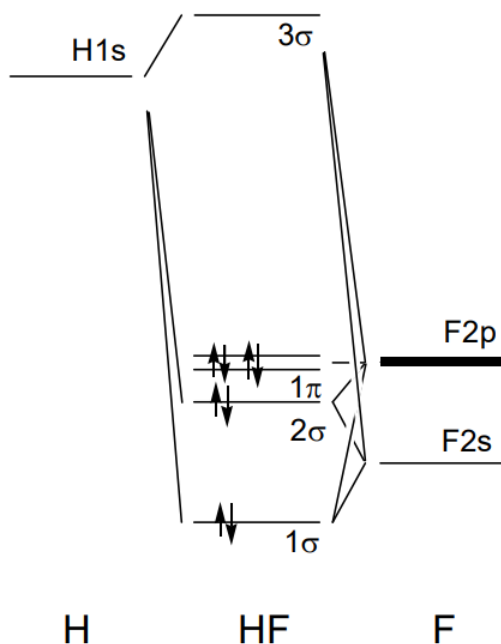
Figure 2.3.21: - Molecular orbitals of HF.

In carbon monoxide, CO, carbon and oxygen have 2s and 2p orbitals resulting in both sigma and pi bonds, and a triple bond is formed between the atoms. Although 8 molecular orbitals in this case are qualitatively the same as those of the isolectronic nitrogen molecule N_2 and 10 electrons occupy the orbital up to 3σ, the energy level of each orbital differs from that of the nitrogen molecule. The bonding 1σ orbital has the 2s character of oxygen because of its larger electronegativity, and the bonding 1π orbital also has the 2p character of oxygen. The antibonding 2π and 4σ orbitals have the 2p character of carbon (Figure 2.3.22).
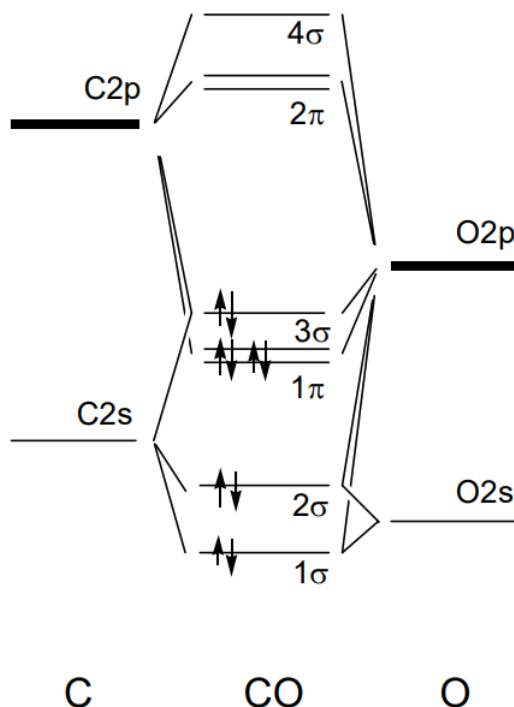

Figure 2.3.22: - Molecular orbitals of CO.

The bond order between atoms is a half of the number of electrons in the bonding orbitals minus those of the antibonding orbitals. For example, in N_2 or CO, it is equal to $\frac{1}{2}(8 - 2) = 3$ and is consistent with the Lewis structure.

> **?** Exercise 2.3.5
>
> Why are the atomic orbitals of oxygen atom in the molecular orbital diagram of carbon monoxide, CO, lower than those of carbon?
>
> **Answer**
>
> It is because the electronegativity of oxygen is larger than that of carbon.

> **✔ problems**
>
> **2.1**
>
> Using the Pauling equation, calculate the electronegativity of chlorine from the bond energies of the hydrogen molecule H_2 (432 kJ mol^{-1}), chlorine molecule Cl_2 (239 kJ mol^{-1}), and hydrogen chloride HCl molecule (428 kJ mol^{-1}) and electronegativity of hydrogen ($\chi = 2.1$).
>
> **2.2**
>
> Why are the energy levels $\sigma_g < \sigma_u$ in the orbitals of sigma character and $\pi_u < \pi_g$ in those of pi character in the molecular orbital diagram of N_2 or O_2?

Great theory and evaluation

Lewis' valence electron theory proposes that a covalent bond is formed with an electron pair and that there are eight valence electrons around each atom. This is a very important concept with which we understand the bonds between the main group elements. However, the theory was not held in high enough regard for a Nobel prize to be awarded to Lewis. One of the reasons of this disregard seems to be that chemists in the United States, Lewis' homeland, ignored his theory at first, and that a Nobel prize laureate, Langmuir, extended Lewis's theory, which was later known as the Lewis-Langmuir theory. N. Bohr, the eminent physicist who had great influence on the Nobel prize selection, evaluated Langmuir's adsorption theory more highly, which suggests that physicists considered Lewis` theory too simplistic.

There is a similar story about the transition state theory of H. Eyring. Physicists and theoretical chemists, who liked mathematical treatment of chemical phenomena, thought Eyring`s theory too unsophisticated. For this reason, the most important concept in chemical kinetics was not considered for a Nobel prize. It is an episode in the history of chemistry which reminds us of the comment of R. Hoffmann, who pointed out that simple concepts are more important than deceptively complicated mathematical theories.