QUANTUM CHEMISTRY

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Book: Quantum Chemistry (Blinder)

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TABLE OF CONTENTS

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CHAPTER OVERVIEW

1: Chapters

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1.1: Atoms and Photons- Origin of the Quantum Theory

Atomic and Subatomic Particles

The notion that the building blocks of matter are invisibly tiny particles called atoms is usually traced back to the Greek philosophers Leucippus of Miletus and Democritus of Abdera in the 5th Century BC. The English chemist John Dalton developed the atomic philosophy of the Greeks into a true scientific theory in the early years of the 19th Century. His treatise *New System of Chemical Philosophy* gave cogent phenomenological evidence for the existence of atoms and applied the atomic theory to chemistry, providing a physical picture of how elements combine to form compounds consistent with the laws of definite and multiple proportions. Table 1.1.1 summarizes some very early measurements (by Sir Humphrey Davy) on the relative proportions of nitrogen and oxygen in three gaseous compounds.

Table 1.1.1: Oxides of Nitrogen

Compound	Percent N	Percent O	Ratio
I	29.50	70.50	0.418
II	44.05	55.95	0.787
III	63.30	36.70	1.725

We would now identify these compounds as NO_2, NO and N_2O, respectively. We see in data such as these a confirmation of Dalton's atomic theory: that compounds consist of atoms of their constituent elements combined in small whole number ratios. The mass ratios in Table 1.1.1 are, with modern accuracy, 0.438, 0.875 and 1.750.

After over 2000 years of speculation and reasoning from indirect evidence, it is now possible in a sense to actually *see* individual atoms, as shown for example in Figure 1.1.1. The word "atom" comes from the Greek *atomos*, meaning literally "indivisible." It became evident in the late 19th Century, however, that the atom was *not* truly the ultimate particle of matter. Michael Faraday's work had suggested the electrical nature of matter and the existence of subatomic particles. This became manifest with the discovery of radioactive decay by Henri Becquerel in 1896 the emission of alpha, beta and gamma particles from atoms. In 1897, J. J. Thompson identified the electron as a universal constituent of all atoms and showed that it carried a negative electrical charge, now designated -*e*.

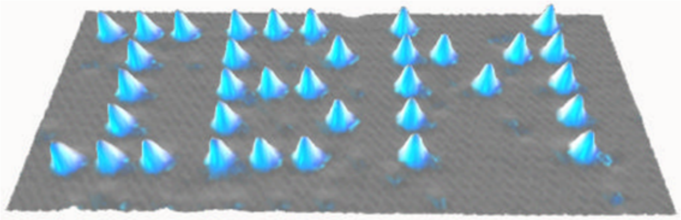
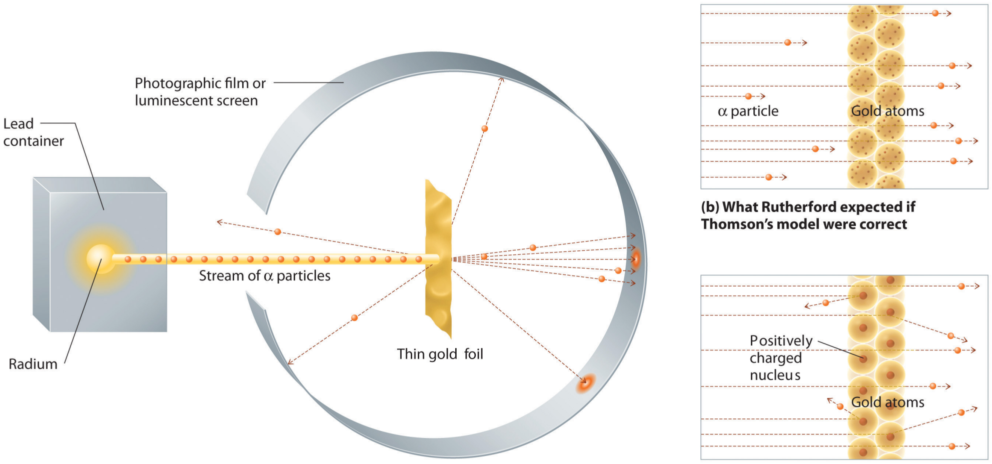


Figure 1.1.1: Image showing electron clouds of individual xenon atoms on a nickel(110) surface produced by a scanning tunneling microscope at IBM Laboratories.

To probe the interior of the atom, Ernest Rutherford in 1911 bombarded a thin sheet of gold with a stream of positively-charged alpha particles emitted by a radioactive source. Most of the high-energy alpha particles passed right through the gold foil, but a small number were strongly detected in a way that indicated the presence a small but massive positive charge in the center of the atom (Figure 1.1.2). Rutherford proposed the nuclear model of the atom. As we now understand it, an electrically-neutral atom of atomic number Z consists of a nucleus of positive charge $+Ze$, containing almost the entire the mass of the atom, surrounded by Z electrons of very small mass, each carrying a charge $-e$. The simplest atom is hydrogen, with $Z = 1$, consisting of a single electron outside a single proton of charge $+e$.



(a) Rutherford's experiment

(b) What Rutherford expected if Thomson's model were correct

(c) What Rutherford actually observed

Figure 1.1.2: A Summary of Rutherford's Experiments*(a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) But a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus.*

With the discovery of the neutron by Chadwick in 1932, the structure of the atomic nucleus was clarified. A nucleus of atomic number *Z* and mass number *A* was composed of *Z* protons and *A-Z* neutrons. Nuclei diameters are of the order of several times 10^{-15}m. From the perspective of an atom, which is 10^5 times larger, a nucleus behaves, for most purposes, like a point charge +*Ze*.

During the 1960's, compelling evidence began to emerge that protons and neutrons themselves had composite structures, with major contributions by Murray Gell-Mann. According to the currently accepted "Standard Model," the protons and neutron are each made of three *quarks*, with compositions *uud* and *udd*, respectively. The up quark *u* has a charge of $+\frac{2}{3}e$, while the down quark *d* has a charge of $-\frac{1}{3}e$. Despite heroic experimental efforts, individual quarks have never been isolated, evidently placing them in the same category with magnetic monopoles. By contrast, the electron maintains its status as an indivisible elementary particle.

Electromagnetic Waves

Perhaps the greatest achievement of physics in the 19th century was James Clerk Maxwell's unification in 1864 of the phenomena of electricity, magnetism and optics. An (optional) summary of Maxwell's equations is given in Supplement 1A. Heinrich Hertz in 1887 was the first to demonstrate experimentally the production and detection of the electromagnetic waves predicted by Maxwell-specifically radio waves-by acceleration of electrical charges. As shown in Figure 1.1.3, electromagnetic waves consist of mutually perpendicular electric and magnetic fields, **E** and **B** respectively, oscillating in synchrony at high frequency and propagating in the direction of **E** x **B**.

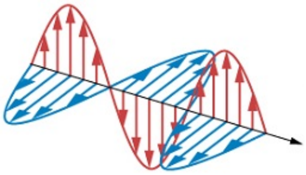


Figure 1.1.3: Schematic representation of monochromatic linearly-polarized electromagnetic wave.

The wavelength λ is the distance between successive maxima of the electric (or magnetic) field. The frequency ν represents the number of oscillations per second observed at a fixed point in space. The reciprocal of frequency $\tau = \frac{1}{\nu}$ represents period of oscillation-the time it takes for one wavelength to pass a fixed point. The speed of propagation of the wave is therefore determined by $\lambda = c\tau$ or in more familiar form

$$\lambda\nu = c \tag{1.1.1}$$

where $c = 2.9979 \times 10^8 m/sec$, usually called the *speed of light*, applies to all electromagnetic waves in vacuum. Frequencies are expressed in hertz (Hz), defined as the number of oscillations per second.

Electromagnetic radiation is now known to exist in an immense range of wavelengths including gamma rays, X-rays, ultraviolet, visible light, infrared, microwaves and radio waves, as shown in Figure 1.1.4.

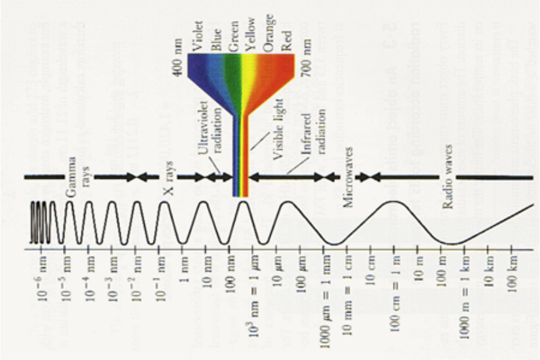


Figure 1.1.4. The electromagnetic spectrum, showing wavelengths of different types of radiation. Adapted from R. A. Freedman and W. J. Kaufmann III, Universe (Freeman, New York, 2001).

Three Failures of Classical Physics

Isaac Newton's masterwork, *Pincipia*, published in 1687, can be considered to mark the beginning of modern physical science. Not only did Newton delineate the fundamental laws governing motion and gravitation but he established a general philosophical worldview which pervaded all scientific theories for two centuries afterwards. This system of thinking about the physical world is known as "Classical Physics." Its most notable feature is the primacy of cause and effect relationships. Given sufficient information about the present state of part of the Universe, it should be possible, at least in principle, to predict its future behavior (as well as its complete history.) This capability is known as *determinism*. For example, solar and lunar eclipses can be predicted centuries ahead, within an accuracy of several seconds. (But interestingly, we can't predict even a couple of days in advance if the weather will be clear enough to view the eclipse!) The other great pillar of classical physics is Maxwell's theory of electromagnetism.

The origin of quantum theory can be marked by three diverse phenomena involving electromagnetic radiation, which could *not* be adequately explained by the methods of classical physics. First among these was blackbody radiation, which led to the contribution of Max Planck in 1900. Next was the photoelectric effect, treated by Albert Einstein in 1905. Third was the origin of line spectra, the hero being Neils Bohr in 1913. A coherent formulation of quantum mechanics was eventually developed in 1925 and 1926, principally the work of Schrödinger, Heisenberg and Dirac. The remainder of this Chapter will describe the early contributions to the quantum theory by Planck, Einstein and Bohr.

Blackbody Radiation

It is a matter of experience that a hot object can emit radiation. A piece of metal stuck into a flame can become "red hot." At higher temperatures, its glow can be described as "white hot." Under even more extreme thermal excitation it can emit predominantly blue light (completing a very patriotic sequence of colors!). Josiah Wedgwood, the famous pottery designer, noted as far back as 1782 that different materials become red hot at the same temperature. The quantitative relation between color and temperature is described by the *blackbody radiation law*. A blackbody is an idealized perfect absorber and emitter of all possible wavelengths λ of the radiation. Figure 1.1.5 shows experimental wavelength distributions of thermal radiation at several temperatures. Consistent with our experience, the maximum in the distribution, which determines the predominant color, increases with temperature. This relation is given by Wien's displacement law, which can be expressed

$$T\lambda_{max} = 2.898 \times 10^6 \; nmK \tag{1.1.2}$$

where the wavelength is expressed in nanometers (nm). At room temperature (300 K), the maximum occurs around $10\mu m$, in the infrared region. In Figure 1.1.5, the approximate values of λ_{max} are 2900 nm at 1000 K, 1450 nm at 2000 K and 500n m at 5800 K, the approximate surface temperature of the Sun. The Sun's λ_{max} is near the middle of the visible range (380-750nm) and is perceived by our eyes as white light.

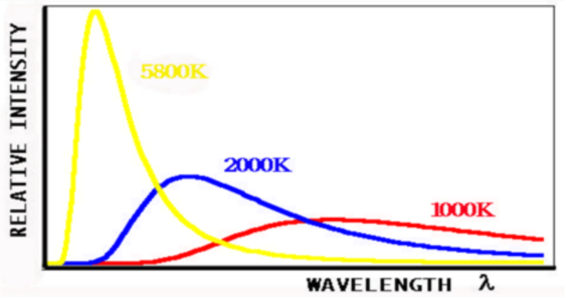


Figure 1.1.5. Intensity distributions of blackbody radiation at three different temperatures. The total radiation intensity varies as T^4 (Stefan-Boltzmann law) so the total radiation at 2000K is actually 2^4 = 16 times that at 1000K.

The origin of blackbody radiation was a major challenge to 19th Century physics. Lord Rayleigh proposed that the electromagnetic field could be represented by a collection of oscillators of all possible frequencies. By simple geometry, the higher-frequency (lower wavelength) modes of oscillation are increasingly numerous since it it possible to fit their waves into an enclosure in a larger number of arrangements. In fact, the number of oscillators increases very rapidly as λ^{-4}. Rayleigh assumed that every oscillator contributed equally to the radiation (the equipartition principle). This agrees fairly well with experiment at low frequencies. But if ultraviolet rays and higher frequencies were really produced in increasing number, we would get roasted like marshmallows by sitting in front of a fireplace! Fortunately, this doesn't happen, and the incorrect theory is said to suffer from an "ultraviolet catastrophe."

Max Planck in 1900 derived the correct form of the blackbody radiation law by introducing a bold postulate. He proposed that energies involved in absorption and emission of electromagnetic radiation did not belong to a continuum, as implied by Maxwell's theory, but were actually made up of discrete bundles which he called "quanta." Planck's idea is traditionally regarded as marking the birth of the quantum theory. A quantum associated with radiation of frequency ν has the energy

$$E = h\nu \tag{1.1.3}$$

where the proportionality factor *h* = 6.626 x 10^{-34} J sec is known as Planck's constant. For our development of the quantum theory of atoms and molecules, we need only this simple result and do not have to follow the remainder of Planck's derivation. If you insist, however, the details are given in Supplement 1B.

The Photoelectric Effect

A familiar device in modern technology is the photocell or "electric eye," which runs a variety of useful gadgets, including automatic door openers. The principle involved in these devices is the photoelectric effect, which was first observed by Heinrich Hertz in the same laboratory in which he discovered electromagnetic waves. Visible or ultraviolet radiation impinging on clean metal surfaces can cause electrons to be ejected from the metal. Such an effect is not, in itself, inconsistent with classical theory since electromagnetic waves are known to carry energy and momentum. But the detailed behavior as a function of radiation frequency and intensity can *not* be explained classically.

The energy required to eject an electron from a metal is determined by its *work function* Φ. For example, sodium has $\Phi = 1.82 eV$. The electron-volt is a convenient unit of energy on the atomic scale: 1 eV = 1.602 x 10^{-19}J. This corresponds to the energy which an electron picks up when accelerated across a potential difference of 1 volt. The classical expectation would be that radiation of sufficient intensity should cause ejection of electrons from a metal surface, with their kinetic energies increasing with the radiation intensity. Moreover, a time delay would be expected between the absorption of radiation and the ejection of electrons. The experimental facts are quite different. It is found that no electrons are ejected, no matter how high the radiation intensity, unless the radiation *frequency* exceeds some threshold value ν_0 for each metal. For sodium ν_0 = 4.39 x 10^{14} Hz (corresponding to a wavelength of 683 nm), as shown in Figure 1.1.6. For frequencies ν above the threshold, the ejected electrons acquire a kinetic energy given by

$$\frac{1}{2}mv^2 = h(\nu - \nu_0) = h\nu - \Phi \tag{1.1.4}$$

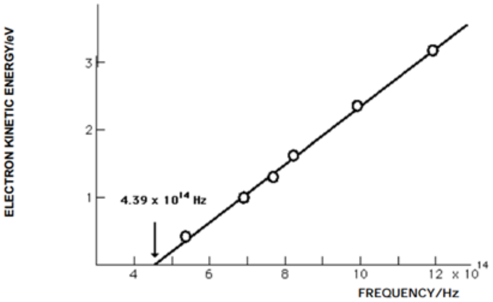


Figure 1.1.6. Photoelectric data for sodium (Millikan, 1916). The threshold frequency ν_0, found by extrapolation, equals 4.39 x 10 ^{14}Hz.

Evidently, the work function Φ can be identified with $h\nu_0$, equal to 3.65 x 10^{-19}J=1.82 eV for sodium. The kinetic energy increases *linearly* with frequency above the threshold but is independent of the radiation intensity. Increased intensity does, however, increase the *number* of photoelectrons.

Einstein's explanation of the photoelectric effect in 1905 appears trivially simple once stated. He accepted Planck's hypothesis that a quantum of radiation carries an energy $h\nu$. Thus, if an electron is bound in a metal with an energy Φ, a quantum of energy $h\nu_0 = \Phi$ will be sufficient to dislodge it. And any excess energy $h(\nu - \nu_0)$ will appear as kinetic energy of the ejected electron. Einstein believed that the radiation field actually did consist of quantized particles, which he named *photons*. Although Planck himself never believed that quanta were real, Einstein's success with the photoelectric effect greatly advanced the concept of energy quantization.

Line Spectra

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.1.7 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure. Blackbody radiation, for example, is a continuum. An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

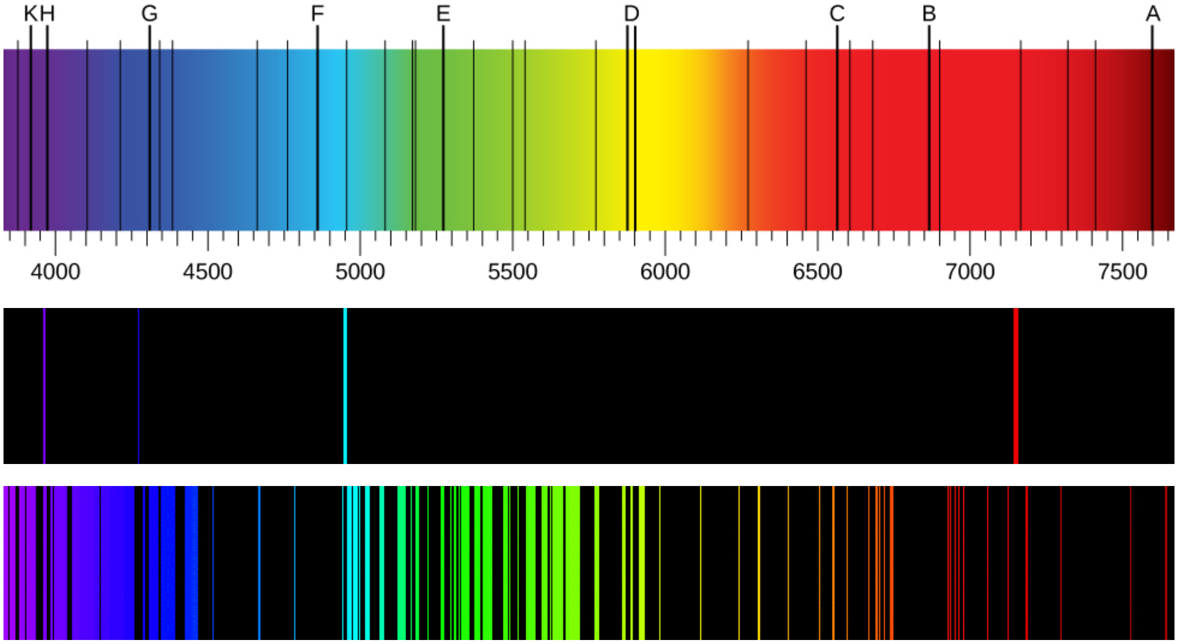


Figure 6.4.1. In the solar emission spectrum in the visible range from 380 nm to 710 nm, Fraunhofer lines are observed as vertical black lines at specific spectral positions in the continuous spectrum. Highly sensitive modern instruments observe thousands of such lines. (middle)The emission spectrum of atomic hydrogen: The spectral positions of emission lines are characteristic for hydrogen atoms. (credit: “Merikanto”/Wikimedia Commons). (bottom The emission spectrum of atomic iron: The spectral positions of emission lines are characteristic for iron atoms. Images used with permission (CC SA-BY; Openstax).

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.1.8.

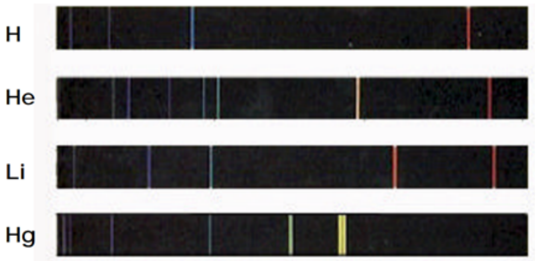


Figure 1.1.8. Emission spectra of several elements.

It is consistent with classical electromagnetic theory that motions of electrical charges within atoms can be associated with the absorption and emission of radiation. What is completely mysterious is how such radiation can occur for discrete frequencies, rather than as a continuum. The breakthrough that explained line spectra is credited to Neils Bohr in 1913. Building on the ideas of Planck and Einstein, Bohr postulated that the energy levels of atoms belong to a discrete set of values E_n, rather than a continuum as in classical mechanics. When an atom makes a downward energy transition from a higher energy level E_m to a lower energy level E_n, it caused the emission of a photon of energy

$$h\nu = E_m - E_n \tag{1.1.5}$$

This is what accounts for the discrete values of frequency ν in emission spectra of atoms. Absorption spectra are correspondingly associated with the annihilation of a photon of the same energy and concomitant excitation of the atom from E_n to E_m. Figure 1.1.9 is a schematic representation of the processes of absorption and emission of photons by atoms. Absorption and emission processes occur at the same set frequencies, as is shown by the two line spectra in Figure 1.1.7.

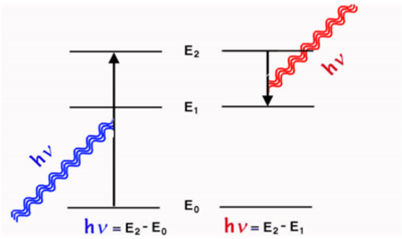


Figure 1.1.9: Origin of line spectra. Absorption of the photon shown in blue causes atomic transition from E_0 to E_2. Transition from E_2 to E_1 causes emission of the photon shown in red.

Rydberg (1890) found that all the lines of the atomic hydrogen spectrum could be fitted to a simple empirical formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), n = 1, 2, 3..., n_2 > n_1 \tag{1.1.6}$$

where R, known as the Rydberg constant, has the value 109,677 cm^{-1}. This formula was found to be valid for hydrogen spectral lines in the infrared and ultraviolet regions, in addition to the four lines in the visible region. No analogously simple formula has been found for any atom other than hydrogen. Bohr proposed a model for the energy levels of a hydrogen atom which agreed with Rydberg's formula for radiative transition frequencies. Inspired by Rutherford's nuclear atom, Bohr suggested a planetary model for the hydrogen atom in which the electron goes around the proton in one of a set of allowed circular orbits, as shown in Fig 8. A more fundamental understanding of the discrete nature of orbits and energy levels had to await the discoveries of 1925-26, but Bohr's model provided an invaluable stepping-stone to the development of quantum mechanics. We will consider the hydrogen atom in greater detail in Chap. 7.

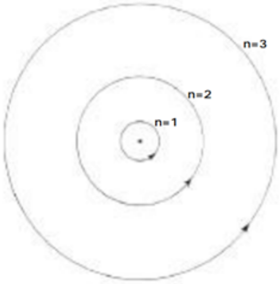


Figure 1.1.10. Bohr model of the hydrogen atom showing three lowest-energy orbits.

Figure 1.1.11. A stylized representation of the Bohr model for a multielectron atom. From the logo of the International Atomic Energy Agency.

Contributors and Attributions

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1.2: Waves and Particles

Quantum mechanics is the theoretical framework which describes the behavior of matter on the atomic scale. It is the most successful quantitative theory in the history of science, having withstood thousands of experimental tests without a single verifiable exception. It has correctly predicted or explained phenomena in fields as diverse as chemistry, elementary-particle physics, solid-state electronics, molecular biology and cosmology. A host of modern technological marvels, including transistors, lasers, computers and nuclear reactors are offspring of the quantum theory. Possibly 30% of the US gross national product involves technology which is based on quantum mechanics. For all its relevance, the quantum world differs quite dramatically from the world of everyday experience. To understand the modern theory of matter, conceptual hurdles of both psychological and mathematical variety must be overcome. A paradox which stimulated the early development of the quantum theory concerned the indeterminate nature of light. Light usually behaves as a wave phenomenon but occasionally it betrays a particle-like aspect, a schizoid tendency known as the wave-particle duality. We consider first the wave theory of light.

The Double-Slit Experiment

Figure $1.2.1$ shows a modernized version of the famous double-slit diffraction experiment first performed by Thomas Young in 1801. Light from a monochromatic (single wavelength) source passes through two narrow slits and is projected onto a screen. Each slit by itself would allow just a narrow band of light to illuminate the screen. But with both slits open, a beautiful interference pattern of alternating light and dark bands appears, with maximum intensity in the center. To understand what is happening, we review some key results about electromagnetic waves.

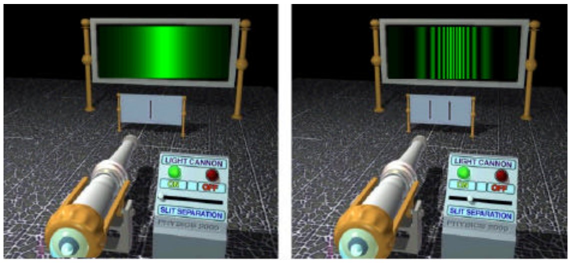

Figure $1.2.1$: Modern version of Young's interference experiment using a laser gun. Single slit (left) produces an intense band of light. Double slit (right) gives a diffraction pattern. See animated applet at www.colorado.edu/physics/2000...twoslitsa.html

Maxwell's theory of electromagnetism was an elegant unification of the diverse phenomena of electricity, magnetism and radiation, including light. Electromagnetic radiation is carried by transverse waves of electric and magnetic fields, propagating in vacuum at a speed $c \approx 3 \times 10^8 m/sec$, known as the "speed of light." As shown in Figure 2, the **E** and **B** fields oscillate sinusoidally, in synchrony with one another. The magnitudes of **E** and **B** are proportional ($B = E/c$ in SI units). The distance between successive maxima (or minima) at a given instant of time is called the wavelength λ. At every point in space, the fields also oscillate sinusoidally as functions of time. The number of oscillations per unit time is called the frequency ν. Since the field moves one wavelength in the time λ/c, the wavelength, frequency and speed for any wave phenomenon are related by

$$\lambda\nu = c \tag{1.2.1}$$

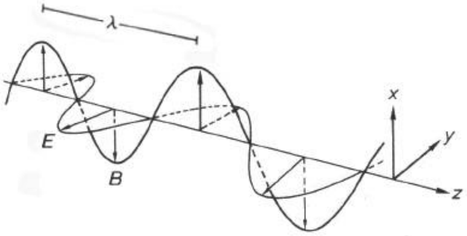

Figure $1.2.2$: Schematic representation of electromagnetic wave. In electromagnetic theory, the intensity of radiation, energy flux incident on a unit area per unit time, is represented by the Poynting vector

$$\vec{S} = \mu_0 \vec{E} \times \vec{B} \tag{1.2.2}$$

The energy density contained in an electromagnetic field, even a static one, is given by

$$\rho=\frac{1}{2}\left(\epsilon_0 E^2+\frac{B^2}{\mu_0}\right) \tag{1.2.3}$$

Note that both of the above energy quantities depend *quadratically* on the fields **E** and **B**. To discuss the diffraction experiments described above, it is useful to define the *amplitude* of an electromagnetic wave at each point in space and time **r**, *t* by the function

$$\Psi(\vec{r},t)=\sqrt{\epsilon_0}E(\vec{r},t)=\frac{B(\vec{r},t)}{\sqrt{\mu_0}} \tag{1.2.4}$$

such that the intensity is given by

$$\rho(\vec{r},t)=[\Psi(\vec{r},t)]^2 \tag{1.2.5}$$

The function $\Psi(\vec{r},t)$ will, in some later applications, have complex values. In such cases we generalize the definition of intensity to

$$\rho(\vec{r},t)=|\Psi(\vec{r},t)|^2=\Psi(\vec{r},t)^*\Psi(\vec{r},t) \tag{1.2.6}$$

where $\Psi(\vec{r},t)^*$ represents the complex conjugate of $\Psi(\vec{r},t)$. In quantum mechanical applications, the function Ψ is known as the *wavefunction*.

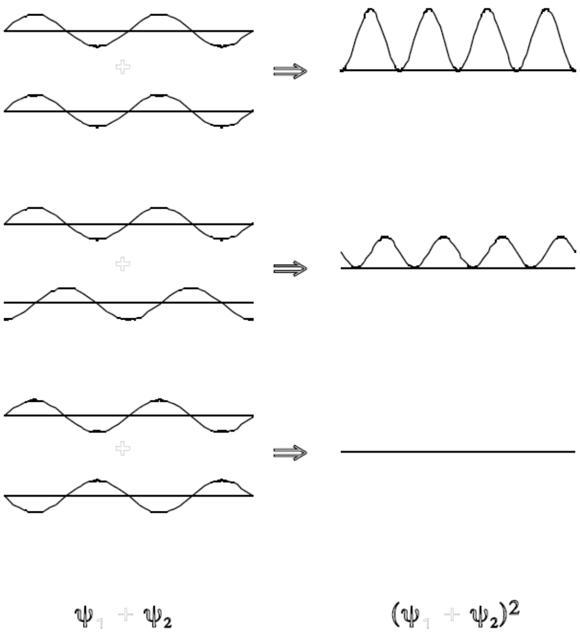

Figure 1.2.1: *Interference of two equal sinusoidal waves. Top: constructive interference. Bottom: destructive interference. Center: intermediate case. The resulting intensities $\rho=\Psi^2$ is shown on the right.*

The electric and magnetic fields, hence the amplitude Ψ, can have either positive and negative values at different points in space. In fact constructive and destructive interference arises from the superposition of waves, as illustrated in Figure 1.2.3. By Equation 1.2.5, the intensity $\rho\geq 0$ everywhere. The light and dark bands on the screen are explained by constructive and destructive interference, respectively. The wavelike nature of light is convincingly demonstrated by the fact that the intensity with both slits open is *not* the sum of the individual intensities, ie, $\rho\neq\rho_1+\rho_2$. Rather it is the wave amplitudes which add:

$$\Psi=\Psi_1+\Psi_2 \tag{1.2.7}$$

with the intensity given by the square of the amplitude:

$$\rho=\Psi^2=\Psi_1^2+\Psi_2^2+2\Psi_1\Psi_2 \tag{1.2.8}$$

The cross term $2\Psi_1\Psi_2$ is responsible for the constructive and destructive interference. Where Ψ_1 and Ψ_2 have the same sign, constructive interference makes the total intensity greater than the the sum of ρ_1 and ρ_2. Where Ψ_1 and Ψ_2 have opposite signs, there is destructive interference. If, in fact, $\Psi_1=-\Psi_2$ then the two waves cancel exactly, giving a dark fringe on the screen.

Wave-Particle Duality

The interference phenomena demonstrated by the work of Young, Fresnel and others in the early 19th Century, apparently settled the matter that light was a wave phenomenon, contrary to the views of Newton a century earlier--case closed! But nearly a century later, phenomena were discovered which could *not* be satisfactorily accounted for by the wave theory, specifically blackbody radiation and the photoelectric effect.

Deviating from the historical development, we will illustrate these effects by a modification of the double slit experiment. Let us equip the laser source with a dimmer switch capable of reducing the light intensity by several orders of magnitude, as shown in Figure $1.2.4$. With each successive filter the diffraction pattern becomes dimmer and dimmer. Eventually we will begin to see localized scintillations at random positions on an otherwise dark screen. It is an almost inescapable conclusion that these scintillations are caused by *photons*, the bundles of light postulated by Planck and Einstein to explain blackbody radiation and the photoelectric effect.

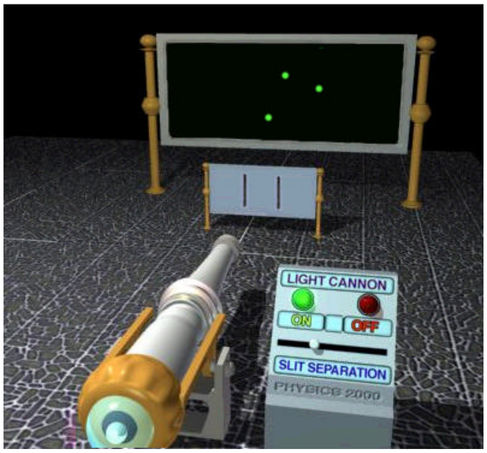

Figure $1.2.1$: Scintillations observed after dimming laser intensity by several orders of magnitude. These are evidently caused by individual photons!

But wonders do not cease even here. Even though the individual scintillations appear at random positions on the screen, their statistical behavior reproduces the original high-intensity diffraction pattern. Evidently the statistical behavior of the photons follows a predictable pattern, even though the behavior of individual photons is unpredictable. This implies that each individual photon, even though it behaves mostly like a particle, somehow carry with it a "knowledge" of the entire wavelike diffraction pattern. In some sense, a single photon must be able to go through *both* slits at the same time. This is what is known as the *wave-particle duality* for light: under appropriate circumstances light can behave as a wave or as a particle.

Planck's resolution of the problem of blackbody radiation and Einstein's explanation of the photoelectric effect can be summarized by a relation between the energy of a photon to its frequency:

$$E = h\nu \tag{1.2.9}$$

where $h = 6.626 \times 10^{-34} Jsec$, known as Planck's constant. Much later, the Compton effect was discovered, wherein an x-ray or gamma ray photon ejects an electron from an atom, as shown in Figure $1.2.5$. Assuming conservation of momentum in a photon-electron collision, the photon is found to carry a momentum *p*, given by

$$p = \frac{h}{\lambda} \tag{1.2.10}$$

Equation 1.2.9 and 1.2.10 constitute quantitative realizations of the wave-particle duality, each relating a particle-like property--energy or momentum--to a wavelike property--frequency or wavelength.

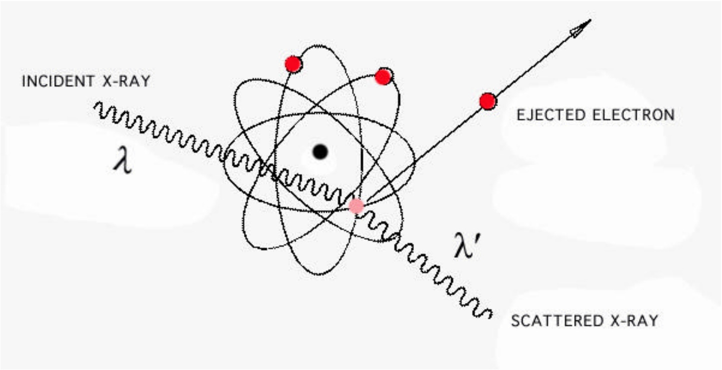

Figure 1.2.1: Compton effect. The momentum and energy carried by the incident x-ray photon are transferred to the ejected electron and the scattered photon.

According to the special theory of relativity, the last two formulas are actually different facets of the same fundamental relationship. By Einstein's famous formula, the equivalence of mass and energy is given by

$$E = mc^2 \tag{1.2.11}$$

The photon's rest mass is zero, but in travelling at speed c, it acquires a finite mass. Equating Equation 1.2.8) and 1.2.11 for the photon energy and taking the photon momentum to be $p = mc$, we obtain

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{1.2.12}$$

Thus, the wavelength-frequency relation (Equation 1.2.1), implies the Compton-effect formula (Equation 1.2.10).

The best we can do is to *describe* the phenomena constituting the wave-particle duality. There is no widely accepted explanation in terms of everyday experience and common sense. Feynman referred to the "experiment with two holes" as the "central mystery of quantum mechanics." It should be mentioned that a number of models have been proposed over the years to rationalize these quantum mysteries. Bohm proposed that there might exist *hidden variables* which would make the behavior of each photon deterministic, ie, particle-like. Everett and Wheeler proposed the "many worlds interpretation of quantum mechanics" in which each random event causes the splitting of the entire universe into disconnected parallel universes in which each possibility becomes the reality. Needless to say, not many people are willing to accept such a metaphysically unwieldy view of reality. Most scientists are content to apply the highly successful computational mechanisms of quantum theory to their work, without worrying unduly about its philosophical underpinnings. Sort of like people who enjoy eating roast beef but would rather not think about where it comes from.

There was never any drawn-out controversy about whether electrons or any other constituents of matter were other than particle-like. Yet a variant of the double-slit experiment using electrons instead of light proves otherwise. The experiment is technically difficult but has been done. An electron gun, instead of a light source, produces a beam of electrons at a selected velocity, which is focused and guided by electric and magnetic fields. Then, everything that happens for photons has its analog for electrons. Individual electrons produce scintillations on a phosphor screen-this is how TV works. But electrons also exhibit diffraction effects, which indicates that they too have wavelike attributes. Diffraction experiments have been more recently carried out for particles as large as atoms and molecules, even for the C_{60} fullerene molecule.

De Broglie in 1924 first conjectured that matter might also exhibit a wave-particle duality. A wavelike aspect of the electron might, for example, be responsible for the discrete nature of Bohr orbits in the hydrogen atom. According to de Broglie's hypothesis, the "matter waves" associated with a particle have a wavelength given by

$$\lambda = h/p \tag{1.2.13}$$

which is identical in form to Compton's result (Equation 1.2.10) (which, in fact, was discovered later). The correctness of de Broglie's conjecture was most dramatically confirmed by the observations of Davisson and Germer in 1927 of diffraction of monoenergetic beams of electrons by metal crystals, much like the diffraction of x-rays. And measurements showed that de Broglie's formula (Equation 1.2.13) did indeed give the correct wavelength (see Figure 1.2.6).

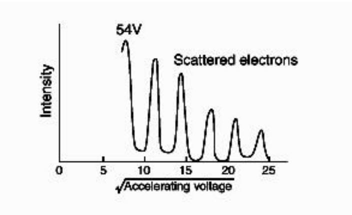

Figure 1.2.16: Intensity of electron scattered at a fixed angle off a nickel crystal, as function of incident electron energy. From C. J. Davisson "Are Electrons Waves?" *Franklin Institute Journal* **205**, 597 (1928).

The Schrödinger Equation

Schrödinger in 1926 first proposed an equation for de Broglie's matter waves. This equation cannot be derived from some other principle since it constitutes a fundamental law of nature. Its correctness can be judged only by its subsequent agreement with observed phenomena (*a posteriori* proof). Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the wave equation

$$\nabla^2\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = 0 \tag{1.2.14}$$

where the Laplacian or "del-squared" operator is defined by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.2.15}$$

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider a very general instance of wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{1.2.16}$$

where $f(\theta)$ represents a sinusoidal function such as $\sin\theta$, $\cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$e^{i\theta} = \cos\theta + i\sin\theta \tag{1.2.17}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever *x* increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{1.2.18}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both *x*- and *t*-dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{1.2.19}$$

representing waves travelling from left to right. Now we make use of the Planck and de Broglie formulas (Equation 1.2.8 and 1.2.13, respectively) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = exp[i(px - Et)/\hbar] \tag{1.2.20}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{1.2.21}$$

Since Planck's constant occurs in most formulas with the denominator 2π, this symbol was introduced by Dirac. Now Equation 1.2.18 represents in some way the wavelike nature of a particle with energy E and momentum *p*. The time derivative of Equation 1.2.20 gives

$$\frac{\partial \Psi}{\partial t} = -(iE/\hbar) \times \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{1.2.22}$$

Thus

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi \tag{1.2.23}$$

Analogously

$$-i\hbar \frac{\partial \Psi}{\partial x} = p\Psi \tag{1.2.24}$$

and

$$-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi \tag{1.2.25}$$

The energy and momentum for a nonrelativistic free particle are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{1.2.26}$$

Thus $\Psi(x,t)$ satisfies the partial differential equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \tag{1.2.27}$$

For a particle with a potential energy $V(x)$,

$$E = \frac{p^2}{2m} + V(x) \tag{1.2.28}$$

we postulate that the equation for matter waves generalizes to

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right] \Psi \tag{1.2.29}$$

For waves in three dimensions should then have

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})\right] \Psi(\vec{r},t) \tag{1.2.30}$$

Here the potential energy and the wavefunction depend on the three space coordinates *x, y, z*, which we write for brevity as **r**. This is the time-dependent Schrödinger equation for the amplitude $\Psi(\vec{r},t)$ of the matter waves associated with the particle. Its formulation in 1926 represents the starting point of modern quantum mechanics. (Heisenberg in 1925 proposed another version known as matrix mechanics.)

For *conservative* systems, in which the energy is a constant, we can separate out the time-dependent factor from (19) and write

$$\Psi(\vec{r},t) = \psi(\vec{r}) e^{-iEt \div \hbar} \tag{1.2.31}$$

where $\psi(\vec{r})$ is a wavefunction dependent only on space coordinates. Putting Equation 1.2.31 into Equation 1.2.30 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})\right] \psi(\vec{r}) = E\psi(\vec{r}) \tag{1.2.32}$$

Most of our applications of quantum mechanics to chemistry will be based on this equation.

The bracketed object in Equation 1.2.32 is called an *operator*. An operator is a generalization of the concept of a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. The Laplacian (∇) is an example of an operator. We usually indicate that an object is an operator by placing a `hat' over it, eg, $\hat{A}$. The action of an operator that turns the function *f* into the function *g* is represented by

$$\hat{A}f = g \tag{1.2.33}$$

Equation 1.2.24 implies that the operator for the *x*-component of momentum can be written

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{1.2.34}$$

and by analogy, we must have

$$\hat{p}_y = -i\hbar\frac{\partial}{\partial y} \tag{1.2.35}$$

and

$$\hat{p}_z = -i\hbar\frac{\partial}{\partial z} \tag{1.2.36}$$

The energy, as in Equation 1.2.28, expressed as a function of position and momentum is known in classical mechanics as the Hamiltonian. Generalizing to three dimensions,

$$\hat{H} = \frac{p^2}{2m} + V(\vec{r}) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \tag{1.2.37}$$

We construct thus the corresponding quantum-mechanical operator

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{1.2.38}$$

The time-independent Schrödinger equation (Equation 1.2.32) can then be written symbolically as

$$\hat{H}\Psi = E\Psi \tag{1.2.39}$$

This form is actually more generally to *any* quantum-mechanical problem, given the appropriate Hamiltonian and wavefunction. Most applications to chemistry involve systems containing many particles--electrons and nuclei. An operator equation of the form

$$\hat{A}\psi = const\psi \tag{1.2.40}$$

is called an eigenvalue equation. Recall that, in general, an operator acting on a function gives another function (e.g., Equation 1.2.33). The special case (Equation 1.2.40) occurs when the second function is a multiple of the first. In this case, ψ is known as an eigenfunction and the constant is called an eigenvalue. (These terms are hybrids with German, the purely English equivalents being `characteristic function' and `characteristic value.') To every dynamical variable A in quantum mechanics, there corresponds an eigenvalue equation, usually written

$$\hat{A}\psi = a\psi \tag{1.2.41}$$

The eigenvalues a represent the possible measured values of the variable A. The Schrödinger Equation (1.2.39) is the best known instance of an eigenvalue equation, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

The Wavefunction

For a single-particle system, the wavefunction $\Psi(\vec{r}, t)$, or $\psi(\vec{r})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. The relationship between amplitude and intensity of electromagnetic waves we developed for Equation 1.2.6 can be extended to matter waves.

The most commonly accepted interpretation of the wavefunction is due to Max Born (1926), according to which $\rho(r)$, the square of the absolute value of $\psi(r)$ is proportional to the probability density (probability per unit volume) that the particle will be found at the position **r**. Probability density is the three-dimensional analog of the diffraction pattern that appears on the two-dimensional screen in the double-slit diffraction experiment for electrons described in the preceding Section. In the latter case we had the relative probability a scintillation would appear at a given point on the screen. The function $\rho(r)$ becomes equal, rather than just proportional to, the probability density when the wavefunction is normalized, that is,

$$\int |\psi(\vec{r})|^2 d\tau = 1 \tag{1.2.42}$$

This simply accounts for the fact that the total probability of finding the particle *somewhere* adds up to unity. The integration in Equation 1.2.42 extends over all space and the symbol $d\tau$ designates the appropriate volume element. For example, the volume differential in Cartesian coordinates, $d\tau = dx\,dy\,dz$ is changed in spherical coordinates to $d\tau = r^2 sin\theta\,dr\,d\theta\,d\phi$. The physical significance of the wavefunctions makes certain demands on its mathematical behavior. The wavefunction must be a single-valued function of all its coordinates, since the probability density ought to be uniquely determined at each point in space.

Moreover, the wavefunction should be finite and continuous everywhere, since a physically-meaningful probability density must have the same attributes. The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"--lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

Contributors and Attributions

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1.3: Quantum Mechanics of Some Simple Systems

The simple quantum-mechanical problem we have just solved can provide an instructive application to chemistry: the *free-electron model* (FEM) for delocalized π-electrons. The simplest case is the 1,3-butadiene molecule

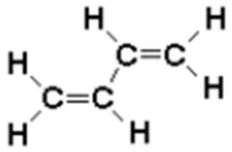


Figure 4) by

$$\rho = 2\psi_1^2 + 2\psi_2^2 \tag{1.3.1}$$

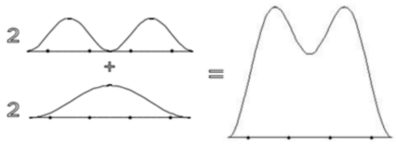
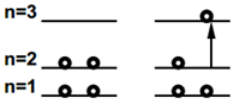


Figure 4. Pi-electron density in butadiene.

A chemical interpretation of this picture might be that, since the π-electron density is concentrated between carbon atoms 1 and 2, and between 3 and 4, the predominant structure of butadiene has double bonds between these two pairs of atoms. Each double bond consists of a π-bond, in addition to the underlying σ-bond. However, this is not the complete story, because we must also take account of the residual π-electron density between carbons 2 and 3. In the terminology of valence-bond theory, butadiene would be described as a *resonance hybrid* with the contributing structures CH_2=CH-CH=CH_2 (the predominant structure) and °CH_2-CH=CH-CH_2° (a secondary contribution). The reality of the latter structure is suggested by the ability of butadiene to undergo 1,4-addition reactions.

The free-electron model can also be applied to the electronic spectrum of butadiene and other linear polyenes. The lowest unoccupied molecular orbital (LUMO) in butadiene corresponds to the n=3 particle-in-a-box state. Neglecting electron-electron interaction, the longest-wavelength (lowest-energy) electronic transition should occur from n=2, the highest occupied molecular orbital (HOMO).



The energy difference is given by

$$\Delta E = E_3 - E_2 = (3^2 - 2^2)\frac{h^2}{8mL^2} \tag{1.3.2}$$

Here *m* represents the mass of an electron (not a butadiene molecule!), 9.1x10^{-31} Kg, and L is the effective length of the box, 4x1.40x10^{-10} m. By the Bohr frequency condition

$$\Delta E = hv = \frac{hc}{\lambda} \tag{1.3.3}$$

The wavelength is predicted to be 207 nm. This compares well with the experimental maximum of the first electronic absorption band, $\lambda_{max} \approx$ 210 nm, in the ultraviolet region.

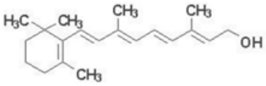
We might therefore be emboldened to apply the model to predict absorption spectra in higher polyenes CH_2=(CH-CH=)$_{n-1}$$CH_2$. For the molecule with 2*n* carbon atoms (*n* double bonds), the HOMO → LUMO transition corresponds to n → n + 1, thus

$$\frac{hc}{\lambda} \approx [\ (n+1)^2 - n^2\ ]\ \frac{h^2}{8m(2nL_{CC})^2} \tag{1.3.4}$$

A useful constant in this computation is the **Compton wavelength**

$$\frac{h}{mc} = 2.426 \times 10^{-12} m. \tag{1.3.5}$$

For *n*=3, hexatriene, the predicted wavelength is 332 nm, while experiment gives $\lambda_{max} \approx$ 250 nm. For *n*=4, octatetraene, FEM predicts 460 nm, while $\lambda_{max} \approx$ 300 nm. Clearly the model has been pushed beyond range of quantitate validity, although the trend of increasing absorption band wavelength with increasing *n* is correctly predicted. Incidentally, a compound should be colored if its absorption includes any part of the visible range 400-700 nm. Retinol (vitamin A), which contains a polyene chain with *n*=5, has a pale yellow color. This is its structure:



Contributors and Attributions

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1.4: Principles of Quantum Mechanics

Here we will continue to develop the mathematical formalism of quantum mechanics, using heuristic arguments as necessary. This will lead to a system of postulates which will be the basis of our subsequent applications of quantum mechanics.

Hermitian Operators

An important property of operators is suggested by considering the Hamiltonian for the particle in a box:

$$\hat{H} = -\frac{h^2}{2m}\frac{d^2}{dx^2} \tag{1.4.1}$$

Let $f(x)$ and $g(x)$ be arbitrary functions which obey the same boundary values as the eigenfunctions of $\hat{H}$, namely that they vanish at $x = 0$ and $x = a$. Consider the integral

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = -\frac{\hbar^2}{2m}\int_0^a f(x)\,g''(x)\,\mathrm{d}x \tag{1.4.2}$$

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,\mathrm{d}x = -\int_0^a f'(x)\,g'(x)\,\mathrm{d}x + \Big[f(x)\,g'(x)\Big]_0^a \tag{1.4.3}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 1.4.3 to

$$\int_0^a f''(x)\,g(x)\,\mathrm{d}x - \Big[f'(x)\,g(x)\Big]_0^a \tag{1.4.4}$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \int_0^a g(x)\,\hat{H}\,f(x)\,\mathrm{d}x \tag{1.4.5}$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,\mathrm{d}x\right)^* \tag{1.4.6}$$

In mathematical terminology, an operator $\hat{A}$ for which

$$\int f^*\,\hat{A}\,g\,\mathrm{d}\tau = \left(\int g^*\,\hat{A}\,f\,\mathrm{d}\tau\right)^* \tag{1.4.7}$$

for all functions f and g which obey specified boundary conditions is classified as *hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a hermitian operator. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are hermitian.

Properties of Eigenvalues and Eigenfunctions

The sets of energies and wavefunctions obtained by solving any quantum-mechanical problem can be summarized symbolically as solutions of the eigenvalue equation

$$\hat{H}\,\psi_n = E_n\,\psi_n \tag{1.4.8}$$

For another value of the quantum number, we can write

$$\hat{H}\,\psi_m = E_m\,\psi_m \tag{1.4.9}$$

Let us multiply Equation 1.4.8 by ψ_m^* and the complex conjugate of Equation 1.4.9 by ψ_n. Then we subtract the two expressions and integrate over $\mathrm{d}\tau$. The result is

$$\int \psi_m^* \, \hat{H} \, \psi_n \, \mathrm{d}\tau - \left(\int \psi_n^* \, \hat{H} \, \psi_m \, \mathrm{d}\tau \right)^* = (E_n - E_m^*) \int \psi_m^* \, \psi_n \, \mathrm{d}\tau \tag{1.4.10}$$

But by the hermitian property (Equation 1.4.6), the left-hand side of Equation 1.4.10 equals zero. Thus

$$(E_n - E_m^*) \int \psi_m^* \, \psi_n \, \mathrm{d}\tau = 0 \tag{1.4.11}$$

Consider first the case $m = n$. The second factor in Equation 1.4.11 then becomes the normalization integral $\int \psi_n^* \, \psi_n \, \mathrm{d}\tau$, which equals 1 (or at least a nonzero constant). Therefore the first factor in Equation 1.4.11 must equal zero, so that

$$E_n^* = E_n \tag{1.4.12}$$

implying that the energy eigenvalues must be real numbers. This is quite reasonable from a physical point of view since eigenvalues represent possible results of measurement. Consider next the case when $E_m \neq E_n$. Then it is the second factor in Equation 1.4.11 that must vanish and

$$\int \psi_m^* \, \psi_n \, \mathrm{d}\tau = 0 \quad when \; E_m \neq E_n \tag{1.4.13}$$

Thus eigenfunctions belonging to different eigenvalues are orthogonal. In the case that ψ_m and ψ_n are degenerate eigenfunctions, so $m \neq n$ but $E_m = E_n$, the above proof of orthogonality does not apply. But it is always possible to construct degenerate functions that are mutually orthogonal. A general result is therefore the orthonormalization condition

$$\int \psi_m^* \, \psi_n \, \mathrm{d}\tau = \delta_{mn} \tag{1.4.14}$$

It is easy to prove that a linear combination of degenerate eigenfunctions is itself an eigenfunction of the same energy. Let

$$\hat{H} \, \psi_{nk} = E_n \, \psi_{nk}, \qquad k = 1, 2, \ldots d \tag{1.4.15}$$

where the ψ_{nk} represent a *d*-fold degenerate set of eigenfunctions with the same eigenvalue E_n. Consider now the linear combination

$$\psi = c_1 \psi_{n,1} + c_2 \psi_{n,2} + \ldots + c_d \psi_{n,d} \tag{1.4.16}$$

Operating on ψ with the Hamiltonian and using (14), we find

$$\hat{H} \, \psi = c_1 \hat{H} \, \psi_{n,1} + c_2 \hat{H} \, \psi_{n,2} + \ldots = E_n (c_1 \psi_{n,1} + c_2 \psi_{n,2} + \ldots) = E_n \, \psi \tag{1.4.17}$$

which shows that the linear combination ψ is also an eigenfunction of the same energy. There is evidently a limitless number of possible eigenfunctions for a degenerate eigenvalue. However, only *d* of these will be linearly independent.

Dirac Notation

The term *orthogonal* has been used both for perpendicular vectors and for functions whose product integrates to zero. This actually connotes a deep connection between vectors and functions. Consider two orthogonal vectors **a** and **b**. Then, in terms of their *x, y, z* components, labeled by 1, 2, 3, respectively, the scalar product can be written

$$\mathbf{a} \cdot \mathbf{b} = a_1 b_1 + a_2 b_2 + a_3 b_3 = 0 \tag{1.4.18}$$

Suppose now that we consider an analogous relationship involving vectors in *n*-dimensional space (which you need not visualize!). We could then write

$$a \cdot b = \sum_{k=0}^{n} a_k b_k = 0 \tag{1.4.19}$$

Finally let the dimension of the space become non-denumerably infinite, turning into a continuum. The sum in Equation 1.4.19 would then be replaced by an integral such as

$$\int a(x) \, b(x) dx = 0 \tag{1.4.20}$$

But this is just the relation for orthogonal functions. A function can therefore be regarded as an abstract vector in a higher-dimensional continuum, known as *Hilbert space*. This is true for eigenfunctions as well. Dirac denoted the vector in Hilbert space corresponding to the eigenfunction ψ_n by the symbol $|n\rangle$. Correspondingly, the complex conjugate ψ_m^* is denoted by $\langle m|$. The integral over the product of the two functions is then analogous to a scalar product (or inner product in linear algebra) of the abstract vectors, written

$$\int \psi_m^* \psi_n \, \mathrm{d}\tau = \langle m| \cdot |n\rangle \equiv \langle m|n\rangle \tag{1.4.21}$$

The last quantity is known as a *bracket*, which led Dirac to designate the vectors $\langle m|$ and $|n\rangle$ as a "bra" and a "ket," respectively. The orthonormality conditions (Equation 1.4.14) can be written

$$\langle m|n\rangle = \delta_{mn} \tag{1.4.22}$$

The integral of a "sandwich" containing an operator $\hat{A}$ can be written very compactly in the form

$$\int \psi_m^* \, \hat{A} \, \psi_n \, \mathrm{d}\tau = \langle m|A|n\rangle \tag{1.4.23}$$

The hermitian condition on $\hat{A}$ [cf. Eq (6)] is therefore expressed as

$$\langle m|A|n\rangle = \langle n|A|m\rangle^* \tag{1.4.24}$$

Expectation Values

One of the extraordinary features of quantum mechanics is the possibility for superpositions of states. The state of a system can sometimes exist as a linear combination of other states, for example,

$$\psi = c_1\psi_1 + c_2\psi_2 \tag{1.4.25}$$

Assuming that all three functions are normalized and that ψ_1 and ψ_2 are orthogonal, we find

$$\int \psi^* \, \psi \, \mathrm{d}\tau = |c_1|^2 + |c_2|^2 = 1 \tag{1.4.26}$$

We can interpret $|c_1|^2$ and $|c_2|^2$ as the probabilities that a system in a state described by ψ can have the attributes of the states ψ_1 and ψ_2, respectively. Suppose ψ_1 and ψ_2 represent eigenstates of an observable A, satisfying the respective eigenvalue equations

$$\hat{A}\psi_1 = a_1\psi_1 \quad \textit{and} \quad \hat{A}\psi_2 = a_2\psi_2 \tag{1.4.27}$$

Then a large number of measurements of the variable A in the state ψ will register the value a_1 with a probability $|c_1|^2$ and the value a_2 with a probability $|c_2|^2$. The average value or *expectation value* of A will be given by

$$\langle A\rangle = |c_1|^2 a_1 + |c_2|^2 a_2 \tag{1.4.28}$$

This can be obtained directly from ψ by the "sandwich construction"

$$\langle A\rangle = \int \psi^* \hat{A} \, \psi \, \mathrm{d}\tau \tag{1.4.29}$$

or, if ψ is not normalized,

$$\langle A\rangle = \frac{\int \psi^* \hat{A} \, \psi \, \mathrm{d}\tau}{\int \psi^* \, \psi \, \mathrm{d}\tau} \tag{1.4.30}$$

Note that the expectation value need not itself be a possible result of a single measurement (like the centroid of a donut, which is located in the hole!). When the operator $\hat{A}$ is a simple function, not containing differential operators or the like, then Equation 1.4.29 reduces to the classical formula for an average value:

$$\langle A\rangle = \int A \, \rho \, \mathrm{d}\tau \tag{1.4.31}$$

More on Operators

An operator represents a prescription for turning one function into another: in symbols, $\hat{A}\psi = \phi$. From a physical point of view, the action of an operator on a wavefunction can be pictured as the process of measuring the observable A on the state ψ. The transformed wavefunction ϕ then represents the state of the system *after* the measurement is performed. In general, ϕ is different from ψ, consistent with the fact that the process of measurement on a quantum system produces an irreducible perturbation of its state. Only in the special case that ψ is an eigenstate of A, does a measurement preserve the original state. The function ϕ is then equal to an eigenvalue a times ψ.

The product of two operators, say $\hat{A}\hat{B}$, represents the successive action of the operators, reading from *right to left*---i.e., first $\hat{B}$ then $\hat{A}$. In general, the action of two operators in the reversed order, say $\hat{B}\hat{A}$, gives a different result, which can be written

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{1.4.32}$$

We say that the operators do not *commute*. This can be attributed to the perturbing effect one measurement on a quantum system can have on subsequent measurements. An example of non-commuting operators from everyday life. In our usual routine each morning, we shower and we get dressed. But the result of carrying out these operations in reversed order will be dramatically different!

The *commutator* of two operators is defined by

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{1.4.33}$$

When $\left[\hat{A}, \hat{B}\right] = 0$, the two operators are said to *commute*. This means their combined effect will be the same whatever order they are applied (like brushing your teeth and showering).

The uncertainty principle for simultaneous measurement of two observables A and B is closely related to their commutator. The uncertainty Δa in the observable A is defined in terms of the mean square deviation from the average:

$$(\Delta a)^2 = \langle(\hat{A} - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2 \tag{1.4.34}$$

It corresponds to the *standard deviation* in statistics. The following inequality can be proven for the product of two uncertainties:

$$\Delta a \Delta b \geq \frac{1}{2}|\langle\left[\hat{A}, \hat{B}\right]\rangle| \tag{1.4.35}$$

The best known application of Equation 1.4.35 is to the position and momentum operators, say $\hat{x}$ and $\hat{p_x}$. Their commutator is given by

$$[\hat{x}, \hat{p_x}] = i\hbar \tag{1.4.36}$$

so that

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{1.4.37}$$

which is known as the *Heisenberg uncertainty principle*. This fundamental consequence of quantum theory implies that the position and momentum of a particle cannot be determined with arbitrary precision--the more accurately one is known, the more uncertain is the other. For example, if the momentum is known exactly, as in a momentum eigenstate, then the position is completely undetermined.

If two operators commute, there is no restriction on the accuracy of their simultaneous measurement. For example, the x and y coordinates of a particle can be known at the same time. An important theorem states that two commuting observables can have simultaneous eigenfunctions. To prove this, write the eigenvalue equation for an operator $\hat{A}$

$$\hat{A}\,\psi_n = a_n\,\psi_n \tag{1.4.38}$$

then operate with $\hat{B}$ and use the commutativity of $\hat{A}$ and $\hat{B}$ to obtain

$$\hat{B}\,\hat{A}\,\psi_n = \hat{A}\,\hat{B}\,\psi_n = a_n\,\hat{B}\,\psi_n \tag{1.4.39}$$

This shows that $\hat{B}\,\psi_n$ is also an eigenfunction of $\hat{A}$ with the same eigenvalue a_n. This implies that

$$\hat{B}\,\psi_n = const\,\psi_n = b_n\,\psi_n \tag{1.4.40}$$

showing that ψ_n is a simultaneous eigenfunction of $\hat{A}$ and $\hat{B}$ with eigenvalues a_n and b_n, respectively. The derivation becomes slightly more complicated in the case of degenerate eigenfunctions, but the same conclusion follows.

After the Hamiltonian, the operators for angular momenta are probably the most important in quantum mechanics. The definition of angular momentum in classical mechanics is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. In terms of its Cartesian components,

$$L_x = yp_z - zp_y \tag{1.4.41}$$

$$L_y = zp_x - xp_z \tag{1.4.42}$$

$$L_z = xp_y - yp_x \tag{1.4.43}$$

In future, we will write such sets of equation as "$L_x = yp_z - zp_y,\ et\ cyc$," meaning that we add to one explicitly stated relation, the versions formed by successive cyclic permutation $x \rightarrow y \rightarrow z \rightarrow x$. The general prescription for turning a classical dynamical variable into a quantum-mechanical operator was developed in Chap 2. The key relations were the momentum components

$$\hat{p_x} = -i\hbar\frac{\partial}{\partial x},\ \ \hat{p_y} = -i\hbar\frac{\partial}{\partial y},\ \ \hat{p_z} = -i\hbar\frac{\partial}{\partial z} \tag{1.4.44}$$

with the coordinates x, y, z simply carried over into multiplicative operators. Applying Equation 1.4.44 to Equation 1.4.43, we construct the three angular momentum operators

$$\hat{L_x} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad et\ cyc \tag{1.4.45}$$

while the total angular momentum is given by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{1.4.46}$$

The angular momentum operators obey the following commutation relations:

$$\left[\hat{L_x},\ \hat{L_y}\right] = i\hbar\hat{L_z} \ \ et\ cyc \tag{1.4.47}$$

but

$$\left[\hat{L}^2,\ \hat{L_z}\right] = 0 \tag{1.4.48}$$

and analogously for $\hat{L_x}$ and $\hat{L_y}$. This is consistent with the existence of simultaneous eigenfunctions of $\hat{L}^2$ and any one component, conventionally designated $\hat{L_z}$. But then these states *cannot* be eigenfunctions of either $\hat{L_x}$ or $\hat{L_y}$.

Postulates of Quantum Mechanics

Our development of quantum mechanics is now sufficiently complete that we can reduce the theory to a set of five postulates.

Postulate 1: Wavefunctions

The state of a quantum-mechanical system is completely specified by a wavefunction Ψ that depends on the coordinates and time. The square of this function $\Psi^*\Psi$ gives the probability density for finding the system with a specified set of coordinate values.

The wavefunction must fulfill certain mathematical requirements because of its physical interpretation. It must be single-valued, finite and continuous. It must also satisfy a normalization condition

$$\int \Psi^*\,\Psi\,d\tau = 1 \tag{1.4.49}$$

Postulate 2: Observables

Every observable in quantum mechanics is represented by a linear, hermitian operator.

The hermitian property was defined in Equation 1.4.7. A linear operator is one which satisfies the identity

$$\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\,\hat{A}\psi_1 + c_2\,\hat{A}\psi_2 \tag{1.4.50}$$

which is required in order to have a superposition property for quantum states. The form of an operator which has an analog in classical mechanics is derived by the prescriptions

$$\hat{\mathbf{r}} = \mathbf{r}, \quad \hat{\mathbf{p}} = -i\hbar\nabla \tag{1.4.51}$$

which we have previously expressed in terms of Cartesian components [cf. Equation 1.4.44].

Postulate 3: Eigenstates

In any measurement of an observable A, associated with an operator $\hat{A}$, the only possible results are the eigenvalues a_n, which satisfy an eigenvalue equation

$$\hat{A}\psi_n = a_n\,\psi_n \tag{1.4.52}$$

This postulate captures the essence of quantum mechanics--the quantization of dynamical variables. A continuum of eigenvalues is not forbidden, however, as in the case of an unbound particle.

Every measurement of A invariably gives one of the eigenvalues. For an arbitrary state (not an eigenstate of A), these measurements will be individually unpredictable but follow a definite statistical law, which is the subject of the fourth postulate:

Postulate 4: Expectation Values

For a system in a state described by a normalized wave function Ψ, the average or expectation value of the observable corresponding to A is given by

$$\langle A\rangle = \int \Psi^*\,\hat{A}\,\Psi\,\mathrm{d}\tau \tag{1.4.53}$$

Finally,

Postulate 5: Time-dependent Evolution

The wavefunction of a system evolves in time in accordance with the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\,\Psi \tag{1.4.54}$$

For time-independent problems this reduces to the time-independent Schrödinger equation

$$\hat{H}\,\psi = E\,\psi \tag{1.4.55}$$

which is the eigenvalue equation for the Hamiltonian operator.

The Variational Principle

Except for a small number of intensively-studied examples, the Schrödinger equation for most problems of chemical interest *cannot* be solved exactly. The variational principle provides a guide for constructing the best possible approximate solutions of a specified functional form. Suppose that we seek an approximate solution for the ground state of a quantum system described by a Hamiltonian $\hat{H}$. We presume that the Schrödinger equation

$$\hat{H}\,\psi_0 = E\,\psi_0 \tag{1.4.56}$$

is too difficult to solve exactly. Suppose, however, that we have a function $\tilde{\psi}$ which we think is an approximation to the true ground-state wavefunction. According to the variational principle (or variational theorem), the following formula provides an *upper bound* to the exact ground-state energy E_0:

$$\tilde{E} \equiv \frac{\int \tilde{\psi}^* \hat{H} \tilde{\psi} \, \mathrm{d}\tau}{\int \tilde{\psi}^* \tilde{\psi} \, \mathrm{d}\tau} \geq E_0 \tag{1.4.57}$$

Note that this ratio of integrals has the same form as the expectation value $\langle H \rangle$ defined by Equation 1.4.30. The better the approximation $\tilde{\psi}$, the lower will be the computed energy $\tilde{E}$, though it will still be greater than the exact value. To prove Equation 1.4.57, we suppose that the approximate function can, in concept, be represented as a superposition of the actual eigenstates of the Hamiltonian, analogous to Equation 1.4.25,

$$\tilde{\psi} = c_0 \psi_0 + c_1 \psi_1 + \dots \tag{1.4.58}$$

This means that $\tilde{\psi}$, the approximate ground state, might be close to the actual ground state ψ_0 but is "contaminated" by contributions from excited states ψ_1, ... Of course, none of the states or coefficients on the right-hand side is actually known, otherwise there would be no need to worry about approximate computations. By Equation 1.4.26, the expectation value of the Hamiltonian in the state Equation 1.4.58 is given by

$$\tilde{E} = |c_0|^2 E_0 + |c_1|^2 E_1 + \dots \tag{1.4.59}$$

Since all the excited states have *higher* energy than the ground state, $E_1, E_2 \ldots \geq E_0$, we find

$$\tilde{E} \geq (|c_0|^2 + |c_1|^2 + \dots) E_0 = E_0 \tag{1.4.60}$$

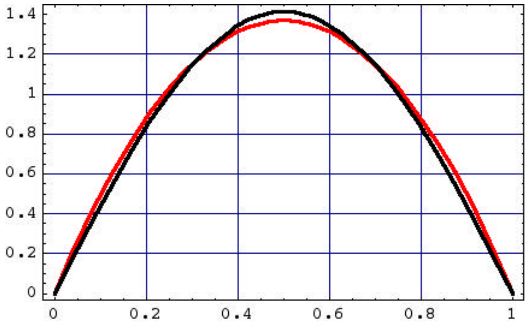
assuming $\tilde{\psi}$ has been normalized. Thus $\tilde{E}$ must be greater than the true ground-state energy E_0, as implied by Equation 1.4.57.

As a very simple, although artificial, illustration of the variational principle, consider the ground state of the particle in a box. Suppose we had never studied trigonometry and knew nothing about sines or cosines. Then a reasonable approximation to the ground state might be an inverted parabola such as the normalized function

$$\tilde{\psi}(x) = \left(\frac{30}{a^5}\right)^{\frac{1}{2}} x(a-x) \tag{1.4.61}$$

Fig. 1 shows this function along with the exact ground-state eigenfunction

$$\psi_1(x) = \left(\frac{2}{a}\right)^{\frac{1}{2}} sin\frac{\pi x}{a} \tag{1.4.62}$$



$$\frac{x}{a} \tag{1.4.63}$$

***Figure 1.4.1**: Variational approximation for particle in a box. Red line represents $\tilde{\psi}$ and black line represents ψ_1*

A variational calculation gives

$$\tilde{E} = \int_0^a \tilde{\psi}(x) \left(-\frac{\hbar^2}{2m}\right) \tilde{\psi}''(x) \, dx = \frac{5}{4\pi^2} \frac{h^2}{ma^2} = \frac{10}{\pi^2} E_1 \approx 1.01321 E_1 \tag{1.4.64}$$

in terms of the exact ground state energy $E_1 = \frac{h^2}{8ma^2}$. In accord with the variational theorem, $\tilde{E} > E_1$. The computation is in error by about 1%.

Contributors and Attributions

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1.5: Harmonic Oscillator

The harmonic oscillator is a model which has several important applications in both classical and quantum mechanics. It serves as a prototype in the mathematical treatment of such diverse phenomena as elasticity, acoustics, AC circuits, molecular and crystal vibrations, electromagnetic fields and optical properties of matter.

Classical Oscillator

A simple realization of the harmonic oscillator in classical mechanics is a particle which is acted upon by a restoring force proportional to its displacement from its equilibrium position. Considering motion in one dimension, this means

$$F = -kx \tag{1.5.1}$$

Such a force might originate from a spring which obeys Hooke's law, as shown in Figure 1.5.1. According to Hooke's law, which applies to real springs for sufficiently small displacements, the restoring force is proportional to the displacement—either stretching or compression—from the equilibrium position.

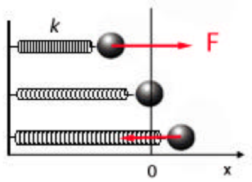

Figure 1.5.1: Spring obeying Hooke's law.

The *force constant* k is a measure of the stiffness of the spring. The variable x is chosen equal to zero at the equilibrium position, positive for stretching, negative for compression. The negative sign in Equation 1.5.1 reflects the fact that F is a *restoring* force, always in the opposite sense to the displacement x.

Applying Newton's second law to the force from Equation 1.5.1, we find x

$$F = m\frac{d^2x}{dx^2} = -kx \tag{1.5.2}$$

where m is the mass of the body attached to the spring, which is itself assumed massless. This leads to a differential equation of familiar form, although with different variables:

$$\ddot{x}(t) + \omega^2 x(t) = 0 \tag{1.5.3}$$

with

$$\omega^2 \equiv \frac{k}{m} \tag{1.5.4}$$

The dot notation (introduced by Newton himself) is used in place of primes when the independent variable is time. The general solution to Equation 1.5.3 is

$$x(t) = A\sin\omega t + B\cos\omega t \tag{1.5.5}$$

which represents periodic motion with a sinusoidal time dependence. This is known as *simple harmonic motion* and the corresponding system is known as a *harmonic oscillator*. The oscillation occurs with a constant angular frequency

$$\omega = \sqrt{\frac{k}{m}} \text{ radians per second} \tag{1.5.6}$$

This is called the *natural frequency* of the oscillator. The corresponding *circular (or angular) frequency* in Hertz (cycles per second) is

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \text{ Hz} \tag{1.5.7}$$

The general relation between force and potential energy in a conservative system in one dimension is

$$F = \frac{-dV}{dx} \tag{1.5.8}$$

Thus the potential energy of a harmonic oscillator is given by

$$V(x) = \frac{1}{2}kx^2 \tag{1.5.9}$$

which has the shape of a parabola, as drawn in Figure 1.5.2. A simple computation shows that the oscillator moves between positive and negative turning points $\pm x_{max}$ where the total energy E equals the potential energy $\frac{1}{2}kx^2_{max}$ while the kinetic energy is momentarily zero. In contrast, when the oscillator moves past $x = 0$, the kinetic energy reaches its maximum value while the potential energy equals zero.

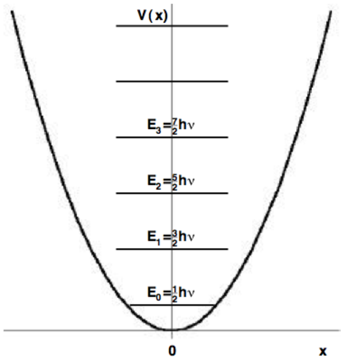

Figure 1.5.2: Potential energy function and first few energy levels for harmonic oscillator.

Harmonic Oscillator in Quantum Mechanics

Given the potential energy in Equation 1.5.9, we can write down the Schrödinger equation for the one-dimensional harmonic oscillator:

$$-\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{1.5.10}$$

For the first time we encounter a differential equation with *non-constant* coefficients, which is a much greater challenge to solve. We can combine the constants in Equation 1.5.10to two parameters

$$\alpha^2 = \frac{mk}{\hbar^2} \tag{1.5.11}$$

and

$$\lambda = \frac{2mE}{\hbar^2\alpha} \tag{1.5.12}$$

and redefine the independent variable as

$$\xi = \alpha^{1/2}x \tag{1.5.13}$$

This reduces the Schrödinger equation to

$$\psi''(\xi) + (\lambda - \xi^2)\psi(\xi) = 0 \tag{1.5.14}$$

The range of the variable x (also ξ) must be taken from $-\infty$ to $+\infty$, there being no finite cutoff as in the case of the particle in a box. A useful first step is to determine the asymptotic solution to Equation 1.5.13, that is, the form of $\psi(\xi)$ as $\xi \to \pm\infty$. For sufficiently large values of $|\xi|$, $\xi^2 \gg \lambda$ and the differential equation is approximated by

$$\psi''(\xi) - \xi^2\psi(\xi) \approx 0 \tag{1.5.15}$$

This suggests the following manipulation:

$$\left(\frac{d^2}{d\xi^2}-\xi^2\right)\psi(\xi)\approx\left(\frac{d}{d\xi}-\xi\right)\left(\frac{d}{d\xi}+\xi\right)\psi(\xi)\approx 0 \tag{1.5.16}$$

The first-order differential equation

$$\psi'(\xi)+\xi\psi(\xi)=0 \tag{1.5.17}$$

can be solved exactly to give

$$\psi(\xi)=\text{const.}\, e^{-\xi^2/2} \tag{1.5.18}$$

Remarkably, this turns out to be an *exact* solution of the Schrödinger equation (Equation 1.5.14) with $\lambda=1$. Using Equation 1.5.12, this corresponds to an energy

$$E=\frac{\lambda\hbar^2\alpha}{2m}=\frac{1}{2}\hbar\sqrt{\frac{k}{m}}=\frac{1}{2}\hbar\omega \tag{1.5.19}$$

where ω is the natural frequency of the oscillator according to classical mechanics. The function in Equation 1.5.18 has the form of a Gaussian, the bell-shaped curve so beloved in the social sciences. The function has no nodes, which leads us to conclude that this represents the ground state of the system.The ground state is usually designated with the quantum number $n=0$ (the particle in a box is a exception, with $n=1$ labeling the ground state). Reverting to the original variable x, we write

$$\psi_0(x)=\text{const}e^{-\alpha x^2/2} \tag{1.5.20}$$

with

$$\alpha=(mk/\hbar^2)^{1/2} \tag{1.5.21}$$

With help of the well-known definite integral (Laplace 1778)

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx=\sqrt{\frac{\pi}{\alpha}} \tag{1.5.22}$$

we find the normalized eigenfunction

$$\psi_0(x)=(\frac{\alpha}{\pi})^{1/4}e^{-\alpha x^2/2} \tag{1.5.23}$$

with the corresponding eigenvalue

$$E_0=\frac{1}{2}\hbar\omega \tag{1.5.24}$$

Drawing from our experience with the particle in a box, we might surmise that the first excited state of the harmonic oscillator would be a function similar to Equation 1.5.23, but with a node at $x=0$, say,

$$\psi_1(x)=const x e^{-\alpha x^2/2} \tag{1.5.25}$$

This is orthogonal to $\psi_0(x)$ by symmetry and is indeed an eigenfunction with the eigenvalue

$$E_1=\frac{3}{2}\hbar\omega \tag{1.5.26}$$

Continuing the process, we try a function with two nodes

$$\psi_2=const(x^2-a)e^{-\alpha x^2/2} \tag{1.5.27}$$

Using the integrals tabulated in the Supplement 5, on Gaussian Integrals, we determine that with $a=\frac{1}{2}$ makes $\psi_2(x)$ orthogonal to $\psi_0(x)$ and $\psi_1(x)$. We verify that this is another eigenfunction, corresponding to

$$E_2=\frac{5}{2}\hbar\omega \tag{1.5.28}$$

The general result, which follows from a more advanced mathematical analysis, gives the following formula for the normalized eigenfunctions:

$$\psi_n(x) = (\frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}})^{1/2} H_n(\sqrt{\alpha} x) e^{-\alpha x^2/2} \tag{1.5.29}$$

where $H_n(\xi)$ represents the Hermite polynomial of degree n. The first few Hermite polynomials are

$$H_0(\xi) = 1 \tag{1.5.30}$$

$$H_1(\xi) = 2\xi \tag{1.5.31}$$

$$H_2(\xi) = 4\xi^2 - 2 \tag{1.5.32}$$

$$H_3(\xi) = 8\xi^3 - 12\xi \tag{1.5.33}$$

The four lowest harmonic-oscillator eigenfunctions are plotted in Figure $1.5.3$. Note the topological resemblance to the corresponding particle-in-a-box eigenfunctions.

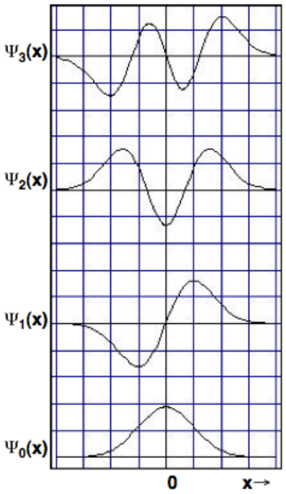

Figure $1.5.3$: Harmonic oscillator eigenfunctions for n=0, 1, 2, 3.

The eigenvalues are given by the simple formula

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \tag{1.5.34}$$

These are drawn in Figure $1.5.2$, on the same scale as the potential energy. The ground-state energy $E_0 = \frac{1}{2}\hbar\omega$ is greater than the classical value of zero, again a consequence of the uncertainty principle. This means that the oscillator is always oscillating.

It is remarkable that the difference between successive energy eigenvalues has a constant value

$$\Delta E = E_{n+1} - E_n = \hbar\omega = h\nu \tag{1.5.35}$$

This is reminiscent of Planck's formula for the energy of a photon. It comes as no surprise then that the quantum theory of radiation has the structure of an assembly of oscillators, with each oscillator representing a mode of electromagnetic waves of a specified frequency.

Contributors and Attributions

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1.6: Angular Momentum

Particle in a Ring

Consider a variant of the one-dimensional particle in a box problem in which the x-axis is bent into a ring of radius R. We can write the same Schrödinger equation

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{1.6.1}$$

There are no boundary conditions in this case since the x-axis closes upon itself. A more appropriate independent variable for this problem is the angular position on the ring given by, $\phi = x/R$. The Schrödinger equation would then read

$$-\frac{\hbar^2}{2mR^2}\frac{d^2\psi(\phi)}{d(\phi)^2} = E\psi(\phi) \tag{1.6.2}$$

The kinetic energy of a body rotating in the xy-plane can be expressed as

$$E = \frac{L_z^2}{2I} \tag{1.6.3}$$

where

$$I = mR^2 \tag{1.6.4}$$

is the moment of inertia and L_z, the *z*-component of angular momentum. (Since $L = r \times p$, if ***r*** and ***p*** lie in the *xy*-plane, ***L*** points in the *z*-direction.) The structure of Equation 1.6.2 suggests that this angular-momentum operator is given by

$$\hat{L_z} = -i\hbar\frac{\partial}{\partial\phi} \tag{1.6.5}$$

This result will follow from a more general derivation in the following Section. The Schrödinger equation (Equation 1.6.2) can now be written more compactly as

$$\psi\prime\prime(\phi) + m^2\psi(\phi) = 0 \tag{1.6.6}$$

where

$$m^2 \equiv 2IE/\hbar^2 \tag{1.6.7}$$

(Please do not confuse this variable m with the mass of the particle!) Possible solutions to (Equation 1.6.6) are

$$\psi(\phi) = \text{const}\, e^{\pm im\phi} \tag{1.6.8}$$

For this wavefunction to be physically acceptable, it must be *single-valued*. Since ϕ increased by any multiple of 2π represents the same point on the ring, we must have

$$\psi(\phi + 2\pi) = \psi(\phi) \tag{1.6.9}$$

and therefore

$$e^{im(\phi+2\pi)} = e^{im\phi} \tag{1.6.10}$$

This requires that

$$e^{2\pi im} = 1 \tag{1.6.11}$$

which is true only if m is an integer:

$$m = 0, \pm 1, \pm 2\ldots \tag{1.6.12}$$

Using Equation 1.6.7, this gives the quantized energy values

$$E_m = \frac{\hbar^2}{2I}m^2 \tag{1.6.13}$$

In contrast to the particle in a box, the eigenfunctions corresponding to $+m$ and $-m$ (Equation 1.6.8) are linearly independent, so both must be accepted. Therefore all eigenvalues, except E_0, are two-fold (or doubly) degenerate. The eigenfunctions can all be written in the form const $e^{im\phi}$, with m allowed to take either positive and negative values (or 0), as in Equation 1.6.11. The normalized eigenfunctions are

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{1.6.14}$$

and can be verified to satisfy the normalization condition containing the complex conjugate

$$\int_0^{2\pi} \psi_m^*(\phi)\psi_m(\phi)d\phi = 1 \tag{1.6.15}$$

where we have noted that $\psi_m^*(\phi) = (2\pi)^{-1/2} e^{-im\phi}$. The mutual orthogonality of the functions (Equation 1.6.14) also follows easily, for

$$\int_0^{2\pi} \psi_{m'}^* \psi_m(\phi)d\phi = \frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi} d\phi \tag{1.6.16}$$

$$= \frac{1}{2\pi}\int_0^{2\pi} [cos(m-m')\phi + isin(m-m')\phi]d\phi = 0 \tag{1.6.17}$$

for $m' \neq m$.

The solutions in Equation 1.6.13 are also eigenfunctions of the angular momentum operator (Equation 1.6.5), with

$$\hat{L}_z \psi_m(\phi) = m\hbar\psi_m(\phi), m = 0, \pm1, \pm2\ldots \tag{1.6.18}$$

This is a instance of a fundamental result in quantum mechanics, that any measured component of orbital angular momentum is restricted to integral multiples of $\hbar$. The Bohr theory of the hydrogen atom, to be discussed in the next Chapter, can be derived from this principle alone.

Free Electron Model for Aromatic Molecules

The benzene molecule consists of a ring of six carbon atoms around which six delocalized *pi*-electrons can circulate. A variant of the FEM for rings predicts the ground-state electron configuration which we can write as $1\pi^2 2\pi^4$, as shown here:

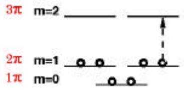

Figure taken from: S. M. Blinder "Introduction to Quantum Mechanics: In Chemistry, Materials Science, and Biology," pg 79, 2004.

The enhanced stability the benzene molecule can be attributed to the complete shells of π-electron orbitals, analogous to the way that noble gas electron configurations achieve their stability. Naphthalene, apart from the central C-C bond, can be modeled as a ring containing 10 electrons in the next closed-shell configuration$1\pi^2 2\pi^4 3\pi^4$. These molecules fulfill Hückel's "4*N*+2 rule" for aromatic stability. The molecules cyclobutadiene $(1\pi^2 2\pi^2)$ and cyclooctatetraene$(1\pi^2 2\pi^4 3\pi^2)$, even though they consist of rings with alternating single and double bonds, do *not* exhibit aromatic stability since they contain partially-filled orbitals.

The longest wavelength absorption in the benzene spectrum can be estimated according to this model as

$$\frac{hc}{\lambda} = E_2 - E_1 = \frac{\hbar^2}{2mR^2}(2^2 - 1^2) \tag{1.6.19}$$

The ring radius *R* can be approximated by the C-C distance in benzene, 1.39 Å. We predict $\lambda \approx$ 210 nm, whereas the experimental absorption has $\lambda_{max} \approx$ 268 nm.

Spherical Polar Coordinates

The motion of a free particle on the surface of a sphere will involve components of angular momentum in three-dimensional space. Spherical polar coordinates provide the most convenient description for this and related problems with spherical symmetry. The position of an arbitrary point ***r*** is described by three coordinates r, θ, ϕ as shown in Figure $1.6.2$.

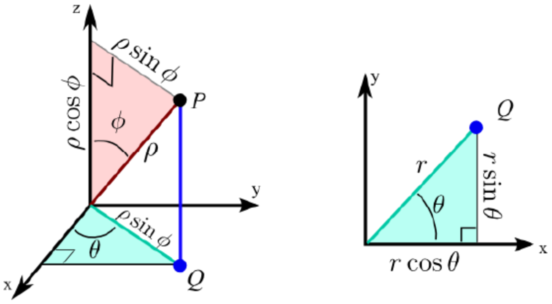

Figure $1.6.2$: Spherical coordinates.

These are connected to Cartesian coordinates by the relations

$$x = r \sin\theta \cos\phi \tag{1.6.20}$$

$$y = r \sin\theta \sin\phi \tag{1.6.21}$$

$$z = r \cos\theta \tag{1.6.22}$$

The radial variable *r* represents the distance from **r** to the origin, or the length of the vector **r**:

$$r = \sqrt{x^2 + y^2 + z^2} \tag{1.6.23}$$

The coordinate θ is the angle between the vector **r** and the *z*-axis, similar to latitude in geography, but with \(\theta= 0 \) and $\theta = \pi$ corresponding to the North and South Poles, respectively. The angle ϕ describes the rotation of **r** about the *z*-axis, running from 0 to 2π, similar to geographic longitude. The volume element in spherical polar coordinates is given by

$$d\tau = r^2 \sin\theta dr d\theta d\phi, \tag{1.6.24}$$

$$r \in \{0, \infty\}, \theta \in \{0, \pi\}, \phi \in \{0, 2\pi\} \tag{1.6.25}$$

and represented graphically by the distorted cube in Figure $1.6.1$.

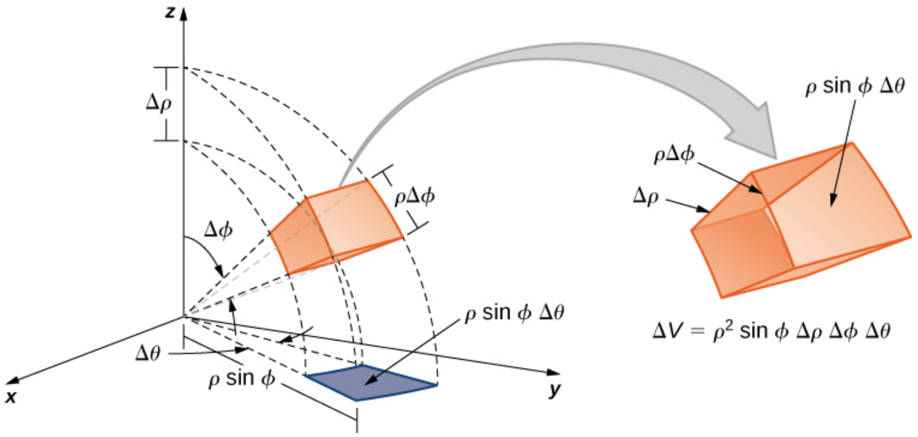

Figure* $1.6.3$*: *Volume element in spherical polar coordinates. (CC BY; OpenStax).*

We also require the Laplacian operator

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{1.6.26}$$

A detailed derivation is given in Supplement 6.

Rotation in Three Dimensions

A particle of mass *M*, free to move on the surface of a sphere of radius *R*, can be located by the two angular variables θ, ϕ. The Schrödinger equation therefore has the form

$$-\frac{\hbar^2}{2M}\nabla^2 Y(\theta,\phi) = EY(\theta,\phi) \tag{1.6.27}$$

with the wavefunction conventionally written as $Y(\theta,\phi)$. These functions are known as *spherical harmonics* and have been used in applied mathematics long before quantum mechanics. Since \(*r* = *R*\), a constant, the first term in the Laplacian does not contribute. The Schrödinger equation reduces to

$$\left\{\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \lambda\right\}Y(\theta,\phi) = 0 \tag{1.6.28}$$

where

$$\lambda = \frac{2MR^2E}{\hbar^2} = \frac{2IE}{\hbar^2} \tag{1.6.29}$$

again introducing the moment of inertia $I = MR^2$. The variables θ and ϕ can be separated in Equation ??? after multiplying through by $sin^2\theta$. If we write

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{1.6.30}$$

and follow the procedure used for the three-dimensional box, we find that dependence on ϕ alone occurs in the term

$$\frac{\Phi''(\phi)}{\Phi(\phi)} = const \tag{1.6.31}$$

This is identical in form to Equation 1.6.6, with the constant equal to $-m^2$, and we can write down the analogous solutions

$$\Phi_m(\phi) = \sqrt{\frac{1}{2\pi}}e^{im\phi}, m = 0, \pm1, \pm2\ldots \tag{1.6.32}$$

Substituting Equation ??? into Equation ??? and cancelling the functions $\Phi(\phi)$, we obtain an ordinary differential equation for $\Theta(\theta)$

$$\left\{\frac{1}{sin\theta}\frac{d}{d\theta}sin\theta\frac{d}{d\theta} - \frac{m^2}{sin^2\theta} + \lambda\right\}\Theta(\theta) = 0 \tag{1.6.33}$$

Consulting our friendly neighborhood mathematician, we learn that the single-valued, finite solutions to (Equation ???) are known as *associated Legendre functions*. The parameters λ and m are restricted to the values

$$\lambda = \ell(\ell+1), \ell = 0, 1, 2\ldots \tag{1.6.34}$$

while

$$m = 0, \pm1, \pm2\ldots\pm\ell(2\ell+1 values) \tag{1.6.35}$$

Putting Equation ??? into Equation ???, the allowed energy levels for a particle on a sphere are found to be

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \tag{1.6.36}$$

Since the energy is independent of the second quantum number *m*, the levels (Equation ???) are $(2\ell+1)$-fold degenerate. The spherical harmonics constitute an orthonormal set satisfying the integral relations

$$\int_0^\pi\int_0^{2\pi} Y^*_{\ell'm'}(\theta,\phi)Y_{\ell m}(\theta,\phi)sin\theta d\theta d\phi = \delta_{\ell\ell'}\delta_{mm'} \tag{1.6.37}$$

The following table lists the spherical harmonics through ℓ = 2, which will be sufficient for our purposes.

$$Spherical Harmonics Y_{\ell m}(\theta,\phi) \tag{1.6.38}$$

$$Y_{00} = \left(\frac{1}{4\pi}\right)^{1/2} \tag{1.6.39}$$

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} cos\theta \tag{1.6.40}$$

$$Y_{1\pm1} = \mp\left(\frac{3}{4\pi}\right)^{1/2} sin\theta e^{\pm i\phi} \tag{1.6.41}$$

$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3cos^2\theta - 1) \tag{1.6.42}$$

$$Y_{2\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} cos\theta sin\theta e^{\pm i\phi} \tag{1.6.43}$$

$$Y_{2\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} sin^2\theta e^{\pm 2i\phi} \tag{1.6.44}$$

A graphical representation of these functions is given in Figure 1.6.4. Surfaces of constant absolute value are drawn, positive where green and negative where red.

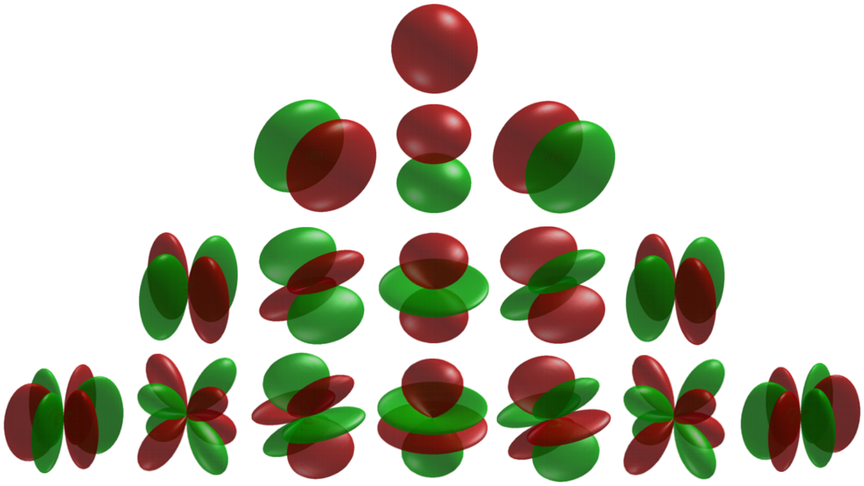

Figure used with permission (CC-SA-BY- 3.0; Sarxos)

Theory of Angular Momentum

Generalization of the energy-angular momentum relation in Equation 1.6.3 to three dimensions gives

$$E = \frac{L^2}{2I} \tag{1.6.45}$$

Thus from Equation ???-??? we can identify the operator for the square of total angular momentum

$$\hat{L}^2 = -\hbar^2 \left\{ \frac{1}{sin\theta}\frac{\partial}{\partial\theta} sin\theta \frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right\} \tag{1.6.46}$$

By Equations ??? and ???, the functions $Y(\theta,\phi)$ are simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ such that

$$\hat{L}^2 Y_{\ell m}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi) \tag{1.6.47}$$

and

$$\hat{L}_z Y_{\ell m}(\theta,\phi) = m\hbar Y_{\ell m}(\theta,\phi) \tag{1.6.48}$$

But the $Y_{\ell m}(\theta,\phi)$ are not eigenfunctions of either L_x and L_y (unless ℓ = 0). Note that the magnitude of the total angular momentum $\sqrt{\ell(\ell+1)}\hbar$ is greater than its maximum observable component in any direction, namely $\ell\hbar$. The quantum-mechanical behavior of the angular momentum and its components can be represented by a vector model, illustrated in Figure 5. The angular momentum vector **L**, with magnitude $\sqrt{\ell(\ell+1)}\hbar$, can be pictured as precessing about the z-axis, with its *z*-component L_z constant. The components L_x and L_y fluctuate in the course of precession, corresponding to the fact that the system is not in an eigenstate of either. There are 2ℓ + 1 different allowed values for L_z, with eigenvalues $m\hbar(m = 0, \pm 1, \pm 2 \ldots \pm \ell)$ equally spaced between $+\ell\hbar$ and $-\ell\hbar$.

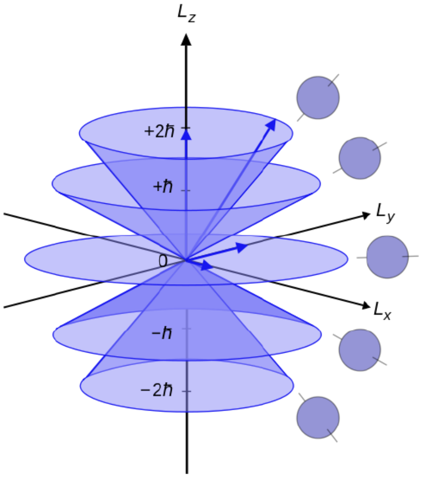

***Figure 1.6.5**: Vector model for angular momentum, showing the case ℓ= 2. (Public Domain; Maschen).*

This discreteness in the allowed directions of the angular momentum vector is called *space quantization*. The existence of simultaneous eigenstates of $\hat{L^2}$ and any one component, conventionally $\hat{L}_z$, is consistent with the commutation relations derived in Chap. 4:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z etcyc \tag{1.6.49}$$

and

$$\left[\hat{L^2}, \hat{L}_z\right] = 0 \tag{1.6.50}$$

Electron Spin

The electron, as well as certain other fundamental particles, possesses an intrinsic angular momentum or *spin*, in addition to its orbital angular momentum. These two types of angular momentum are analogous to the daily and annual motions, respectively, of the Earth around the Sun. To distinguish the spin angular momentum from the orbital, we designate the quantum numbers as *s* and m_s, in place of ℓ and *m*. For the electron, the quantum number *s* always has the value $\frac{1}{2}$, while m_s can have one of two values, $\pm\frac{1}{2}$. The electron is said to be an elementary particle of spin $\frac{1}{2}$. The proton and neutron also have spin $\frac{1}{2}$ and belong to the classification of particles called *fermions*, which are governed by the Pauli exclusion principle. Other particles, including the photon, have integer values of spin and are classified as *bosons*. These do *not* obey the Pauli principle, so that an arbitrary number can occupy the same quantum state. A complete theory of spin requires relativistic quantum mechanics. For our purposes, it is sufficient to recognize the two possible internal states of the electron, which can be called `spin up' and `spin down.' These are designated, respectively, by α and β as factors in the electron wavefunction. Spins play an essential role in determining the possible electronic states of atoms and molecules.

1.7: Hydrogen Atom

Atomic Spectra

When gaseous hydrogen in a glass tube is excited by a 5000-volt electrical discharge, four lines are observed in the visible part of the emission spectrum: red at 656.3 nm, blue-green at 486.1 nm, blue violet at 434.1 nm and violet at 410.2 nm:

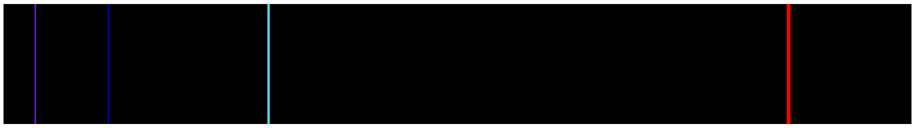

Figure 1.7.1: Visible spectrum of atomic hydrogen.

Other series of lines have been observed in the ultraviolet and infrared regions. Rydberg (1890) found that all the lines of the atomic hydrogen spectrum could be fitted to a single formula

$$\frac{1}{\lambda}=\mathcal{R}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right), \quad n_1=1,\ 2,\ 3\ldots,\ n_2>n_1 \tag{1.7.1}$$

where $\mathcal{R}$, known as the Rydberg constant, has the value $109,677$ cm^{-1} for hydrogen. The reciprocal of wavelength, in units of cm^{-1}, is in general use by spectroscopists. This unit is also designated *wavenumbers*, since it represents the number of wavelengths per cm. The Balmer series of spectral lines in the visible region, shown in Figure $1.7.1$, correspond to the values $n_1=2,\ n_2=3,\ 4,\ 5$ and 6. The lines with $n_1=1$ in the ultraviolet make up the Lyman series. The line with $n_2=2$, designated the Lyman alpha, has the longest wavelength (lowest wavenumber) in this series, with $1/\lambda=82.258$ cm^{-1} or $\lambda=121.57$ nm.

Other atomic species have line spectra, which can be used as a "fingerprint" to identify the element. However, no atom other than hydrogen has a simple relation analogous to Equation 1.7.1 for its spectral frequencies. Bohr in 1913 proposed that all atomic spectral lines arise from transitions between discrete energy levels, giving a photon such that

$$\Delta E=h\nu=\frac{hc}{\lambda} \tag{1.7.2}$$

This is called the *Bohr frequency condition*. We now understand that the atomic transition energy ΔE is equal to the energy of a photon, as proposed earlier by Planck and Einstein.

The Bohr Atom

The nuclear model proposed by Rutherford in 1911 pictures the atom as a heavy, positively-charged nucleus, around which much lighter, negatively-charged electrons circulate, much like planets in the Solar system. This model is however completely untenable from the standpoint of classical electromagnetic theory, for an accelerating electron (circular motion represents an acceleration) should radiate away its energy. In fact, a hydrogen atom should exist for no longer than 5×10^{-11} sec, time enough for the electron's death spiral into the nucleus. This is one of the worst quantitative predictions in the history of physics. It has been called the Hindenberg disaster on an atomic level. (Recall that the Hindenberg, a hydrogen-filled dirigible, crashed and burned in a famous disaster in 1937.)

Bohr sought to avoid an atomic catastrophe by proposing that certain orbits of the electron around the nucleus could be exempted from classical electrodynamics and remain stable. The Bohr model was quantitatively successful for the hydrogen atom, as we shall now show.

We recall that the attraction between two opposite charges, such as the electron and proton, is given by Coulomb's law

$$F=\begin{cases}-\dfrac{e^2}{r^2} & \text{(gaussian units)}\\ -\dfrac{e^2}{4\pi\epsilon_0 r^2} & \text{(SI units)}\end{cases} \tag{1.7.3}$$

We prefer to use the Gaussian system in applications to atomic phenomena. Since the Coulomb attraction is a central force (dependent only on r), the potential energy is related by

$$F = -\frac{dV(r)}{dr} \tag{1.7.4}$$

We find therefore, for the mutual potential energy of a proton and electron,

$$V(r) = -\frac{e^2}{r} \tag{1.7.5}$$

Bohr considered an electron in a circular orbit of radius r around the proton. To remain in this orbit, the electron must be experiencing a centripetal acceleration

$$a = -\frac{v^2}{r} \tag{1.7.6}$$

where v is the speed of the electron. Using Equations 1.7.4 and 1.7.6 in Newton's second law, we find

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \tag{1.7.7}$$

where m is the mass of the electron. For simplicity, we assume that the proton mass is infinite (actually $m_p \approx 1836 m_e$) so that the proton's position remains fixed. We will later correct for this approximation by introducing reduced mass. The energy of the hydrogen atom is the sum of the kinetic and potential energies:

$$E = T + V = \frac{1}{2}mv^2 - \frac{e^2}{r} \tag{1.7.8}$$

Using Equation 1.7.7, we see that

$$T = -\frac{1}{2}V \qquad \text{and} \qquad E = \frac{1}{2}V = -T \tag{1.7.9}$$

This is the form of the virial theorem for a force law varying as r^{-2}. Note that the energy of a bound atom is *negative*, since it is lower than the energy of the separated electron and proton, which is taken to be zero.

For further progress, we need some restriction on the possible values of r or v. This is where we can introduce the quantization of angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. Since $\mathbf{p}$ is perpendicular to $\mathbf{r}$, we can write simply

$$L = rp = mvr \tag{1.7.10}$$

Using Equation 1.7.9, we find also that

$$r = \frac{L^2}{me^2} \tag{1.7.11}$$

We introduce angular momentum quantization, writing

$$L = n\hbar, \qquad n = 1,\ 2... \tag{1.7.12}$$

excluding $n = 0$, since the electron would then not be in a circular orbit. The allowed orbital radii are then given by

$$r_n = n^2 a_0 \tag{1.7.13}$$

where

$$a_0 \equiv \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11}\ \text{m} = 0.529 \text{Å} \tag{1.7.14}$$

which is known as the *Bohr radius*. The corresponding energy is

$$E_n = -\frac{e^2}{2a_0 n^2} = -\frac{me^4}{2\hbar^2 n^2}, \qquad n = 1,\ 2... \tag{1.7.15}$$

Rydberg's formula (Equation 1.7.1) can now be deduced from the Bohr model. We have

$$\frac{hc}{\lambda} = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.7.16}$$

and the Rydbeg constant can be identified as

$$\mathcal{R} = \frac{2\pi^2 m e^4}{h^3 c} \approx 109,737\ \text{cm}^{-1} \tag{1.7.17}$$

The slight discrepency with the experimental value for hydrogen $(109,677)$ is due to the finite proton mass. This will be corrected later.

The Bohr model can be readily extended to hydrogenlike ions, systems in which a single electron orbits a nucleus of arbitrary atomic number Z. Thus $Z = 1$ for hydrogen, $Z = 2$ for He^+, $Z = 3$ for Li^{++}, and so on. The Coulomb potential 1.7.5 generalizes to

$$V(r) = -\frac{Ze^2}{r}, \tag{1.7.18}$$

the radius of the orbit (Equation 1.7.13) becomes

$$r_n = \frac{n^2 a_0}{Z} \tag{1.7.19}$$

and the energy Equation 1.7.15 becomes

$$E_n = -\frac{Z^2 e^2}{2 a_0 n^2} \tag{1.7.20}$$

De Broglie's proposal that electrons can have wavelike properties was actually inspired by the Bohr atomic model. Since

$$L = rp = n\hbar = \frac{nh}{2\pi} \tag{1.7.21}$$

we find

$$2\pi r = \frac{nh}{p} = n\lambda \tag{1.7.22}$$

Therefore, each allowed orbit traces out an integral number of de Broglie wavelengths.

Wilson (1915) and Sommerfeld (1916) generalized Bohr's formula for the allowed orbits to

$$\oint p\, dr = nh, \qquad n = 1,\ 2\ldots \tag{1.7.23}$$

The Sommerfeld-Wilson quantum conditions Equation 1.7.23 reduce to Bohr's results for circular orbits, but allow, in addition, elliptical orbits along which the momentum p is variable. According to Kepler's first law of planetary motion, the orbits of planets are ellipses with the Sun at one focus. Figure $1.7.2$ shows the generalization of the Bohr theory for hydrogen, including the elliptical orbits. The lowest energy state $n = 1$ is still a circular orbit. But $n = 2$ allows an elliptical orbit in addition to the circular one; $n = 3$ has three possible orbits, and so on. The energy still depends on n alone, so that the elliptical orbits represent degenerate states. Atomic spectroscopy shows in fact that energy levels with $n > 1$ consist of multiple states, as implied by the splitting of atomic lines by an electric field (Stark effect) or a magnetic field (Zeeman effect). Some of these generalized orbits are drawn schematically in Figure $1.7.2$.

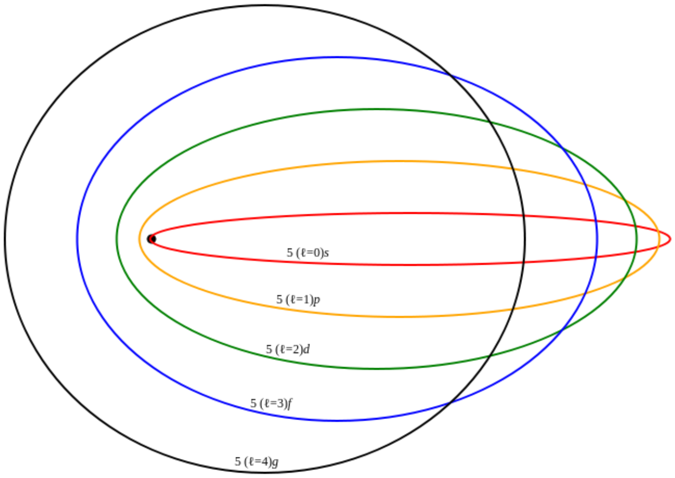

Figure 1.7.1: Elliptical orbits with the same energy and quantized angular momentum **in** Bohr-Sommerfield orbits for $n = 1,\ 2,\ 3$ (not to scale). (Public Domain; Pieter Kuiper)

The Bohr model was an important first step in the historical development of quantum mechanics. It introduced the quantization of atomic energy levels and gave quantitative agreement with the atomic hydrogen spectrum. With the Sommerfeld-Wilson generalization, it accounted as well for the degeneracy of hydrogen energy levels. Although the Bohr model was able to sidestep the atomic "Hindenberg disaster," it cannot avoid what we might call the "Heisenberg disaster." By this we mean that the assumption of well-defined electronic orbits around a nucleus is completely contrary to the basic premises of quantum mechanics. Another flaw in the Bohr picture is that the angular momenta are all too large by one unit, for example, the ground state actually has zero orbital angular momentum (rather than $\hbar$).

> *The assumption of well-defined electronic orbits around a nucleus in the Bohr atom is completely contrary to the basic premises of quantum mechanics.*

Quantum Mechanics of Hydrogenlike Atoms

In contrast to the particle in a box and the harmonic oscillator, the hydrogen atom is a real physical system that can be treated exactly by quantum mechanics. In addition to their inherent significance, these solutions suggest prototypes for atomic orbitals used in approximate treatments of complex atoms and molecules.

For an electron in the field of a nucleus of charge $+Ze$, the Schrӧdinger equation can be written

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right\}\psi(r) = E\psi(r) \tag{1.7.24}$$

It is convenient to introduce *atomic units* in which length is measured in bohrs:

$$a_0 = \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11}\ \text{m} \equiv 1\ \text{bohr} \tag{1.7.25}$$

and energy in hartrees:

$$\frac{e^2}{a_0} = 4.358 \times 10^{-18}\ \text{J} = 27.211\ \text{eV} \equiv 1\ \text{hartree} \tag{1.7.26}$$

Electron volts (eV) are a convenient unit for atomic energies. One eV is defined as the energy an electron gains when accelerated across a potential difference of $1\ \text{volt}$. The ground state of the hydrogen atom has an energy of $-1/2\ \text{hartree}$ or $-13.6\ \text{eV}$. Conversion to atomic units is equivalent to setting

$$\hbar = e = m = 1 \tag{1.7.27}$$

in all formulas containing these constants. Rewriting the Schrӧdinger equation in atomic units, we have

$$\left\{-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right\}\psi(r) = E\psi(r) \tag{1.7.28}$$

Since the potential energy is spherically symmetrical (a function of r alone), it is obviously advantageous to treat this problem in spherical polar coordinates $r,\ \theta,\ \phi$. Expressing the Laplacian operator in these coordinates [cf. Eq (6-20)],

$$-\frac{1}{2}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} \times\psi(r,\ \theta,\ \phi)-\frac{Z}{r}\psi(r,\ \theta,\ \phi)=E\psi(r,\ \theta,\ \phi) \tag{1.7.29}$$

Equation 1.7.29 shows that the second and third terms in the Laplacian represent the angular momentum operator $\hat{L}^2$. Clearly, Equation 1.7.29 will have separable solutions of the form

$$\psi(r,\ \theta,\ \phi)=R(r)Y_{\ell m}(\theta,\ \phi) \tag{1.7.30}$$

Substituting Equation 1.7.30 into Equation 1.7.29 and using the angular momentum eigenvalue Equation Equation ???, we obtain an ordinary differential equation for the radial function $R(r)$:

$$\left\{-\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr}+\frac{\ell(\ell+1)}{2r^2}-\frac{Z}{r}\right\}R(r)=ER(r) \tag{1.7.31}$$

Note that in the domain of the variable r, the angular momentum contribution $\ell(\ell+1)/2r^2$ acts as an effective addition to the potential energy. It can be identified with *centrifugal force*, which pulls the electron outward, in opposition to the Coulomb attraction. Carrying out the successive differentiations in Equation 1.7.32 and simplifying, we obtain

$$\frac{1}{2}R''(r)+\frac{1}{r}R'(r)+\left[\frac{Z}{r}-\frac{\ell(\ell+1)}{2r^2}+E\right]R(r)=0 \tag{1.7.32}$$

another second-order linear differential equation with non-constant coefficients. It is again useful to explore the asymptotic solutions to Equation 1.7.32, as $r\to\infty$. In the asymptotic approximation,

$$R''(r)-2r|E|R(r)\approx 0 \tag{1.7.33}$$

having noted that the energy E is negative for bound states. Solutions to Equation 1.7.33 are

$$R(r)\approx\textsf{const}\ e^{\pm\sqrt{2|E|}r} \tag{1.7.34}$$

We reject the positive exponential on physical grounds, since $R(r)\to\infty$ as $r\to\infty$, in violation of the requirement that the wavefunction must be finite everywhere. Choosing the negative exponential and setting $E=-Z^2/2$ the ground state energy in the Bohr theory (in atomic units), we obtain

$$R(r)\approx\textsf{const}\ e^{-Zr} \tag{1.7.35}$$

It turns out, very fortunately, that this asymptotic approximation is also an *exact* solution of the Schrödinger equation (Equation \(\ref{29}\)) with $\ell=0$, just what happened for the harmonic-oscillator problem in Chap. 5. The solutions to Equation 1.7.32, designated $R_{n\ell}(r)$, are labeled by n, known as the *principal quantum number*, as well as by the angular momentum ℓ, which is a parameter in the radial equation. The solution in Equation 1.7.35 corresponds to $R_{10}(r)$. This should be normalized according to the condition

$$\int_0^\infty[R_{10}(r)]^2\,r^2\,dr=1 \tag{1.7.36}$$

A useful definite integral is

$$\int_0^\infty r^n\,e^{-\alpha r}\,dr=\frac{n!}{\alpha^{n+1}} \tag{1.7.37}$$

The normalized radial function is thereby given by

$$R_{10}(r)=2Z^{3/2}e^{-Zr} \tag{1.7.38}$$

Since this function is nodeless, we identify it with the ground state of the hydrogenlike atom. Multipying Equation 1.7.38 by the spherical harmonic $Y_{00}=1/\sqrt{4\pi}$, we obtain the total wavefunction (Equation 1.7.30)

$$\psi_{100}(r,\theta,\phi)=\left(\frac{Z^3}{\pi}\right)^{1/2}e^{-Zr}\tag{1.7.39}$$

This is conventionally designated as the 1s function $\psi_{1s}(r)$.

Integrals in spherical-polar coordinates over a spherically-symmetrical integrand (like the 1s orbital) can be significantly simplified. We can do the reduction

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}f(r)\,r^2\,\sin\theta\,dr\,d\theta\,d\phi=\int_0^\infty f(r)\,4\pi r^2\,dr\tag{1.7.40}$$

since integration over θ and ϕ gives 4π, the total solid angle of a sphere. The normalization of the 1s wavefunction can thus be written as

$$\int_0^\infty[\psi_{1s}(r)]^2\,4\pi r^2\,dr=1\tag{1.7.41}$$

Hydrogen Atom Ground State

There are a number of different ways of representing hydrogen-atom wavefunctions graphically. We will illustrate some of these for the 1s ground state. In atomic units,

$$\psi_{1s}(r)=\frac{1}{\sqrt{\pi}}e^{-r}\tag{1.7.42}$$

is a decreasing exponential function of a single variable r, and is simply plotted in Figure 3.

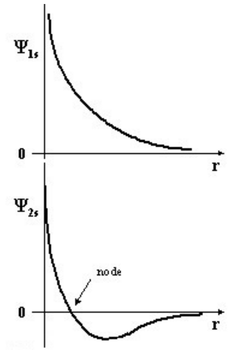

Figure 1.7.3. Wavefunctions for 1s and 2s orbitals for atomic hydrogen. The 2s-wavefunction (scaled by a factor of 2) has a node at $r=2$ bohr. Taken from voh.chem.ucla.edu/vohtar/wint.../lecture3.html

Figure 1.7.3 gives a somewhat more pictorial representation, a three-dimensional contour plot of $\psi_{1s}(r)$ as a function of x and y in the x, y-plane.

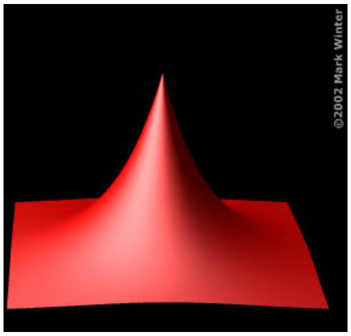

Figure 1.7.4: Contour map of 1s orbital in the x-, y-plane. Taken from winter.group.shef.ac.uk/orbit...s/wave-fn.html

According to Born's interpretation of the wavefunction, the probability per unit volume of finding the electron at the point (r, θ, ϕ) is equal to the square of the normalized wavefunction

$$\rho_{1s}(r)=[\psi_{1s}(r)]^2=\frac{1}{\pi}e^{-2r}\tag{1.7.43}$$

This is represented in Figure 5 by a scatter plot describing a possible sequence of observations of the electron position. Although results of individual measurements are not predictable, a statistical pattern does emerge after a sufficiently large number of measurements.

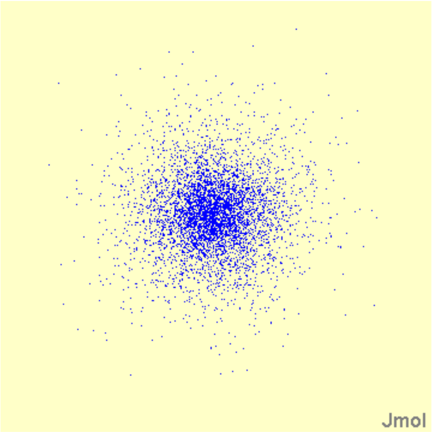

Figure 1.7.5: Scatter plot of electron position measurements in hydrogen $1s$ orbital. Taken from winter.group.shef.ac.uk/orbit...sity-dots.html

The probability density is normalized such that

$$\int_0^\infty \rho_{1s}(r)\,4\pi r^2\,dr = 1 \tag{1.7.44}$$

In some ways $\rho(r)$ does *not* provide the best description of the electron distribution, since the region around $r = 0$, where the wavefunction has its largest values, is a relatively small fraction of the volume accessible to the electron. Larger radii r represent larger physical regions since, in spherical polar coordinates, a value of r is associated with a shell of volume $4\pi r^2\,dr$. A more significant measure is therefore the *radial distribution function*

$$D_{1s}(r) = 4\pi r^2[\psi_{1s}(r)]^2 \tag{1.7.45}$$

which represents the probability density within the entire shell of radius r, normalized such that

$$\int_0^\infty D_{1s}(r)\,dr = 1 \tag{1.7.46}$$

The functions $\rho_{1s}(r)$ and $D_{1s}(r)$ are both shown in Figure $1.7.6$. Remarkably, the $1s$ RDF has its maximum at $r = a_0$, equal to the radius of the first Bohr orbit

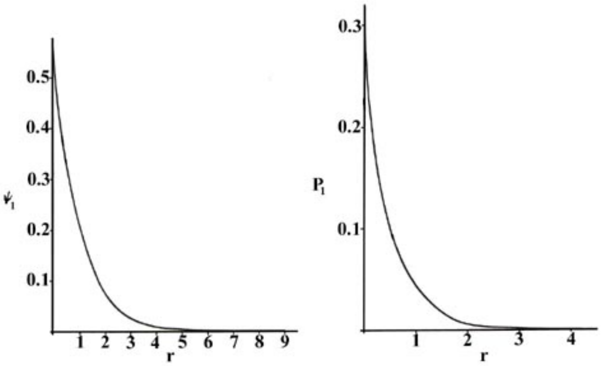

Figure 1.7.6: The wavefunction and probability distribution as functions of r for the n = 1 level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures. Image used with permisison (Bader).

Atomic Orbitals

The general solution for $R_{n\ell}(r)$ has a rather complicated form which we give without proof:

$$R_{n\ell}(r) = N_{n\ell}\,\rho^{\ell}\,L_{n+\ell}^{2\ell+1}(\rho)e^{-\rho/2} \qquad \rho \equiv \frac{2Zr}{n} \tag{1.7.47}$$

Here L_β^α is an associated Laguerre polynomial and $N_{n\ell}$, a normalizing constant. The angular momentum quantum number ℓ is by convention designated by a code: *s* for $\ell = 0$, *p* for $\ell = 1$, *d* for $\ell = 2$, *f* for $\ell = 3$, *g* for $\ell = 4$, and so on. The first four letters come from an old classification scheme for atomic spectral lines: *sharp*, *principal*, *diffuse* and *fundamental*. Although these designations have long since outlived their original significance, they remain in general use. The solutions of the hydrogenic Schrödinger equation in spherical polar coordinates can now be written in full

$$\begin{gathered}\psi_{n\ell m}(r,\,\theta,\,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\,\phi) \\ n = 1,\,2\ldots \qquad \ell = 0,\,1\ldots n-1 \qquad m = 0,\,\pm 1,\,\pm 2\ldots \pm\ell\end{gathered} \tag{1.7.48}$$

where $Y_{\ell m}$ are the spherical harmonics tabulated in Chap. 6. Table 1 below enumerates all the hydrogenic functions we will actually need. These are called *hydrogenic atomic orbitals*, in anticipation of their later applications to the structure of atoms and molecules.

Table 1. Real hydrogenic functions in atomic units.

$\psi_{1s} = \dfrac{1}{\sqrt{\pi}} e^{-r}$	(1.7.49)
$\psi_{2s} = \dfrac{1}{2\sqrt{2\pi}} \left(1 - \dfrac{r}{2}\right) e^{-r/2}$	(1.7.50)
$\psi_{2p_z} = \dfrac{1}{4\sqrt{2\pi}} z\, e^{-r/2}$	(1.7.51)
$\psi_{2p_x},\ \psi_{2p_y} \qquad \text{analogous}$	(1.7.52)
$\psi_{3s} = \dfrac{1}{81\sqrt{3\pi}} (27 - 18r + 2r^2) e^{-r/3}$	(1.7.53)
$\psi_{3p_z} = \dfrac{\sqrt{2}}{81\sqrt{\pi}} (6 - r) z\, e^{-r/3}$	(1.7.54)
$\psi_{3p_x},\ \psi_{3p_y} \qquad \text{analogous}$	(1.7.55)
$\psi_{3d_{z^2}} = \dfrac{1}{81\sqrt{6\pi}} (3z^2 - r^2) e^{-r/3}$	(1.7.56)
$\psi_{3d_{zx}} = \dfrac{\sqrt{2}}{81\sqrt{\pi}} zx\, e^{-r/3}$	(1.7.57)
$\psi_{3d_{yz}},\ \psi_{3d_{xy}} \qquad \text{analogous}$	(1.7.58)
$\psi_{3d_{x^2-y^2}} = \dfrac{1}{81\sqrt{\pi}} (x^2 - y^2) e^{-r/3}$	(1.7.59)

The energy levels for a hydrogenic system are given by

$$E_n = -\frac{Z^2}{2n^2} \text{ hartrees} \tag{1.7.60}$$

and depends on the principal quantum number alone. Considering all the allowed values of ℓ and m, the level E_n has a degeneracy of n^2. Figure 7 shows an energy level diagram for hydrogen $(Z=1)$. For $E \geq 0$, the energy is a continuum, since the electron is in fact a free particle. The continuum represents states of an electron and proton in interaction, but not bound into a stable atom. Figure $1.7.7$ also shows some of the transitions which make up the Lyman series in the ultraviolet and the Balmer series in the visible region.

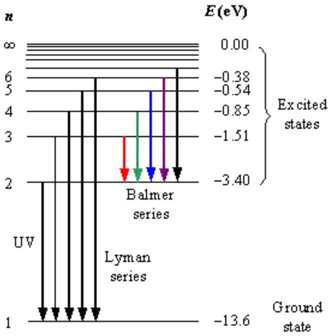

Figure 1.7.7: Energy levels of atomic hydrogen. Taken from http://eilat.sci.brooklyn.cuny.edu/c...hws/hw2d_c.htm

The ns orbitals are all spherically symmetrical, being associated with a constant angular factor, the spherical harmonic $Y_{00} = 1/\sqrt{4\pi}$. They have $n-1$ radial nodes—spherical shells on which the wavefunction equals zero. The 1*s* ground state is nodeless and the number of nodes increases with energy, in a pattern now familiar from our study of the particle-in-a-box and harmonic oscillator. The 2*s* orbital, with its radial node at $r=2$ bohr, is also shown in Figure $1.7.3$.

p- and d-Orbitals

The lowest-energy solutions deviating from spherical symmetry are the 2*p*-orbitals. Using Equations 1.7.47, 1.7.48 and the $\ell = 1$ spherical harmonics, we find three degenerate eigenfunctions:

$$\psi_{210}(r,\ \theta,\ \phi) = \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos\theta \tag{1.7.61}$$

and

$$\psi_{21\pm1}(r,\ \theta,\ \phi) = \mp\frac{1}{4\sqrt{2\pi}} r e^{-r/2} \sin\theta e^{\pm i\phi} \tag{1.7.62}$$

The function ψ_{210} is real and contains the factor $r\cos\theta$, which is equal to the cartesian variable z. In chemical applications, this is designated as a $2p_z$ orbital:

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} z e^{-r/2} \tag{1.7.63}$$

A contour plot is shown in Figure $1.7.8$. Note that this function is cylindrically-symmetrical about the z-axis with a node in the x, y-plane. The $\psi_{21\pm1}$ are complex functions and not as easy to represent graphically. Their angular dependence is that of the spherical harmonics $Y_{1\pm1}$, shown in Figure 6-4. As noted in Chap. 4, any linear combination of degenerate eigenfunctions is an equally-valid alternative eigenfunction. Making use of the Euler formulas for sine and cosine

$$\cos\phi = \frac{e^{i\phi}+e^{-i\phi}}{2} \quad \text{and} \quad \sin\phi = \frac{e^{i\phi}-e^{-i\phi}}{2} \tag{1.7.64}$$

and noting that the combinations $\sin\theta\cos\phi$ and $\sin\theta\sin\phi$ correspond to the cartesian variables x and y, respectively, we can define the alternative 2*p* orbitals

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{21-1} - \psi_{211}) = \frac{1}{4\sqrt{2\pi}} x e^{-r/2} \tag{1.7.65}$$

and

$$\psi_{2p_y} = -\frac{i}{\sqrt{2}}(\psi_{21-1} + \psi_{211}) = \frac{1}{4\sqrt{2\pi}} y e^{-r/2} \tag{1.7.66}$$

Clearly, these have the same shape as the $2p_z$-orbital, but are oriented along the x- and y-axes, respectively. The threefold degeneracy of the p-orbitals is very clearly shown by the geometric equivalence the functions $2p_x$, $2p_y$ and $2p_z$, which is not obvious for the spherical harmonics. The functions listed in Table 1 are, in fact, the real forms for all atomic orbitals, which are more useful in chemical applications. All higher p-orbitals have analogous functional forms $x\,f(r)$, $y\,f(r)$ and $z\,f(r)$ and are likewise 3-fold degenerate.

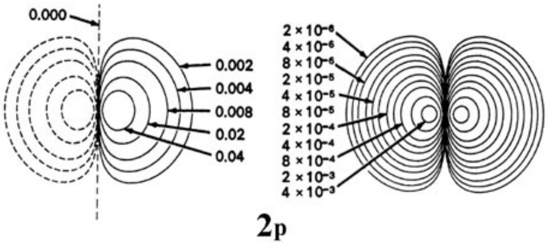

Figure $1.7.8$: Contour plot of $2p_z$ orbital. (Bader).

The orbital ψ_{320} is, like ψ_{210}, a real function. It is known in chemistry as the d_{z^2}-orbital and can be expressed as a cartesian factor times a function of r:

$$\psi_{3d_{z^2}} = \psi_{320} = (3z^2 - r^2) f(r) \tag{1.7.67}$$

A contour plot is shown in Figure $1.7.9$. This function is also cylindrically symmetric about the z-axis with *two* angular nodes—the conical surfaces with $3z^2 - r^2 = 0$. The remaining four $3d$ orbitals are complex functions containing the spherical harmonics $Y_{2\pm1}$ and $Y_{2\pm2}$ pictured in Figure 6-4. We can again construct real functions from linear combinations, the result being four geometrically equivalent "four-leaf clover" functions with two perpendicular planar nodes. These orbitals are designated $d_{x^2-y^2}$, d_{xy}, d_{zx} and d_{yz}. Two of them are shown in Figure 9. The d_{z^2} orbital has a different shape. However, it can be expressed in terms of two non-standard d-orbitals, $d_{z^2-x^2}$ and $d_{y^2-z^2}$. The latter functions, along with $d_{x^2-y^2}$ add to zero and thus constitute a linearly *dependent* set. *Two* combinations of these three functions can be chosen as independent eigenfunctions.

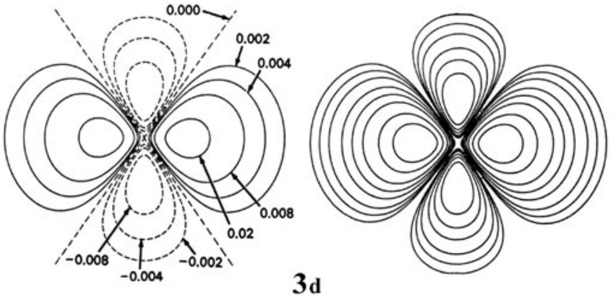

Figure $1.7.8$: Contour plot of $3d_{xy}$ orbital.

Summary

The atomic orbitals listed in Table 1 are illustrated in Figure $1.7.20$. Blue and red indicate, respectively, positive and negative regions of the wavefunctions (the radial nodes of the $2s$ and $3s$ orbitals are obscured). These pictures are intended as stylized representations of atomic orbitals and should *not* be interpreted as quantitatively accurate.

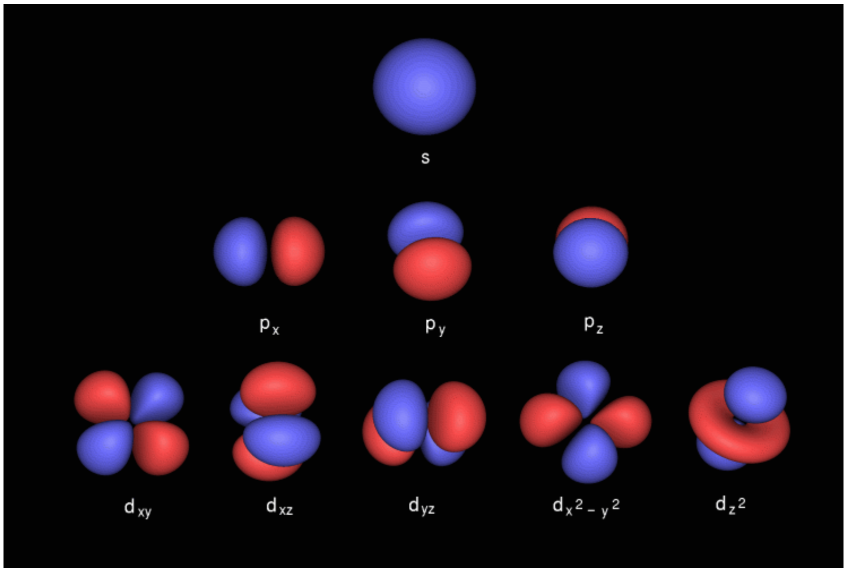

Figure 1.7.20: Hydrogenic atomic orbitals. Taken from www.chemcomp.com/journal/molorbs.htm

The electron charge distribution in an orbital $\psi_{n\ell m}(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = |\psi_{n\ell m}(\mathbf{r})|^2 \tag{1.7.68}$$

which for the *s*-orbitals is a function of r alone. The radial distribution function can be defined, even for orbitals containing angular dependence, by

$$D_{n\ell}(r) = r^2 [R_{n\ell}(r)]^2 \tag{1.7.69}$$

This represents the electron density in a shell of radius r, including all values of the angular variables θ, ϕ. Figure 1.7.11 shows plots of the RDF for the first few hydrogen orbitals.

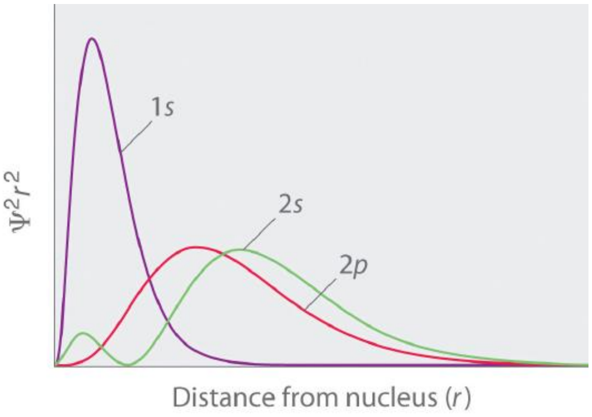

Figure 1.7.22: Some radial distribution functions.

Contributors and Attributions

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1.8: Helium Atom

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

The helium atom has two electrons bound to a nucleus with charge Z = 2. The successive removal of the two electrons can be diagrammed as

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{1.8.1}$$

The *first ionization energy* I_1, the minimum energy required to remove the first electron from helium, is experimentally 24.59 eV. The second ionization energy, I_2, is 54.42 eV. The last result can be calculated exactly since He^+ is a hydrogen-like ion. We have

$$I_2 = -E_{1s}(\mathrm{He}^+) = \frac{Z^2}{2n^2} = 2\text{ hartrees} = 54.42\text{ eV} \tag{1.8.2}$$

The energy of the three separated particles on the right side of Equation 1.8.1 is, by definition, zero. Therefore the ground-state energy of helium atom is given by $E_0 = -(I_1 + I_2) = -79.02\text{ eV} = -2.90372\text{ hartrees}$. We will attempt to reproduce this value, as close as possible, by theoretical analysis.

Schrödinger Equation and Variational Calculations

The Schrödinger equation for He atom, again using atomic units and assuming infinite nuclear mass, can be written

$$\left\{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right\}\psi(\mathrm{r}_1, \mathrm{r}_2) = E\psi(\mathrm{r}_1, \mathrm{r}_2) \tag{1.8.3}$$

The five terms in the Hamiltonian represent, respectively, the kinetic energies of electrons 1 and 2, the nuclear attractions of electrons 1 and 2, and the repulsive interaction between the two electrons. It is this last contribution which prevents an exact solution of the Schrödinger equation and which accounts for much of the complication in the theory. In seeking an approximation to the ground state, we might first work out the solution in the absence of the $1/r_{12}$-term. In the Schrödinger equation thus simplified, we can separate the variables $\mathbf{r_1}$ and $\mathbf{r_2}$ to reduce the equation to two independent hydrogen-like problems. The ground state wavefunction (not normalized) for this hypothetical helium atom would be

$$\psi(\mathrm{r}_1, \mathrm{r}_2) = \psi_{1s}(r_1)\psi_{1s}(r_2) = e^{-Z(r_1+r_2)} \tag{1.8.4}$$

and the energy would equal $2 \times (-Z^2/2) = -4$ hartrees, compared to the experimental value of -2.90 hartrees. **Neglect of electron repulsion evidently introduces a very large error.**

A significantly improved result can be obtained with the functional form (Equation 1.8.4), but with Z replaced by a adjustable parameter α, thus:

$$\tilde{\psi}(r_1, r_2) = e^{-\alpha(r_1+r_2)} \tag{1.8.5}$$

Using this function in the variational principle [cf. Eq (4.53)], we have

$$\tilde{E} = \frac{\int \psi(r_1, r_2)\hat{H}\psi(r_1, r_2)d\tau_1\tau_2}{\int \psi(r_1, r_2)\psi(r_1, r_2)d\tau_1 d\tau_2} \tag{1.8.6}$$

where $\hat{H}$ is the full Hamiltonian as in Equation 1.8.3, including the $1/r_{12}$-term. The expectation values of the five parts of the Hamiltonian work out to

$$\left\langle -\frac{1}{2}\nabla_1^2 \right\rangle = \left\langle -\frac{1}{2}\nabla_2^2 \right\rangle = \frac{\alpha^2}{2} \tag{1.8.7}$$

$$\left\langle -\frac{Z}{r_1} \right\rangle = \left\langle -\frac{Z}{r_2} \right\rangle = -Z\alpha, \left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8}\alpha \tag{1.8.8}$$

The sum of the integrals in Equation 1.8.8 gives the variational energy

$$\tilde{E}(\alpha)=\alpha^2-2Z\alpha+\frac{5}{8}\alpha \tag{1.8.9}$$

This will be always be an upper bound for the true ground-state energy. We can optimize our result by finding the value of α which *minimizes* the energy (Equation 1.8.9). We find

$$\frac{d\tilde{E}}{d\alpha}=2\alpha-2Z+\frac{5}{8}=0 \tag{1.8.10}$$

giving the optimal value

$$\alpha=Z-\frac{5}{16} \tag{1.8.11}$$

This can be given a physical interpretation, noting that the parameter α in the wavefunction (Equation 1.8.5) represents an *effective* nuclear charge. Each electron partially shields the other electron from the positively-charged nucleus by an amount equivalent to $5/8$ of an electron charge. Substituting Equation 1.8.11 into Equation 1.8.9, we obtain the optimized approximation to the energy

$$\tilde{E}=-\left(Z-\frac{5}{16}\right)^2 \tag{1.8.12}$$

For helium ($Z=2$), this gives -2.84765 hartrees, an error of about 2% ($E_0=-2.90372$). Note that the inequality $\tilde{E}>E_0$ applies in an *algebraic* sense.

In the late 1920's, it was considered important to determine whether the helium computation could be improved, as a test of the validity of quantum mechanics for many electron systems. The table below gives the results for a selection of variational computations on helium.

wavefunction	**parameters**	**energy**
$e^{-Z(r_1+r_2)}$	$Z=2$	-2.75
$e^{-\alpha(r_1+r_2)}$	$\alpha=1.6875$	-2.84765
$\psi(r_1)\psi(r_2)$	best $\psi(r)$	-2.86168
$e^{-\alpha(r_1+r_2)}(1+cr_{12})$	best α, c	-2.89112
Hylleraas (1929)	10 parameters	-2.90363
Pekeris (1959)	1078 parameters	-2.90372

The third entry refers to the *self-consistent field* method, developed by Hartree. Even for the best possible choice of one-electron functions $\psi(r)$, there remains a considerable error. This is due to failure to include the variable r_{12} in the wavefunction. The effect is known as *electron correlation*.

The fourth entry, containing a simple correction for correlation, gives a considerable improvement. Hylleraas (1929) extended this approach with a variational function of the form

$$\psi(r_1,r_2,r_{12})=e^{-\alpha(r_1+r_2)}\times\text{polynomial in} r_1,r_2,r_{12} \tag{1.8.13}$$

and obtained the nearly exact result with 10 optimized parameters. More recently, using modern computers, results in essentially perfect agreement with experiment have been obtained.

Spinorbitals and the Exclusion Principle

The simpler wavefunctions for helium atom in Equation 1.8.5, can be interpreted as representing two electrons in hydrogen-like 1s orbitals, designated as a $1s^2$ configuration. According to Pauli's exclusion principle, which states that no two electrons in an atom can have the same set of four quantum numbers, the two 1s electrons must have *different* spins, one spin-up or α, the other spin-down or β. A product of an orbital with a spin function is called a *spinorbital*. For example, electron 1 might occupy a spinorbital which we designate

$$\phi(1)=\psi_{1s}(1)\alpha(1) \text{or} \psi_{1s}(1)\beta(1) \tag{1.8.14}$$

Spinorbitals can be designated by a single subscript, for example, ϕ_a or ϕ_b, where the subscript stands for a *set* of four quantum numbers. In a two electron system the occupied spinorbitals ϕ_a and ϕ_b must be different, meaning that at least one of their four quantum numbers must be unequal. A two-electron spinorbital function of the form

$$\Psi(1,2)=\frac{1}{2}\Big(\phi_a(1)\phi_b(2)-\phi_b(1)\phi_a(2)\Big) \tag{1.8.15}$$

automatically fulflls the Pauli principle since it vanishes if $a=b$. Moreover, this function associates each electron equally with each orbital, which is consistent with the *indistinguishability* of identical particles in quantum mechanics. The factor $1/\sqrt{2}$ normalizes the two-particle wavefunction, assuming that ϕ_a and ϕ_b are normalized and mutually orthogonal. The function (Equation 1.8.15) is *antisymmetric* with respect to interchange of electron labels, meaning that

$$\Psi(2,1)=-\Psi(1,2) \tag{1.8.16}$$

This antisymmetry property is an elegant way of expressing the Pauli principle.

We note, for future reference, that the function in Equation 1.8.15 can be expressed as a 2×2 determinant:

$$\Psi(1,2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_a(1) & \phi_b(1)\\ \phi_a(2) & \phi_b(2)\end{vmatrix} \tag{1.8.17}$$

For the $1s^2$ configuration of helium, the two orbital functions are the same and Equation 1.8.15 can be written

$$\Psi(1,2)=\psi_{1s}(1)\psi_{1s}(2)\times\frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2)-\beta(1)\alpha(2)\Big) \tag{1.8.18}$$

For two-electron systems (but *not* for three or more electrons), the wavefunction can be factored into an orbital function times a spin function. The two-electron spin function

$$\sigma_{0,0}(1,2)=\frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2)-\beta(1)\alpha(2)\Big) \tag{1.8.19}$$

represents the two electron spins in opposing directions (antiparallel) with a total spin angular momentum of zero. The two subscripts are the quantum numbers S and M_S for the total electron spin. Eqution 1.8.18 is called the *singlet* spin state since there is only a single orientation for a total spin quantum number of zero. It is also possible to have both spins in the *same* state, provided the orbitals are different. There are three possible states for two parallel spins:

$$\sigma_{1,1}(1,2)=\alpha(1)\alpha(2) \tag{1.8.20}$$

$$\sigma_{1,0}(1,2)=\frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2)+\beta(2)\alpha(2)\Big) \tag{1.8.21}$$

$$\sigma_{1,-1}(1,2)=\beta(1)\beta(2) \tag{1.8.22}$$

These make up the *triplet* spin states, which have the three possible orientations of a total angular momentum of 1.

Excited States of Helium

The lowest excited state of helium is represented by the electron configuration $1s\ 2s$. The $1s\ 2p$ configuration has higher energy, even though the $2s$ and $2p$ orbitals in hydrogen are degenerate, because the $2s$ penetrates closer to the nucleus, where the potential energy is more negative. When electrons are in different orbitals, their spins can be either parallel or antiparallel. In order that the wavefunction satisfy the antisymmetry requirement (Equation 1.8.16), the two-electron orbital and spin functions must have *opposite* behavior under exchange of electron labels. There are four possible states from the $1s\ 2s$ configuration: a singlet state

$$\Psi^+(1,2)=\frac{1}{\sqrt{2}}\Big(\psi_{1s}(1)\psi_{2s}(2)+\psi_{2s}(1)\psi_{1s}(2)\Big)\sigma_{0,0}(1,2) \tag{1.8.23}$$

and three triplet states

$$\Psi^-(1,2)=\frac{1}{\sqrt{2}}\Big(\psi_{1s}(1)\psi_{2s}(2)-\psi_{2s}(1)\psi_{1s}(2)\Big)\begin{cases}\sigma_{1,1}(1,2)\\ \sigma_{1,0}(1,2)\\ \sigma_{1,-1}(1,2)\end{cases} \tag{1.8.24}$$

Using the Hamiltonian in Equation 1.8.3, we can compute the approximate energies

$$E^{\pm} = \iint \Psi^{\pm}(1,2)\hat{H}\Psi^{\pm}(1,2)d\tau_1 d\tau_2 \tag{1.8.25}$$

After evaluating some fierce-looking integrals, this reduces to the form

$$E^{\pm} = I(1s) + I(2s) + J(1s,2s) \pm K(1s,2s) \tag{1.8.26}$$

in terms of the one electron integrals

$$I(a) = \int \psi_a(\mathrm{r}) \left\{ -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right\} \psi_a(\mathrm{r}) d\tau \tag{1.8.27}$$

the Coulomb integrals

$$J(a,b) = \iint \psi_a(\mathrm{r}_1)^2 \frac{1}{r_{12}} \psi_b(\mathrm{r}_2)^2 d\tau_1 d\tau_2 \tag{1.8.28}$$

and the exchange integrals

$$K(a,b) = \iint \psi_a(\mathrm{r}_1)\psi_b(\mathrm{r}_1) \frac{1}{r_{12}} \psi_a(\mathrm{r}_2)\psi_b(\mathrm{r}_2) d\tau_1 d\tau_2 \tag{1.8.29}$$

The Coulomb integral represents the repulsive potential energy for two interacting charge distributions $\psi_a(\mathbf{r}_1)^2$ and $\psi_b(\mathbf{r}_2)^2$. The exchange integral, which has no classical analog, arises because of the exchange symmetry (or antisymmetry) requirement of the wavefunction. Both J and K can be shown to be positive quantities. Therefore the lower sign in (22) represents the state of lower energy, making the triplet state of the configuration 1s 2s lower in energy than the singlet state. This is an almost universal generalization and contributes to Hund's rule, to be discussed in the next Chapter.

Contributors and Attributions

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1.9: Atomic Structure and The Periodic Law

Quantum mechanics can account for the periodic structure of the elements, by any measure a major conceptual accomplishment for any theory. Although accurate computations become increasingly more challenging as the number of electrons increases, the general patterns of atomic behavior can be predicted with remarkable accuracy.

Slater Determinants

According to the orbital approximation, which was introduced in the last Chapter, an N-electron atom contains N occupied spinorbitals, which can be designated ϕ_a, ϕ_b . . . ϕ_n. In accordance with the Pauli exclusion principle, no two of these spinorbitals can be identical. Also, every electron should be equally associated with every spinorbital. A very neat mathematical representation for these properties is a generalization of the two-electron wavefunction (8.13) or (8.15) called a *Slater determinant*

$$\Psi(1,2\ldots N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_a(1) & \phi_b(1) & \ldots & \phi_n(1)\\ \phi_a(2) & \phi_b(2) & \ldots & \phi_n(2)\\ & & \vdots & \\ \phi_a(N) & \phi_b(N) & \ldots & \phi_n(N)\end{vmatrix} \tag{1.9.1}$$

Since interchanging any two rows (or columns) of a determinant multiplies it by -1, the antisymmetry property (8.15) is fulfilled, for *every* pair of electrons.

The Hamiltonian for an atom with N electrons around a nucleus of charge Z can be written

$$\hat{H}=\sum_{i=1}^{N}\left\{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right\}+\sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{1.9.2}$$

The sum over electron repulsions is written so that each pair $\{i,j\}$ is counted just once. The energy of the state represented by a Slater determinant (Equation 1.9.1) can be obtained after a lengthy derivation. We give just the final result

$$\tilde{E}=\sum_a I_a+\frac{1}{2}\sum_{a,b}(J_{ab}-K_{ab}) \tag{1.9.3}$$

where the sums run over all occupied spinorbitals. The one-electron, Coulomb and exchange integrals have the same form as those defined for helium atom in Eqs (8.22-24). The only difference is that an exchange integral equals zero unless the spins of orbitals a and b are both α or both β. The factor $^1/_2$ corrects for the double counting of pairs of spinorbitals in the second sum. The contributions with $a = b$ can be omitted since $J_{aa} = K_{aa}$. This effectively removes the Coulomb interaction of an orbital with itself, which is spurious.

The Hartree-Fock or self-consistent field (SCF) method is a procedure for optimizing the orbital functions in the Slater determinant (1), so as to minimize the energy (Equation 1.9.3). SCF computations have been carried out for all the atoms of the periodic table, with predictions of total energies and ionization energies generally accurate in the $1-2\%$ range.

Aufbau Principles and Periodic Structure

Aufbau means "building-up." Aufbau principles determine the order in which atomic orbitals are filled as the atomic number is increased. For the hydrogen atom, the order of increasing orbital energy is given by $1s < 2s = 2p < 3s = 3p = 3d$, etc. The dependence of energy on n alone leads to extensive degeneracy, which is however removed for orbitals in many-electron atoms. Thus $2s$ lies below $2p$, as already observed in helium. Similarly, $3s$, $3p$ and $3d$ increase energy in that order, and so on. The $4s$ is lowered sufficiently that it becomes comparable to $3d$. The general ordering of atomic orbitals is summarized in the following scheme:

$$\begin{gathered}1s<2s<2p<3s<3p<4s\sim 3d<4p<5s\sim 4d\\ <5p<6s\sim 5d\sim 4f<6p<7s\sim 6d\sim 5f\end{gathered} \tag{1.9.4}$$

and illustrated in Figure 1. This provides enough orbitals to fill the ground states of all the atoms in the periodic table. For orbitals designated as comparable in energy, e.g., $4s \sim 3d$, the actual order depends which other orbitals are occupied. The sequence of orbitals pictured above increases in the order $n+\frac{1}{2}\,l$, except that $l = 4$ (rather than 3) is used for an f-orbital.

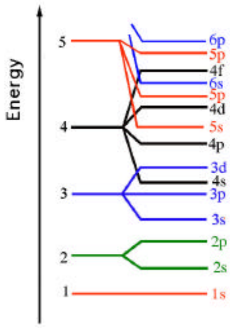


Figure 1: Approximate order of atomic orbital energy levels.

The tabulation below shows the ground-state electron configuration and term symbol for selected elements in the first part of the periodic table. From the term symbol, one can read off the total orbital angular momentum L and the total spin angular momentum S. The code for the total orbital angular momentum mirrors the one-electron notation, but using upper-case letters, as follows:

L = 0 1 2 3 4
S P D F G

The total spin S is designated, somewhat indirectly, by the spin multiplicity $2S + 1$ written as a superscript *before* the S, P, D. . . symbol. For example ^{1}S (singlet S) ,^{1}P (singlet P). . . mean $S = 0$; ^{2}S (doublet S) ,^{2}P (doublet P). . . mean $S = 1/2$; ^{3}S (triplet S) ,^{3}P (triplet P). . . mean $S = 1$, and so on. Please do not confuse the spin quantum number S with the orbital designation S.

Atom	Z	Electron Configuration	Term Symbol
H	1	$1s$	$^2S_{1/2}$
He	2	$1s^2$	$^1S_0$
Li	3	$[He]2s$	$^2S_{1/2}$
Be	4	$[He]2s^2$	$^1S_0$
B	5	$[He]2s^22p$	$^2P_{1/2}$
C	6	$[He]2s^22p^2$	$^3P_0$
N	7	$[He]2s^22p^3$	$^4S_{3/2}$
O	8	$[He]2s^22p^4$	$^3P_2$
F	9	$[He]2s^22p^5$	$^2P_{3/2}$
Ne	10	$[He]2s^22p^6$	$^1S_0$
Na	11	$[Ne]3s$	$^2S_{1/2}$
Cl	17	$[Ne]3s^23p^5$	$^2P_{3/2}$
Ar	18	$[Ne]3s^23p^6$	$^1S_0$
K	19	$[Ar]4s$	$^2S_{1/2}$
Ca	20	$[Ar]4s^2$	$^1S_0$
Sc	21	$[Ar]4s^23d$	$^2D_{3/2}$
Ti	22	$[Ar]4s^23d^2$	$^3F_2$
V	23	$[Ar]4s^23d^3$	$^4F_{3/2}$
Cr	24	$[Ar]4s3d^5$	$^7S_3$
Mn	25	$[Ar]4s^23d^5$	$^6S_{5/2}$

Atom	Z	Electron Configuration	Term Symbol
Fe	26	$[\mathrm{Ar}]4s^23d^6$	$^5\mathrm{D}_4$
Co	27	$[\mathrm{Ar}]4s^23d^7$	$^4\mathrm{F}_{9/2}$
Ni	28	$[\mathrm{Ar}]4s^23d^8$	$^3\mathrm{F}_4$
Cu	29	$[\mathrm{Ar}]4s3d^{10}$	$^2\mathrm{S}_{1/2}$
Zn	30	$[\mathrm{Ar}]4s^23d^{10}$	$^1\mathrm{S}_0$
Ga	31	$[\mathrm{Ar}]4s^23d^{10}4p$	$^2\mathrm{P}_{1/2}$
Br	35	$[\mathrm{Ar}]4s^23d^{10}4p^5$	$^2\mathrm{P}_{3/2}$
Kr	36	$[\mathrm{Ar}]3d^{10}4s^24p^6$	$^1\mathrm{S}_0$

The vector sum of the orbital and spin angular momentum is designated

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{1.9.5}$$

The possible values of the total angular momentum quantum number J runs in integer steps between $|L - S|$ and $L + S$. The J value is appended as a subscript on the term symbol, eg, $^1\mathrm{S}_0$, $^2\mathrm{P}_{1/2}$, $^2\mathrm{P}_{3/2}$. The energy differences between J states is a result of *spin-orbit interaction*, a magnetic interaction between the circulating charges associated with orbital and spin angular momenta. For atoms of low atomic number, the spin-orbit coupling is a relatively small correction to the energy, but it can become increasingly significant for heavier atoms.

We will next consider in some detail the Aufbau of ground electronic states starting at the beginning of the periodic table. Hydrogen has one electron in an *s*-orbital so its total orbital angular momentum is also designated S. The single electron has $s = 1/2$, thus $S = 1/2$. The spin multiplicity $2S + 1$ equals 2, thus the term symbol is written $^2\mathrm{S}$. In helium, a second electron can occupy the 1*s* shell, provided it has the opposite spin. The total spin angular momentum is therefore zero, as is the total orbital angular momentum. The term symbol is $^1\mathrm{S}$, as it will be for all other atoms with complete electron shells. In determining the total spin and orbital angular moments, we need consider only electrons outside of closed shells. Therefore lithium and beryllium are a reprise of hydrogen and helium. The angular momentum of boron comes from the single 2*p* electron, with $l = 1$ and $s = 1/2$, giving a $^2\mathrm{P}$ state.

To build the carbon atom, we add a second 2*p* electron. Since there are three degenerate 2*p* orbitals, the second electron can go into either the already-occupied 2*p* orbital or one of the unoccupied 2*p* orbitals. Clearly, two electrons in different 2*p* orbitals will have less repulsive energy than two electrons crowded into the same 2*p* orbital. In terms of the Coulomb integrals, we would expect, for example

$$J(2px, 2py) < J(2px, 2px) \tag{1.9.6}$$

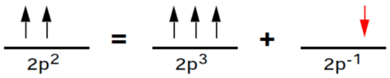
For nitrogen atom, with three 2*p* electrons, we expect, by the same line of reasoning, that the third electron will go into the remaining unoccupied 2*p* orbital. The half-filled $2p^3$ subshell has an interesting property. If the three occupied orbitals are $2p_x$, $2p_y$ and $2p_z$, then their total electron density is given by

$$\rho_{2p} = \psi^2_{2p_x} + \psi^2_{2p_y} + \psi^2_{2p_z} = \left(x^2 + y^2 + z^2\right) \times \text{function of r} = \text{function of r} \tag{1.9.7}$$

noting that $x^2 + y^2 + z^2 = r^2$. But spherical symmetry implies zero angular momentum, like an *s*-orbital. In fact, any half filled subshell, such as p^3, d^5, f^7, will contribute zero angular momentum. The same is, of course true as well for *filled* subshells, such as p^6, d^{10}, f^{14}. These are all S terms.

Another way to understand this vector cancelation of angular momentum is to consider the alternative representation of the degenerate 2*p*-orbitals: $2p_{-1}$; $2p_0$ and $2p_1$. Obviously, the *z*-components of angular momentum now add to zero, and since only this one component is observable, the total angular momentum must also be zero.

Returning to our unfinished consideration of carbon, the $2p^2$ subshell can be regarded, in concept, as a half-filled $2p^3$ subshell plus an electron "hole." The advantage of this picture is that the total orbital angular momentum must be equal to that of the hole, namely $l = 1$. This is shown below:



Thus the term symbol for the carbon ground state is P. It remains to determine the total spins of these subshells. Recall that exchange integrals K_{ab} are non-zero only if the orbitals a and b have the same spin. Since exchange integrals enter the energy formula (3) with negative signs, the more nonvanishing K integrals, the lower the energy. This is achieved by having the maximum possible number of electrons with *unpaired* spins. We conclude that $S = 1$ for carbon and $S = 3/2$ for nitrogen, so that the complete term symbols are ^{3}P and ^{4}S, respectively.

The allocation electrons among degenerate orbitals can be formalized by *Hund's rule*: For an atom in its ground state, the term with the highest multiplicity has the lowest energy.

Resuming Aufbau of the periodic table, oxygen with four 2p electrons must have one of the 2p-orbitals doubly occupied. But the remaining two electrons will choose unoccupied orbitals with parallel spins. Thus oxygen has, like carbon, a ^{3}P ground state. Fluorine can be regarded as a complete shell with an electron hole, thus a ^{2}P ground state. Neon completes the 2s2p shells, thus term symbol ^{1}S. The chemical stability and high ionization energy of all the noble-gas atoms can be attributed to their electronic structure of complete shells. The third row of the periodic table is filled in complete analogy with the second row. The similarity of the outermost electron shells accounts for the periodicity of chemical properties. Thus, the alkali metals Na and K belong in the same family as Li, the halogens Cl and Br are chemically similar to F, and so forth.

The transition elements, atomic numbers 21 to 30, present further challenges to our understanding of electronic structure. A complicating factor is that the energies of the 4s and 3d orbitals are very close, so that interactions among occupied orbitals often determines the electronic state. Ground-state electron configurations can be deduced from spectroscopic and chemical evidence, and confirmed by accurate self-consisent field computations. The 4s orbital is the first to be filled in K and Ca. Then come 3d electrons in Sc, Ti and V. A discontinuity occurs at Cr. The groundstate configuration is found to be $4s3d^5$, instead of the extrapolated $4s^23d^4$. This can be attributed to the enhanced stability of a half-filled $3d^5$-shell. All six electrons in the valence shells have parallel spins, maximizing the number of stabilizing exchange integrals and giving the observed ^{6}S term. An analogous discontinuity occurs for copper, in which the 4s subshell is again raided to complete the $3d^{10}$ subshell.

The order in which orbitals are filled is not necessarily consistent with the order in which electrons are removed. Thus, in all the positive ions of transition metals, the two 4s-electrons are removed first. The inadequacy of any simple generalizations about orbital energies is demonstrated by comparing the three ground-state electron configurations: Ni $4s^23d^8$, Pd $5s^04d^{10}$ and Pt $6s5d^9$.

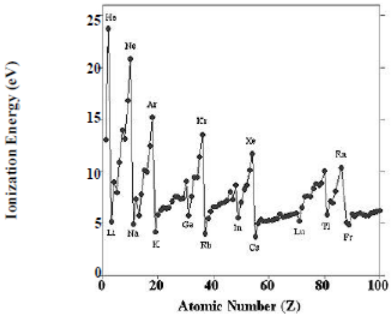


Figure 2. Periodic trends in ionization energy.

The periodic structure of the elements is evident for many physical and chemical properties, including chemical valence, atomic radius, electronegativity, melting point, density, and hardness. The classic prototype for periodic behavior is the variation of the first ionization energy with atomic number, which is plotted in in Figure 2.

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1.10: The Chemical Bond

The Hydrogen Molecule

This four-particle system, two nuclei plus two electrons, is described by the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \tag{1.10.1}$$

in terms of the coordinates shown in Figure 1.10.1. We note first that

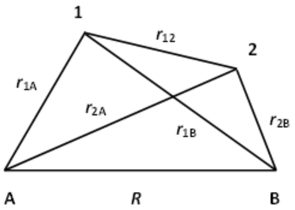


Figure 1.10.1: Coordinates used for hydrogen molecule.

the masses of the nuclei are much greater than those of the electrons, M_{proton} = 1836 atomic units, compared to m_{electron} = 1 atomic unit. Therefore nuclear kinetic energies will be negligibly small compared to those of the electrons. In accordance with the Born-Oppenheimer approximation, we can first consider the electronic Schrödinger equation

$$\hat{H}_{elec}\psi(r_1, r_2, R) = E_{elec}(R)\psi(r_1, r_2, R) \tag{1.10.2}$$

where

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \tag{1.10.3}$$

The internuclear separation R occurs as a parameter in this equation so that the Schrödinger equation must, in concept, be solved for each value of the internuclear distance R. A typical result for the energy of a diatomic molecule as a function of R is shown in Figure 1.10.2. For a bound state, the energy minimum occurs at for $R = R_e$, known as the *equilibrium internuclear distance*. The depth of the potential well at R_e is called the *binding energy* or *dissociation energy* D_e. For the H_2 molecule, D_e = 4.746 eV and R_e=1.400 bohr = 0.7406 Å. Note that as $R \to 0$, $E(R) \to \infty$, since the $1/R$ nuclear repulsion will become dominant.

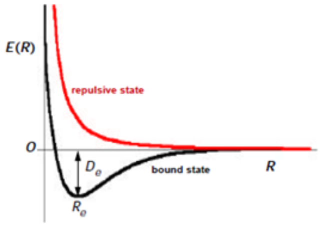


Figure 1.10.2. Energy curves for a diatomic molecule.

The more massive nuclei move much more slowly than the electrons. From the viewpoint of the nuclei, the electrons adjust almost instantaneously to any changes in the internuclear distance. The electronic energy $E_{\text{elec}}(R)$ therefore plays the role of a *potential energy* in the Schrödinger equation for nuclear motion

$$\left\{-\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 + V(R)\right\}\chi(r_A, r_B) = E\chi(r_A, r_B) \tag{1.10.4}$$

where

$$V(R) = E_{elec}(R) \tag{1.10.5}$$

from solution of Equation 1.10.2. Solutions of Equation 1.10.4 determine the vibrational and rotational energies of the molecule. These will be considered elsewhere. For the present, we are interested in the obtaining electronic energy from Equation 1.10.2 and 1.10.3. We will thus drop the subscript "elec" on $\hat{H}$ and $E(R)$ for the remainder this Chapter.

The first quantum-mechanical account of chemical bonding is due to Heitler and London in 1927, only one year after the Schrödinger equation was proposed. They reasoned that, since the hydrogen molecule H_2 was formed from a combination of hydrogen atoms A and B, a first approximation to its electronic wavefunction might be

$$\psi(r_1, r_2) = \psi_{1s}(r_{1A})\psi_{1s}(r_{2B}) \tag{1.10.6}$$

Using this function into the variational integral

$$\tilde{E}(R) = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau} \tag{1.10.7}$$

the value $R_e \approx 1.7$ bohr was obtained, indicating that the hydrogen atoms can indeed form a molecule. However, the calculated binding energy $D_e \approx 0.25$ eV, is much too small to account for the strongly-bound H_2 molecule. Heitler and London proposed that it was necessary to take into account the *exchange* of electrons, in which the electron labels in Equation 1.10.6 are reversed. The properly symmetrized function

$$\psi(r_1, r_2) = \psi_{1s}(r_{1A})\psi_{1s}(r_{2B}) + \psi_{1s}(r_{1B})\psi_{1s}(r_{2A}) \tag{1.10.8}$$

gave a much more realistic binding energy value of 3.20 eV, with R_e = 1.51 bohr. We have already used exchange symmetry (and antisymmetry) in our treatment of the excited states of helium. The variational function (Equation 1.10.8) was improved (Wang, 1928) by replacing the hydrogen 1s functions e^{-r} by $e^{-\zeta r}$. The optimized value ζ = 1.166 gave a binding energy of 3.782 eV. The quantitative breakthrough was the computation of James and Coolidge (1933). Using a 13-parameter function of the form

$$\psi(r_1, r_2) = e^{-\alpha(\xi_1+\xi_2)} \text{ x polynomial in} \{\xi_1, \xi_2, \eta_1, \eta_2, \rho\}, \xi_i \equiv \frac{r_{iA} + r_{iB}}{R}, \eta_i \equiv \frac{r_{iA} + r_{iB}}{R}, \rho \equiv \frac{r_{12}}{R} \tag{1.10.9}$$

they obtained R_e = 1.40 bohr, D_e = 4.720 eV. In a sense, this result provided a proof of the validity of quantum mechanics for molecules, in the same sense that Hylleraas' computation on helium was a proof for many-electron atoms.

The Valence Bond Theory

The basic idea of the Heitler-London model for the hydrogen molecule can be extended to chemical bonds between any two atoms. The orbital function (8) must be associated with the singlet spin function $\sigma_{0,0}(1,2)$ in order that the overall wavefunction be antisymmetric. This is a quantum-mechanical realization of the concept of an electron-pair bond, first proposed by G. N. Lewis in 1916. It is also now explained why the electron spins must be paired, i.e., antiparallel. It is also permissible to combine an antisymmetric orbital function with a triplet spin function but this will, in most cases, give a repulsive state, as shown by the red curve in Figure 1.10.2.

According to valence-bond theory, unpaired orbitals in the valence shells of two adjoining atoms can combine to form a chemical bond if they overlap significantly and are symmetry compatible. A σ-bond is cylindrically symmetrical about the axis joining the atoms. Two s AO's, two p_z AO's or an s and a p_z can contribute to a σ-bond, as shown in Figure 1.10.3. The z-axis is chosen along the internuclear axis. Two p_x or two p_y AO's can form a π-bond, which has a nodal plane containing the internuclear axis. Examples of symmetry-incompatible AO's would be an s with a p_x or a p_x with a p_y. In such cases the overlap integral would vanish because of cancelation of positive and negative contributions. Some possible combinations of AO's forming σ and π bonds are shown in Figure 1.10.3.

Bonding in the HCl molecule can be attributed to a combination of a hydrogen 1s with an unpaired 3p_z on chlorine. In Cl_2, a sigma bond is formed between the 3p_z AO's on each chlorine. As a first approximation, the other doubly-occupied AO's on chlorine-the inner shells and the valence-shell lone pairs-are left undisturbed.

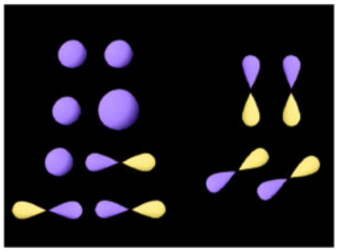


Figure 1.10.3. Formation of σ and π bonds.

The oxygen atom has two unpaired $2p$-electrons, say $2p_x$ and $2p_y$. Each of these can form a σ-bond with a hydrogen $1s$ to make a water molecule. It would appear from the geometry of the p-orbitals that the HOH bond angle would be 90°. It is actually around 104.5°. We will resolve this discrepency shortly. The nitrogen atom, with three unpaired $2p$ electrons can form three bonds. In NH_3, each $2p$-orbital forms a σ-bond with a hydrogen $1s$. Again 90° HNH bond angles are predicted, compared with the experimental 107°. The diatomic nitrogen molecule has a triple bond between the two atoms, one σ bond from combining $2p_z$ AO's and two π bonds from the combinations of $2p_x$'s and $2p_y$'s, respectively.

Hybrid Orbitals and Molecular Geometry

To understand the bonding of carbon atoms, we must introduce additional elaborations of valence-bond theory. We can write the valence shell configuration of carbon atom as $2s^2 2p_x 2p_y$, signifying that two of the $2p$ orbitals are unpaired. It might appear that carbon would be divalent, and indeed the species CH_2 (carbene or methylene radical) does have a transient existence. But the chemistry of carbon is dominated by tetravalence. Evidently it is a good investment for the atom to promote one of the $2s$ electrons to the unoccupied $2p_z$ orbital. The gain in stability attained by formation of four bonds more than compensates for the small excitation energy. It can thus be understood why the methane molecule CH_4 exists. The molecule has the shape of a regular tetrahedron, which is the result of *hybridization*, mixing of the s and three p orbitals to form four sp^3 hybrid atomic orbitals. Hybrid orbitals can overlap more strongly with neighboring atoms, thus producing stronger bonds. The result is four C-H σ-bonds, identical except for orientation in space, with 109.5° H-C-H bond angles.

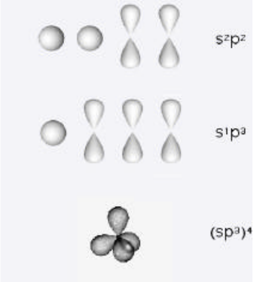
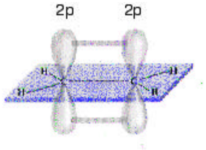
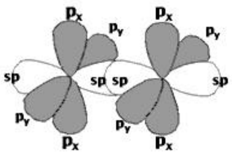


Figure 1.10.4. Promotion and hybridization of atomic orbitals in carbon atom.

Other carbon compounds make use of two alternative hybridization schemes. The s AO can form hybrids with *two* of the p AO's to give three sp^2 hybrid orbitals, with one p-orbital remaining unhybridized. This accounts for the structure of ethylene (ethene):



The C-H and C-C σ-bonds are all trigonal sp^2 hybrids, with 120° bond angles. The two unhybridized p-orbitals form a π-bond, which gives the molecule its rigid planar structure. The two carbon atoms are connected by a double bond, consisting of one σ and one π. The third canonical form of sp-hybridization occurs in C-C triple bonds, for example, acetylene (ethyne). Here, two of the p AO's in carbon remain unhybridized and can form two π-bonds, in addition to a σ-bond, with a neighboring carbon:



Acetylene H-C≡C-H is a linear molecule since sp-hybrids are oriented 180° apart.

The deviations of the bond angles in H_2O and NH_3 from 90° can be attributed to fractional hybridization. The angle H-O-H in water is 104.5° while H-N-H in ammonia is 107°. It is rationalized that the p-orbitals of the central atom acquire some s-character and increase their angles towards the tetrahedral value of 109.5°. Correspondingly, the lone pair orbitals must also become hybrids. Apparently, for both water and ammonia, a model based on tetrahedral orbitals on the central atoms would be closer to the actual behavior than the original selection of s- and p-orbitals. The hybridization is driven by repulsions between the electron densities of neighboring bonds.

Valence Shell Model

An elementary, but quite successful, model for determining the shapes of molecules is the *valence shell electron repulsion theory* (VSEPR), first proposed by Sidgewick and Powell and popularized by Gillespie. The local arrangement of atoms around each multivalent center in the molecule can be represented by $AX_{n\text{-}k}E_k$, where X is another atom and E is a lone pair of electrons. The geometry around the central atom is then determined by the arrangement of the *n* electron pairs (bonding plus nonbonding), which minimizes their mutual repulsion. The following geometric configurations satisfy this condition:

n	*shape*		
2	linear	5	trigonal bipyramid
3	trigonal planar	6	octahedral
4	tetrahedral	7	pentagonal bipyramid

The basic geometry will be distorted if the *n* surrounding pairs are not identical. The relative strength of repulsion between pairs follows the order E-E > E-X > X-X. In ammonia, for example, which is NH_3E, the shape will be tetrahedral to a first approximation. But the lone pair E will repel the N-H bonds more than they repel one another. Thus the E-N-H angle will increase from the tetrahedral value of 109.5°, causing the H-N-H angles to decrease slightly. The observed value of 107° is quite well accounted for. In water, OH_2E_2, the opening of the E-O-E angle will likewise cause a closing of H-O-H, and again, 104.5° seems like a reasonable value.

Valence-bond theory is about 90% successful in explaining much of the descriptive chemistry of ground states. VB theory fails to account for the triplet ground state of O_2 or for the bonding in electron-deffcient molecules such as diborane, B_2H_6. It is not very useful in consideration of excited states, hence for spectroscopy. Many of these deficiencies are remedied by molecular orbital theory, which we take up in the next Chapter.

1.11: Molecular Orbital Theory

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

The Hydrogen Molecule-Ion

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry. It also has been detected in outer space. The Schrödinger equation forHH_2^+ can be solved exactly within the Born-Oppenheimer approximation. For fixed internuclear distance *R*, this reduces to a problem of one electron in the field of two protons, designated A and B. We can write

$$\left\{-\frac{1}{2}\nabla^2\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right\}\psi(r)=E\psi(r) \tag{1.11.1}$$

where r_A and r_B are the distances from the electron to protons A and B, respectively. This equation was solved by Burrau (1927), after separating the variables in prolate spheroidal coordinates. We will write down these coordinates but give only a pictorial account of the solutions. The three prolate spheroidal coordinates are designated ξ, η, ϕ. the first two are defined by

$$\xi=\frac{r_A+r_B}{R} \tag{1.11.2}$$

and

$$\eta=\frac{r_A-r_B}{R} \tag{1.11.3}$$

while ϕ is the angle of rotation about the internuclear axis. The surfaces of constant ξ and η are, respectively, confocal ellipsoids and hyperboloids of revolution with foci at A and B. The two-dimensional analog should be familiar from analytic geometry, an ellipse being the locus of points such that the sum of the distances to two foci is a constant. Analogously, a hyperbola is the locus whose *difference* is a constant. Figure $1.11.1$shows several surfaces of constant ξ, η and ϕ. The ranges of the three coordinates are $\xi\in\{1,\infty\}$, $\eta\in\{-1,1\}$, $\phi\in\{0,2\pi\}$. The prolate-spheroidal coordinate system conforms to the natural symmetry of the H_2^+ problem in the same way that spherical polar coordinates were the appropriate choice for the hydrogen atom.

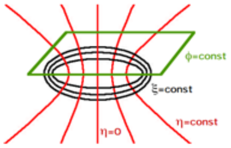


Figure 1.11.1: Prolate spheroidal coordinates.

The first few solutions of the H_2^+ Schrödinger equation are sketched in Figure $1.11.2$, roughly in order of increasing energy. The ϕ-dependence of the wavefunction is contained in a factor

$$\Phi(\phi)=e^{i\lambda\phi},\qquad\lambda=0,\pm1,\pm2,\ldots \tag{1.11.4}$$

which is identical to the ϕ-dependence in atomic orbitals. In fact, the quantum number λ represents the component of orbital angular momentum along the internuclear axis, the only component which has a definite value in systems with axial (cylindrical) symmetry. The quantum number λ determines the basic shape of a diatomic molecular orbital, in the same way that ℓ did for an atomic orbital. An analogous code is used σ for λ = 0, π for λ = ±1, δ for λ = ±2, and so on. We are already familiar with σ- and π-orbitals from valence-bond theory. A second classification of the H_2^+ eigenfunctions pertains to their symmetry with respect to inversion through the center of the molecule, also known as *parity*. If ψ(-r) = +ψ(r), the function is classified *gerade* or even parity, and the orbital designation is given a subscript *g*, as in σ_g or π_g. If ψ(-r) = -ψ(r), the function is classified as *ungerade* or odd parity, and we write instead σ_u or π_u. Atomic orbitals can also be classified by inversion symmetry. However, all *s* and *d* atomic orbitals are g, while all p and f orbitals are u, so no further designation is necessary. The molecular orbitals of a given symmetry are numbered in order of increasing energy, for example, $1\sigma_g$, $2\sigma_g$, $3\sigma_g$.

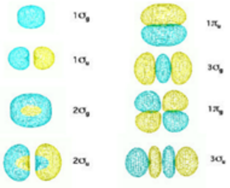


Figure 1.11.2: H_2^+ molecular orbitals.

The lowest-energy orbital, as we have come to expect, is nodeless. It obviously must have cylindrical symmetry (λ = 0) and inversion symmetry (g). It is designated $1\sigma_g$ since it is the first orbital of this classification. The next higher orbital has a nodal plane, with η = 0, perpendicular to the axis. This function still has cylindrical symmetry (σ) but now changes sign upon inversion (u). It is designated $1\sigma_u$, as the first orbital of this type. The next higher orbital has an inner ellipsiodal node. It has the same symmetry as the lowest orbital and is designated $2\sigma_g$. Next comes the $2\sigma_u$ orbital, with both planar and ellipsoidal nodes. Two degenerate π-orbitals come next, each with a nodal plane containing the internuclear axis, with ϕ=const. Their classification is $1\pi_u$. The second $1\pi_u$-orbital, not shown in Figure 1.11.2, has the same shape rotated by 90°. The $3\sigma_g$ orbital has two hyperbolic nodal surfaces, where η = ±const. The $1\pi_g$, again doubly-degenerate, has two nodal planes, η = 0 and ϕ=const. Finally, the $3\sigma_u$, the last orbital we consider, has three nodal surfaces where η=const.

An molecular orbital is classified as a *bonding orbital* if it promotes the bonding of the two atoms. Generally a bonding molecular orbital has a significant accumulation of electron charge in the region between the nuclei and thus reduces their mutual repulsion. The $1\sigma_g$, $2\sigma_g$, $1\pi_u$ and $3\sigma_g$ are evidently bonding orbitals. An molecular orbital which does *not* significantly contribute to nuclear shielding is classified as an *antibonding orbital*. The $1\sigma_u$, $2\sigma_u$, $1\pi_g$ and $3\sigma_u$ belong in this category. Often an antibonding molecular orbital is designated by σ* or π*.

The actual ground state of H_2^+ has the $1\sigma_g$ orbital occupied. The equilibrium internuclear distance R_e is 2.00 bohr and the binding energy D_e is 2.79 eV, which represents quite a strong chemical bond. The $1\sigma_u$ is a repulsive state and a transition from the ground state results in dissociation of the molecule.

The LCAO Approximation

In Figure 1.11.3, the $1\sigma_g$ and $1\sigma_u$ orbitals are plotted as functions of z, along the internuclear axis. Both functions have cusps, discontinuities in slope, at the positions of the two nuclei A and B. The $1s$ orbitals of hydrogen atoms have the same cusps. The shape of the $1\sigma_g$ and $1\sigma_u$ suggests that they can be approximated by a sum and difference, respectively, of hydrogen $1s$ orbitals, such that

$$\psi(1\sigma_{g,u}) \approx \psi(1s_A) \pm \psi(1s_B) \tag{1.11.5}$$

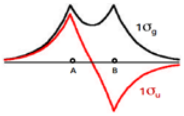


Figure 1.11.3: H_2^+ orbitals along internuclear axis.

This *linear combination of atomic orbitals* is the basis of the so-called LCAO approximation. The other orbitals pictured in Figure 1.11.2 can likewise be approximated as follows:

$$\psi(2\sigma_{g,u}) \approx \psi(2s_A) \pm \psi(2s_B) \tag{1.11.6}$$

$$\psi(3\sigma_{g,u}) \approx \psi(2p\sigma_A) \pm \psi(2p\sigma_B) \tag{1.11.7}$$

$$\psi(1\pi_{u,g}) \approx \psi(2p\pi_A) \pm \psi(2p\pi_B) \tag{1.11.8}$$

The $2p\sigma$ atomic orbital refers to $2p_z$, which has the axial symmetry of a σ-bond. Likewise $2p\pi$ refers to $2p_x$ or $2p_y$, which are positioned to form π-bonds. An alternative notation for diatomic molecular orbitals which specifies their atomic origin and bonding/antibonding character is the following:

$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$3\sigma_u$	$1\pi_u$	$1\pi_g$

$\sigma 1s$	$\sigma^* 1s$	$\sigma 2s$	$\sigma^* 2s$	$\sigma 2p$	$\sigma^* 2p$	$\pi 2p$	$\pi^* 2p$

Almost all applications of molecular-orbital theory are based on the LCAO approach, since the exact H_2^+ functions are far too complicated to work with.

The relationship between molecular orbitals and their constituent atomic orbitals can be represented in correlation diagrams, show in Figure 1.11.4

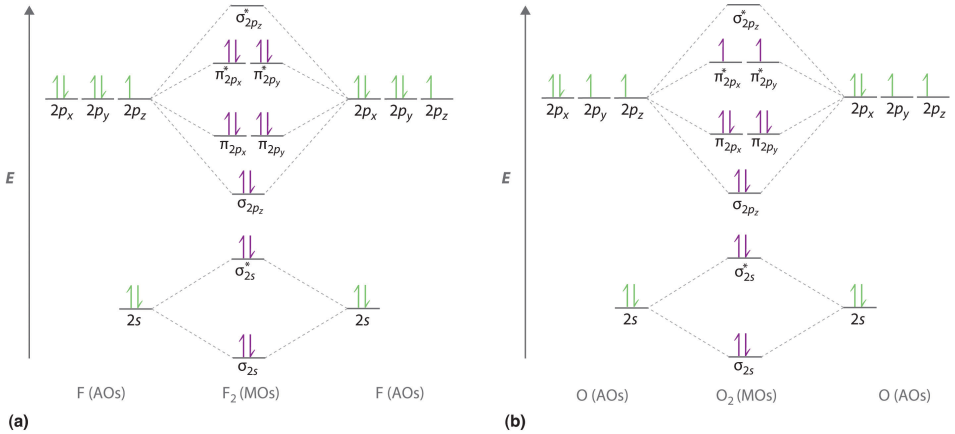


Figure 1.11.4: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^\star_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x},\ \pi^\star_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

MO Theory of Homonuclear Diatomic Molecules

A sufficient number of orbitals is available for the *Aufbau* of the ground states of all homonuclear diatomic species from H_2 to Ne_2. Table 1 summarizes the results. The most likely order in which the molecular orbitals are filled is given by

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g \sim 1\pi_u < 1\pi_g < 3\sigma_u \tag{1.11.9}$$

The relative order of $3\sigma_g$ and $1\pi_u$ depends on which other molecular orbitals are occupied, much like the situation involving the 4*s* and 3*d* atomic orbitals. The results of photoelectron spectroscopy indicate that $1\pi_u$ is lower up to and including N_2, but $3\sigma_g$ is lower thereafter.

The term symbol $\Sigma, \Pi, \Delta \ldots$, analogous to the atomic S, P, D. . . symbolizes the axial component of the total orbital angular momentum. When a π-shell is filled (4 electrons) or half-filled (2 electrons), the orbital angular momentum cancels to zero and we find a Σ term. The spin multiplicity is completely analogous to the atomic case. The total parity is again designated by a subscript *g* or *u*. Since the many electron wavefunction is made up of products of individual MO's, the total parity is odd only if the molecule contains an *odd* number of *u* orbitals. Thus a σ_u^2 or a π_u^2 subshell transforms like *g*.

For Σ terms, the superscript $\pm$ denotes the sign change of the wavefunction under a reflection in a plane containing the internuclear axis. This is equivalent to a sign change in the variable $\phi \rightarrow -\phi$. This symmetry is needed when we deal with spectroscopic selection rules. In a spin-paired π_u^2 subshell the triplet spin function is symmetric so that the orbital factor must be antisymmetric, of the form

$$\frac{1}{\sqrt{2}}\left(\pi_x(1)\pi_y(2) - \pi_y(1)\pi_x(2)\right) \tag{1.11.10}$$

This will change sign under the reflection, since $x \rightarrow x$ but $y \rightarrow -y$. We need only remember that a π_u^2 subshell will give the term symbol $^3\Sigma_g^-$.

The net bonding effect of the occupied molecular orbitals is determined by the *bond order*, half the excess of the number bonding minus the number antibonding. This definition brings the molecular orbital results into correspondence with the Lewis (or valence-bond) concept of single, double and triple bonds. It is also possible in molecular orbital theory to have a bond order of 1/2, for example, in H_2^+ which is held together by a single bonding orbital. A bond order of zero generally indicates no stable chemical bond, although helium and neon atoms can still form clusters held together by much weaker van der Waals forces. Molecular-orbital theory successfully accounts for the transient stability of a ${}^3\Sigma_u^+$ excited state of He_2, in which one of the antibonding electrons is promoted to an excited bonding orbital. This species has a lifetime of about 10^{-4} sec, until it emits a photon and falls back into the unstable ground state. Another successful prediction of molecular orbital theory concerns the relative binding energy of the positive ions N_2^+ and O_2^+, compared to the neutral molecules. Ionization weakens the N–N bond since a bonding electron is lost, but it strengthens the O–O bond since an antibonding electron is lost.

One of the earliest triumphs of molecular orbital theory was the prediction that the oxygen molecule is paramagnetic. Figure 1.11.5 shows that liquid O_2 is a magnetic substance, attracted to the region between the poles of a permanent magnet. The paramagnetism arises from the half-filled $1\pi_g^2$ subshell. According to Hund's rules the two electrons singly occupy the two degenerate $1\pi_g$ orbitals with their spins aligned *parallel*. The term symbol is ${}^3\Sigma_g^-$ and the molecule thus has a nonzero spin angular momentum and a net magnetic moment, which is attracted to an external magnetic field. Linus Pauling invented the paramagnetic oxygen analyzer, which is extensively used in medical technology.

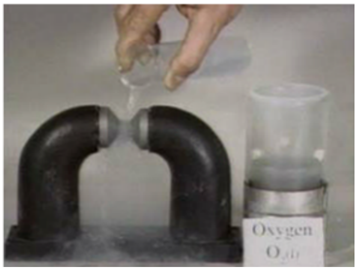


Figure 1.11.5. Demonstration showing blue liquid O_2 attracted to the poles of a permanent magnet. From jchemed.chem.wisc.edu/jcesoft.../PARANIO/9.HTM

Variational Computation of Molecular Orbitals

Thus far we have approached molecular orbital theory from a mainly descriptive point of view. To begin a more quantitative treatment, recall the LCAO approximation to the H_2^+ ground state, Equation 1.11.5, which can be written

$$\psi = c_A\psi_A + c_B\psi_B \tag{1.11.11}$$

Using this as a trial function in the variational principle, we have

$$E(c_A, c_B) = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau} \tag{1.11.12}$$

where $\hat{H}$ is the Hamiltonian from Equation 1.11.1. In fact, these equations can be applied more generally to construct *any* molecular orbital, not just solutions for H_2^+. In the general case, $\hat{H}$ will represent an effective one-electron Hamiltonian determined by the molecular environment of a given orbital. The energy expression involves some complicated integrals, but can be simplified somewhat by expressing it in a standard form. Hamiltonian matrix elements are defined by

$$H_{AA} = \int \psi_A \hat{H} \psi_A d\tau \tag{1.11.13}$$

$$H_{BB} = \int \psi_B \hat{H} \psi_B d\tau \tag{1.11.14}$$

$$H_{AB} = H_{BA} = \int \psi_A \hat{H} \psi_B d\tau \tag{1.11.15}$$

while the overlap integral is given by

$$S_{AB} = \int \psi_A \psi_B d\tau \tag{1.11.16}$$

Presuming the functions ψ_A and ψ_B to be normalized, the variational energy (Equation 1.11.12) reduces to

$$E(c_Ac_B) = \frac{c_A^2 H_{AA} + 2c_Ac_BH_{AB} + c_B^2 H_{BB}}{c_A^2 + 2c_Ac_BS_{AB} + c_B^2} \tag{1.11.17}$$

To optimize the MO, we find the minimum of E wrt variation in c_A and c_B, as determined by the two conditions

$$\frac{\partial E}{\partial c_A} = 0, \quad \frac{\partial E}{\partial c_B} = 0 \tag{1.11.18}$$

The result is a *secular equation* determining two values of the energy:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0 \tag{1.11.19}$$

For the case of a homonuclear diatomic molecule, for example H_2^+, the two Hamiltonian matrix elements H_{AA} and H_{BB} are equal, say to α. Setting $H_{AB} = \beta$ and $S_{AB} = S$, the secular equation reduces to

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0 \tag{1.11.20}$$

with the two roots

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S} \tag{1.11.21}$$

The calculated integrals α and β are usually negative, thus for the bonding orbital

$$E^{+} = \frac{\alpha + \beta}{1 + S} \quad (bonding) \tag{1.11.22}$$

while for the antibonding orbital

$$E^{-} = \frac{\alpha - \beta}{1 - S} \quad (antibonding) \tag{1.11.23}$$

Note that $(E^- - \alpha) > (\alpha - E^+)$, thus the energy increase associated with antibonding is slightly greater than the energy decrease for bonding. For historical reasons, α is called a *Coulomb integral* and β, a *resonance integral*.

Heteronuclear Molecules

The variational computation leading to Equation 1.11.19can be applied as well to the heteronuclear case in which the orbitals ψ_A and ψ_B are *not* equivalent. The matrix elements H_{AA} and H_{BB} are approximately equal to the energies of the atomic orbitals ψ_A and ψ_B, respectively, say E_A and E_B with $E_A > E_B$. It is generally true that $|E_A|, |E_B| \gg |H_{AB}|$. With these simplifications, secular equation can be written

$$\begin{vmatrix} E_A - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & E_B - E \end{vmatrix} = (E_A - E)(E_B - E) - (H_{AB} - ES_{AB})^2 = 0 \tag{1.11.24}$$

This can be rearranged to

$$E - E_A = \frac{(H_{AB} - ES_{AB})^2}{E - E_B} \tag{1.11.25}$$

To estimate the root closest to E_A, we can replace E by E_A on the right hand side of the equation. This leads to

$$E^- \approx E_A + \frac{(H_{AB} - E_AS_{AB})^2}{E_A - E_B} \tag{1.11.26}$$

and analogously for the other root,

$$E^+ \approx E_B - \frac{(H_{AB} - E_BS_{AB})^2}{E_A - E_B} \tag{1.11.27}$$

The following correlation diagram represents the relative energies of these atomic orbitals and MO's:

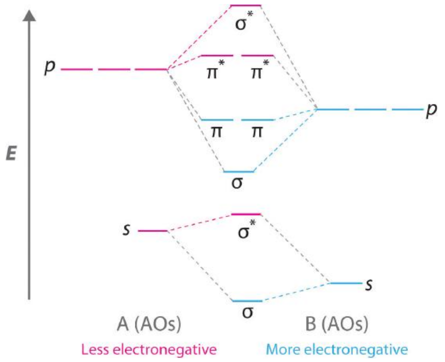


Figure 1.11.6: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A simple analysis of Equations 1.11.24 implies that, in order for two atomic orbitals ψ_A and ψ_B to form effective molecular orbitals the following conditions must be met:

I. (The atomic orbitals must have compatible symmetry. For example, ψ_A and ψ_B can be either *s* or $p\sigma$ orbitals to form a σ-bond or both can be $p\pi$ (with the same orientation) to form a π-bond.
II. The charge clouds of ψ_A and ψ_B should overlap as much as possible. This was the rationale for hybridizing the *s* and *p* orbitals in carbon. A larger value of S_{AB} implies a larger value for H_{AB}.
III. The energies E_A and E_B must be of comparable magnitude. Otherwise, the denominator in (20) and (21) will be too large and the molecular orbitals will not differ significantly from the original AO's. A rough criterion is that E_A and E_B should be within about 0.2 hartree or 5 eV. For example, the chlorine 3*p* orbital has an energy of -13.0 eV, comfortably within range of the hydrogen 1*s*, with energy -13.6 eV. Thus these can interact to form a strong bonding (plus an antibonding) molecular orbital in HCl. The chlorine 3*s* has an energy of -24.5 eV, thus it could not form an effective bond with hydrogen even if it were available.

Hückel Molecular Orbital Theory

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of σ-bonds. This is, in fact, a more sophisticated version of a free-electron model. We again illustrate the model using butadiene CH_2=CH-CH=CH_2. From four *p* atomic orbitals with nodes in the plane of the carbon skeleton, one can construct four π molecular orbitals by an extension of the LCAO approach:

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 \tag{1.11.28}$$

Applying the linear variational method, the energies of the molecular orbitals are the roots of the 4 x 4 secular equation

$$\begin{vmatrix} H_{11}-E & H_{12}-ES_{12} & \dots \\ H_{12}-ES_{12} & H_{22}-E & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \tag{1.11.29}$$

Four simplifying assumptions are now made

I. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the *p*-orbitals are directed perpendicular to the direction of their bonds.
II. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
III. All resonance integrals H_{ij} between neighboring atoms are set equal to β.
IV. All coulomb integrals H_{ii} are set equal to α.

The secular equation thus reduces to

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{1.11.30}$$

Dividing by β^4 and defining

$$x = \frac{\alpha - E}{\beta} \tag{1.11.31}$$

the equation simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{1.11.32}$$

This is essentially the connection matrix for the molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{1.11.33}$$

Noting that this is a quadratic equation in x^2, the roots are found to be $x^2 = (3 \pm \sqrt{5})/2$, so that $x = \pm 0.618, \pm 1.618$ This corresponds to the four MO energy levels

$$E = \alpha \pm 1.618\beta, \quad \alpha \pm 0.618\beta \tag{1.11.34}$$

Since α and β are negative, the lowest molecular orbitals have

$$E(1\pi) = \alpha + 1.618\beta \tag{1.11.35}$$

and

$$E(2\pi) = \alpha + 0.618\beta \tag{1.11.36}$$

and the total π-electron energy of the $1\pi^2 2\pi^2$ configuration equals

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta \tag{1.11.37}$$

The simplest application of Hückel theory, to the ethylene molecule $CH_2=CH_2$ gives the secular equation

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \tag{1.11.38}$$

This is easily solved for the energies $E = \alpha \pm \beta$. The lowest orbital has $E(1\pi) = \alpha + \beta$ and the $1\pi^2$ ground state has $E_\pi = 2(\alpha + \beta)$. If butadiene had two localized double bonds, as in its dominant valence-bond structure, its π-electron energy would be given by $E_\pi = 4(\alpha + \beta)$. Comparing this with the Hückel result (Equation 1.11.37), we see that the energy lies lower than the that of two double bonds by 0.48β. The thermochemical value is approximately -17 kJmol^{-1}. This stabilization of a conjugated system is known as the *delocalization energy*. It corresponds to the resonance-stabilization energy in valence-bond theory.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular equation

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{1.11.39}$$

with the **six roots** $x = \pm 2, \pm 1, \pm 1$. The energy levels are $E = \alpha \pm 2\beta$ and two-fold degenerate $E = \alpha \pm \beta$. With the three lowest molecular orbitals occupied, we have

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \tag{1.11.40}$$

Since the energy of three localized double bonds is $6\alpha + 6\beta$, the delocalization energy equals 2β. The thermochemical value is -152 kJmol^{-1}.

Contributors

- Seymour Blinder (Professor Emeritus of Chemistry and Physics at the University of Michigan, Ann Arbor)

1.12: Molecular Symmetry

In many cases, the symmetry of a molecule provides a great deal of information about its quantum states, even without a detailed solution of the Schrödinger equation. A geometrical transformation which turns a molecule into an indistinguishable copy of itself is called a *symmetry operation*. A symmetry operation can consist of a rotation about an axis, a reflection in a plane, an inversion through a point, or some combination of these.

The Ammonia Molecule

We shall introduce the concepts of symmetry and group theory by considering a concrete example–the ammonia molecule NH_3. In any symmetry operation on NH_3, the nitrogen atom remains fixed but the hydrogen atoms can be permuted in 3!=6 different ways. The axis of the molecule is called a C_3 axis, since the molecule can be rotated about it into 3 equivalent orientations, 120° apart. More generally, a C_n axis has n equivalent orientations, separated by $2\pi/n$ radians. The axis of highest symmetry in a molecule is called the *principal axis*. Three mirror planes, designated $\sigma_1, \sigma_2, \sigma_3$, run through the principal axis in ammonia. These are designated as σ_v or *vertical* planes of symmetry. Ammonia belongs to the symmetry group designated C_{3v}, characterized by a three-fold axis with three vertical planes of symmetry.

Let us designate the orientation of the three hydrogen atoms in Figure 1.12.1 as {1, 2, 3}, reading in clockwise order from the bottom. A counterclockwise rotation by 120°, designated

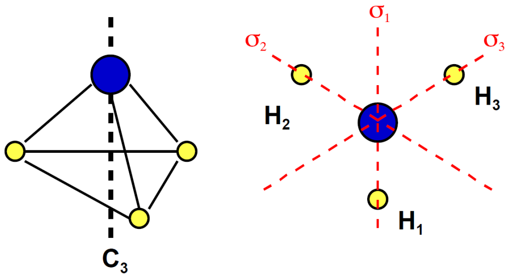


Figure 1.12.1: Two views of the ammonia molecule.

by the operator C_3, produces the orientation {2, 3, 1}. A second counterclockwise rotation, designated C_3^2, produces {3, 1, 2}. Note that two successive counterclockwise rotations by 120° is equivalent to one clockwise rotation by 120°, so the last operation could also be designated C_3^{-1}. The three reflection operations $\sigma_1, \sigma_2, \sigma_3$, applied to the original configuration {1, 2, 3} produces {1, 3, 2}, {3, 2, 1} and {2, 1, 3}, respectively. Finally, we must include the identity operation, designated E, which leaves an orientation unchanged. The effects of the six possible operations of the symmetry group C_{3v} can be summarized as follows:

$$E\{1,2,3\} = \{1,2,3\} C_3\{1,2,3\} = \{2,3,1\} \tag{1.12.1}$$

$$C_3^2\{1,2,3\} = \{3,1,2\} \sigma_1\{1,2,3\} = \{1,3,2\} \tag{1.12.2}$$

$$\sigma_2\{1,2,3\} = \{3,2,1\} \sigma_3\{1,2,3\} = \{2,1,3\} \tag{1.12.3}$$

We have thus accounted for all 6 possible permutations of the three hydrogen atoms.

The successive application of two symmetry operations is equivalent to some single symmetry operation. For example, applying C_3, then σ_1 to our starting orientation, we have

$$\sigma_1 C_3\{1,2,3\} = \sigma_1\{2,3,1\} = \{2,1,3\} \tag{1.12.4}$$

But this is equivalent to the single operation σ_3. This can be represented as an algebraic relation among symmetry operators

$$\sigma_1 C_3 = \sigma_3 \tag{1.12.5}$$

Note that successive operations are applied in the order *right to left* when represented algebraically. For the same two operations in reversed order, we find

$$C_3 \sigma_1\{1,2,3\} = C_3\{1,3,2\} = \{3,2,1\} = \sigma_2\{1,2,3\} \tag{1.12.6}$$

Thus symmetry operations do *not*, in general commute

$$AB \not\equiv BA \tag{1.12.7}$$

although they *may* commute, for example, C_3 and C_3^2.

The algebra of the group C_{3v} can be summarized by the following multiplication table.

$$\begin{array}{ccccccc}
 & 1^{st} & E & C_3 & C_3^2 & \sigma_1 & \sigma_2 & \sigma_3 \\
2^{nd} & & & & & & & \\
E & & E & C_3 & C_3^2 & \sigma_1 & \sigma_2 & \sigma_3 \\
C_3 & & C_3 & C_3^2 & E & \sigma_3 & \sigma_1 & \sigma_2 \\
C_3^2 & & C_3^2 & E & C_3 & \sigma_2 & \sigma_3 & \sigma_1 \\
\sigma_1 & & \sigma_1 & \sigma_2 & \sigma_3 & E & C_3 & C_3^2 \\
\sigma_2 & & \sigma_2 & \sigma_3 & \sigma_1 & C_3^2 & E & C_3 \\
\sigma_3 & & \sigma_3 & \sigma_1 & \sigma_2 & C_3 & C_3^2 & E
\end{array} \tag{1.12.8}$$

Notice that each operation occurs once and only once in each row and each column.

Group Theory

In mathematics, a *group* is defined as a set of g elements $\mathcal{G} \equiv \{G_1, G_2 \ldots G_h\}$ together with a rule for combination of elements, which we usually refer to as a *product*. The elements must fulfill the following four conditions.

I. The product of any two elements of the group is another element of the group. That is $G_iG_j = G_k$ with $G_k \in \mathcal{G}$
II. Group multiplication obeys an associative law, $G_i(G_jG_k) = (G_iG_j)G_k \equiv G_iG_jG_k$
III. There exists an *identity element* E such that $EG_i = G_iE = G_i$ for all *i*.
IV. Every element G_i has a unique inverse G_i^{-1}, such that $G_iG_i^{-1} = G_i^{-1}G_i = E$ with $G_i^{-1} \in \mathcal{G}$.

The number of elements *h* is called the *order* of the group. Thus C_{3v} is a group of order 6.

A set of quantities which obeys the group multiplication table is called a *representation* of the group. Because of the possible noncommutativity of group elements [cf. Eq (1)], simple numbers are not always adequate to represent groups; we must often use matrices. The group C_{3v} has three *irreducible representations*, or IR's, which cannot be broken down into simpler representations. A trivial, but nonetheless important, representation of any group is the *totally symmetric representation*, in which each group element is represented by 1. The multiplication table then simply reiterates that $1 \times 1 = 1$. For C_{3v} this is called the A_1 representation:

$$A_1 : E = 1, C_3 = 1, C_3^2 = 1, \sigma_1 = 1, \sigma_2 = 1, \sigma_3 = 1 \tag{1.12.9}$$

A slightly less trivial representation is A_2:

$$A_2 : E = 1, C_3 = 1, C_3^2 = 1, \sigma_1 = -1, \sigma_2 = -1, \sigma_3 = -1 \tag{1.12.10}$$

Much more exciting is the E representation, which requires 2×2 matrices:

$$\begin{gathered}
E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \\
C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \sigma_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \\
\sigma_2 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}
\end{gathered} \tag{1.12.11}$$

The operations C_3 and C_3^2 are said to belong to the same *class* since they perform the same geometric function, but for different orientations in space. Analogously, σ_1, σ_2 and σ_3 are obviously in the same class. E is in a class by itself. The class structure of the group is designated by $\{E, 2C_3, 3\sigma_v\}$. We state without proof that the number of irreducible representations of a group is equal to the number of classes. Another important theorem states that the sum of the squares of the dimensionalities of the irreducible representations of a group adds up to the order of the group. Thus, for C_{3v}, we find $1^2 + 1^2 + 2^2 = 6$.

The *trace* or *character* of a matrix is defined as the sum of the elements along the main diagonal:

$$\chi(M) \equiv \sum_k M_{kk} \tag{1.12.12}$$

For many purposes, it suffices to know just the characters of a matrix representation of a group, rather than the complete matrices. For example, the characters for the E representation of C_{3v} in Eq (4) are given by

$$\begin{gathered}\chi(E)=2, \quad \chi(C_3)=-1, \quad \chi(C_3^2)=-1, \\ \chi(\sigma_1)=0, \quad \chi(\sigma_2)=0, \quad \chi(\sigma_3)=0\end{gathered} \tag{1.12.13}$$

It is true in general that the characters for all operations in the same class are equal. Thus Eq (6) can be abbreviated to

$$\chi(E)=2, \quad \chi(C_3)=-1, \quad \chi(\sigma_v)=0 \tag{1.12.14}$$

For one-dimensional representations, such as A_1 and A_2, the characters are equal to the matrices themselves, so Equations 1.12.9 and 1.12.10can be read as a table of characters.

The essential information about a symmetry group is summarized in its *character table*. We display here the character table for C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	$(xy, x^2-y^2), (xz, yz)$

(1.12.15)

The last two columns show how the cartesian coordinates x, y, z and their products transform under the operations of the group.

Group Theory and Quantum Mechanics

When a molecule has the symmetry of a group $\mathcal{G}$, this means that each member of the group commutes with the molecular Hamiltonian

$$[\hat{G}_i, \hat{H}]=0 \quad i=1\ldots h \tag{1.12.16}$$

where we now explicitly designate the group elements G_i as operators on wavefunctions. As was shown in Chap. 4, commuting operators can have simultaneous eigenfunctions. A representation of the group of dimension d means that there must exist a set of d degenerate eigenfunctions of $\hat{H}$ that transform among themselves in accord with the corresponding matrix representation. For example, if the eigenvalue E_n is d-fold degenerate, the commutation conditions (Equation 1.12.9) imply that, for $i=1\ldots h$,

$$\hat{G}_i\hat{H}\psi_{nk}=\hat{H}\hat{G}_i\psi_{nk}=E_n\hat{G}_i\psi_{nk} \text{ for } k=1\ldots d \tag{1.12.17}$$

Thus each $\hat{G}_i\psi_{nk}$ is also an eigenfunction of $\hat{H}$ with the same eigenvalue E_n, and must therefore be represented as a linear combination of the eigenfunctions ψ_{nk}. More precisely, the eigenfunctions transform among themselves according to

$$\hat{G}_i\psi_{nk}=\sum_{m=1}^{d} D(G_i)_{km}\psi_{nm} \tag{1.12.18}$$

where $D(G_i)_{km}$ means the $\{k,m\}$ element of the matrix representing the operator $\hat{G}_i$.

The character of the identity operation E immediately shows the degeneracy of the eigenvalues of that symmetry. The C_{3v} character table reveals that NH_3, and other molecules of the same symmetry, can have only nondegenerate and two-fold degenerate energy levels. The following notation for symmetry species was introduced by Mulliken:

I. One dimensional representations are designated either A or B. Those symmetric wrt rotation by $2\pi/n$ about the C_n principal axis are labeled A, while those antisymmetric are labeled B.
II. Two dimensional representations are designated E; 3, 4 and 5 dimensional representations are designated T, F and G, respectively. These latter cases occur only in groups of high symmetry: cubic, octahedral and icosohedral.
III. In groups with a center of inversion, the subscripts g and u indicate even and odd parity, respectively.
IV. Subscripts 1 and 2 indicate symmetry and antisymmetry, respectively, wrt a C_2 axis perpendicular to C_n, or to a σ_v plane.
V. Primes and double primes indicate symmetry and antisymmetry to a σ_h plane.

For individual orbitals, the lower case analogs of the symmetry designations are used. For example, MO's in ammonia are classified a_1, a_2 or e.

For ammonia and other C_{3v} molecules, there exist three species of eigenfunctions. Those belonging to the classification A_1 are transformed into themselves by all symmetry operations of the group. The 1s, 2s and $2p_z$ AO's on nitrogen are in this category. The z-axis is taken as the 3-fold axis. There are no low-lying orbitals belonging to A_2. The nitrogen $2p_x$ and $2p_y$ AO's form a two-dimensional representation of the group C_{3v}. That is to say, any of the six operations of the group transforms either one of these AO's into a linear combination of the two, with coefficients given by the matrices (4). The three hydrogen 1s orbitals transform like a 3×3 representation of the group. If we represent the hydrogens by a column vector {H1,H2,H3}, then the six group operations generate the following algebra

$$\begin{array}{cc} E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \\ C_3^2 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} & \sigma_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \sigma_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} & \sigma_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array} \tag{1.12.19}$$

Let us denote this representation by Γ. It can be shown that Γ is a *reducible* representation, meaning that by some unitary transformation the 3×3 matrices can be factorized into blockdiagonal form with 2×2 plus 1×1 submatrices. The reducibility of Γ can be deduced from the character table. The characters of the matrices (Equation 1.12.19) are

$$\Gamma: \qquad \chi(E) = 3, \quad \chi(C_3) = 0, \quad \chi_{(}\sigma_v) = 1 \tag{1.12.20}$$

The character of each of these permutation operations is equal to the number of H atoms left untouched: 3 for the identity, 1 for a reflection and 0 for a rotation. The characters of Γ are seen to equal the sum of the characters of A_1 plus E. This reducibility relation is expressed by writing

$$\Gamma = A_1 \oplus E \tag{1.12.21}$$

The three H atom 1s functions can be combined into LCAO functions which transform according to the IR's of the group. Clearly the sum

$$\psi = \psi_{1s}(1) + \psi_{1s}(2) + \psi_{1s}(3) \tag{1.12.22}$$

transforms like A_1. The two remaining linear combinations which transform like E must be orthogonal to (Equation 1.12.22) and to one another. One possible choice is

$$\psi' = \psi_{1s}(2) - \psi_{1s}(3), \quad \psi'' = 2\psi_{1s}(1) - \psi_{1s}(2) - \psi_{1s}(3) \tag{1.12.23}$$

Now, Equation 1.12.22can be combined with the N 1s, 2s and $2p_z$ to form MO's of A_1 symmetry, while Equation 1.12.23can be combined with the N $2p_x$ and $2p_y$ to form MO's of E symmetry. Note that no hybridization of AO's is predetermined, it emerges automatically in the results of computation.

Contributors and Attributions

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1.13: Molecular Spectroscopy

Our most detailed knowledge of atomic and molecular structure has been obtained from spectroscopy-study of the emission, absorption and scattering of electromagnetic radiation accompanying transitions among atomic or molecular energy levels. Whereas atomic spectra involve only electronic transitions, the spectroscopy of molecules is more intricate because vibrational and rotational degrees of freedom come into play as well. Early observations of absorption or emission by molecules were characterized as band spectra-in contrast to the line spectra exhibited by atoms. It is now understood that these bands reflect closely-spaced vibrational and rotational energies augmenting the electronic states of a molecule. With improvements in spectroscopic techniques over the years, it has become possible to resolve individual vibrational and rotational transitions. This has provided a rich source of information on molecular geometry, energetics and dynamics. Molecular spectroscopy has also contributed significantly to analytical chemistry, environmental science, astrophysics, biophysics and biochemistry.

Reduced Mass

Consider a system of two particles of masses m_1 and m_2 interacting with a potential energy which depends only on the separation of the particles. The classical energy is given by

$$E=\frac{1}{2}m_1\dot{\vec{r}}_1^{\,2}+\frac{1}{2}m_2\dot{\vec{r}}_2^{\,2}+V(|\vec{r}_2-\vec{r}_1|) \tag{1.13.1}$$

the dots signifying derivative wrt time. Introduce two new variables, the particle separation $\vec{r}$ and the position of the center of mass $\vec{R}$:

$$\vec{r}=\vec{r}_2-\vec{r}_1, \qquad \vec{R}=\frac{m_1\vec{r}_1+m_2\vec{r}_2}{m} \tag{1.13.2}$$

where $m=m_1+m_2$. In terms of the new coordinates

$$\vec{r}_1=\vec{R}+\frac{m_2}{m}\vec{r}, \qquad \vec{r}_2=\vec{R}-\frac{m_1}{m}\vec{r} \tag{1.13.3}$$

and

$$E=\frac{1}{2}m\dot{\vec{R}}^2+\frac{1}{2}\mu\dot{\vec{r}}^2+V(r) \tag{1.13.4}$$

where $r=|\vec{r}|$ and μ is called the $reduced\ mass$

$$\mu\equiv\frac{m_1m_2}{m_1+m_2} \tag{1.13.5}$$

An alternative relation for reduced mass is

$$\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2} \tag{1.13.6}$$

reminiscent of the formula for resistance of a parallel circuit. Note that, if $m_2\to\infty$, then $\mu\to m_1$. The term containing $\dot{\vec{R}}$ represents the kinetic energy of a single hypothetical particle of mass μ located at the center of mass $\vec{R}$. The remaining terms represent the $relative$ motion of the two particles. It was the appearance of a $single$ particle of effective mass μ moving in the potential field $V(r)$.

$$E_{rel}=\frac{1}{2}\mu\dot{\vec{r}}^2+V(r)=\frac{\vec{p}^2}{2\mu}+V(r) \tag{1.13.7}$$

We can thus write the Schrödinger equation for the relative motion

$$\left\{-\frac{\hbar^2}{2\mu}\bigtriangledown^2+V(r)\right\}\psi(\vec{r})=E\psi(\vec{r}) \tag{1.13.8}$$

When we treated the hydrogen atom, it was assumed that the nuclear mass was infinite. In that case we can set $\mu=m$, the mass of an electron. The Rydberg constant for infinite nuclear mass was calculated to be

$$R_\infty = \frac{2\pi^2 me^4}{h^3 c} = 109,737\mathrm{cm}^{-1} \tag{1.13.9}$$

If instead, we use the reduced mass of the electron-proton system

$$\mu = \frac{mM}{m+M} \approx \frac{1836}{1837} m \approx 0.999456\, m \tag{1.13.10}$$

.

This changes the Rydberg constant for hydrogen to

$$R_H \approx 109,677\, cm^{-1} \tag{1.13.11}$$

in perfect agreement with experiment.

In 1931, H. C. Urey evaporated four liters of hydrogen down to one milliliter and measured the spectrum of the residue. The result was a set of lines displaced slightly from the hydrogen spectrum. This amounted to the discovery of deuterium, or heavy hydrogen, for which Urey was awarded in 1934 Nobel Prize in Chemistry. Estimating the mass of the deuteron, $^2H_1$, as twice that of the proton, gives

$$R_D \approx 109,707\, cm^{-1} \tag{1.13.12}$$

Another interesting example involving reduced mass concerns positronium, a short-lived combination of an electron and a positron-the electron's antiparticle. The electron and position mutually annihilate with a half-life of approximately 10^{-7} sec. and positroium decays into gamma rays. The reduced mass of positronium is

$$\mu = \frac{m \times m}{m+m} = \frac{m}{2} \tag{1.13.13}$$

half the mass of the electron. Thus the ionization energy equals 6.80 eV, half that of hydrogen atom. Positron emission tomography (PET) provides a sensitive scanning technique for functioning living tissue, notably the brain. A compound containing a positron-emitting radionuclide, for example, ^{11}C, ^{13}N, ^{15}O or ^{18}F, is injected into the body. The emitted positrons attach to electrons to form short-lived positronium, and the annihilation radiation is monitored.

Vibration of Diatomic Molecules

A diatomic molecule with nuclear masses M_A, M_B has a reduced mass

$$\mu = \frac{M_A M_B}{M_A + M_B} \tag{1.13.14}$$

Figure 1. Jens Zorn sculpture depicting positronium annihilation. Outside University of Michigan Physics Building.

Solution of the electronic Schrödinger equation gives the energy as a function of internuclear distance E_{elec}(R). This plays the role of a potential energy function for motion of the nuclei V(R), as sketched in Fig. 2. We can thus write the Schrödinger equation for vibration

$$\left\{ -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V(R) \right\} \chi(R) = E_\chi(R) \tag{1.13.15}$$

If the potential energy is expanded in a Taylor series about R = R_e

$$V(R) = V(R_e) + (R - R_e)V'(R_e) + \frac{1}{2}(R - R_e)^2 V\,''\,(R_e) + \ldots \tag{1.13.16}$$

An approximation for this expansion has the form of a harmonic oscillator with

$$V(R) \approx \frac{1}{2}k(R-R_e)^2 \tag{1.13.17}$$

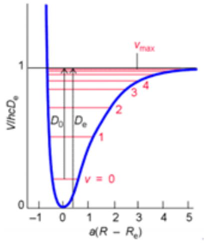


Figure 2. Vibrational energies of a diatomic molecule, as approximated by a Morse oscillator.

The energy origin can be chosen so V (R_e) = 0. At the minimum of the potential, V'(R_e) = 0. The best fit to the parabola (17) is obtained with a force constant set equal to

$$k \approx \frac{d^2V(R)}{dR^2}|_{R=R_e} \tag{1.13.18}$$

From the solution for the harmonic oscillator, we identify the ground state vibrational energy, with quantum number $\nu = 0$

$$E_0 = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}} \tag{1.13.19}$$

The actual dissociation energy from the ground vibrational state is then approximated by

$$D_0 \approx D_e - \frac{1}{2}\hbar\omega \tag{1.13.20}$$

In wavenumber units

$$hcD_0 \approx hcD_e - \frac{1}{2}\tilde{\nu}\ cm^{-1} \tag{1.13.21}$$

An improved treatment of molecular vibration must account for *anharmonicity*, deviation from a harmonic oscillator. Anharmonicity results in a finite number of vibrational energy levels and the possibility of dissociation of the molecule at sufficiently high energy. A very successful approximation for the energy of a diatomic molecule is the Morse potential:

$$V(R) = hcD_e\{\,1 - e^{a(R-R_e)}\,\}^2 \quad a = \left(\frac{\mu\omega^2}{2hcD_e}\right)^{\frac{1}{2}} \tag{1.13.22}$$

Note that V (R_e) = 0 at the minimum of the potential well. The Schrödinger equation for a Morse oscillator can be solved to give the energy levels

$$E_v = (v+\frac{1}{2})\hbar\omega - (v+\frac{1}{2})^2\hbar\omega x_e \tag{1.13.23}$$

or, expressed in wavenumber units,

$$hcE_v = (v+\frac{1}{2})\tilde{\nu} - (v+\frac{1}{2})^2 x_e\tilde{\nu} \tag{1.13.24}$$

Higher vibrational energy levels are spaced closer together, just as in real molecules. Vibrational transitions of diatomic molecules occur in the infrared, roughly in the range of 50-12,000 cm^{-1}. A molecule will absorb or emit radiation only if it has a non-zero dipole moment. Thus HCl is *infrared active* while H_2 and Cl_2 are not.

Vibration of Polyatomic Molecules

A molecule with N atoms has a total of 3N degrees of freedom for its nuclear motions, since each nucleus can be independently displaced in three perpendicular directions. Three of these degrees of freedom correspond to translational motion of the center of mass. For a nonlinear molecule, three more degrees of freedom determine the orientation of the molecule in space, and thus its rotational motion. This leaves 3N - 6 vibrational modes. For a linear molecule, there are just two rotational degrees of freedom, which leaves 3N - 5 vibrational modes. For example, the nonlinear molecule H_2O has three vibrational modes while the linear molecule CO_2 has four vibrational modes. The vibrations consist of coordinated motions of several atoms in such a way as to keep the center of mass stationary and nonrotating. These are called the *normal modes*. Each normal mode has a characteristic resonance frequency $\tilde{\nu}_i$, which is usually determined experimentally. To a reasonable approximation, each normal mode behaves as an independent harmonic oscillator of frequency $\tilde{\nu}_i$. The normal modes of H_2O and CO_2 are pictured below.

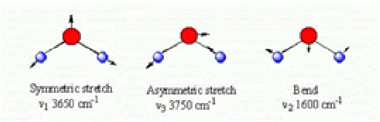


Figure 3. Normal modes of H_2O.

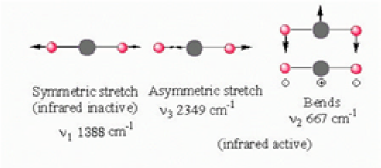


Figure 4. Normal modes of CO_2.

A normal mode will be infrared active only if it involves a change in the dipole moment. All three modes of H_2O are active. The symmetric stretch of CO_2 is inactive because the two C-O bonds, each of which is polar, exactly compensate. Note that the bending mode of CO_2 is doubly degenerate. Bending of adjacent bonds in a molecule generally involves less energy than bond stretching, thus bending modes generally have lower wavenumbers than stretching modes.

Rotation of Diatomic Molecules

The rigid rotor model assumes that the internuclear distance *R* is a constant. This is not a bad approximation since the amplitude of vibration is generally of the order of 1% of *R*. The Schrödinger equation for nuclear motion then involves the three-dimensional angular momentum operator, written $\hat{J}$ rather than $\hat{L}$ when it refers to molecular rotation. The solutions to this equation are already known and we can write

$$\frac{\hat{J}^2}{2\mu R^2} Y_{JM}(\theta,\phi) = E_J Y_{JM}(\theta,\phi) \quad J = 0,1,2\ldots \quad M = 0,\pm 1\ldots \pm J \tag{1.13.25}$$

where $Y_{JM}(\theta,\phi)$ are spherical harmonics in terms of the quantum numbers *J* and *M*, rather than *l* and *m*. Since the eigenvalues of $\hat{J}^2$ are $J(J+1)\hbar^2$, the rotational energy levels are

$$E_J = \frac{\hbar^2}{2I} J(J+1) \tag{1.13.26}$$

The moment of inertia is given by

$$I = \mu R^2 = M_A R_A^2 + M_B R_B^2 \tag{1.13.27}$$

where R_A and R_B are the distances from nuclei A and B, respectively, to the center of mass. In wavenumber units, the rotational energy is expressed

$$hcE_J = BJ(J+1)cm^{-1} \tag{1.13.28}$$

where *B* is the rotational constant. The rotational energy-level diagram is shown in Fig.5. Each level is (2J + 1)-fold degenerate. Again, only polar molecules can absorb or emit radiation in the course of rotational transitions. The radiation is in the microwave or far infrared region. The selection rule for rotational transitions is ΔJ = ±1.

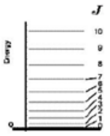
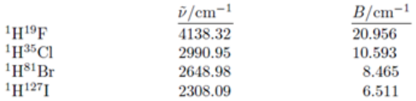


Figure 5. Rotational Energies
$hcE_J = BJ(J+1)$

Molecular Parameters from Spectroscopy

Following is a table of spectroscopic constants for the four hydrogen halides:



	$\tilde{\nu}/\mathrm{cm}^{-1}$	B/cm^{-1}
$^1H^{19}F$	4138.32	20.956
$^1H^{35}Cl$	2990.95	10.593
$^1H^{81}Br$	2648.98	8.465
$^1H^{127}I$	2308.09	6.511

The force constant can be found from the vibrational constant. Equating the energy quantities $\hbar\omega = hc\tilde{\nu}$, we find

$$\omega = 2\pi c\tilde{\nu} = \sqrt{\frac{k}{\mu}} \tag{1.13.29}$$

Thus

$$k = (2\pi c\tilde{\nu})^2\mu \tag{1.13.30}$$

with

$$\mu = \frac{m_A m_B}{m_A + m_B} = \frac{M_A M_B}{M_A + M_B} u \tag{1.13.31}$$

where u = 1.66054 x 10^{-27} kg, the atomic mass unit. M_A and M_B are the conventional atomic weights of atoms A and B (on the scale $^{12}C = 12$). Putting in numerical factors

$$k = 58.9 \times 10^{-6}(\tilde{\nu}/cm^{-1})^2 \frac{M_A M_B}{M_A + M_B} N/m \tag{1.13.32}$$

This gives 958.6, 512.4, 408.4 and 311.4 N/m for HF, HCl, HBr and HI, respectively. These values do *not* take account of anharmonicity.

The internuclear distance *R* is determined by the rotational constant. By definition,

$$hcB = \frac{\hbar^2}{2I} \tag{1.13.33}$$

Thus

$$B = \frac{\hbar}{4\pi c I} \tag{1.13.34}$$

with

$$I = \mu R^2 = \frac{m_A m_B}{m_A + m_B} R^2 = \frac{M_A M_B}{M_A + M_B} u R^2 \;\; kg\, m^2 \tag{1.13.35}$$

Solving for R,

$$R = 410.6 / \sqrt{\frac{M_A M_B}{M_A + M_B}(B/cm^{-1})} \;\, pm \tag{1.13.36}$$

For the hydrogen halides, HF, HCl, HBr, HI, we calculate *R* = 92.0, 127.9, 142.0, 161.5 pm, respectively.

Rotation of Nonlinear Molecules

A nonlinear molecule has three moments of inertia about three principal axes, designated I_a, I_b and I_c. The classical rotational energy can be written

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{1.13.37}$$

where J_a, J_b, J_c are the components of angular momentum about the principal axes. For a spherical rotor, such as CH_4 or SF_6, the three moments of inertia are equal to the same value I. The energy simplifies to $J^2/2I$ and the quantum-mechanical Hamiltonian is given by

$$\hat{H} = \frac{\hat{J}^2}{2I} \tag{1.13.38}$$

The eigenvalues are

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2.. \tag{1.13.39}$$

just as for a linear molecule. But the levels of a spherical rotor have degeneraciesof $(2J + 1)^2$ rather than $(2J + 1)$.

A symmetric rotor has two equal moments of inertia, say $I_c = I_b \neq I_a$. The molecules NH_3, CH_3Cl and C_6H_6 are examples. The Hamiltonian takes the form

$$\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2 + \hat{J}_c^2}{2I_b} = \frac{\hat{J}^2}{2I_b} + \left(\frac{1}{2I_a} - \frac{1}{2I_b}\right)\hat{J}_a^2 \tag{1.13.40}$$

Since it is possible to have simultaneous eigenstates of $\hat{J}^2$ and one of its components $\hat{J}_a$, the energies of a symmetric rotor have the form

$$E_{JK} = \frac{J(J+1)}{2I_b} + \left(\frac{1}{2I_a} - \frac{1}{2I_b}\right)K^2 \quad J = 0, 1, 2... \quad K = 0 \pm 1, \pm 2, \ldots \pm J \tag{1.13.41}$$

There is, in addition, the $(2J + 1)$-fold M degeneracy.

Electronic Excitations in Diatomic Molecules

The quantum states of molecules are composites of rotational, vibrational and electronic contributions. The energy spacing characteristic of these different degrees of freedom vary over many orders of magnitude, giving rise to very different spectroscopic techniques for studying rotational, vibrational and electronic transitions. Electronic excitations are typically of the order of several electron volts, 1 eV being equivalent to approximately 8000 cm^{-1} or 100 kJ mol^{-1}. As we have seen, typical energy differences are of the order of 1000 cm^{-1} for vibration and 10 cm^{-1} for rotation. Fig. 6 gives a general idea of the relative magnitudes of these energy contributions. Each electronic state has a vibrational structure, characterized by vibrational quantum numbers v and each vibrational state has a rotational structure, characterized by rotational quantum numbers J and M.

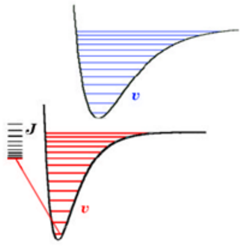


Figure 6. Schematic representation of the electronic ground state and an excited state of a diatomic molecule. Vibrational levels of the ground state are shown in red, those of the excited state, in blue. The rotational levels for $v = 0$ are also shown.

Every electronic transition in a molecule is accompanied by changes in vibrational and rotational states. Generally, in the liquid state, individual vibrational transitions are not resolved, so that electronic spectra consist of broad bands comprising a large number of overlapping vibrational and rotational transitions. Spectroscopy on the gas phase, however, can often resolve individual vibrational and even rotational transitions.

When a molecule undergoes a transition to a different electronic state, the electrons rearrange themselves much more rapidly than the nuclei. To a very good approximation, the electronic state can be considered to occur instantaneously, while the nuclear configuration remains fixed. This is known as the *Franck-Condon principle*. It has the same physical origin as the Born-Oppenheimer approximation, namely the great disparity in the electron and nuclear masses. On a diagram showing the energies of the ground and excited states as functions of internuclear distance, Franck-Condon behavior is characterized by *vertical transitions*, in which *R* remains approximately constant as the molecule jumps from one potential curve to the other.

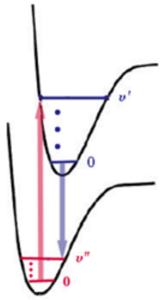


Figure 7. Franck-Condon principle

In a vibrational state $v = 0$ the maximum of probability for the internuclear distance R is near the center of the potential well. For all higher values vibrational states, maxima of probability occur near the two turning points of the potential-where the total energy equals the potential energy. These correspond on the diagrams to the end points of the horizontal dashes inside the potential curve.

Contributors and Attributions

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1.14: Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a versatile and highly-sophisticated spectroscopic technique which has been applied to a growing number of diverse applications in science, technology and medicine. This chapter will consider, for the most part, magnetic resonance involving protons.

Magnetic Properties of Nuclei

In all our previous work, it has been sufficient to treat nuclei as structureless point particles characterized fully by their mass and electric charge. On a more fundamental level, as was discussed in Chap. 1, nuclei are actually composite particles made of nucleons (protons and neutrons) and the nucleons themselves are made of quarks. The additional properties of nuclei which will now become relevant are their spin angular momenta and magnetic moments. Recall that electrons possess an intrinsic or spin angular momentum s which can have just two possible projections along an arbitrary spacial direction, namely $\pm\frac{1}{2}\hbar$. Since $\hbar$ is the fundamental quantum unit of angular momentum, the electron is classified as a particle of spin one-half. The electron's spin state is described by the quantum numbers $s = 1$ and $m_s = \pm 1$. A circulating electric charge produces a magnetic moment $\vec{\boldsymbol{\mu}}$ proportional to the angular momentum **J**. Thus

$$\vec{\mu} = \gamma \vec{J} \tag{1.14.1}$$

where the constant of proportionality γ is known as the magnetogyric ratio. The z-component of $\vec{\mu}$ has the possible values

$$\vec{\mu}_z = \gamma \hbar m_J \text{where} m_J = -J, -J+1, \ldots, +J \tag{1.14.2}$$

determined by space quantization of the angular momentum J. The energy of a magnetic dipole in a magnetic field B is given by

$$E = -\vec{\mu} \cdot \vec{B} = -\vec{\mu}_z B \tag{1.14.3}$$

where magnetic field defines the z-axis. The SI unit of magnetic field (more correctly, magnetic induction) is the tesla, designated T. Electromagnets used in NMR produce fields in excess of 10 T. Small iron magnets have fields around .01 T, while some magnets containing rare-earth elements such as NIB (niobium-iron-boron) reach 0.2 T. The Earth's magnetic field is approximately 5×10^{-5}T (0.5 gauss in alternative units), dependent on geographic location. At the other extreme, a neutron star, which is really a giant nucleus, has a field predicted to be of the order of 10^{8} T. The energy relation (3) determines the most conveniently units for magnetic moment, namely joules per tesla, J T^{-1}.

For orbital motion of an electron, where the angular momentum is l, the magnetic moment is given by

$$\vec{\mu}_z = -\frac{e\hbar}{2m} m_l = -\vec{\mu}_B m_l \tag{1.14.4}$$

where the minus sign reflects the *negative* electric charge. The Bohr *magneton* is defined by

$$\vec{\mu}_B = -\frac{e\hbar}{2m} = 9.274 \times 10^{-24} J T^{-1} \tag{1.14.5}$$

The magnetic moment produced by electron spin is written

$$\vec{\mu}_z = -g \vec{\mu}_B m_s \tag{1.14.6}$$

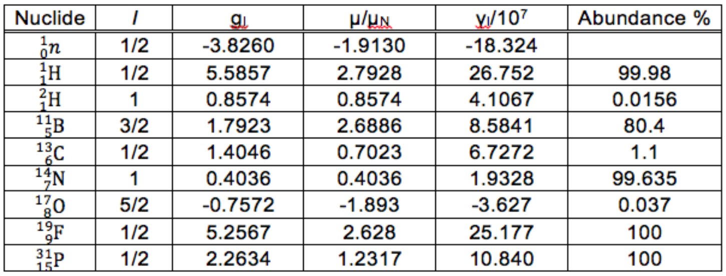
with introduction of the g-factor. Eq (4) implies g = 1 for orbital motion. For electron spin, however, g = 2 (more exactly, 2.0023). The factor 2 compensates for ms = 1 such that spin and *l* = 1 orbital magnetic moments 2 are both equal to one Bohr magneton.

Many nuclei possess spin angular momentum, analogous to that of the electron. The nuclear spin, designated *I*, has an integral or half-integral value: 0, 1 , 1, 3 , and so on. **Table 1** lists some nuclei of importance in chemical applications of NMR. The proton and the neutron both are spin 2 particles, like the electron. Complex nuclei have angular momenta which are resultants of the spins of their component nucleons. The deuteron ^{2}H, with *I* = 1, evidently has parallel proton and neutron spins. The ^{4}He nucleus has *I* = 0, as do ^{12}C, ^{16}O, ^{20}Ne, ^{28}Si and ^{32}S. These nuclei contain filled shells of protons and neutrons with the vector sum of the component angular momenta equal to zero, analogous to closed shells of electrons in atoms and molecules. In fact, all even-even nuclei have spins of zero. Nuclear magnetic moments are of the order of a *nuclear magneton*

$$\vec{\mu}_N = \frac{e\hbar}{2M} = 5.051 \times 10^{-27} J T^{-1} \tag{1.14.7}$$

where M is the mass of the proton. The nuclear magneton is smaller than the Bohr magneton by a factor m/M ≈ 1836.

Table 1: Some common nuclei in NMR spectroscopy



Nuclide	I	g_I	μ/μ_N	$\gamma_I/10^7$	Abundance %
^1_0n	1/2	-3.8260	-1.9130	-18.324	
^1_1H	1/2	5.5857	2.7928	26.752	99.98
^2_1H	1	0.8574	0.8574	4.1067	0.0156
$^{11}_5B$	3/2	1.7923	2.6886	8.5841	80.4
$^{13}_6C$	1/2	1.4046	0.7023	6.7272	1.1
$^{14}_7N$	1	0.4036	0.4036	1.9328	99.635
$^{17}_8O$	5/2	-0.7572	-1.893	-3.627	0.037
$^{19}_9F$	1/2	5.2567	2.628	25.177	100
$^{31}_{15}P$	1/2	2.2634	1.2317	10.840	100

In analogy with Equations 1.14.2 and 1.14.6, nuclear moments are represented by

$$\vec{\mu}_z = g_I \vec{\mu}_N m_I = \hbar \gamma_I m_I \tag{1.14.8}$$

where g_I is the nuclear g-factor and γ_I, the magnetogyric ratio. Most nuclei have positive g-factors, as would be expected for a rotating positive electric charge. It was long puzzling that the neutron, although lacking electric charge, has a magnetic moment. It is now understood that the neutron is a composite of three charged quarks, *udd*. The negatively-charged d- quarks are predominantly in the outermost regions of the neutron, thereby producing a negative magnetic moment, like that of the electron. The g- factor for ^{17}O, and other nuclei dominated by unpaired neutron spins, is consequently also negative.

Nuclear Magnetic Resonance

The energy of a nuclear moment in a magnetic field, according to Equation 1.14.3, is given by

$$E_{m_I} = -\hbar \gamma_I m_I B \tag{1.14.9}$$

For a nucleus of spin I, the energy of a nucleus in a magnetic field is split into $2I+1$ Zeeman levels. A proton and other nuclei with spin $\frac{1}{2}$ particles will have just two possible levels:

$$E_{\pm\frac{1}{2}} = \pm\frac{1}{2}\hbar\gamma B \tag{1.14.10}$$

with the α-spin state ($m_I = -\frac{1}{2}$) lower in energy than the β-spin state ($m_I = +\frac{1}{2}$) by

$$\Delta E = \hbar \gamma B \tag{1.14.11}$$

Fig. 1 shows the energy of a proton as a function of magnetic field. In zero field (B = 0), the two spin states are degenerate. In a field B, the energy splitting corresponds to a photon of energy $\Delta E = \hbar\omega = h\nu$ where

$$\omega_L = \gamma_B \text{ or } \nu_L = \gamma_B \tag{1.14.12}$$

known as the Larmor frequency of the nucleus. For the proton in a field of 1 T, ν_L = 42.576 MHz, as the proton spin orientation flips from $+\frac{1}{2}$ to $-\frac{1}{2}$. This transition is in the radiofrequency region of the electromagnetic spectrum. NMR spectroscopy consequently exploits the technology of radiowave engineering.

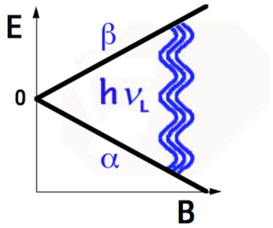


***Figure 1**. Energies of spin $\frac{1}{2}$ in magnetic field showing NMR transition at Larmor frequency ν_L.*

A transition cannot occur unless the values of the radiofrequency and the magnetic field accurately fulfill Eq (12). This is why the technique is categorized as a resonance phenomenon. If some resonance condition is not satisfied, no radiation can be absorbed or emitted by the nuclear spins. In the earlier techniques of NMR spectroscopy, it was found more convenient keep the radiofrequency fixed and sweep over values of the magnetic field B to detect resonances. These have been largely supplanted by modern pulse techniques, to be described later.

The transition probability for the upward transition (absorption) is equal to that for the downward transition (stimulated emission). (The contribution of spontaneous emission is neglible at radiofrequencies.) Thus if there were equal populations of nuclei in the α and β spin states, there would be zero net absorption by a macroscopic sample. The possibility of observable NMR absorption depends on the lower state having at least a slight excess in population. At thermal equilibrium, the ratio of populations follows a Boltzmann distribution

$$\frac{N_\beta}{N_\alpha} = \frac{e^{\frac{-E_\beta}{kT}}}{e^{\frac{-E_\alpha}{kt}}} = e^{-\frac{\hbar\gamma B}{kT}} \tag{1.14.13}$$

Thus the relative population difference is given by

$$\frac{\Delta N}{N_\alpha} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\hbar\gamma B}{2kT} \tag{1.14.14}$$

Since nuclear Zeeman energies are so small, the populations of the α and β spin states differ very slightly. For protons in a 1 T field, $\Delta N/N \approx 3\times10^{-6}$. Although the population excess in the lower level is only of the order of parts per million, NMR spectroscopy is capable of detecting these weak signals. Higher magnetic fields and lower temperatures are favorable conditions for enhanced NMR sensitivity.

The Chemical Shift

NMR has become such an invaluable technique for studying the structure of atoms and molecules because nuclei represent ideal noninvasive probes of their electronic environment. If all nuclei of a given species responded at their characteristic Larmor frequencies, NMR might then be useful for chemical analysis, but little else. The real value of NMR to chemistry comes from minute differences in resonance frequencies dependent on details of the electronic structure around a nucleus. The magnetic field induces orbital angular momentum in the electron cloud around a nucleus, thus, in effect, partially shielding the nucleus from the external field B. The actual or local value of the magnetic field at the position of a nucleus is expressed

$$B_{loc} = (1-\sigma)B \tag{1.14.15}$$

where the fractional reduction of the field is denoted by σ, the shielding constant, typically of the order of parts per million. The actual resonance frequency of the nucleus in its local environment is then equal to

$$\nu = (1-\sigma)\frac{\gamma B}{2\pi} \tag{1.14.16}$$

A classic example of this effect is the proton NMR spectrum of ethanol CH_3CH_2OH, shown in Fig. 2. The three peaks, with intensity ratios 3:2:1 can be identified with the three chemically-distinct environments in which the protons find themselves: three methyl protons (CH_3), two methylene protons (CH_2) and one hydroxyl proton (OH).

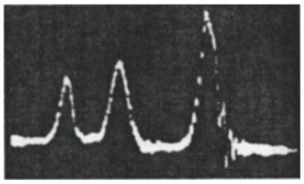


***Figure 2**. Oscilloscope trace showing the first NMR spectrum of ethanol, taken at Stanford University in 1951. Courtesy Varian Associates, Inc.*

The variation in resonance frequency due to the electronic environment of a nucleus is called the chemical shift. Chemical shifts on the delta scale are defined by

$$\delta = \frac{\nu - \nu^O}{\nu^O} \times 10^6 \tag{1.14.17}$$

where ν_o represents the resonance frequency of a reference compound, usually tetramethylsilane $Si(CH_3)_4$, which is rich in highly-shielded chemically-equivalent protons, as well as being unreactive and soluble in many liquids. By definition δ = 0 for TMS and almost everything else is “downfield” with positive values of δ. Most compounds have delta values in the range of 0 to 12 (hydrogen halides have negative values, e.g. δ ≈ −13 for HI). The hydrogen atom has δ ≈ 13 while the bare proton would have δ ≈ 31. Conventionally, the δ-scale is plotted as increasing from right to left, in the opposite sense to the magnitude of the magnetic field. Nuclei with larger values of δ are said to be more deshielded, with the bare proton being the ultimate limit. Fig. 3 shows some typical values of δ for protons in some common organic compounds.

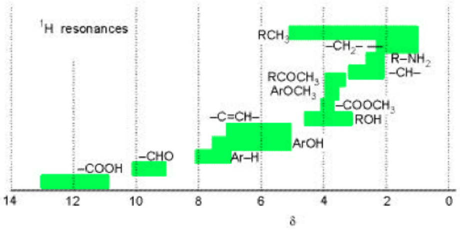


***Figure 3**. Ranges of proton chemical shifts for common functional groups. From P. Atkins, Physical Chemistry, (Freeman, New York, 2002).*

Fig. 4 shows a high-resolution NMR spectrum of ethanol, including a δ-scale. The “fine structure” splittings of the three chemically-shifted components will be explained in the next Section. The chemical shift of a nucleus is very difficult to treat theoretically. However, certain empirical regularities, for example those represented in Fig. 3, provide clues about the chemical environment of the nucleus. We will not consider these in any detail except to remark that often increased deshielding of a nucleus (larger δ) can often be attributed to a more electronegative neighboring atom. For example the proton in the ethanol spectrum (Fig. 4) with δ ≈ 5 can be identified as the hydroxyl proton, since the oxygen atom can draw significant electron density from around the proton.

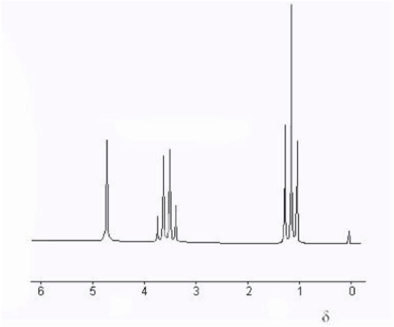


***Figure 4**. High-resolution NMR spectrum of ethanol showing δ scale of chemical shifts. The line at δ = 0 corresponds to the TMS trace added as a reference.*

Neighboring groups can also contribute to the chemical shift of a given atom, particularly those with mobile π-electrons. For example, the ring current in a benzene ring acts as a secondary source of magnetic field. Depending on the location of a nucleus, this can contribute either shielding or deshielding of the external magnetic field, as shown in Fig. 5. The interaction of neighboring groups can be exploited to obtain structural information by using lanthanide shift reagents. Lanthanides (elements 58 through 71) contain 4f-electrons, which are not usually involved in chemical bonding and can give large paramagnetic contributions. Lanthanide complexes which bind to organic molecules can thereby spread out pro- ton resonances to simplify their analysis. A popular chelating complex is Eu(dpm)3, tris(dipivaloylmethanato)europium, where dpm is the group $(CH_3)_3C–CO=CH–CO–C(CH_3)_3$.

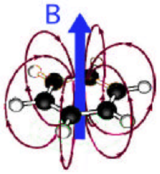
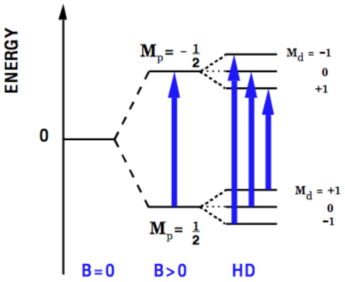


Figure 5. Magnetic field produced by ring current in benzene, shown as red loops. Where the arrows are parallel to the external field B, including protons directly attached to the ring, the effect is deshielding. However, any nuclei located within the return loops

will experience a shielding effect.

Spin-Spin Coupling

Two of the resonances in the ethanol spectrum shown in Fig. 4 are split into closely-spaced multiplets—one triplet and one quartet. These are the result of spin-spin coupling between magnetic nuclei which are relatively close to one another, say within two or three bond separations. Identical nuclei in identical chemical environments are said to be equivalent. They have equal chemical shifts and do not exhibit spin-spin splitting. Nonequivalent magnetic nuclei, on the other hand, can interact and thereby affect one another's NMR frequencies. A simple example is the HD molecule, in which the spin-1proton can interact with the spin-1 deuteron, even though the atoms are chemically equivalent. The proton's energy is split into two levels by the external magnetic field, as shown in Fig. 1. The neighboring deuteron, itself a magnet, will also contribute to the local field at the pro- ton. The deuteron's three possible orientations in the external field, with MI = −1,0,+1, with different contributions to the magnetic field at the proton, as shown in Fig. 6. The proton's resonance is split into three evenly spaced, equally intense lines (a triplet), with a separation of 42.9 Hz. Corespondingly the deuteron's resonance is split into a 42.9 Hz doublet by its interaction with the proton. These splittings are independent of the external field B, whereas chemical shifts are proportional to B. Fig. 6 represents the energy levels and NMR transitions for the proton in HD.



- ***Figure 6***. *Nuclear energy levels for proton in HD molecule. The two Zeeman levels of the proton when B > 0 are further split by interaction with the three possible spin orientations of the deuteron* M_d*= −1, 0, +1. The proton NMR transition, represented by blue arrows, is split into a triplet with separation 42.9 Hz.*

  Nuclear-spin phenomena in the HD molecule can be compactly represented by a spin Hamiltonian

$$\hat{H} = -\hbar\gamma_H M_H (1-\sigma_H) - \hbar\gamma_D M_D (1-\sigma_D) B + hJ_{HD} I_H \cdot I_D \tag{1.14.18}$$

- The shielding constants σ_H and σ_D are, in this case, equal since the two nuclei are chemically identical. For sufficiently large magnetic fields B, the last term is effectively equal to $hJ_{HD}M_HM_D$. The spin-coupling constant J can be directly equated to the splitting expressed in Hz. We consider next the case of two equivalent protons, for example, the CH_2 group of ethanol. Each proton can have two possible spin states with $M_I = \pm\frac{1}{2}$, giving a total of four composite spin states. Just as in the case of 2 electron spins, these combine to give singlet and triplet nuclear-spin states with M = 0 and 1, respectively. Also, just as for electron spins, transitions between singlet and triplet states are forbidden. The triplet state allows NMR transitions with $\Delta M = \pm 1$ to give a single resonance frequency, while the singlet state is inactive. As a consequence, spin-spin splittings do not occur among identical nuclei. For example, the H_2 molecule shows just a single NMR frequency. And the CH_2 protons in ethanol do not show spin- spin interactions with one another. They can however cause a splitting of the neighboring CH_3 protons. Fig. 7 (left side) shows the four possible spin states of two equivalent protons, such as those in the methylene group CH_2, and the triplet with intensity ratios 1:2:1 which these produce in nearby protons. Also shown (right side) are the eight possible spin states for three equivalent protons, say those in a methyl group CH_3, and the quartet with intensity ratios 1:3:3:1 which these produce. In general, n equivalent protons will give a splitting pattern of n + 1 lines in the ratio of binomial coefficients 1:n:n(n − 1)/2 . . . The tertiary hydrogen in isobutane $(CH_3)_3CH*$, marked with an asterisk, should be split into 10 lines by the 9 equivalent methyl protons.

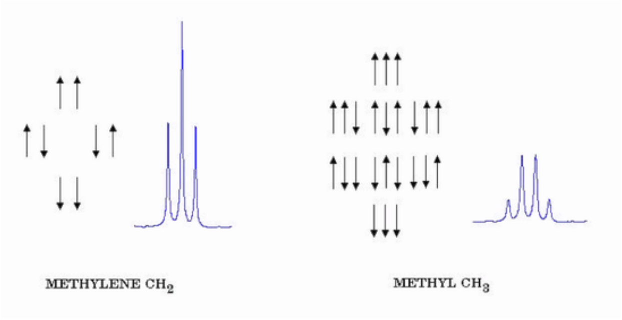
- 

Figure 7. *Splitting patterns from methylene and methyl protons.*

The NMR spectrum of ethanol CH_3CH_2OH (Fig. 4) can now be interpreted. The CH_3 protons are split into a 1:2:1 triplet by spin-spin interaction with the neighboring CH_2. Conversely, the CH_2 protons are split into a 1:3:3:1 quartet by interaction with the CH_3. The OH (hydroxyl) proton evidently does not either cause or undergo spin-spin splitting. The explanation for this is hydrogen bonding, which involves rapid exchange of hydroxyl protons among neighboring molecules. If this rate of exchange is greater than or comparable to the NMR radiofrequency, then the splittings will be "washed out." Only one line with a motion-averaged value of the chemical shift will be observed. NMR has consequently become a useful tool to study intramolecular motions.

Contributors and Attributions

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Index

Index

Glossary

Sample Word 1 | Sample Definition 1

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