Quantum Chemistry

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Contents

Chapter 1

Quantum Theory and The Wave Equation

In the last year of the nineteenth century, some experimental results concerned with thermal radiation were found to be incompatible with the theory of physics in those years. In order to overcome this difficulty, a new theory known as quantum theory was developed, and in the nineteen twenties, quantum mechanics was founded. The quantum theory was then applied to various problems in chemistry such as chemical bonding and chemical reactions, and today quantum chemistry has become an important field of chemistry.

In this chapter, we shall see the scope of quantum chemistry at first, and then interactions between charged particles as well as wave phenomena will be introduced as preliminary background of the theory. After learning a short history of the quantum theory, we shall study foundations of quantum mechanics.

1.1 What is quantum chemistry?

Quantum chemistry is an application of quantum mechanics to chemistry. Quantum chemistry enables us to understand and predict structures, properties, and reaction mechanisms in various substances. For these purposes, mathematical techniques are essential. Since electronic computers had not yet been created in the early days when quantum mechanics was born, the scope of chemical phenomena to which quantum chemistry can be applied in practice, was considerably limited to a very small range of problems. However, very rapid progress of modern computing instruments in recent years has prompted a remarkable extension of the scope of quantum chemistry. In this part, we shall see what can be clarified and predicted after having studied quantum chemistry.

(1) Origin of characteristics of chemical elements can be elucidated. (cf.$2.5, 2.6, 6.1, 6.2$)

There are several groups of elements with similar properties: alkali metals easily lose an electron (highly electropositive), halogens tend to accept an electron (highly electronegative), and noble gases are inert. Although periodic characteristics of elements are to be studied in middle or high school, how these properties of elements originate from natural laws cannot be explained at the level of school chemistry. There is an explanation that noble gases are inert because of their stable electron configurations. Why the electron configurations of noble gases are particularly stable? It was discovered in 1962 that even a noble gas can react to yield its compounds, though the fact is usually disregarded in school chemistry. Why can an "inert" noble gas undergo reactions? Are there any conditions for its reactivity? The origin of characteristic properties of chemical elements including the mysterious reactivity of noble gases can be elucidated with quantum mechanics.

(2) Molecular structures can be predicted. (cf. $4.4, 5.4$–5.7)

In every textbook for school chemistry, a chart of molecular structures such as fig:1.1 is shown. These structures were of course determined by experimental studies. Skeletal structures, such as a tetrahedron for methane, an isosceles triangle for water, and a hexagon with six equivalent CH bonds extending externally for benzene, are all very interesting. Why is methane not a cross?

Why is water not linear? Why in benzene do all CC bonds as well as all CH bonds have the same bond lengths? Such questions can be answered by quantum chemistry. Bond lengths and angles can be obtained by quantum chemical calculations.

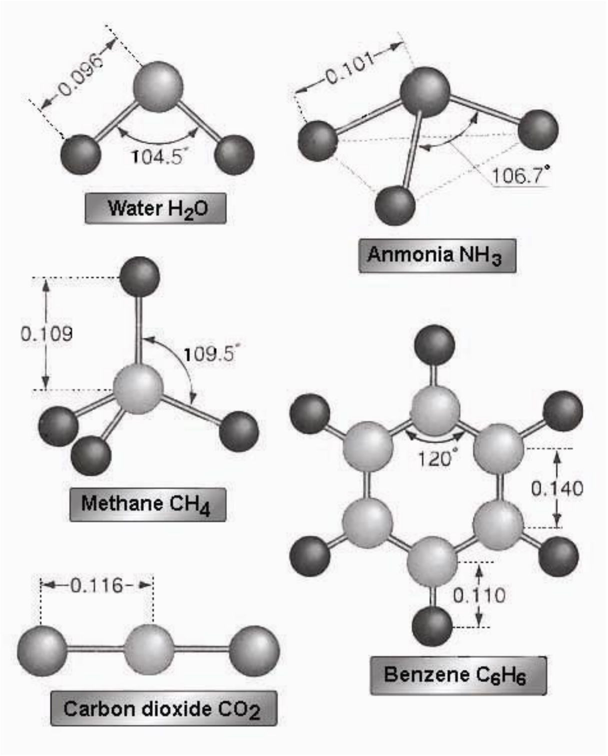


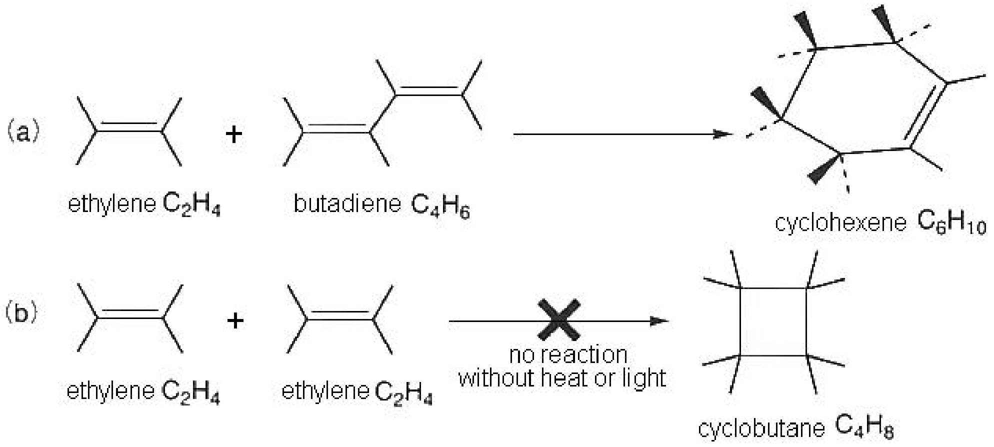
Figure 1.1: Skeletal structures of molecules. Numerical figures are bond lengths in nm and bond angles in degree.

(3) Molecular spectra can be predicted. (cf. 4. 4)
We can see vivid pictures demonstrating characteristic colors of various materials in textbooks for school chemistry. Colorful pictures on TV also are chemical products, controlled electrically. Colors of matter are inherently determined by spectra of light, i.e. by electromagnetic waves. The mechanisms by which colors are produced in solutions and solids containing molecules and ions can be understood by quantum chemistry. The wavelengths of infrared and microwave radiation that are absorbed or emitted by water and carbon monoxide molecules can be calculated by quantum chemical theories. By comparing observed spectra in interstellar space with quantum chemical calculations, molecules producing those spectra have been identified.

(4) Heats of reaction can be predicted (cf. 4. 4)
The heat of a chemical reaction need not necessarily be deduced from some data on reactions including related compounds and Hess's Law of Constant Heat Summation. Without experimental data, heats of chemical reactions can be obtained by quantum chemical calculations.

(5) What will be produced and how the reactions will proceed can be predicted (cf. 6. 3, 6. 4)
Vinyl compounds having a double bond undergo addition reactions or addition polymerization, as can be seen in a textbook for school chemistry. Polyethylene and polybutadiene are polymerized products of a single monomer unit of ethylene and butadiene, respectively. In 1928 it was discovered that a mixture of ethylene and butadiene leads to a unique production of a cyclohexene ring (Reaction Scheme I). Such a reaction is very useful to obtain a six-membered ring of carbon atoms, since the reaction easily occurs to yield the desired product selectively without useless consumption of the reactants. Why do ethylene molecules not easily react with each other to produce a four-membered cyclobutane ring (Reaction scheme Ib)? The explanation can be elucidated by

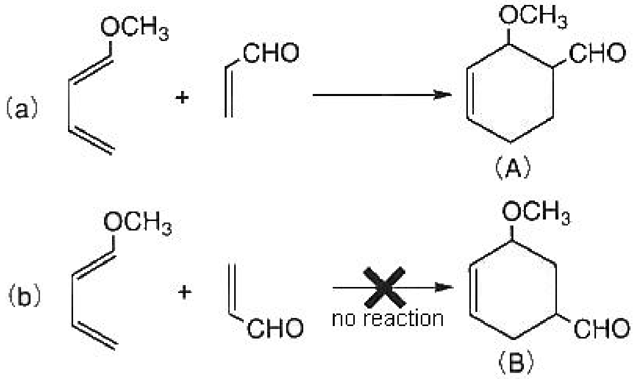
quantum chemical theory.



Reaction scheme I

(End-atoms are H atoms)

Moreover, two types of ring products (A) and (B) in the Reaction scheme II can be assumed to be produced from ethylene and butadiene derivatives in which a hydrogen atom is substituted by a formyl group (-CHO) and a methoxy group (-OCH_3), respectively. However, only (A) can be produced in the real reaction. If several products are formed, we need to make efforts to separate them with a considerable loss of reactants. Therefore, a reaction producing only one product is very useful in chemical synthesis. Quantum chemistry can provide theoretical designs of reaction schemes leading to selective production of compounds.



Reaction scheme II

(CH bonds are omitted)

The above examples are only part of the full range of modern applications of quantum chemistry. Recent developments in computing instruments have rapidly extended the applicable range of quantum chemistry. Mathematical and computing methods for quantum chemistry have been developed in various levels, from primitive and qualitative methods to the most sophisticated and very quantitative methods. In the 21st century, the applicable range of quantum chemistry will be continuously expanded to cover uncultivated areas.

1.2 Charged particles constituting matter and the Coulomb force

The elements of all matter are nuclei and electrons with positive and negative electric charges, respectively. Combinations and interactions of these particles give various structures, properties, and reactions of matter. First of all, it is important to understand fundamental aspects of electric interactions. An atom is composed of a nucleus and some electrons; the positive electric charge of the nucleus and the number of electrons surrounding the nucleus are both equal to the atomic number (Z). When an atom loses or gains an electron, it becomes a positive or negative ion, respectively. The tendency of an atom to become an ion by losing or gaining an electron is different depending on the kind of the chemical element classified by the atomic number. This tendency is closely related to the chemical properties of the element.

Example 1.1 Calculate e, the electric charge of an electron, using Faraday's constant of $96485\,\mathrm{C\,mol^{-1}}$ and Avogadro's constant of $6.022 \times 10^{23}\,\mathrm{mol^{-1}}$. (1 C is the electric charge that is carried by an electric current of 1 A for 1 s)

(Solution) The electric charge of 1 mole of electrons is $96485\,\mathrm{C\,mol^{-1}}$ from Faraday's constant, and the number of particles per 1 mol is from Avogadro's constant. Using these numbers, the electric charge of an electron is calculated as

$$e = \frac{96485\,\mathrm{C\,mol^{-1}}}{6.022 \times 10^{23}\,\mathrm{mol^{-1}}} = 1.602 \times 10^{-19}\,\mathrm{C}$$

In general, matter losing an electron carries a positive charge, and matter gaining an electron carries a negative charge. Matter carrying electric charges exert forces one another along the directions connecting them. A pair of charges with the same sign repel each other, and charges with opposite signs attract mutually. The force F exerted on the charges has a magnitude proportional to the product of the charges of Q_1 and Q_2 and inversely proportional to the square of the distance r. This is called Coulomb's law and expressed as

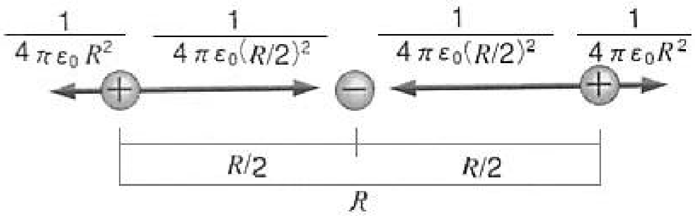
$$F = \frac{Q_1 \cdot Q_2}{4\pi\varepsilon_0 r^2} \tag{1.1}$$

Here, ε_0 is a fundamental physical constant called permittivity of vacuum (cf. Appendix 1).

Although Coulomb's law was discovered by observing forces between charged bodies, this law can also be applied to very small particles such as electrons and nuclei. Therefore, Coulomb's law is deeply related to atomic properties of both physical (e.g. color of absorbed and emitted light) and chemical (tendency of ionization and reactivity) types.

Particles with masses exert attractive forces known as universal gravitation toward one another. However, for particles with small masses such as electrons and molecular ions, gravitational forces are negligibly small in comparison with those given by Coulomb's law (Coulomb forces).

Example 1.2 When a unit negative charge is placed at the midpoint between a pair of unit positive charges separated by a distance R, which force acting on a positive charge is the larger, the force exerted by the negative charge or the force caused by the other positive charge? Find the direction to which the positive charge tends to move.



(Solution) A positive charge undergoes an attractive force of $F^- = -1/4\pi\varepsilon_0(R/2)^2$ by the negative charge placed at the distance of $R/2$ and a repulsive force of $F^+ = 1/4\pi\varepsilon_0 R^2$ by the other positive charge at the distance R. Since the former is 4 times larger than the latter, each positive charge tends to move toward the other positive charge. (By the action of the intervening negative charge, the positive charges tend to bind one to the other. This is related to the phenomenon that nuclei with positive charges can be held together under the action of electrons.)

When a charged particle is placed at a position between a pair of metallic plates with a certain electric potential difference (voltage), then a positive charge undergoes a force toward the plate of lower voltage and a negative charge toward the higher one. The magnitude of the force is proportional to the absolute value of the electric charge. Thus, under the same potential difference, the force acting on an electron and that on a monovalent positive ion have the same magnitude, though the directions are opposite.

When an electron in a resting state is accelerated from a metal plate of a low voltage to another metal plate of higher voltage with an electric potential difference of 1 volt (V), the kinetic energy of the electron becomes 1 electron volt (eV). The work to carry a positive electric charge of 1 Coulomb (C) up to a position where the voltage is 1 V higher than the starting point is 1 Joule (J), $1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$. A Brown tube for a TV set (cathode ray tube or CRT) is equipped with an electron gun (cathode) from which electrons are emitted and accelerated by a potential difference of ca. 10 kV. Such a beam of electrons is then focused onto the fluorescent screen by the action of an electron lens made of magnetic deflection coils and displays a spot of light emission.

Example 1.3 Calculate the velocity of an electron with a kinetic energy of 1 eV.

(Solution) The kinetic energy of an electron (mass of an electron is m) is expressed as $\frac{1}{2}mv^2$, and $1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$. Thus, $\frac{1}{2}mv^2 = 1.602 \times 10^{-19}\,\mathrm{J}$. By using the mass of electron $m = 9.109 \times 10^{-31}\,\mathrm{kg}$, the velocity of the electron v is obtained as

$$v = \left(\frac{2 \times 1.602 \times 10^{-19}}{9.109 \times 10^{-31}}\right)^{1/2} = 5.93 \times 10^5\,\mathrm{m\,s^{-1}}$$

As can be seen from the above Example 1, the velocity of an electron of 1 eV is about $600\,\mathrm{kms^{-1}}$. Velocities of ions, with a kinetic energy of 1 eV are considerably slower in comparison with the velocity of an electron. This is because the mass of an ion M is considerably larger than the mass of an electron m. Even for the lightest ion, i.e. a hydrogen ion (proton), M is ca. 1836 times larger than m. Hence, the velocity of a proton with a kinetic energy of 1 eV is about $1.38 \times 10^4\,\mathrm{m\,s^{-1}}$. Kinetic energy analyses (Velocity analyses) of electrons or ions ejected from sample materials are useful for studying their structures and masses.

1.3 Waves and oscillations

A basic equation for waves was utilized to discover the fundamental equation for quantum mechanics, which became the basis of quantum chemistry. Let us first consider basic properties of waves.

A typical wave depending on the position x and time t is expressed as the following sine wave.

$$\Psi(x,t) = A \sin 2\pi \left(\frac{x}{\lambda} - \frac{t}{T}\right) \tag{1.2}$$

Here, Ψ is a quantity indicating the displacement at the position x and time t, A is the amplitude, T is the frequency, λ is the wave length, and $2\pi\,(x/\lambda - t/T)$ is the phase of the wave. Time-development of this wave (Fig.2a) can be understood easily by considering the behavior at a given point, for example at $x = 0$. This wave oscillates in the range between $\pm A$, and its frequency per second is expressed as

$$\nu = \frac{1}{T} \tag{1.3}$$

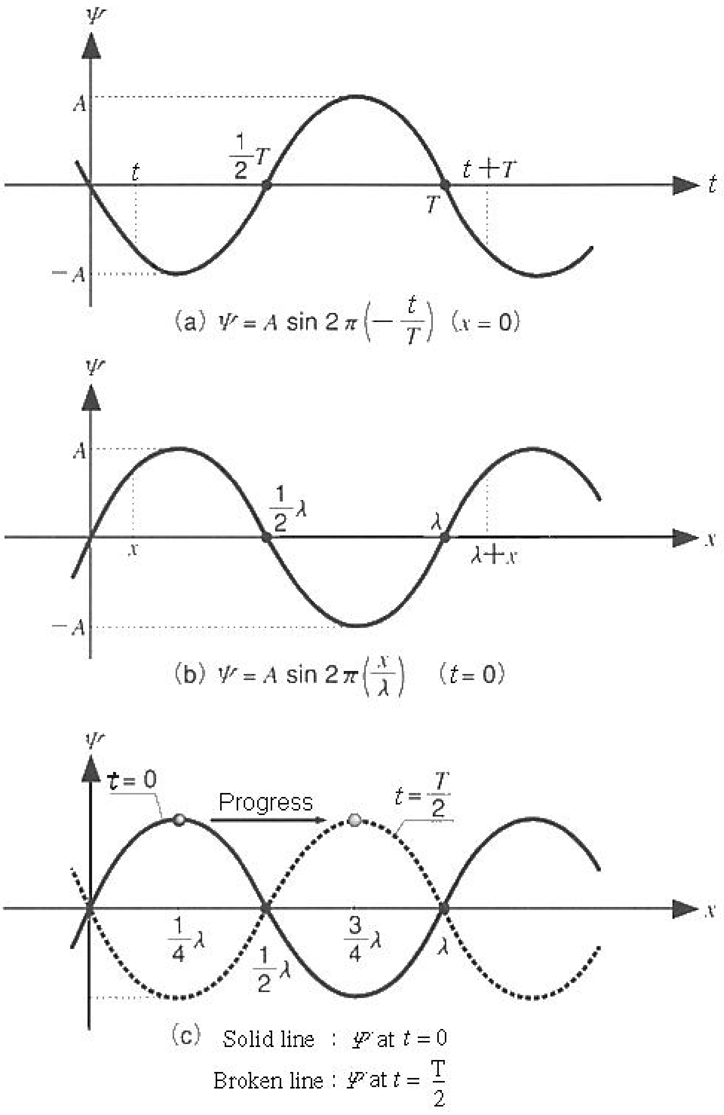


Figure 1.2: Sine waves

The unit for the frequency is s^{-1} or Hz (Hertz). The motion of the wave in the coordinate space at a given time (for example at $t = 0$) is shown in Fig.2b, in which periodic behavior of the wave can be seen with an interval of the wavelength λ. Considering a peak of the wave which should satisfy $\Psi = A$ in eq.(2), we obtain

$$2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right) = \frac{\pi}{2}$$

Thus, the value for x with this condition is given by

$$x(t) = \lambda\left(\frac{t}{T} + \frac{1}{4}\right)$$

The x-coordinate for the peak of the wave increases as function of time t as can be seen in Fig.2c. Therefore, this wave proceeds toward the positive direction along the x-axis. Since its velocity v is expressed as $v = dx/dt$, we obtain

$$v = \frac{\lambda}{T} \tag{1.4}$$

Using eq.(3), we obtain

$$v = \nu\lambda \tag{1.5}$$

This is the fundamental equation for a wave. A wave with a wavelength λ oscillating ν times per second reaches a position in a distance of $\nu\lambda$, which is the velocity of this wave. As for electromagnetic waves or light, the velocity v becomes the light velocity c, and we obtain

$$c = \nu\lambda \tag{1.6}$$

This is the fundamental equation of electromagnetic waves.

A mathematical relation for a complex number with an angle θ,

$$\exp(i\theta) = \cos\theta + i\sin\theta \tag{1.7}$$

can be used to extend a wave with a frequency ν and wavelength λ to a wave expressed by an exponential function with a complex value. Using eq.7 as well as $\theta = 2\pi(x/\lambda - t/T) = 2\pi(x/\lambda - \nu t)$, we obtain an equation for $\Psi = A\exp(i\theta)$.

$$\Psi(x,t) = A\exp 2\pi i\left(\frac{x}{\lambda} - \nu t\right) \tag{1.8}$$

This equation will be used later for introducing the fundamental equation of quantum mechanics.

Example 1.4 A carbon dioxide molecule absorbs infrared radiation with a wave number of $667\,\mathrm{cm}^{-1}$ (wave number is defined as the number of waves per unit length of 1 cm). Calculate the wavelength and the frequency of this wave.

(Solution) Using relations $\lambda\sigma = 1$ and $\lambda\nu = c$ among wave number σ, wavelength λ, frequency

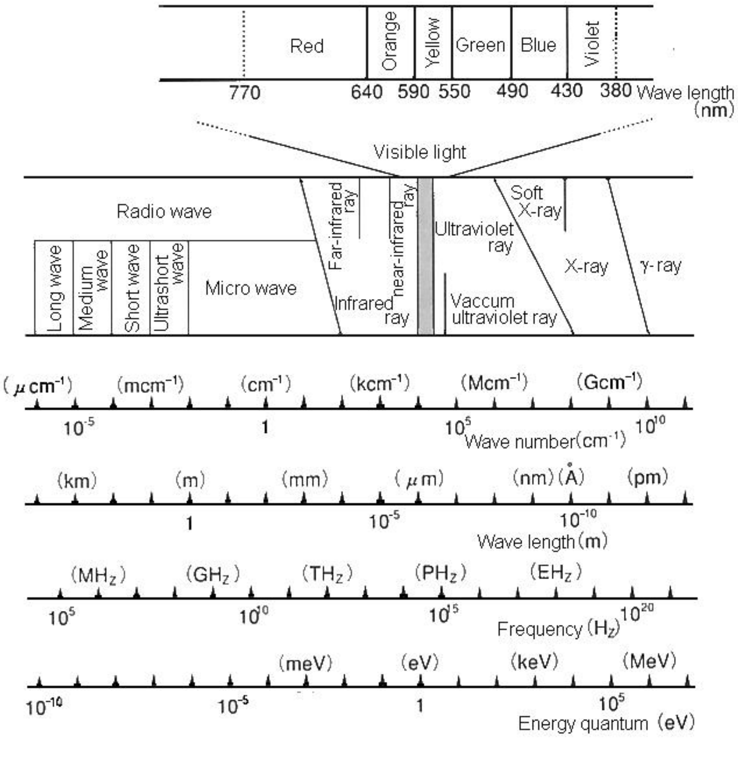


Figure 1.3: Classification of electromagnetic waves

ν, and light velocity c, we obtain $\lambda = 1/\sigma$ and $\nu = c\sigma$. In the case of infrared radiation[1] with a wave number of $667\,\mathrm{cm}^{-1}$,

$$\lambda = \frac{1}{667\,\mathrm{cm}^{-1}} = 1.50 \times 10^{-3}\,\mathrm{cm} = 15.0\,\mu\mathrm{m} = 1.50 \times 10^{-5}\,\mathrm{m}$$
$$\nu = (3.00 \times 10^{8}\,\mathrm{m\,s}^{-1}) \times (66700\,\mathrm{m}^{-1}) = 2.00 \times 10^{13}\,\mathrm{s}^{-1}$$

1.4 Quantum theory of energy

The concept of matter being composed of small elements has been established by the discovery of atoms, electrons, and nuclei. Further studies on thermal radiation and photoelectric effects have revealed the indivisible minimum unit of energy called an energy quantum.

The phenomenon of light (electromagnetic wave) emission from matter heated to a high temperature, such as iron in a furnace or a heater in an electric stove, is called thermal radiation. Thermal radiation from a completely black body is an ideal case that does not include reflection and is called black-body-radiation. Spectroscopic measurements of intensities of emitted electromagnetic waves as functions of wavelength λ or frequency ν give characteristic features of the spectra. The spectra for black-body-radiation shows a characteristic shape at a given temperature, and their features change depending on the temperature, as can be seen in Fig.1.4.

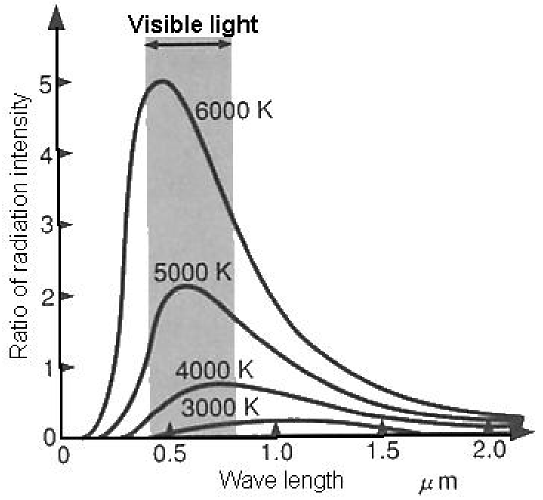


Figure 1.4: Spectra of black body radiation

The wavelength at the maximum $\lambda_{\max}$ shifts toward shorter wavelengths upon increasing absolute temperature T. The product of $\lambda_{\max}$ and T becomes approximately constant.

$$\lambda_{\max} T = \text{constant} \tag{1.9}$$

This is Wien's displacement law.

In the several years starting from the end of the nineteenth century to the beginning of the twentieth century, no theoretical explanations of thermal radiation were successful, though some trials were made on the basis of physical laws known before. Thus, physicists in those years became deeply perplexed. In 1900, Planck successfully introduced the new concept of an energy quantum, which yielded a satisfactory formula for thermal radiation. Planck's theory includes an elementary unit of energy proportional to the frequency ν for every oscillator, and the allowed

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[1] Typical wavelengths for infrared radiation are $1 \sim 100\,\mu\mathrm{m}$ ($1\,\mu m = 10^{-6}\,m$). Relationship between wavelengths or wave numbers and photon energies can be seen in Fig.1.3.

energy of an oscillator is assumed to be an integer multiple of the frequency ν, $nh\nu$. This minimum unit of energy $h\nu$ is called the energy quantum, and h is called Planck constant. The experimental value of h is $h = 6.6262 \times 10^{-34}$ Js.

Example 1.5 The maximum wavelength of thermal radiation from a crystalline plate of gallium arsenide (GaAs) heated in a vacuum chamber for production of semiconductor was $5.0\,\mu$m at $308\,^\circ$C. Calculate the maximum wavelength when the plate is heated at $400\,^\circ$C.

(Solution) Wien's displacement law gives a value of the product of the maximum wavelength λ_{max} and the absolute temperature T as

$$\lambda_{\text{max}} T = (5.0\,\mu\text{m})(308 + 273\,\text{K}) = 2905\,\mu\text{m}\,\text{K}$$

Thus, we obtain the maximum wavelength λ_{max} at $400\,^\circ$C as follows.

$$\lambda_{\text{max}} = \frac{2905\,\mu\text{m}\,\text{K}}{400 + 273\,\text{K}} = 4.3\,\mu\text{m} = 4.3 \times 10^{-6}\,\text{m}$$

The concept of the energy quantum was applied to the explanation of the photoelectric effect by Einstein, and the minimum unit of energy $h\nu$ for a light of frequency ν was then called a light quantum or a photon.

The photoelectric effect is a phenomenon where an electron is ejected from matter illuminated by light, which is associated with consumption of light energy. The ejected electron is called a photoelectron. Photoelectric currents of a photoelectric tube produced by irradiating the surface of the cathode were extensively studied by Lenard (Fig.1.5), and interesting features were revealed for the photoelectric effects.

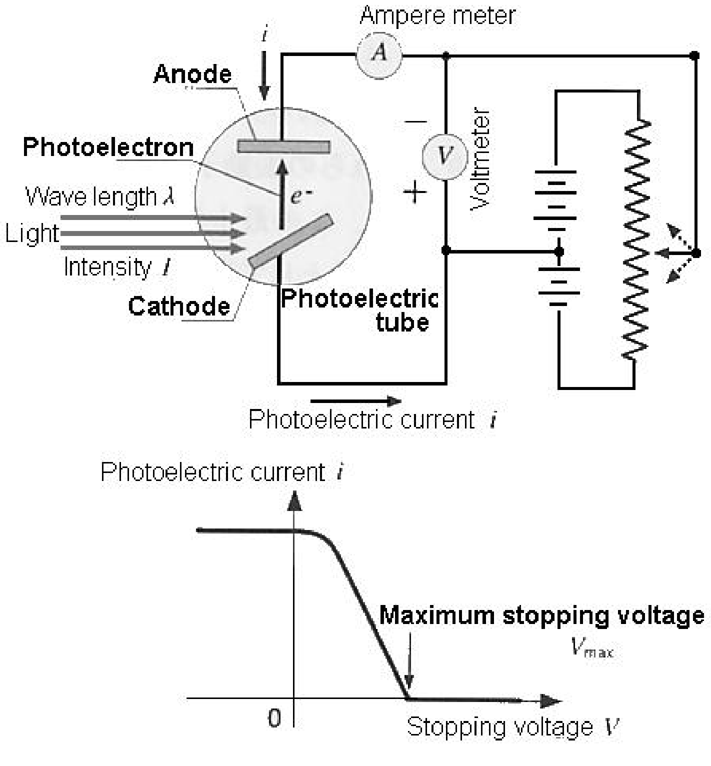


Figure 1.5: The relationship between the photocurrent and the retarding voltage in the photoelectric effect

(1) There is a threshold wavelength λ_{t}. Regardless of how strong the light intensity, when the wavelength is longer than the threshold value, no photoelectric effect can be observed

(Fig.1.6a-b). Threshold wavelengths(λ_{t} or$\lambda_{\mathrm{t}'}$) are different depending on the materials of the cathode (Fig.1.6a), andλ_{t} for an alkali metal is at a longer wavelength in comparison with other materials.

(2) A photoelectric current is observed at the instant just after light is introduced, even if the intensity of the light is very weak (Fig.1.6c). The photoelectric current, i, is proportional to the light intensity, I (Fig.1.6b).

(3) When a stopping voltage V is applied between the anode and the cathode so that the photoelectron ejected from the cathode may be repelled before reaching the anode, the photoelectric current becomes vanishing at a certain voltage of V_{max} (maximum stopping voltage). V_{max} corresponds to the maximum value of the kinetic energies of the photoelectrons, $\{(1/2)mv^2\}_{\mathrm{max}} = V_{\mathrm{max}}$. The maximum stopping voltage does not change even if the intensity of the light introduced onto the cathode is increased. The maximum stopping voltage depends on the kind of material, and the shorter the wavelength (or the larger the frequency), the larger it becomes (Fig.1.6d).

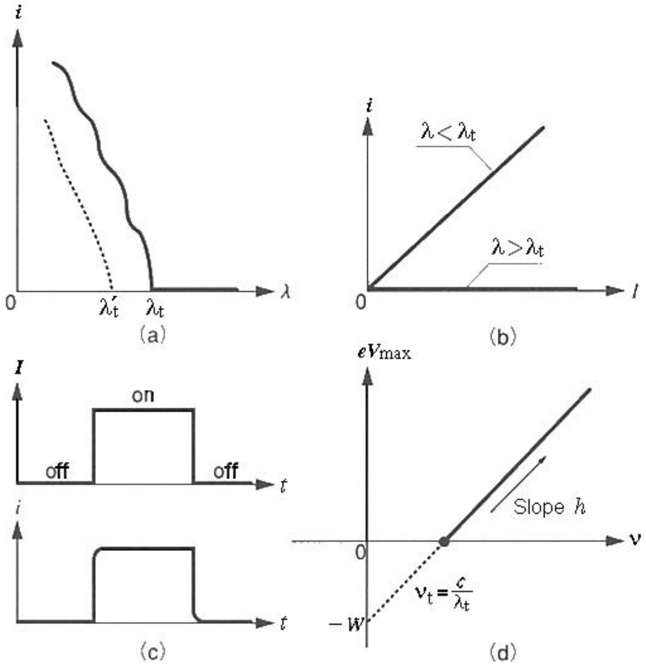


Figure 1.6: Observed features of the photoelectric effect

These experimental features of the photoelectric effect could not be explained in terms of naive ideas that electrons in matter would be ejected under the disturbing actions of electromagnetic waves. For example, the general tendency for the action of electromagnetic waves to increase with the increase of their intensity clearly contradicts feature (1). Since low intensity light has insufficient energy to kick out an electron, a certain time would be required for ejection of a photoelectron after irradiation, and hence this is not consistent with feature (2). On the other hand, intense light would seem to increase the velocity of the photoelectron in contradiction to feature (3).

In 1905 Einstein showed that the photoelectric effect can be explained consistently in terms of the law of conservation of energy, as a photon energy of $h\nu$ is consumed to generate a photoelectron. Since a certain amount of work W is required for extracting an electron from matter, the energy of an electron in matter E_{in} ($E_{\mathrm{in}} < 0$) should be $-W$, provided that the energy of a resting electron free from external forces is set to be 0.

$$E_{\mathrm{in}} = -W \tag{1.10}$$

The magnitude of W ($W > 0$) depends on the kind of the substance. W is called a work function for a metal, and it corresponds to ionization energy or ionization potential when the substance ejecting an electron is an atom or a molecule. The kinetic energy of an ejected photoelectron with a mass m and a velocity v is expressed as $\frac{1}{2}mv^2$. When an electron in the state of $E_{\text{in}} = -W$ is given a photon energy $h\nu$ to be ejected as an photoelectron, the law of conservation of energy leads to the following equation.

$$h\nu - W = \frac{1}{2}mv^2 \tag{1.11}$$

The left-hand side of this equation is the sum of energies for a photon and an electron, and the right side corresponds to the state of an outgoing photoelectron after the consumption of a photon. The kinetic energy of the photoelectron in the right side of Eq.(11) is positive, and thus $h\nu \geq W$. By using a relation for light velocity c with frequency ν and wavelength λ,we obtain

$$\lambda \leq \frac{hc}{W} \tag{1.12}$$

This explains the reason why the photoelectric effect cannot occur unless the wavelength is shorter than the threshold value of $\lambda_{\text{t}} = hc/W$.

As indicated in Table 1.1, the work function W is a characteristic quantity of the matter. It is therefore reasonable that the threshold wavelength varies depending on the individual matter. Since a photoelectron is produced at the expense of a photon, the photoelectron is ejected on the instant even if the light intensity is low, and the larger the number of photons becomes with intense light, the larger the photoelectric current becomes with the increase of the photoelectrons. The equation for the energy conservation, $eV_{\text{max}} = h\nu - W$, explains the experimental facts in Fig.1.6d. Thus, the light with a frequency ν became understood to behave as photons like particles with a characteristic energy of $h\nu$.

Example 1.6. The threshold wavelength for a copper plate was determined to be 255 nm in an experiment of the photoelectric effect. Obtain the work function of copper in units of J or eV.

(Solution) The formula for the photoelectric effect leads to the following relationship between the work function W and the threshold wavelength λ_{t}.

$$\lambda_{\text{t}} = \frac{hc}{W}$$

Thus,

$$\begin{aligned} W &= \frac{hc}{\lambda_{\text{t}}} = \frac{(6.63 \times 10^{-34}\,\text{J s})(3.00 \times 10^{8}\,\text{m s}^{-1})}{255 \times 10^{-9}\,\text{m}} \\ &= 7.45 \times 10^{-19}\,\text{J} \qquad \cdots \text{(answer in units of J)} \\ &= \frac{7.45 \times 10^{-19}\,\text{J}}{1.602 \times 10^{-19}\,\text{J eV}^{-1}} \\ &= 4.65\,\text{eV} \qquad \cdots \text{(answer in units of eV)} \end{aligned}$$

1.5 Atomic spectra and energy levels

In the middle of the nineteenth century, studies of spectra of light emitted from flame and gas discharges have revealed atomic spectra characteristic of the chemical element. At the early stage of the twentieth century, studies of internal structures of atoms have developed to elucidate the mechanism of characteristic atomic spectra.

A gaseous discharge of hydrogen gives brilliant lines of the atomic spectrum of the hydrogen atom with a series of four wavelengths in the visible region($400 \sim 800\,\text{nm}$); the wavelength values

Table 1.1: The work functions W for various metals

Metal		Work function/eV	Metal		Work function/eV
cesium	Cs	1.95	aluminum	Al	4.28
potassium	K	2.28	tin	Sn	4.42
sodium	Na	2.36	iron	Fe	4.5
calcium	Ca	2.9	tungsten	W	4.6
zinc	Zn	3.63	copper	Cu	4.65
magnesium	Mg	3.66	gold	Au	5.1
lead	Pb	4.25	nickel	Ni	5.15
silver	Ag	4.26	platinum	Pt	5.64

Table 1.2: The spectral line series of the hydrogen atom (wavelength in nm)

series	m	n	wavelength for $n = m + 1$	wavelength for $n \to \infty$
Lyman	1	2,3,4,$\cdots$	121.6	91.18
Balmer	2	3,4,5,$\cdots$	656.5	364.7
Paschen	3	4,5,6,$\cdots$	1876	820.6
Brackett	4	5,6,7,$\cdots$	4052	1459
Pfund	5	6,7,8,$\cdots$	7460	2279

corrected to the vacuum are $\lambda_1 = 656.47$ nm, $\lambda_2 = 486.28\,\text{nm}$, $\lambda_3 = 434.17\,\text{nm}$, $\lambda_4 = 410.29\,\text{nm}$. In 1885 Balmer discovered the following formula (Balmer's formula), which fits the wavelengths of the brilliant lines.

$$\lambda_k = \frac{a(k+2)^2}{(k+2)^2 - 4} \qquad (a = 364.7\,\text{nm}) \tag{1.13}$$

Here, $\lambda_k$is the wavelength of the k-th line for $k = 1 \sim 4$ in the visible spectrum, and lines for $k = 5$ can also be observed in the ultraviolet region. A series of spectral lines corresponding to eq.(1.13) is called the Balmer series, which converge to $a = 364.7\,\text{nm}$ when $k \to \infty$. Some other series (Table 1.2) were also observed in the infrared and ultraviolet regions. These series were found commonly to fit in with the following formula (Rydberg's formula).

$$\frac{1}{\lambda} = \frac{R}{m^2} - \frac{R}{n^2} \tag{1.14}$$

Here, m and n are positive integers, which should be assigned to a particular spectral line, and R is the Rydberg constant. Rydberg's formula can be applied not only to emission spectra but also to absorption spectra, which are observed as the loss of light intensity after passing through the sample.

Example 1.7 Using Balmer's formula with its constant $a = 364.7\,\text{nm}$ in comparison with Rydberg's formula, obtain the Rydberg constant R.

(Solution) Transforming eq.(1.14) into a form similar to eq.(1.13), we obtain

$$\lambda = \frac{1}{R} \cdot \frac{n^2 \cdot m^2}{n^2 - m^2}$$

A comparison of this equation with eq.(1.13) leads to $n = 2$, $m = k + 2$, and

$$a = \frac{n^2}{R} = \frac{4}{R}$$

Thus, we obtain

$$R = \frac{4}{a} = \frac{4}{364.7 \times 10^{-9}\,\text{m}} = 1.097 \times 10^7\,\text{m}^{-1}$$

Let us consider the significance of Rydberg's formula based on the quantum theory by Planck and Einstein. The essence of absorption or emission of light (electromagnetic wave) is a process of taking or giving photons $h\nu$, in which the law of conservation of energy is considered to hold. Multiplying both sides of eq.(1.14) by hc and using a relation of $c = \nu\lambda$, the photon energy $h\nu$ upon light absorption or emission can be expressed as a difference of two terms as follows.

$$h\nu = \frac{Rhc}{m^2} - \frac{Rhc}{n^2} \tag{1.15}$$

In connection with the interpretation of the photoelectric effect that the energy balance of an electron equals to hν, each term in the right hand side of eq.(1.15) is suggested to correspond to the energy of the electronic state before or after the light absorption or emission. Since the energy of an electron captured in matter is negative as in the case of eq.(1.10), a formula for the energy level of an electron in hydrogen atom can be obtained as follows,

$$E_n = -\frac{Rhc}{n^2} \tag{1.16}$$

where n is a positive integer $1, 2, 3, \cdots$. By using this formula for the energy levels, eq.(1.15) can be generalized in the following form with an assumption of $E_n > E_m$.

$$h\nu = E_n - E_m \quad \text{or} \quad E_m + h\nu = E_n \tag{1.17}$$

As shown by arrows in Fig.1.7, upon light absorption an electron steps up from the lower level to the higher level, and upon light emission an electron steps down from the higher level to the lower level.

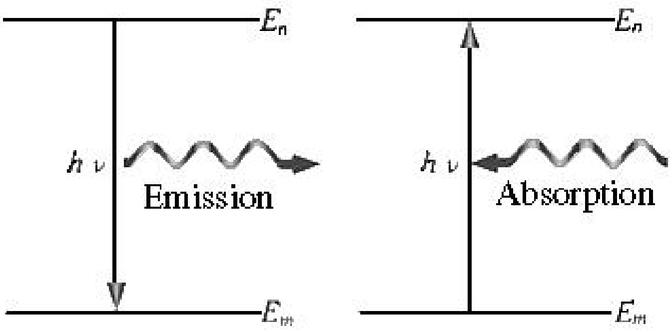


Figure 1.7: Light absorption and emission and Bohr's frequency condition

Eq.(1.17) leads to the following equation for the frequency ν.

$$\nu = \frac{E_n - E_m}{h} \tag{1.18}$$

This equation was first proposed by N.H.D. Bohr in 1913 and called Bohr's frequency condition. Now, let us consider the meaning of eq.(1.16) and Fig.1.7. The electronic state of $n = 1$ is the lowest energy state and is called the ground state. Higher energy states of $n \geq 2$ are called excited states. In a state of $n \to \infty$the electron energy becomes 0, and the electron is released from the attractive force by the nucleus. This state corresponds to the ionic state (ionized state) in which a proton and an electron in a hydrogen atom are separated in the infinite distance. Thus, the ionization energy of hydrogen W_H is given by the next formula.

$$W_\mathrm{H} = E_\infty - E_1 = 0 - (-Rhc) = Rhc \tag{1.19}$$

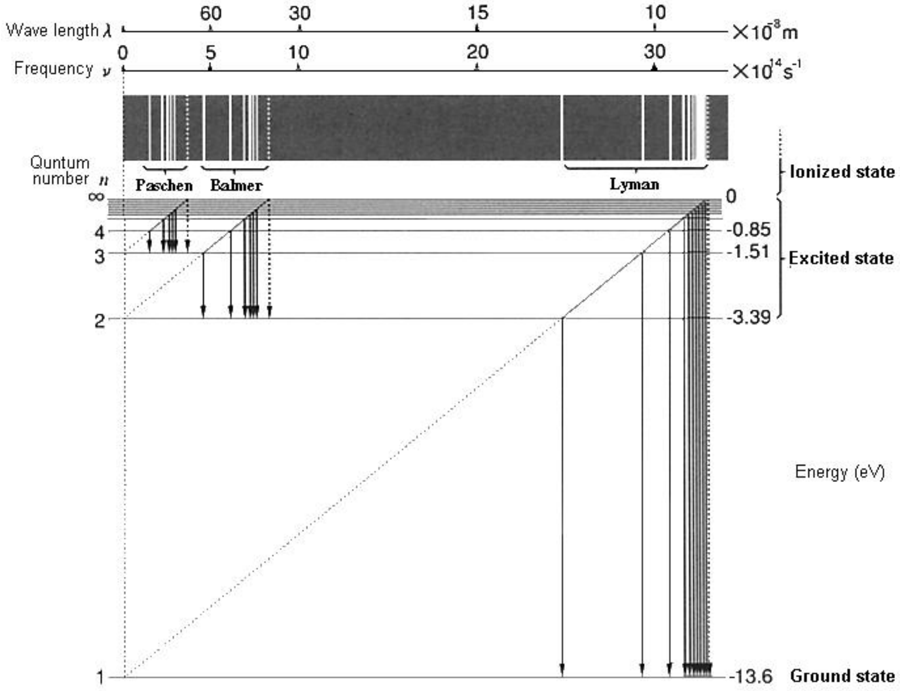


Figure 1.8: Energy levels and spectra of hydrogen atom

Example1.8 Using the value of Rydberg constant R obtained in the Example 1.7, obtain the ionization energy of hydrogen atom W_H in units of J, eV, and J mol^{-1}.

(Solution) Equation (1.19) gives $W_\mathrm{H} = Rhc$, and we obtain

$$\begin{aligned} W_\mathrm{H} &= (1.097 \times 10^{7}\,\mathrm{m}^{-1})(6.626 \times 10^{-34}\,\mathrm{J\,s})(2.998 \times 10^{8}\,\mathrm{m\,s}^{-1}) \\ &= 2.179 \times 10^{-18}\,\mathrm{J} \\ &= \frac{2.179 \times 10^{-18}\,\mathrm{J}}{1.602 \times 10^{-19}\,\mathrm{J\,eV}^{-1}} = 13.60\,\mathrm{eV} \end{aligned}$$

For 1 mol,

$$(2.179 \times 10^{-18}\,\mathrm{J})(6.022 \times 10^{23}\,\mathrm{mol}^{-1}) = 1312\,\mathrm{kJ\,mol}^{-1}$$

In 1911, E. Rutherford proposed a model of the atomic structure based on experimental studies of α particles (stream of helium nuclei) scattered by metallic foil such as gold foil. In this model, a hydrogen atom is composed of a proton and an electron moving round it.

Bohr derived a successful formula for energy levels of hydrogen atom in 1913 by introducing new ideas into a physical system of an electron moving round a proton at a constant distance of r. A circular motion of an electron with a velocity v around a proton at a radius of r gives the following equation between the electric force due to Coulomb's law and the centripetal force of the circular motion.

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r} \tag{1.20}$$

Here, the left-hand side is the Coulomb force, and the right-hand side is the centripetal force. In general, the force equals (mass) × (acceleration), according to Newton's law of motion. In this case, the mass is the electron mass m, and the centripetal acceleration is v^2/r. Bohr assumed a quantum condition that requires a product of momentum (mass $m \times$ velocity$v$) and the circumference of

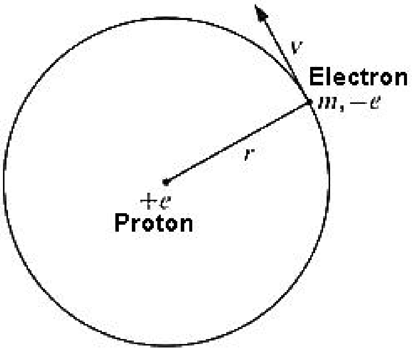


Figure 1.9: Bohr's model

the circle ($2\pi r$) to be an integer multiple of Planck constant h.

$$(mv)(2\pi r) = nh \qquad (n = 1, 2, 3, \cdots) \tag{1.21}$$

Unless this condition is fulfilled, the system cannot be in a stable stationary state. From equations (1.20) and (1.21), the radius of the circular orbit in the stationary state is derived as follows.

$$r = \frac{n^2 \varepsilon_0 h^2}{\pi m e^2} = n^2 a_{\mathrm{B}} \qquad (n = 1, 2, 3, \cdots) \tag{1.22}$$

Here, $a_{\mathrm{B}} = \varepsilon_0 h^2/\pi m e^2$ is the orbital radius in the stationary state of $n = 1$ and called Bohr radius. The value of a_{B} is 5.292×10^{-11} m, and this distance may be considered as the size of a hydrogen atom. The total energy E of an electron is the sum of its kinetic energy $mv^2/2$ and its potential energy U. The potential energy $U(r)$ of an electron under the Coulomb force in the left-hand side of eq.(1.20) can be obtained as follows. The potential energy at the infinite distance $U(\infty)$ is taken to be 0 as the reference energy. Then, the work required for removing the electron from the distance r to the infinite distance against the Coulomb attraction equals $U(\infty) - U(r)$

$$\begin{aligned} U(r) &= U(\infty) - \int_r^\infty \frac{e^2}{4\pi\varepsilon_0 r^2} \mathrm{d}r = \left[\frac{e^2}{4\pi\varepsilon_0 r}\right]_r^\infty \\ &= -\frac{e^2}{4\pi\varepsilon_0 r} \end{aligned}$$

Using eq.(1.20), the energy becomes

$$E = \frac{mv^2}{2} - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{8\pi\varepsilon_0 r}$$

Substituting eq.(1.22) for r, we obtain a formula for the n-th energy level E_n as follows.

$$E_n = -\frac{me^4/8{\varepsilon_0}^2 h^2}{n^2} \tag{1.23}$$

A comparison of this equation with eq.(1.16) gives a theoretical representation of the Rydberg constant R.

$$R = \frac{me^4}{8{\varepsilon_0}^2 h^3 c} \tag{1.24}$$

1.6 Particles and wave characters

According to Einstein's idea, a photon with an energy $h\nu$ (frequency ν and wavelength λ) has a linear momentum along its propagating direction of the following magnitude p.

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{1.25}$$

In 1923 A. H. Compton verified this idea using scattering experiments of X-rays and electrons. Thus, the behavior of photons having a momentum h/λ together with an energy $h\nu$ was revealed. In 1923 de Broglie postulated conversely that a particle can have a wavelength corresponding to its momentum via eq.(1.25) in which the momentum and the wavelength are related from one to the other and vice versa. The wave behavior of electrons is called an electron wave, and in general the wave behavior of matter is called a matter wave or de Broglie wave. The wavelength λ for a matter wave is given by the following equation, which is equivalent to eq.(1.25).

$$\lambda = \frac{h}{p} \tag{1.26}$$

This relationship is called de Broglie relation.

Example 1.9 Calculate the wavelength of the electron beam given by acceleration of electrons from 0 V to 150 V.

(Solution) The kinetic energy E is an energy gained through acceleration by the potential difference that is the applied voltage of 150 V.

$$E = 150\,\mathrm{eV} = (150\,\mathrm{eV})(1.602 \times 10^{-19}\,\mathrm{J\,eV^{-1}}) = 2.403 \times 10^{-17}\,\mathrm{J}$$

In general there are the following equations for the electron mass m, velocity v, momentum p, and kinetic energy E.

$$E = \frac{1}{2}mv^2, \qquad p = mv$$

Using the de Broglie relation $\lambda = h/p$, we obtain

$$\begin{aligned} \lambda &= \frac{h}{mv} = h(2mE)^{-1/2} \\ &= (6.626 \times 10^{-34}\,\mathrm{J\,s})(2 \times (9.109 \times 10^{-31}\,\mathrm{kg})(2.403 \times 10^{-17}\,\mathrm{J}))^{-1/2} \\ &= 1.00 \times 10^{-10}\,\mathrm{m} \end{aligned}$$

(A useful formula to obtain the wavelength λ of an electron wave with a kinetic energy of Z eV is given as $\lambda = \sqrt{150/Z} \times 10^{-10}$ m) Beautiful spots as shown in Fig.1.10 were observed by M. T. F. Laue in 1912, when X-rays were irradiated on a crystal. This demonstrates the diffraction of X-rays that behave as electromagnetic waves. X-rays reflected by regular arrays of atoms with a spacing d (Fig.1.11) are enhanced, if the following condition is fulfilled.

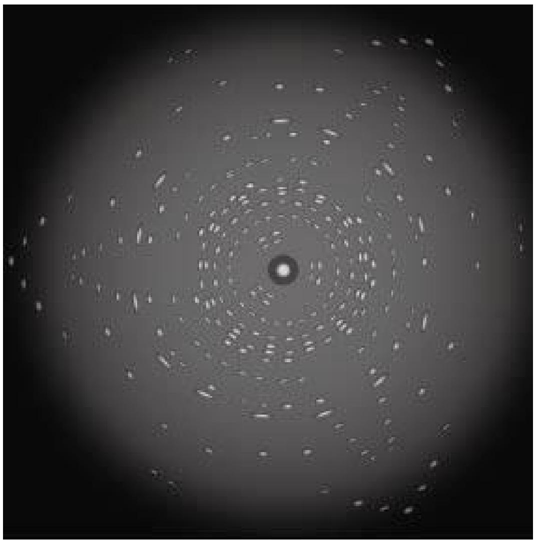


Figure 1.10: Laue spots of calcium carbonate (provided by Rigaku Denki)

$$2d\sin\theta = n\lambda \qquad (n = 1, 2, 3, \cdots) \tag{1.27}$$

This is called the Bragg condition of reflection (Bragg's law), and n is called the order of reflection.

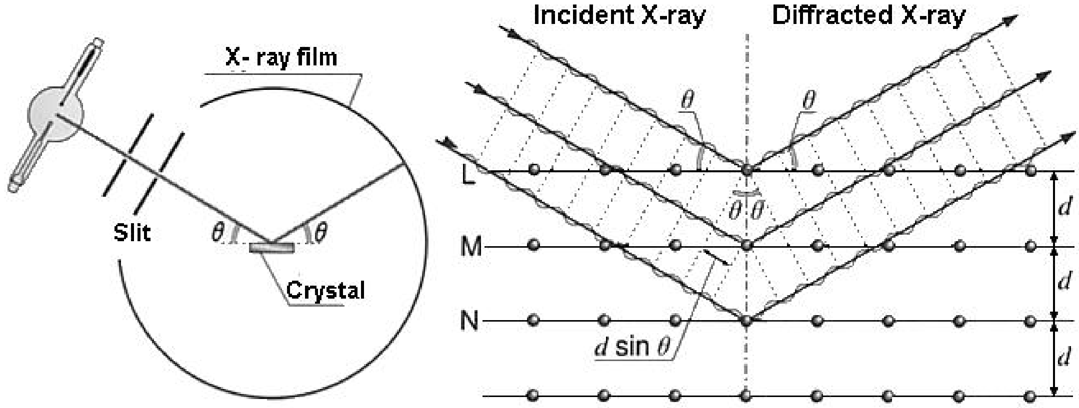


Figure 1.11: X-ray diffraction by crystal lattice

Similarly, electron waves were experimentally confirmed to produce diffraction phenomena with regular arrays of atoms in crystals by C. J. Davisson and L. H. Germer in 1925 and also by G. P. Thomson in 1927. A typical pattern of electron diffraction is shown in Fig.1.12. The spatially inhomogeneous distribution created by the interference of electron waves is closely related with the production and destruction of chemical bonding.

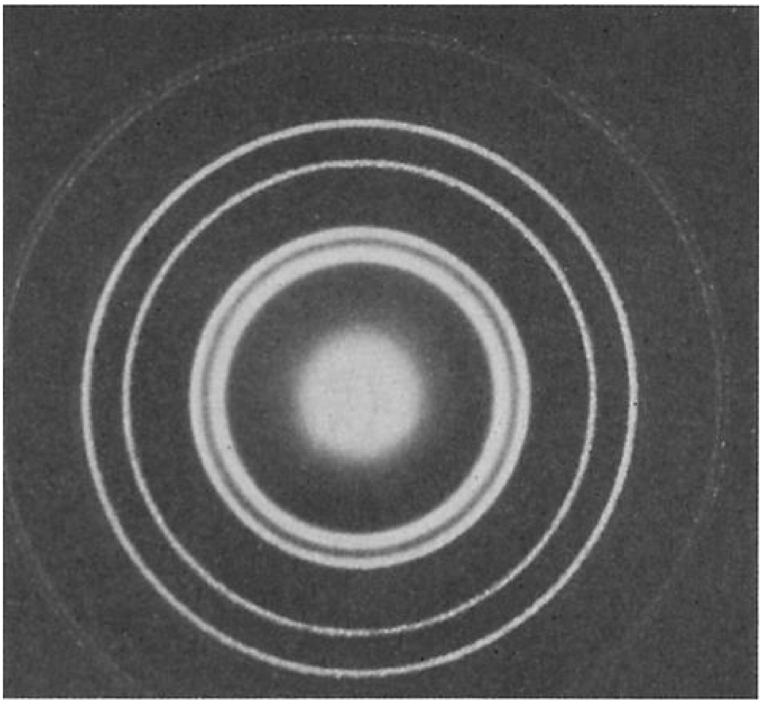


Figure 1.12: Electron diffraction pattern of gold polycrystals

1.7 Wave equations

In 1926 fundamental equations inclusively describing both particle and wave characteristics were proposed in terms of wave mechanics by Schrödinger and matrix mechanics by Heisenberg. Though their mathematical forms were different, these theories were proved to be equivalent in their physical significance by E. Schrödinger. In this textbook, the fundamental equation for quantum mechanics is treated in terms of wave mechanics.

As we have already studied in section 1.3, a typical example for waves with a frequency ν and a wavelength λ is represented by

$$\Psi(x,t) = A\, e^{2\pi i\left(\frac{x}{\lambda} - \nu t\right)}$$

Using a formula for differentiation of an exponential function ($\mathrm{d}e^{ax}/\mathrm{d}x = ae^{ax}$), derivatives with respect to time t or position x lead to the following equations, respectively.

$$\frac{\partial \Psi}{\partial t} = -i(2\pi\nu)\Psi$$

$$\frac{\partial \Psi}{\partial x} = i\left(\frac{2\pi}{\lambda}\right)\Psi$$

It should be noted that the partial differentiation symbol ∂ is used in place of d when numbers of variables are more than one. Using the equations connecting particle and wave characteristics, $E = h\nu$ and $p = h/\lambda$, we obtain the following simultaneous differential equations that do not include ν and λ explicitly.

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{1.28}$$

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{1.29}$$

Here, $\hbar$ is a constant denoting $(h/2\pi)$. Equations (1.28) and (1.29) connect particle quantities E and p with a wave function Ψ. Let us study the mathematical properties of these equations before applying them to some systems. The equation (1.28) shows that the operation of $i\hbar\partial/\partial t$ on Ψ from the left is equivalent to a simple multiplication of Ψ by the energy E. The equation (1.29) indicates that the operation of $-i\hbar\partial/\partial x$ on Ψ from the left is equal to a simple multiplication of Ψ by the momentum p. Mathematical operations, such as $i\hbar\partial/\partial t$ and $-i\hbar\partial/\partial x$, are called operators. Namely, these operators stand for the energy E and the momentum p, respectively.

$$i\hbar\frac{\partial}{\partial t} \leftrightarrow E$$

$$-i\hbar\frac{\partial}{\partial x} \leftrightarrow p$$

In order to apply these simultaneous equations to particular problems, it is necessary to know a relation between E and p. In classical mechanics before the birth of quantum mechanics, an important relation between E and p was known as the Hamilton function, which represents the energy of the system as a function of the momentum p, the position x, and time t.

$$E = H(p,x,t) \tag{1.30}$$

With the help of the Hamilton function H, the equations (1.28) and (1.29) can be united into a single equation. In order to do this, let us first derive a Hamilton function for a system in which a particle of mass m moves with a kinetic energy $\frac{1}{2}mv^2$ under a potential energy of U. Noting that the momentum of this particle is $p = mv$, we obtain

$$H = \frac{1}{2}mv^2 + U = \frac{1}{2}m\left(\frac{p}{m}\right)^2 + U = \frac{p^2}{2m} + U \tag{1.31}$$

Substitution of this equation into the right side of eq.(1.28) with using eq.(1.30) leads to the following result.

$$\begin{aligned} i\hbar\frac{\partial\Psi}{\partial t} &= \left(\frac{p^2}{2m}+U\right)\Psi = \frac{p}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi + U\Psi \\ &= \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2\Psi + U\Psi \\ &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U\right)\Psi \end{aligned} \tag{1.32}$$

As can be seen from this example, equations (1.28) and (1.29) can be combined into one equation when the energy E in the right side of eq.(1.28) is replaced by the corresponding Hamilton function H in which the momentum p should be replaced by the respective operator $\hat{p}$.

$$\hat{H} = H(\hat{p}, x, t) \tag{1.33}$$

In general, replacing the momentum p in the expression of Hamilton function by the respective operator $\hat{p}$ in eq.(1.33) we obtain the quantum mechanical Hamilton function $\hat{H}$.

$$\hat{H} = H(\hat{p}, x, t) \tag{1.34}$$

$\hat{H}$ is called Hamilton operator or Hamiltonian. Using this operator, two equations (1.28) and (1.29) are unified into one equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \tag{1.35}$$

This equation is the most fundamental equation of the quantum mechanics and is called the Schrödinger equation after the name of the discoverer. The wave function Ψ in this equation represents the state in which the system of matter exists. The physical significance of Ψ will be discussed in the later sections.

Although eq.(1.35) could be derived from a simple wave function, this equation is known to be applicable to general problems. Generalization of the Hamiltonian and the wave function in eq.(1.35) will be studied later. Procedures for solving the wave equation and the meanings of the solutions will also be studied in the later sections.

1.8 Wave functions and probabilities of finding particles

In the photoelectric effect, the more the light intensity (the square of the amplitude of the electromagnetic wave) increases, the more the number of photons increases linearly. Namely, the number of photons is proportional to the square of the amplitude. In 1926 Born generalized this idea to propose that the square of the absolute value of the wavefunction Ψ is proportional to the probability of finding the particle. The absolute value should be used for the general wave, because the wave may be a complex function rather than a real function. The square of the absolute value of the complex wave function Ψ is obtained by the following equation.

$$|\Psi|^2 = \Psi \cdot \Psi^* \tag{1.36}$$

Here, Ψ^* is the complex conjugate of Ψ, and it is given via simple replacement of every imaginary unit i included in the mathematical expression of Ψ by $-i$.

$$\Psi^* = \Psi(i \to -i) \tag{1.37}$$

The probability of finding a particle moving along the x axis in a particular region between x and $x + \mathrm{d}x$ is expressed as $|\Psi(x,t)|^2\mathrm{d}x$ by using the wavefunction $\Psi(x,t)$. Since the probability finding the particle in the region from $x = -\infty$ to $x = +\infty$ is equal to 1, the next integral must be 1.

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \mathrm{d}x = 1 \tag{1.38}$$

This is the normalization condition of the wavefunction. If this condition is satisfied, the wavefunction is said to be normalized.

When a wavefunction is a solution of eq.(1.35), any multiplication of the wavefunction by an arbitrary constant also yields a solution of eq.(1.35). Solutions of the wave equation are therefore arbitrary for their proportionality constants. The normalization condition removes the arbitrariness of a real wavefunction except for its sign. In the case of a complex wavefunction, an ambiguity of the phase factor of $e^{i\theta}$ remains. However, the phase factor does not change the square of the absolute value, and the physical meaning of the wavefunction is irrelevant with the phase factor. Thus, one may choose arbitrarily the value of θ in the phase factor, for example θ can be set equal to be 0.

Since the first derivatives of the wavefunction are related to the energy E and the momentum p according to eqs.(1.28)-(1.29), the wavefunction representing a state with finite energy and momentum should be continuous with respect to the time and the position. This important characteristic of acceptable wave functions should not be disregarded, when one needs to obtain a wavefunction by solving the wave equation.

Before closing this section, it is important to note the quantum mechanical significance of the wavefunction.

1. The state of a system is described by the wavefunction.
2. The probability that a particle will be found at a position is proportional to the square of the absolute value of the wavefunction.
3. The wavefunction evolves in time according to the equation

$$i\hbar\tfrac{\partial\Psi}{\partial t} = \hat{H}\Psi.$$

1.9 Stationary states and eigenvalue equations

If the energy E is independent of time t, the probability of finding a particle is also independent of t. States of this kind are called stationary states. When the energy E is a constant, irrespective of time t, eq.(1.28) is easily integrated for t to yield the following solution.

$$\Psi(x,t) = \psi(x)\cdot\exp\left(-i\frac{Et}{\hbar}\right) \tag{1.39}$$

The symbol $\psi(x)$ is the integration constant arising from the integration with respect to t, and thus $\psi(x)$ is independent of t, though it depends on the position coordinate x. Although the wave function for the stationary state $\Psi(x,t)$ in eq.(1.39) oscillates as a function of t, the square of the absolute value of $\Psi(x,t)$, that is the product $\Psi(x,t) * \Psi(x,t)$, remains constant.

$$\begin{aligned}|\Psi(x,t)|^2 &= \psi(x)\cdot\exp\left(-i\frac{Et}{\hbar}\right)\cdot\psi(x)^*\cdot\exp\left(i\frac{Et}{\hbar}\right)\\ &= \psi(x)\cdot\psi(x)^* = |\psi(x)|^2 \end{aligned} \tag{1.40}$$

Therefore, the probability of finding a particle in the stationary state is independent of t and calculated to be the same even if the time-independent function $\psi(x)$ is used in place of $\Psi(x,t)$. Thus $\psi(x)$ is called the wavefunction of the stationary state. Inserting $\Psi(x,t)$ in eq.(1.39) into the wave equation (1.35) and rearranging the formula, we obtain

$$(\hat{H}\psi - E\psi)\exp\left(-i\frac{Et}{\hbar}\right) = 0$$

Thus the following equation determining the wavefunction of the stationary $\psi(x)$ state is given.

$$\hat{H}\psi = E\psi \tag{1.41}$$

This is called the Schrödinger equation for stationary states or the time-independent Schrödinger equation.

Example 1.10 Write the time-independent Schrödinger equation for a one-dimensional harmonic oscillator that contains a particle with a mass m moving on the x-axis under the potential energy of $U(x) = \frac{1}{2}kx^2 (k > 0)$.

(Solution) The time-independent Schrödinger equation is expressed as $\hat{H}\psi = E\psi$. In this case the motion of the particle is restricted to the x-axis, the wavefunction is a function of x and represented as $\psi = \psi(x)$. The Hamiltonian $\hat{H}$ of this system is obtained from the Hamilton function H composed of the sum of the kinetic energy and the potential energy. For this system, The momentum p of the particle leads to the kinetic energy of $p^2/2m$ and the potential energy is $\frac{1}{2}kx^2$, and we obtain

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

Thus the Hamiltonian $\hat{H}$ is derived by simply replacing the momentum p with the operator $\hat{p} = -i\hbar\partial/\partial x$ in the expression of H. This replacement must be made twice for $p^2/2m$, and we obtain

$$\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

The potential energy $\frac{1}{2}kx^2$ can be left as it is, since it does not contain the momentum p. Therefore the Hamiltonian $\hat{H}$ is expressed as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

Inserting this $\hat{H}$ into $\hat{H}\psi = E\psi$, the time-independent Schrödinger equation for a one-dimensional harmonic oscillator is given as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right)\psi(x) = E\psi(x)$$

note $F(x) = -\mathrm{d}U(x)/\mathrm{d}x = -kx$ $(k > 0)$ represents the force acting on the particle. A particle in a harmonic oscillator undergoes a returning force (restoring force) proportional to its displacement from the equilibrium and oscillates around the equilibrium position. The displacement of an elastic body such as a spring is proportional to the applied force. This is called Hooke's law.

$\hat{p}$ and $\hat{H}$ are operators corresponding to the momentum and the energy, respectively. An operator $\hat{F}$ corresponding to an arbitrary observable $F(p, x)$ is introduced as $F(\hat{p}, x)$ by inserting eq.(1.33) ($\hat{p} = -i\hbar\partial/\partial x$ in place of p) in $F(p, x)$. The operator $\hat{x}$ corresponding to a Cartesian coordinate x is simply expressed as $\hat{x} = x$, since no momentum p is contained in x.

In general, a suitable choice of a function ϕ yields a $\hat{F}\phi$ proportional to ϕ and equal to a constant multiple of ϕ itself.

$$\hat{F}\phi = f\phi \tag{1.42}$$

The multiplying constant f is the eigenvalue of the operator $\hat{F}$, and the function ϕ is the eigenfunction of $\hat{F}$ corresponding to the eigenvalue f. When some eigenfunctions (e.g. ϕ_1 and ϕ_2) corresponding to the same eigenvalue f are linearly independent of each other (e.g. ϕ_1 is not proportional to ϕ_2), the eigenvalue f is said to be degenerate. The number of independent eigenfunctions corresponding to the same eigenvalue is the degree of the degeneracy. The equation (1.42) including a set of an eigenfunction ϕ and an eigenvalue f for the operator $\hat{F}$ is called the eigenvalue equation of $\hat{F}$. The wave equation (1.41) for stationary states (the time-independent Schrödinger equation) is the eigenvalue equation of the Hamiltonian operator $\hat{H}$ corresponding to the energy. The equation (1.41) gives possible sets of eigenfunctions ψ and eigenvalues E for the energy.

In a stationary state, the energy E and the probability of finding the particle are independent of time t. However, we should not consider that the particle rests at a certain position. Even in a stationary state, motion of a particle is taken into account as the oscillation of the phase factor in eq.(1.39) satisfying the time-dependent wave equation of (1.35).

1.10 A particle in a one-dimensional box

The best way to understand procedures for solving wave equations and the significance of the solutions is to study typical examples. Let us solve the time-independent Schrödinger equation $\hat{H}\psi = E\psi$ for a particle with a mass m, which is confined in a region $(0 < x < L)$ on the x-axis (one-dimensional box). The Hamiltonian of this system is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$$

$U(x)$ is the potential energy of the system. The limitation of the particle motion is imposed on $U(x)$ as follows (Fig.1.13).

$$\begin{array}{lll} \text{Inside the box} & (0 < x < L) & U(x) = 0 \\ \text{Outside the box} & (x \leq 0 \text{ or } x \geq L) & U(x) = +\infty \end{array} \tag{1.43}$$

This treatment naturally leads to no probability of finding the particle outside the box. If $\psi(x) \neq 0$ at $U(x) = +\infty$, then both sides of $\hat{H}\psi = E\psi$ become divergent.

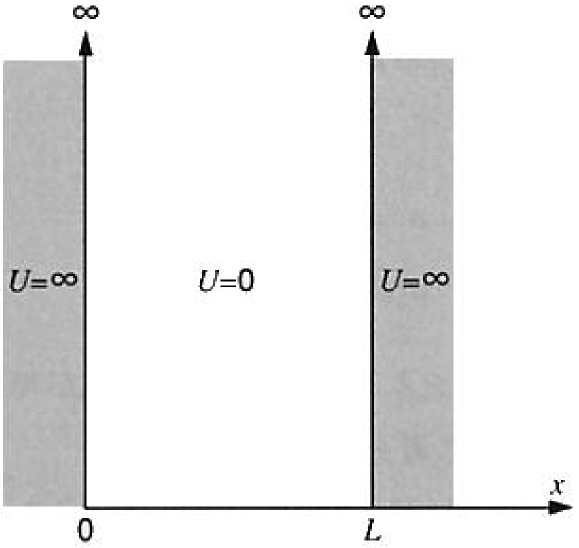


Figure 1.13: Potential energy U(x) for a particle in a one-dimensional box

Since $U(x) = 0$ inside the box, the wave equation $\hat{H}\psi = E\psi$ becomes a very simple form as

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\kappa^2\psi \tag{1.44}$$

where

$$\kappa = \left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} \tag{1.45}$$

The general solution of eq.(1.44) is well known, and it is given by

$$\psi(x) = a \cdot \mathrm{e}^{i\kappa x} + b \cdot \mathrm{e}^{-i\kappa x} \tag{1.46}$$

Substitution of this expression into the left side of eq.(1.44) will lead the right side.

In order to adapt $\psi(x)$ in eq.(1.46) to the physical interpretation of the quantum theory, we need to consider the continuous properties of wavefunctions. In this case, $\psi(x)$ must be continuous at both ends of the box ($x = 0$ and $x = L$). Thus, the following conditions are required.

At an end of the box ($x = 0$), $\psi(0) = a + b = 0$,
and at another end of the box ($x = L$), $\psi(L) = a \cdot \mathrm{e}^{i\kappa L} + b \cdot \mathrm{e}^{-i\kappa L} = 0$.
Therefore, we obtain

$$a = -b \tag{1.47}$$

$$a(\mathrm{e}^{i\kappa L} - \mathrm{e}^{-i\kappa L}) = 0 \tag{1.48}$$

Since the possible values for the energy eigenvalue E are not apparent, we must classify the possible cases as follows.

1) ($E < 0$)

From eq.(1.45) κ is a pure imaginary number, and hence the parenthesis in the left of eq.(1.48) cannot be equal to 0. This leads to $a + b = 0$, and then $\psi(x) = a\,e^{i\kappa x} + b\,e^{-i\kappa x} = 0$ for all $x(0 < x < L)$. Clearly this is not consistent with our assumption of a particle in a box.

2) ($E = 0$)

From eq.(1.45) $\kappa = 0$ and $\psi(x) = a + b = 0$ for all $x(0 < x < L)$. This is also incompatible with the assumption of a particle in a box.

3) ($E > 0$)

In this case $\kappa > 0$, and hence the parenthesis in the left of eq.(1.48) can be equal to 0. This condition is

$$\mathrm{e}^{i\kappa L} = \mathrm{e}^{-i\kappa L} \quad \text{or} \quad \mathrm{e}^{2i\kappa L} = 1 \tag{1.49}$$

It should be noted that $\mathrm{e}^{2k\pi i} = 1$ for an arbitrary integer k. Thus the possible values for $\kappa(\kappa > 0)$ should satisfy the following condition.

$$\kappa L = n\pi \qquad (n = 1, 2, 3, \cdots) \tag{1.50}$$

Inserting this κ into eq.(1.45), we obtain the possible values for the energy E with an integer n.

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{1.51}$$

This is the formula of the energy levels for a one-dimensional particle in a box. For any energies other than the special values in eq.(1.51) there are no solutions. The appearance of discrete levels is a consequence of quantization of energy. Quantized energy levels are classified with the positive integer n. These numbers representing quantized states are said to be quantum numbers.

The wavefunction corresponding to the energy level E_n, can be determined from equations (1.46), (1.47), and (1.50).

Outside the box ($x < 0$ or $x > L$) $\psi_n(x) = 0$

Inside the box ($0 < x < L$) $\psi_n(x) = a(\mathrm{e}^{i\kappa x} - \mathrm{e}^{-i\kappa x}) = 2ai \sin \kappa x = c \sin(n\pi x/L)$

Here, the formula $\mathrm{e}^{i\theta} = \cos\theta + i \sin\theta$ is used, and $2ai$ is denoted as c. The value of c is determined by the normalization condition.

$$\int_{-\infty}^{\infty} |\psi|^2 \mathrm{d}x = |c|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x = 1$$

The value of the last integral is $L/2$, and $c^2 \cdot (L/2) = 1$. Thus, $c = \sqrt{2/L}$, and we obtain the solution within the box.

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad (n = 1, 2, 3, \cdots) \tag{1.52}$$

The energy levels E_n and the wavefunctions $\psi_n(x)$ for a particle in a one-dimensional box with a length L are shown in Fig.1.14.

The lowest energy state with the quantum number $n = 1$ is the ground state of a particle in a box. The probability finding the particle is largest at the middle of the box and decreases on going to both ends. In the macroscopic world, we can place a particle at any place in a box. On the other hand in the quantum world, only probabilities can be determined. It is very strange

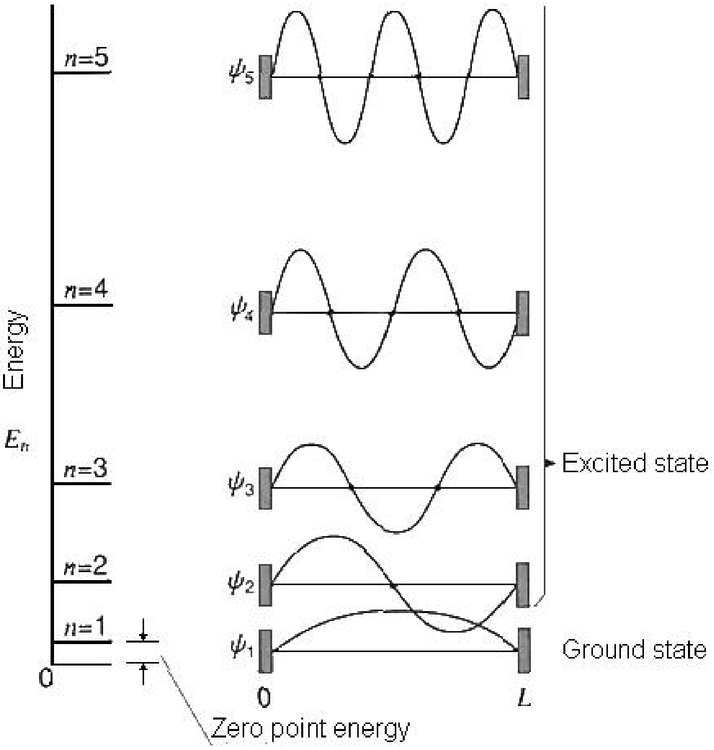


Figure 1.14: The energy levels $E_n = n^2h^2/8mL^2$ and the wavefunctions $\psi_n(x)$ for a particle in a one-dimensional box

that the ground-state energy $E_1 = h^2/8mL^2 > 0$ is larger than the given potential energy of $U = 0$. In a macroscopic system, the minimum energy state of a particle is a state with no motion and the energy equal to the minimum potential energy U_{min} (in this case $U_{\text{min}} = 0$). The fact that $E_1 - U_{\text{min}} > 0$ indicates that a particle can move with the energy of $E_1 - U_{\text{min}}$, even at the absolute zero temperature where no energy can be removed from the system any more. Therefore, the energy of $E_1 - U_{\text{min}}$ is called the zero-point energy, and the motion in the ground state is called the zero-point motion. In the macroscopic world, the mass m of the matter and the length L of the box are very large, and hence $E_1 = h^2/8mL^2$ can be disregarded as negligibly small. It follows that zero-point energies and zero-point motion can be neglected for macroscopic systems. Definite discrete values are only allowed for excited-state energies of a particle in a box by contrast with a particle in the macroscopic world for which any energy values can be allowed. Energy levels for a macroscopic system can be considered as continuous because of very large m and L. As can be seen from wave functions shown in Fig.1.14, there are some positions with no probability of finding a particle in an excited state, even though the particle moves in the box. The geometrical position where $\psi = 0$ is said to be a node. The number of nodes in the box is $n-1$, which increases with the increase of the quantum number n. Waves with more nodes generally have more energy. This propensity should be noted, and it will be helpful for understanding the nature of electron waves moving in matter.

Example 1.11 Show the following relation between wavefunctions $\psi_n(x)$ and $\psi_m(x)$ for a particle in a one-dimensional box.

$$\int_{-\infty}^{\infty} \psi_n(x)^* \psi_m(x) \mathrm{d}x = \delta_{nm}$$

δ_{nm} is Kronecker's delta, which equals to 1 for $n = m$ and 0 for $n \neq m$.

(Solution) The wavefunction with a quantum number n for a box ($0 < x < L$) with a length L, is given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad (n = 1, 2, 3, \cdots)$$

For the outside of the box $\psi_n(x) = 0$. Let us denote the integral of this problem as I_{nm}.

$$I_{nm} = \int_{-\infty}^{\infty} \psi_n(x)^* \psi_m(x) \mathrm{d}x = \int_0^L \left(\frac{2}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) \mathrm{d}x$$

The additivity formula for trigonometrical functions

$$\cos(A \pm B) = \cos A \cos B \mp \sin A \sin B$$

leads to

$$\sin A \sin B = \frac{1}{2}(\cos(A - B) - \cos(A + B))$$

Thus

$$I_{nm} = I(-) - I(+)$$

Here

$$I(\pm) = \left(\frac{1}{L}\right) \int_0^L \cos\left(\frac{(n \pm m)\pi x}{L}\right) \mathrm{d}x$$

Introducing $\theta = \pi x/L$ and using $\mathrm{d}\theta = (\pi/L)\mathrm{d}x$, we obtain

$$I(\pm) = \frac{1}{\pi} \int_0^\pi \cos\{(n \pm m)\theta\} \mathrm{d}\theta$$

When $(n \pm m)$ is not equal to 0,

$$I(\pm) = \left[\frac{1}{\pi} \left\{\frac{1}{n \pm m}\right\} \sin(n \pm m)\theta\right]_0^\pi = 0$$

When $n = m \, (n - m = 0)$,

$$I(-) = \frac{1}{\pi} \int_0^\pi \mathrm{d}\theta = \frac{\pi}{\pi} = 1$$

Therefore,
(1) for $n = m$, $I_{nm} = 1 - 0 = 1$ and
(2) for $n \neq m$, $I_{nm} = 0 - 0 = 0$ Using Kronecker's delta, we obtain $I_{nm} = \delta_{nm}$

The integral of this example for $n = m$ is the normalization condition, provided that the wavefunction has already been normalized. For $n \neq m$ the integral is 0, where two wavefunctions are said to be mutually orthogonal and to obey the orthogonality. The orthogonality holds in general between arbitrary wavefunctions corresponding to different eigenvalues. When functions are normalized for themselves and mutually orthogonal, such a set of functions is said to be orthonormal and to obey orthonormality.

1.11 Generalization of the wave equation

Now, let us extend the simple wave equation for a particle in a one-dimensional space to the more general case.

(a) Extension to the three-dimension

The extension from one-dimension to three-dimensions requires three coordinates x, y, and z in place of only one variable of x. It follows that the wavefunction is denoted as $\Psi(x, y, z, t)$ in place of $\Psi(x, t)$. Accordingly the velocity v and the momentum p are denoted by vectors with three components, (v_x, v_y, v_z) and (p_x, p_y, p_z), respectively. The replacement formula corresponding to eq.(1.33) is extended to be as follows.

$$\begin{aligned}\hat{p}_x &= -i\hbar\frac{\partial}{\partial x}\\ \hat{p}_y &= -i\hbar\frac{\partial}{\partial y}\\ \hat{p}_z &= -i\hbar\frac{\partial}{\partial z}\end{aligned} \tag{1.53}$$

For a particle with a mass m in three-dimensions, the kinetic energy needed to produce the Hamiltonian operator is expressed as follows.

$$\frac{p^2}{2m} = \frac{1}{2m}({p_x}^2 + {p_y}^2 + {p_z}^2) = -\frac{\hbar^2}{2m}\Delta$$

Here, Δ is an operator called the Laplacian. Its expression for one-dimension is

$$\Delta = \frac{\partial^2}{\partial \mathrm{x}^2}$$

and for three-dimensions

$$\Delta = \frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2} + \frac{\partial^2}{\partial \mathrm{z}^2}$$

With the Laplacian symbol Δ, the Hamiltonian for one particle with a mass m can be written, irrespective of the dimension, in the same expression as

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + \mathrm{U} \tag{1.54}$$

It should be noted that the potential energy U for one-dimension or three-dimensions is $U(x)$ or $U(x, y, z)$, respectively.

The Laplacian Δ may be replaced by ∇^2 or $\nabla \cdot \nabla$, where ∇ is a mathematical symbol called nabla, which is given by the next formula.

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

Thus, the Laplacian Δ is equal to an inner product or a scalar product .

$$\Delta = \nabla \cdot \nabla \tag{1.55}$$

Although both of these expressions may be used, Δ is used in this book.

(b) Extension to N-particle system

The wavefunction of a system with N-particles is a function of $3N$ spatial coordinates $(x_1, y_1, z_1, \cdots, x_N, y_N, z_N)$ and time t, and it contains information on the probability of finding the particles. It is convenient to use a symbol q in place of the $3N$ variables. The wavefunction $\Psi(q, t)$ for an N-particle system satisfies the same wave equation as the one-particle wavefunction.

$$i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{1.56}$$

A possible state that happens in the real world is only limited to Ψ satisfying this equation and is called an eigenstate. The probability of finding each particle in a volume of $\mathrm{d}x_i\mathrm{d}y_i\mathrm{d}z_i$ corresponding to a particular region of $x_i \sim x_i + \mathrm{d}x_i$,$y_i \sim y_i + \mathrm{d}y_i$, $z_i \sim z_i + \mathrm{d}z_i$ is given for the eigenstate Ψ by

$$|\Psi(q, t)|^2 \mathrm{d}q \tag{1.57}$$

The integration of eq.(1.57) over the entire region of $3N$ dimensional space should be equal to 1, since it is the total summation of the probabilities (normalization condition).

$$\int |\Psi(q, t)|^2 \mathrm{d}q = 1 \tag{1.58}$$

Here,

$$\mathrm{d}q = \mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1 \cdots \mathrm{d}x_N\mathrm{d}y_N\mathrm{d}z_N \tag{1.59}$$

represents the volume element of $3N$-dimension, and the corresponding integration should be taken for all of the $3N$ variables over the entire space. The integral in eq.(1.58) is simply expressed with a single $\int$ in stead of using $3N \int$, corresponding to the abbreviation for the volume element dq. The range of the integration for each variable x_i, y_i, or z_i is from $-\infty$ to ∞.

$\hat{H}$ in eq.(1.56) is the Hamiltonian operator for an N-particle system, which can be easily constructed from a classical energy expression of the Hamilton function $H(p,\, q,\, t)$ by using the following replacement formula for $\hat{p}$ in place of the momentum p.

$$\hat{p} = -i\hbar\frac{\partial}{\partial q} \tag{1.60}$$

Thus,

$$\hat{H} = H(\hat{p}, q, t) \tag{1.61}$$

For a stationary state in which $H(p,\, q,\, t) = E$ (a constant at any time t),

$$\Psi(q,t) = \psi(q)\exp\left(-i\frac{Et}{\hbar}\right) \tag{1.62}$$

$$|\Psi(q,t)|^2 = |\psi(q)|^2 \tag{1.63}$$

The wavefunction for a stationary state $\psi(q)$ satisfies

$$\hat{H}\psi = E\psi \tag{1.64}$$

The normalization condition for $\psi(q)$ is

$$\int |\psi(q)|^2\mathrm{d}q = 1 \tag{1.65}$$

1.12 The motion in two-particle systems

Many particles need to be considered in general for the application of the wave equation to chemical problems. In order to see an outlook of the application to molecular systems, let us first deal with two-particle systems. Problems in two-particle systems can be reduced to one-particle problems, when the relative motion and the motion of the center of gravity are separated.

(a) Separation of the relative motion from the translation

Let us suppose that the energy of two particles E is expressed as a sum of kinetic energies E_1 and E_2 for the particles and the potential energy U,

$$E = E_1 + E_2 + U \tag{1.66}$$

where

$$E_1 = \frac{1}{2}m_1\,\boldsymbol{V}_1^2$$
$$E_2 = \frac{1}{2}m_2\,\boldsymbol{V}_2^2$$

and m_i, $\boldsymbol{V}_i$ are the mass and the velocity of the i-th particle ($i = 1$ or 2), respectively. Coordinates for the center of gravity (X, Y, Z) are related to coordinates for each particle (x_i, y_i, z_i).

$$\begin{aligned} X &= \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \\ Y &= \frac{m_1y_1 + m_2y_2}{m_1 + m_2} \\ Z &= \frac{m_1z_1 + m_2z_2}{m_1 + m_2} \end{aligned} \tag{1.67}$$

Since the particle velocity $\boldsymbol{V}_i$ is a vector composed of time-derivatives of the Cartesian coordinates for the particle, the velocity for the center of gravity $\boldsymbol{V}_G$ is represented with the particle velocities.

$$\boldsymbol{V}_{\mathrm{G}} = \frac{m_1\,\boldsymbol{V}_1 + m_2\,\boldsymbol{V}_2}{m_1 + m_2}$$

The relative coordinates can be introduced as the positions of the second particle with respect to the first particle

$$\begin{aligned} x &= x_2 - x_1 \\ y &= y_2 - y_1 \\ z &= z_2 - z_1 \end{aligned} \tag{1.68}$$

The relative velocity $\boldsymbol{V}$, which is defined as the time-derivative of the relative position, is given by

$$\boldsymbol{V} = \boldsymbol{V}_2 - \boldsymbol{V}_1 \tag{1.69}$$

The motion of the center of gravity, which is independent of the relative motion between the particles, corresponds to parallel motion keeping relative geometries between the particles and is called the translational motion or translation.

The energy of the two-particle system is expressed as the sum of energies for the relative motion and the translation.

$$E = \frac{1}{2}(m_1 + m_2)\,{\boldsymbol{V}_{\mathrm{G}}}^2 + \frac{1}{2}\mu\,\boldsymbol{V}^2 + U \tag{1.70}$$

The first term represents the kinetic energy of the translation, and the second term represents the kinetic energy of the relative motion, where μ is the reduced mass defined by the following formula.

$$\mu = \frac{1}{1/m_1 + 1/m_2} \tag{1.71}$$

Since we may choose an arbitrary coordinate system, the motion of two-particle systems with respect to coordinates fixed at the center of gravity can be simply expressed as

$$E = \frac{1}{2}\mu\,\boldsymbol{V}^2 + U \tag{1.72}$$

where $\boldsymbol{V} = 0$. This is the energy of a particle with a mass μ and a velocity $\boldsymbol{V}$ moving under the potential energy U. Therefore, the motion of a two-particle system is reduced to that of one particle with a reduced mass μ. Thus, the corresponding Hamiltonian of the relative motion of this system is represented with a Laplacian Δ as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta + \mathrm{U} \tag{1.73}$$

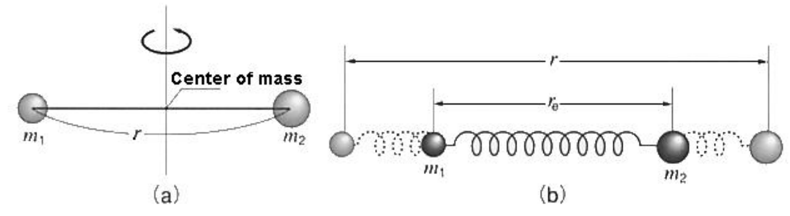


Figure 1.15: Relative motion of two-particle systems (a) Rotational motion with a fixed r (b) Vibrational motion

(b) Separation of rotation and vibration

The relative motion of two-particle systems can be divided into rotation and vibration. The rotational motion can be imagined by the rotation of a dumbbell. A prototype of the vibrational motion is the vibration of two balls connected with a spring, as shown in Fig.1.15. Angles are suitable variables for rotation. Let us transform Cartesian coordinates into polar coordinates using (r, θ, ϕ) in three-dimension, as shown in Fig.1.16.

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned} \tag{1.74}$$

r is the distance from the origin of the coordinates and said to be the radial distance. θ is the angle of the inclination from the z-axis and said to be the polar angle. ϕ is the angle around the z-axis and said to be the azimuthal angle. The spatial orientation is specified by the two angles θ and ϕ. In the polar coordinate system, variations in the angles (θ, ϕ) and the distance (r) represent rotational and vibrational motion, respectively. In the Cartesian coordinate, rotation and vibration cannot be separated.

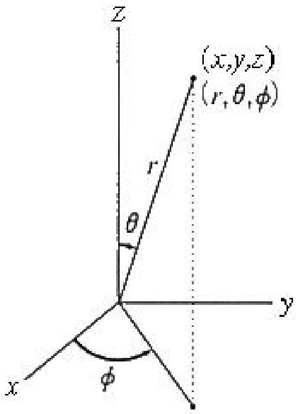


Figure 1.16: The polar coordinates

(c) Wave equation in the polar coordinates

The Laplacian for the relative motion of a two-particle system is given by

$$\Delta = \frac{1}{\mathrm{r}^2}\frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r}^2\frac{\partial}{\partial \mathrm{r}}\right) + \frac{1}{\mathrm{r}^2}\Lambda \tag{1.75}$$

Λ is an operator for angles and is known as the Legendrian.

$$\Lambda = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{1.76}$$

By using these equations, the Hamiltonian for the relative motion is written as

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \Lambda\right) + U \tag{1.77}$$

This Hamiltonian can be applied to important problems in chemistry. Let us see some typical examples of the wave equations, their energy eigenvalues, and wavefunctions.

(1) Reduced mass and energy levels of a hydrogen atom

A typical example is a hydrogen atom, which is a two-particle system of a proton and an electron. Equation (1.71) leads to the reduced mass for this system with the proton mass of M and the electron mass m as follows.

$$\mu = \frac{1}{1/M + 1/m} \tag{1.78}$$

Since m/M is as small as about 1/1836, $1/M$ is negligibly small in comparison with $1/m$ in the denominator of the eq.(78). With this approximation, $\mu = m$, and hence the Hamiltonian in eq.(1.73) is clearly the same as that for the electronic motion in a hydrogen atom with the fixed nucleus (Bohr's model). Rigorously, the reduced mass μ should be used without using m in the approximation of $M \to \infty$. Much better agreement with observed spectra will be obtained in Bohr's model, if we use μ in place of m.

When eq.(1.77) is used, energy eigenvalues satisfying $\hat{H}\psi = E\psi$ become equal to those for Bohr's model using μ in place of m, and they are given as

$$E_n = -\frac{W_{\mathrm{H}}}{n^2} \qquad (n = 1, 2, 3, \cdots) \tag{1.79}$$

$$W_{\mathrm{H}} = \frac{\mu e^4}{8\varepsilon_0 h^2} \tag{1.80}$$

W_{H} is the ionization energy of a hydrogen atom. The rigorous Rydberg constant R using the reduced mass μ is expressed as follows.

$$R = \frac{W_{\mathrm{H}}}{hc} = \frac{\mu e^4}{8\varepsilon_0 h^3 c} \tag{1.81}$$

This expression reduces to eq.(1.24) for Bohr's model, when we use $\mu = m$ in the approximation of $M \to \infty$. On account of this reason, the Rydberg constant for the case of $M \to \infty$ is sometimes denoted as R_∞.

(2) Molecular rotation of a diatomic molecule

The Hamiltonian in eq.(1.77) can be applied to molecular rotation of a diatomic molecule, which is the rotational motion around an axis passing through the center of gravity. The distance r of the bonded atoms, which is called the bond length, can be fixed at its equilibrium value, and we neglect external forces. Then, the Hamiltonian for the rotational motion of a diatomic molecule is expressed as

$$\hat{H} = -\frac{\hbar^2}{2I}\Lambda \tag{1.82}$$

I is the moment of inertia and given by

$$I = \mu r^2 \tag{1.83}$$

The reduced mass in this case is the same as eq.(1.71) for mass of two particles, m_1 and m_2. Equation (1.82) can be applied to a circular motion of a particle with mass μ attached at one end of a hard stick of length r, which is fixed at the other end to the origin of the coordinates. This circular motion of the particle is restricted to the surface of the sphere. This kind of a rotational system is called a rigid rotor. Stationary states of such a rigid rotor or the molecular rotation are described by wavefunctions of two angles θ and ϕ.

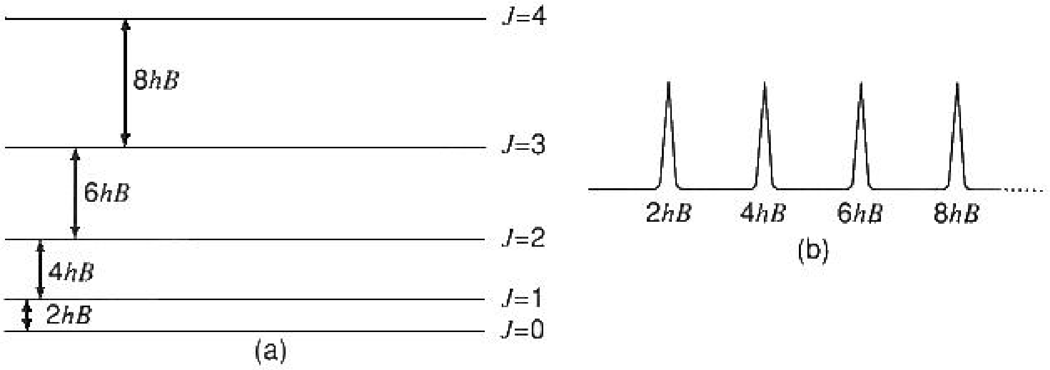


Figure 1.17: The rotational energy levels (a) and the rotational spectrum (b). The rotational constant, $B = \frac{h}{8\pi^2 \mu r^2}$. The selection rule for rotational transitions, $\Delta J = \pm 1$.

By solving $\hat{H}\psi = E\psi$ with eq.(1.82), energy levels are obtained as follows (Fig. 1.17).

$$E_J = \frac{\hbar^2}{2I} J(J+1) \qquad (J = 0, 1, 2, 3, \cdots) \tag{1.84}$$

Here, J is the rotational quantum number. The formula for rotational energy levels can be applied to molecular rotations of diatomic molecules. Photons corresponding to the energy difference between the J-th and $(J+1)$-th energy levels, which is expressed as ΔE in eq.(1.85), can be absorbed or emitted to yield molecular rotational spectra.

$$\Delta E = E_{J+1} - E_J = (J+1)\frac{\hbar^2}{I} = 2(J+1)hB \tag{1.85}$$

Transitions among rotational levels are called rotational transitions. B in eq.(1.85) is the rotational constant, which is defined by the following equation.

$$B = \frac{h}{8\pi^2 \mu r^2} \tag{1.86}$$

Associated with the increase of J=0,1,2,3, the corresponding energies of the rotational transitions expressed as ΔE in eq.(1.85) increase with a constant spacing of $(\hbar^2/I)$. In many cases, rotational spectra of molecules appear in the microwave or far infrared regions. When the moment of inertia I is obtained from observed spectra, the bond length r can be determined from eq.(1.83) given the value of the reduced mass. Though analyses become complicated, geometrical structures of polyatomic molecules can also be determined from rotational spectra. Electromagnetic waves from interstellar media in the universe contain those emitted as molecular rotational spectra. Rotational transition probabilities depend on the electric polarization of the molecule. Rotational transitions cannot occur for nitrogen and hydrogen molecules, since these molecules have no electric polarization.

(3) Molecular vibration of a diatomic molecule

The Hamiltonian in eq.(1.77) can also be applied to the molecular vibration of a diatomic molecule, which is the stretching motion of the bond-length r around its equilibrium distance of r_e. Fixing the rotational angles θ and ϕ, the Hamiltonian for the vibrational motion of a diatomic molecule is expressed as

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + U(r) \tag{1.87}$$

Since the wavefunction $\psi(r)$ is a function of r satisfying $\hat{H}\psi = E\psi$, we can write $\psi(r)$ using a function $\phi(r)$ as follows.

$$\psi(r) = \frac{\phi(r)}{r} \tag{1.88}$$

Then, we obtain from the eq.(1.87) the following equation.

$$\left(-\frac{\hbar^2}{2\mu}\cdot\frac{\partial^2}{\partial r^2} + U(r)\right)\phi(r) = E\phi(r) \tag{1.89}$$

For vibrational motion according to Hooke's law, the potential energy U is proportional to the square of the displacement Q from the equilibrium position (fig.1.18), and it is given by

$$U = \frac{1}{2}kQ^2 \tag{1.90}$$

Here, k is a constant related to the strength of the spring, which is called the force constant. The displacement Q is given by the difference between the bond length r and its equilibrium value r_e.

$$Q = r - r_\mathrm{e} \tag{1.91}$$

Using the displacement Q as the variable, the wave equation for the vibrational motion of a diatomic molecule is expressed as follows.

$$\left(-\frac{\hbar^2}{2\mu}\cdot\frac{\partial^2}{\partial Q^2} + \frac{1}{2}kQ^2\right)\phi(Q) = E\phi(Q) \tag{1.92}$$

By solving this equation, energy levels for one-dimensional harmonic oscillator are given by the following equation (fig.1.18).

$$E_v = \left(v + \frac{1}{2}\right)h\nu \qquad (v = 0, 1, 2, 3, \cdots) \tag{1.93}$$

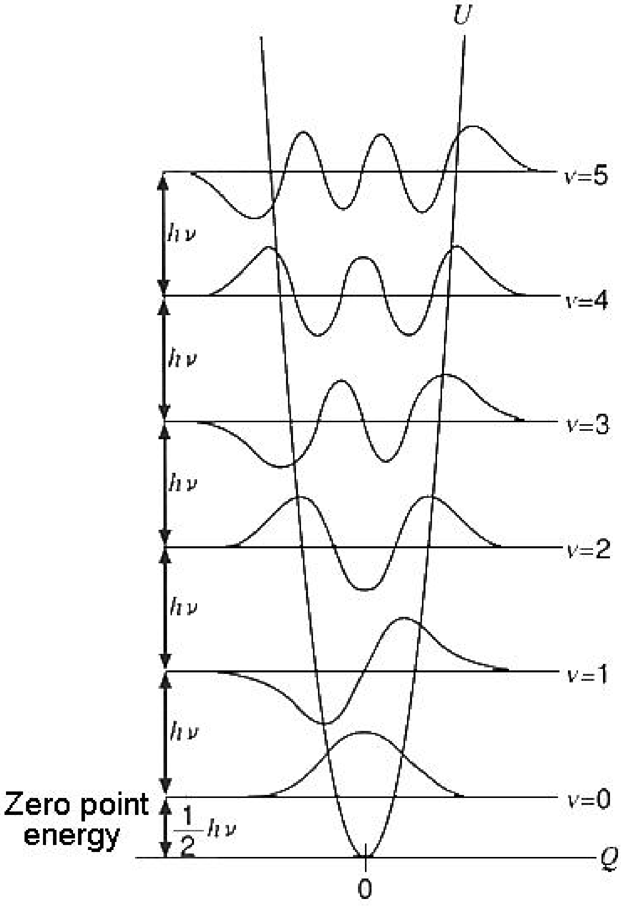


Figure 1.18: Potential energy $U = \frac{1}{2}kQ^2$ as well as energy levels and wavefunctions for a one-dimensional harmonic oscillator

Here, v is the vibrational quantum number, and ν is the fundamental frequency of the vibrational motion, which is given by the following formula.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.94}$$

This frequency is equal to the fundamental frequency of a one-dimensional harmonic oscillator with a force constant k and a reduced mass μ.

In the case of a classical harmonic oscillator, the energy of a vibrating spring may change continuously. While for an oscillator in the quantum theory, only quantized energy values in eq.(1.93) can be allowed. Energy levels of a harmonic oscillator are equally spaced, and the energy spacing $h\nu$ is called the energy quantum of vibration. The energy of the ground state is $E_0 = \frac{1}{2}h\nu$, and this energy is one half of the energy quantum of vibration, which is called the zero-point energy of vibration. The vibrational motion in the ground state is called the zero-point oscillation.

As can be seen from eq.(1.94), molecular vibrations oscillate slowly for massive systems and quickly for strongly bonded systems. Photons of the energy difference between the $(v+1)$-th and v-th energy levels, which is expressed as ΔE in eq.(1.95), can be absorbed or emitted to yield molecular vibrational spectra.

$$\Delta E = E_{v+1} - E_v = h\nu \tag{1.95}$$

Vibrational spectra of molecules are usually in the infrared region. Molecular vibrations associated with changes of electric polarization tend to undergo vibrational transitions with greater probability. Vibrations without changes in electric polarization do not undergo vibrational transitions.

Although the details of wavefunctions for harmonic oscillators are not described here, their general characteristics can be seen in fig.1.18. The number of nodal points in the wavefunctions of harmonic oscillators increases with the increase of the quantum number, one by one, similarly to the nodal points in the wavefunctions of a particle in the one-dimensional box.

1.13 The angular momentum

Angular momentum is an important physical quantity, especially for problems of energy levels and spectra of atoms and molecules. In this section, angular momentum is defined, and its properties are described.

The angular momentum of a particle is defined as an outer product (vector product) $\boldsymbol{r} \times \boldsymbol{p}$ of the position vector $\boldsymbol{r}$ representing its position (x, y, z) and its momentum $\hat{\boldsymbol{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$.

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} \tag{1.96}$$

This equation can be rewritten with components.

$$\begin{aligned} l_x &= yp_z - zp_y \\ l_y &= zp_x - xp_z \\ l_z &= xp_y - yp_x \end{aligned} \tag{1.97}$$

The angular momentum introduced here is called the orbital angular momentum, since it is related to the classical orbital motion of the particle.

Example 1.12 Obtain the orbital angular momentum $\boldsymbol{l}$ of a particle of a mass m circulating in the x–y plane with a constant velocity of v and a radius r. Then, rewrite Bohr's condition of quantization in eq.(1.21) for the restriction of the magnitude of the angular momentum $|\,\boldsymbol{l}\,|$.

(Solution) Since $z = 0,\ p_z = 0$ for the circular motion around the origin O in the x–y plane as shown in the figure, the x and y components of $\boldsymbol{l}$ are both vanishing.

$$\begin{aligned} l_x &= yp_z - zp_y = y \cdot 0 - 0 \cdot p_y = 0 \\ l_y &= zp_x - xp_z = 0 \cdot p_x - x \cdot 0 = 0 \end{aligned}$$

Taking the angle θ and the direction of the velocity v as in the figure, we obtain the following equations.

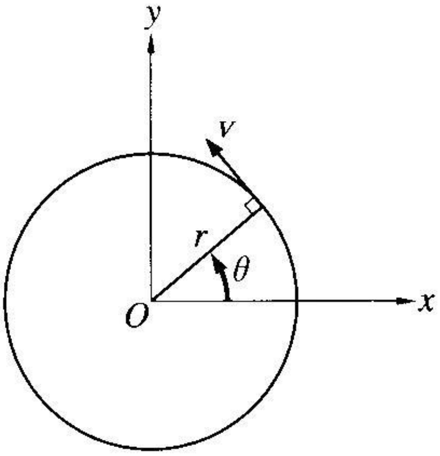
$$\begin{aligned} x &= r\cos\theta \\ y &= r\sin\theta \\ p_x &= mv_x = -mv\sin\theta \\ p_y &= mv_y = mv\cos\theta \end{aligned}$$

The z component of $\boldsymbol{l}$ becomes

$$l_z = xp_y - yp_x = mvr \cdot \cos^2\theta + mvr \cdot \sin^2\theta = mvr$$

Thus, three components of the orbital angular momentum $\boldsymbol{l}$ are expressed as

$$\boldsymbol{l} = (0, 0, mvr)$$



According to eq.(1.21), Bohr's condition of quantization is

$$(mv)(2\pi r) = nh \qquad (n = 1, 2, 3, \cdots)$$

Noting $|\,\boldsymbol{l}\,| = mvr$ in the above equation, we obtain

$$|\,\boldsymbol{l}\,| = n\hbar$$

Thus, Bohr's condition of quantization indicates that the magnitude of the orbital angular momentum of the circular motion is quantized to be proportional to the integer multiple of $\hbar$.

The operator $\hat{\boldsymbol{l}} = (\hat{l}_x,\, \hat{l}_y,\, \hat{l}_z)$ corresponding to $\boldsymbol{l}$ can be obtained using a formula of eq.(1.53), which was used for the derivation of the Hamiltonian operator. Using polar coordinates $(r,\, \theta,\, \phi)$, we obtain the following equations.

$$\begin{aligned} \hat{l}_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ \hat{l}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ \hat{l}_z &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned} \tag{1.98}$$

These equations lead to a useful expression for the square of the angular momentum $\boldsymbol{l}^2 = {l_x}^2 + {l_y}^2 + {l_z}^2$. Thus , $\hat{\boldsymbol{l}}^2$ which is proportional to the Legendre operator Λ.

$$\hat{\boldsymbol{l}}^2 = -\hbar^2 \cdot \Lambda \tag{1.99}$$

Characteristic properties of the operator Λ have been studied very well in connection with the spherical harmonics $Y_{l,m}$. Some examples for $Y_{l,m}$ are shown in Table 1.3. The following relation is very important.

$$\Lambda Y_{l,m} = -l(l+1)Y_{l,m} \tag{1.100}$$

or

$$\hat{\boldsymbol{l}}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m} \tag{1.101}$$

This is the eigen equation for $\hat{\boldsymbol{l}}^2$; $Y_{l,m}$ is the eigen function, and $l(l+1)\hbar^2$ is the eigen value. l is the quantum number determining the magnitude of the orbital angular momentum. This is the quantum number for the square of $\boldsymbol{l}$ and is restricted to be $l = 0, 1, 2, 3, \cdots$.

The following relation for the z component of the angular momentum $\hat{l}_z$ can be confirmed in Table 1.3.

$$\hat{l}_z Y_{l,m} = m\hbar Y_{l,m} \tag{1.102}$$

This is the eigen equation for $\hat{l}_z$; $Y_{l,m}$ is the eigen function, and $m\hbar$ is the eigen value. m is the quantum number for the z component of the orbital angular momentum, and its $2l+1$ possible

Table 1.3: Spherical harmonics $Y_{l,m}(\theta,\phi)$

$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$	$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \mathrm{e}^{\pm i2\phi}$
$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$	$Y_{3,0} = \sqrt{\frac{7}{16\pi}} (5\cos^3\theta - 3\cos\theta)$
$Y_{1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin\theta \mathrm{e}^{\pm i\phi}$	$Y_{3,\pm 1} = \sqrt{\frac{21}{64\pi}} (5\cos^2\theta - 1) \sin\theta \mathrm{e}^{\pm i\phi}$
$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$	$Y_{3,\pm 2} = \sqrt{\frac{105}{32\pi}} \cos\theta \sin^2\theta \mathrm{e}^{\pm i2\phi}$
$Y_{2,\pm 1} = \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \mathrm{e}^{\pm i\phi}$	$Y_{3,\pm 3} = \sqrt{\frac{35}{64\pi}} \sin^3\theta \mathrm{e}^{\pm i3\phi}$

values associated with the quantum number l are in the range from $-l$ to $+l$. For example for $l = 1$, allowed values are $m = -1, 0, 1$. Such characteristics of l and m are related to the behavior of electrons in atoms. A similar relationship is also important in the description of molecular rotational states. As studied in the rigid rotor of a diatomic molecule, the Hamiltonian operator is proportional to the Legendrian operator Λ in eq.(1.100), the wavefunctions for the molecular rotation become spherical harmonics $Y_{l,m}$.

1.14 Measured values and expectation values

The eigen values (energy eigen values) that satisfy the wave equation for stationary states are the allowed energies of the system, namely the energy levels. Therefore, the measured energy values for the stationary states should agree with an energy eigen value. In other words, any value different from the energy eigen values cannot be measured in principle, except for discrepancies due to experimental errors. How about the eigen values of the momentum and those of the angular momentum? It has been confirmed by experiments that the possible values to be measured for an observable physical quantity should be eigen values of the operator of that observable.

If a system is in a stationary state, the energy should become a definite value, whenever it is measured. This is because the wave function representing a state of the system is a particular eigen function belonging to the respective eigen value. The momentum or the angular momentum is not always definite, and their measured values may be different. This is related to the nature of the wave function which does not need to be (or be proportional to)particular eigen functions of the momentum or the angular momentum.

Quantum theoretical investigations of the uncertainty in measured quantities led to the following rules.

(1) The wave function $\Psi(q,t)$ can be expressed as the following form of a linear combination of $\{\phi_i\}$, which are eigen functions of the physical quantity F.

$$\Psi(q,t) = \sum_i c_i(t)\phi_i(q) \tag{1.103}$$

Here, the eigen equation for F is given as

$$\hat{F}\phi_i(q) = f_i\phi_i(q) \tag{1.104}$$

(2) Measured values of a physical quantity F should agree with one of eigen values for its operator $\hat{F}$. The probability $P(f_i)$ of finding the i-th eigen value f_i is given by the square of the i-th coefficient c_i in the above expansion in terms of normalized eigen functions $\{\phi_i\}$.

$$P(f_i) = a|c_i|^2 \tag{1.105}$$

Since the total probability should be equal to unity,

$$\sum_i P(f_i) = 1 \tag{1.106}$$

then the constant a in eq.(1.105) should be normalized as follows.

$$a = \frac{1}{\sum_i |c_i|^2} \tag{1.107}$$

From the above two rules, the average of the measured values $\langle f \rangle$ is expected to be given by the following formula.

$$\langle f \rangle = \sum_i f_i P(f_i) \tag{1.108}$$

The value of the right-hand side of this equation is determined by the magnitude of the expansion coefficients $\{c_i\}$ which represent the amounts of the respective components included in the state of Ψ. If all $c_i (i \neq 1)$ except for $c_1 (i = 1)$ are 0, then $\langle f \rangle = f_1$. In this case, Ψ is a pure state of $\Psi = c_1 \phi_1$, which includes only the first eigen function, and $P(f_1) = 1$ for $i = 1$, while $P(f_i) = 0$ for $i \neq 1$. When a particular eigen value f_i among the whole eigen values $\{f_i\}$ of $\hat{F}$ is always observed, the state Ψ is the eigen state of the physical quantity F, and this physical quantity F has always a certain value f. On the other hand for the more general cases of mixed states in which Ψ contains several components among $\{\phi_i\}$, measured values distribute over different eigen values rather than fixed at a certain value.

The average of measured values $\langle f \rangle$ can be directly calculated by the quantum mechanical expectation value $\langle F \rangle$ defined by the following formula.

$$\langle F \rangle = \frac{\int \Psi^* \hat{F} \Psi \mathrm{d}q}{\int \Psi^* \Psi \mathrm{d}q}. \tag{1.109}$$

The integration should be taken for all variables symbolized as q over the entire ranges of the variables of Ψ. When Ψ is already normalized, the denominator becomes unity and thus it may be omitted.

1.15 The commutation relation and the uncertainty principle

Whether a pair of physical quantities F and G can have certain measured values simultaneously or not is governed by the properties of the corresponding operators $\hat{F}$ and $\hat{G}$. In general, if there exists a class of common eigen functions $\{\phi_i\}$, then the following relationship holds.

$$\hat{F}\hat{G} = \hat{G}\hat{F} \tag{1.110}$$

Conversely, if this relationship holds, then there exists a class of common eigen functions $\{\phi_i\}$ for $\hat{F}$ and $\hat{G}$. The above relationship indicates that the operators $\hat{F}$ and $\hat{G}$ commute and that the order is interchangeable.

Let us consider a special case where an operator $\hat{F}$ commutes with the Hamiltonian operator $\hat{H}$. In this case, there exists a function Ψ which is simultaneously an eigen function of both $\hat{F}$ and $\hat{H}$, and then a pair of equations $\hat{F}\Psi = f\Psi$ and $\hat{H}\Psi = E\Psi$ are compatible for the same function Ψ. In such a special case, the wave function Ψ of the eigen function of $\hat{H}$ with an eigen value E is also the eigen function of $\hat{F}$ with an eigen value f. In a sense, this state of Ψ is a pure state in which the physical quantity F has always a certain value f. The physical quantity F can have a certain value, only if the corresponding operator $\hat{F}$ commutes with $\hat{H}$. If $\hat{F}$ and $\hat{H}$ do not commute, F does not have a certain value, and a measured value f_i will be observed at a probability of $P(f_i)$, according to the rule mentioned above.

Example 1.13 Confirm that the operator of the position coordinate $\hat{x}$ and the operator of the x-component of the linear momentum $\hat{p}_x$ do not commute.

(Solution) Since $\hat{x} = x$ and $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, we obtain the following equations for an arbitrary function $\phi(x)$.

$$\hat{x}\hat{p}_x\phi = x\left(-i\hbar\frac{\partial}{\partial x}\right)\phi = -i\hbar x\frac{\partial\phi}{\partial x}$$

$$\hat{p}_x\hat{x}\phi = -i\hbar\frac{\partial}{\partial x}(x\phi) = -i\hbar\phi - i\hbar x\frac{\partial\phi}{\partial x}$$

It follows that

$$(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\phi = i\hbar\phi$$

Noting that ϕ is a function of x,

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

Since the right-hand side is not vanishing, we can conclude that $\hat{x}$ and $\hat{p}_x$ do not commute.

Similarly to the above example, $\hat{y}$ and $\hat{p}_y$ and also $\hat{z}$ and $\hat{p}_z$ do not commute. Therefore, the position coordinate and the linear momentum cannot have certain values simultaneously. Uncertainties of measured values were studied by W. K. Heisenberg. He found the following relationship in 1927.

$$\Delta q\Delta p \geq \frac{1}{2}\hbar \tag{1.111}$$

Here, Δq and Δp denote the uncertainties for the position q and the corresponding momentum p. Because of this relation, if we want to specify the position, measured values for the momentum become uncertain with distributed values. Conversely, if we want to specify the momentum, measured values for the position become uncertain. An analogous relationship was also found for the uncertainty of the energy ΔE and the time interval Δt necessary to measure.

$$\Delta E\Delta t \geq \frac{1}{2}\hbar \tag{1.112}$$

This means that we need the infinite time to determine the energy precisely. When the time interval is very short, the energy becomes obscured rather than to be determined at a certain value. The above two inequalities are called the uncertainty principle.

Exercises

1.1 Associated with a collision of an excited atom with the surface of an electrode in vacuum, an electron can be emitted as a secondary electron from the surface, and such electrons can be captured with a metal plate. Using such an apparatus with an ammeter, the electric current through the circuit connecting the electrode with the metal plate was measured to be 160 pA (1 C is the electric charge that the electric current of 1 A carries for 1 second). Calculate the number of excited atoms per second, provided that one excited atom produces one secondary electron.

1.2 The velocity of a nitrogen molecule travelling in the atmosphere at ambient temperature is ca. 500 ms^{-1}. Calculate the kinetic energy of a nitrogen molecule with this velocity in units of J or eV.

1.3 A group of infrared rays with wavelengths of 3.3, 6.2, 7.7, 8.6, and 11.3 μm are emitted from various interstellar matters. It has been a long standing question to determine the substance that emits these infrared rays. It is well known that infrared spectra of unsaturated hydrocarbon molecules contain spectral lines of $3000\,\mathrm{cm}^{-1}$ of CH stretching modes, $1600\,\mathrm{cm}^{-1}$ and $1300\,\mathrm{cm}^{-1}$ of CC stretching modes, and $1140\,\mathrm{cm}^{-1}$ and $890\,\mathrm{cm}^{-1}$ of CCH angle bending modes. Which of these wave numbers correspond to the unidentified infrared wavelengths from the interstellar matter?

1.4 Estimate the surface temperature of a star emitting the thermal radiation with a maximum wavelength of 500 nm. Answer this question consulting Example 1.5.

1.5 A photon emitted from a hydrogen atom in the excited state of principal quantum number $n = 2$ hit another hydrogen atom in the state $n = 2$, and a photoelectron was ejected. Calculate the kinetic energy of this photoelectron.

1.6 An electron beam produced by acceleration of electrons with a potential difference of 600 V was projected onto a crystal surface of Ni. The second order reflection was observed at an angle of 34.5°. Calculate the interval of the adjacent lattice planes of the crystal.

1.7 Write the wave equation for stationary states of a particle with a mass m moving under a potential energy of $U(r) = \frac{1}{2}kr^2\ (k > 0)$ depending only on the distance r. Indicate the dependence on the three dimensional coordinates (x, y, z) explicitly.

1.8 The next two functions ψ_1 and ψ_2 are wavefunctions for stationary states of a one-dimensional harmonic oscillator. A, B, and $a\,(a > 0)$ are constants.

$$\psi_1(x) = A\mathrm{e}^{-ax^2}$$
$$\psi_2(x) = Bx\mathrm{e}^{-ax^2}$$

Concerning these two functions, answer the next questions (1) and (2).

(1) Normalize ψ_1 and ψ_2. Using a formula of $\int_{-\infty}^{\infty} \mathrm{e}^{-x^2}\mathrm{d}x = \sqrt{\pi}$, determine constants A and B, so as to satisfy the normalization condition.

(2) Substitute ψ_1 and ψ_2 into the wave equation for stationary states of an oscillating particle with a mass m and a force constant k. Obtain eigen values for ψ_1 and ψ_2 by transforming substituted equations into a form proportional to the respective wavefunction.

1.9 Obtain the expectation value of the position coordinate for a particle in a one-dimensional box with a length L.

1.10 Show that spherical harmonics functions of $Y_{1,1}$, $Y_{1,0}$, and $Y_{1,-1}$ are eigen functions of the operator for the square of the orbital angular momentum. Confirm that the eigen values for these three functions coincide. Verify that any linear combination of these three functions is also an eigen function of the operator for the square of the orbital angular momentum, and that its eigen value also agrees with the eigen value of the three functions.

Chapter 2

Atom

Chemical elements, which are chemical varieties of atoms, are classified by atomic numbers. Atoms of the same element are called isotopes, when total numbers of protons and neutrons in the nuclei (mass numbers) are different. Although phenomena concerning with masses depnend on isotopes and their abundance, chemcical properties are usually irrespective of the isotopes. This is due to decisive roles of electrons which are small and mobile. Probabilities of electron transfer are governed by numbers of electrons around nuclei. Electronic motion depends on the attractive force caused by the nucleus charges. Since the number of electrons and the nucleus charge are chararacteristic to each atomic number, chemical properties of atoms are closely related to the atomic numbers.

In this chapter, we will study how characteristic properties of atoms appear dependning on the atomic number. In the last section of this chapter, we will aslo study excited states and spectra of atoms.

2.1 The hydrogenic atom

Let us first consider a hydrogenic atom, in which an electron is moving around a nucleus as shown in fig.2.1. Based on such a simple system, we will study the fundamental characteristics of energy levels and wavefunctions.

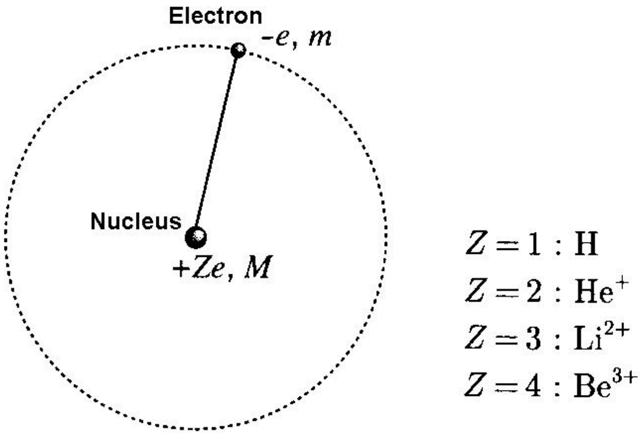


Figure 2.1: A hydrogenic atom. Z: atomic number, M: mass of the nucleus, m: mass of the electron

The electric charge of the nucleus is represented by the product of the atomic number Z and the elementary charge e. The potential energy U is given by $U = -Ze^2/4\pi\varepsilon_0 r$. Using the formula (1.73) for a two-particle system introduced in section 1.12, the Hamiltonian operator $\hat{H}$ of this system is expressed by the following equation.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{2.1}$$

Here, μ is the reduced mass, which is given for the mass of the nucleus M and the mass of the electron m by the following equation.

$$\mu = \frac{1}{1/M + 1/m} \tag{2.2}$$

When $1/M$ in the denominator of this equation for μ is neglected by noting $M \gg m$, the equation reduces to $\mu = m$, and the system becomes a simple model that an electron moves around the resting nucleus. Errors due to this approximation are not very large, as can be seen below from the Example 2.1. It follows that solutions of the wave equation of the Hamiltonian in eq.(1.73), which are rigorously for the relative motion, can be understood to represent motions of the electron in the atom.

A comparison with the case of a hydrogen atom ($Z = 1$) indicates that e^2 is simply replaced by Ze^2 in the expression for the potential energy. Therefore, from eqs.(1.79) and (1.80), the energy levels are given by the following equations.

$$E_n = -\frac{W(Z)}{n^2} \qquad (n = 1, 2, 3, \cdots) \tag{2.3}$$

$$W(Z) = \frac{\mu Z^2 e^4}{8{\varepsilon_0}^2 h^2} \tag{2.4}$$

Here, n is the principal quantum number that determines the energy level. $W(Z)$ is the energy required for removing one electron from the hydrogenic atom. This quantity for $Z = 1$ corresponds to the ionization energy of hydrogen atom W_{H}.

Example 2.1 How many times the energy is required for producing a di-positive ion of helium (He^{2+}) by removing an electron from a helium ion (He^{+}) in comparison with the ionization energy of hydrogen atom ?

(Solution) Ionization energy of an atom depends on the reduced mass μ and the atomic number Z. Approximating the mass ratio of a proton and an electron as 1836 : 1 and also approximating the mass ratio of a hydrogen nucleus and a helium nucleus as 1 : 4, we obtain the ratio of the reduced masses as

$$\frac{\mu(\mathrm{He})}{\mu(\mathrm{H})} = \frac{1/1836 + 1}{1/(1836 \times 4) + 1} = \frac{4 \times (1 + 1836)}{1 + 1836 \times 4} = 1.00041$$

For the difference of the atomic numbers, $Z(\mathrm{He})^2/Z(\mathrm{H})^2 = 2^2/1^2 = 4$. It follows that the ratio obtained becomes 4.0016.

$$W(2) = 4 \times 1.00041 \times W_{\mathrm{H}} = 4.00164$$

If the difference of the reduced masses is neglected as $\mu(\mathrm{He}) = \mu(\mathrm{H}) = m$, then $W(2) = 4W_{\mathrm{H}}$, which leads to an answer of 4 as the ratio to be obtained.

Using the Hamiltonian operator in eq.(1.77), the wave equation can be expressed in terms of polar coordinates as follows.

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \Lambda\right)\Psi = (E - U)\Psi \tag{2.5}$$

As studied for the angular momentum, Legendrian Λ only includes angular coordinates (θ, ϕ), and it satisfies the following equation with the spherical harmonic functions $Y_{l,m}$.

$$\Lambda Y_{l,m} = -l(l+1)Y_{l,m} \tag{2.6}$$

Noting this equation, let us take the wave function in the following form.

$$\Psi = R(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.7}$$

From eqs.(2.5)-(2.7) we obtain

$$\left[-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - l(l+1)\right)R(r) + (U-E)R(r)\right]Y_{l,m} = 0 \tag{2.8}$$

The Ψ introduced in eq.(2.7) is able to become the solution of the wave equation of the hydrogenic atom, provided that the function $R(r)$ is determined to satisfy $[\quad] = 0$. In this way, the wave function of the hydrogenic atom is given in a form of a product of the radial part $R(r)$ and the angular part $Y_{l,m}(\theta, \phi)$.

The equation determining $R(r)$ is given by as follows.

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - l(l+1)\right)R(r) = (E-U)R(r) \tag{2.9}$$

By solving this differential equation to obtain continuous and finite functions, energy eigen values E agree with eqs.(1.79) and (1.80), and the following restrictions to n and l are derived.

$$n = l+1, l+2, l+3, \cdots \qquad (n = 1, 2, 3, \cdots) \tag{2.10}$$

Functions $R(r)$ for the radial part are expressed in terms of mathematically well known Laguerre polynomials L_α and a function of r given below as ρ.

$$\rho = \frac{2Zr}{na_0} \tag{2.11}$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2} \tag{2.12}$$

$$R_{n,l}(\rho) = -\sqrt{\frac{4(n-l-1)!}{n^4[(n+l)!]^3}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^l \mathrm{e}^{-\rho/2} L_{n+l}{}^{2l+1}(\rho) \tag{2.13}$$

$$L_\alpha{}^\beta(\rho) = \frac{\mathrm{d}^\beta}{\mathrm{d}\rho^\beta}L_\alpha(\rho) \qquad (\beta = 0, 1, 2, \cdots,\ \beta \le \alpha) \tag{2.14}$$

$$L_\alpha(\rho) = \mathrm{e}^\rho \frac{\mathrm{d}^\alpha}{\mathrm{d}\rho^\alpha}(\rho^\alpha \mathrm{e}^{-\rho}) \qquad (\alpha = 0, 1, 2, \cdots) \tag{2.15}$$

Table 2.1: The radial part of the wave functions $R_{n,l}(r)$

$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2}\mathrm{e}^{-(Z/a_0)r}$$

$$R_{2,0} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)\mathrm{e}^{-(Z/2a_0)r}$$

$$R_{2,1} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}\mathrm{e}^{-(Z/2a_0)r}$$

$$R_{3,0} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - \frac{18Zr}{a_0} + \frac{2Z^2r^2}{a_0{}^2}\right)\mathrm{e}^{-(Z/3a_0)r}$$

$$R_{3,1} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{6Zr}{a_0} - \frac{Z^2r^2}{a_0}\right)\mathrm{e}^{-(Z/3a_0)r}$$

$$R_{3,2} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0{}^2}\mathrm{e}^{-(Z/3a_0)r}$$

Here, $L_\alpha{}^\beta$ are associated Laguerre polynomials. a_0 is a constant, which is equal to the Bohr radius $a_{\rm B}$, when $\mu = m$. As can be seen from Example 2.1, errors due to the approximation of $\mu = m$ are as small as less than 0.1%. Thus, a_0 may be considered to be equal to the Bohr radius $a_{\rm B}$. Table 2.1 shows the radial part of the wave functions $R_{n,l}$ which can be obtained from eqs.(2.11)-(2.15). Graphs of $R_{n,l}$ for hydrogen are shown in fig.2.2.

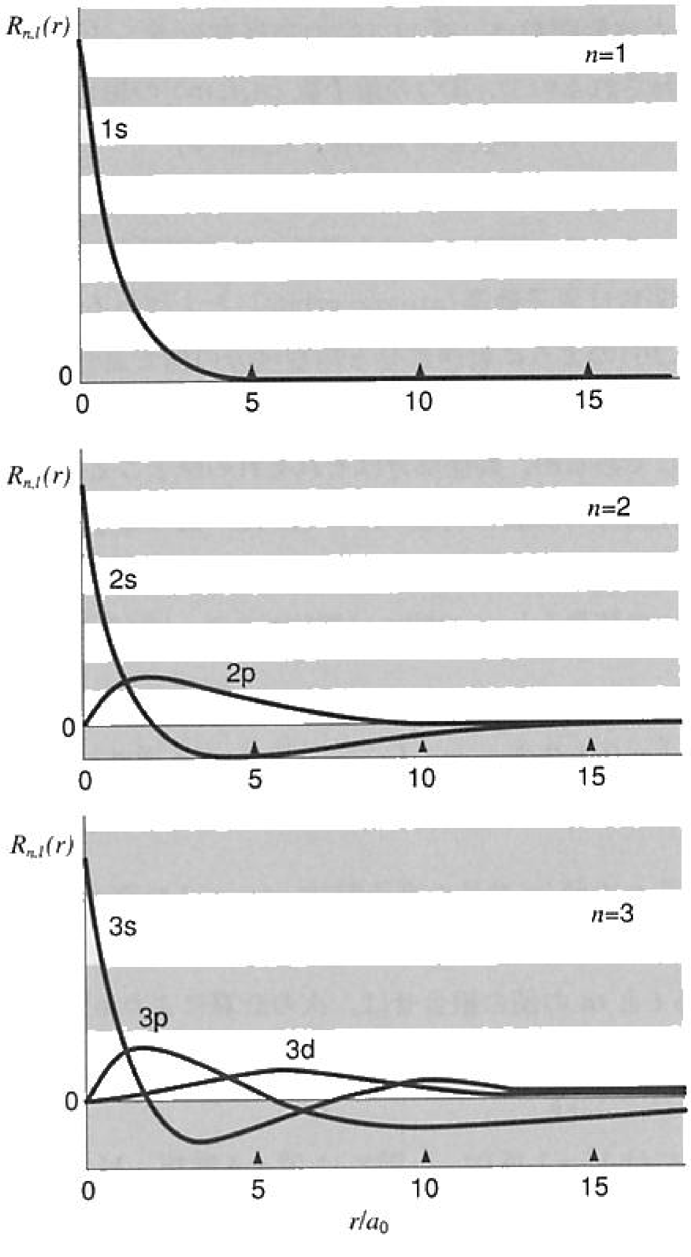


Figure 2.2: Radial part $R_{n,l}(r)$ of hydrogenic wave functions.

Since the square of the absolute value of the wave function is proportional to the probability finding a particle, the form of $R_{n,l}(r)$ determines the behavior of an electron in the atom with respect to the distance r from the nucleus. This has a great significance in various chemical phenomena in connection with the behavior of electrons in a general atom. As can be seen from Table 2.1 and fig.2.2, the radial part of the wave functions $R_{n,l}$ have mathematical properties listed below. In connection with these properties, characteristic remarks on the r-dependence of the probability finding an electron in the atom are shown in [ ]. As will be seen in Section 2.2, the r-dependence of the probability of finding an electron is proportional to $r^2 {R_{n,l}}^2$.

[Mathematical properties of the radial part of the wave functions and the r-dependence of the probability of finding an electron]

(1) Because of an exponential factor, the functional value approaches 0 asymptotically associated with the increase of r [moving outward from the nucleus, the probability of finding an electron becomes to be vanishing].

(2) The coefficient of r in the exponent becomes smaller for the larger principal quantum number n, and it follows that the functional value approaches 0 more slowly for the larger n [The probability of finding an electron extends into the more outer regions on going from $n = 1$, $n = 2$, and $n = 3$].

(3) The functional value at $r = 0$ is 0 except for $l = 0$ [There is no possibility of finding an electron at the nuclear position except for $l = 0$].

(4) There are $n - l - 1$ distances (spheres) where no electron can be found with the functional value being vanishing [In cases of $n - l > 1$, the probability of finding an electron decreases to the outer regions with an oscillating behavior].

The principal quantum number n has an important significance that classifies the energy levels, and it also characterizes the spatial behavior of the probability of finding an electron. It follows that electrons in an atom extend outwards in forming electron shells of the K shell ($n = 1$), the L shell ($n = 2$), the M shell ($n = 3$), the N shell ($n = 4$), the O shell ($n = 5$), the P shell ($n = 6$) and so on. This propensity corresponds to the orbital radius in the Bohr model becoming larger, associated with the increase of n.

In the Bohr model, the motion of an electron belonging to each electron shell is limited to a simple circular orbit. In quantum mechanics, electronic motion becomes more complex because forms of the wave functions depend not only on n but also on l and m. l and m are also quantum numbers that specify atomic states and wave functions. l is called the azimuthal quantum number, and m is called the magnetic quantum number. l is related to the directions and forms of wave functions, and m is concerned with the phenomena that energy levels may vary with the applied magnetic field.

The wave functions $\{\Psi\}$ of a hydrogenic atom are expressed as a product of the radial part $R_{n,l}(r)$ in eq.(2.13) and the spherical harmonics functions $Y_{l,m}$, and thus $\{\Psi\}$ are specified by a combination of three quantum numbers (n, l, m).

$$\Psi_{n,l,m} = R_{n,l}(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.16}$$

(r, θ, ϕ) are electron coordinates with respect to the nuclear position, and $\Psi_{n,l,m}$ represents the electronic motion in the atom. According to the correspondence with the orbital motion of the electron in the Bohr model, wave functions for an electron in an atom are called atomic orbitals. Atomic orbitals for general atoms are also expressed as a product of the radial part and the angular part(spherical harmonics) as eq.(2.16) and are specified by three quantum numbers (n, l, m). Although the angular part of atomic orbitals is the same for both hydrogenic atoms and general atoms, the radial part is different for each atom. The characteristic properties of the radial part (1)-(4) given above are common for all atoms.

As mentioned for the angular momentum, there are some restrictions for the two integers l and m associated with the spherical harmonics functions $Y_{l,m}$. Taking into account the relation between l and n in eq.(2.10), we obtain the following equations.

$$l = 0, 1, 2, 3, \cdots, n-1 \qquad (n\,\text{cases}) \tag{2.17}$$

$$m = -l, -l+1, \cdots, 0, \cdots, l-1, l \qquad (2l+1\,\text{cases}) \tag{2.18}$$

There are n cases of l values for the same n (the n-th electron shell), and there are $2l+1$ cases of m values for the same l. It follows that the acceptable combinations of l and m for a particular electron shell such as the n-th shell are determined to be n^2 by the following calculation.

$$\sum_{l=0}^{n-1}(2l+1) = \frac{2 \times n(n-1)}{2} + n = n^2 \tag{2.19}$$

Thus, there are $1^2 = 1$ wave functions for the K shell, $2^2 = 4$ for the L shell, and $3^2 = 9$ for the M shell. These numbers are related to the upper limits of numbers of electrons that can be incorporated in a particular electron shell, as will be seen below in Section 2.5.

Although energy levels of hydrogenic atoms depend only on the principal quantum number n as can be seen from eq.(2.3), wave functions representing the statistical nature of particles depend on l and m as well as on n to have varieties of functional forms; there are one type for $n = 1$, four types for $n = 2$, and nine types for $n = 3$, respectively. In other words, there are n^2 different types of wave functions with the same energy eigen value of E_n for all excited states $(n > 1)$ except for the ground state $(n = 1)$. Wave functions have a four fold degeneracy for $n = 2$ and a nine fold degeneracy for $n = 3$.

2.2 Forms of atomic orbitals

The creation and destruction of chemical bonds occurs under the action of interference among electron waves. Their mechanisms are related to the forms of atom orbital functions. In this section, classification and characteristics of orbital forms are discussed for atomic orbitals of hydrogenic atoms as typical examples.

2.2.1 Classification of atomic orbitals

Atomic orbitals are wave functions representing electronic motion in an atom, and atomic orbitals are classified into several types with the principal quantum number n and the azimuthal quantum number l, as listed in Table 2.2.

Table 2.2: Classification of atomic orbitals

electron shell	principal quantum number n	azimuthal quantum number l					
		0 s	1 p	2 d	3 f	4 g	5 h
K	1	1s					
L	2	2s	2p				
M	3	3s	3p	3d			
N	4	4s	4p	4d	4f		
O	5	5s	5p	5d	5f	5g	
P	6	6s	6p	6d	6f	6g	6h

The azimuthal quantum number is related to the characteristic features of spectral series in atomic spectra. It follows that the first letters of the names for spectral series, such as sharp, principal, diffuse, and fundamental, have been used as s for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$.

2.2.2 s,p,d functions for the angular part

The names s, p, d for atomic orbitals are used for classification of the angular part. Although prototypes of the angular part functions are spherical harmonic functions $Y_{l,m}(\theta, \phi)$, in actual calculations and considerations conventional functions shown in Table 2.3 are used instead for some reasons described below. The angular part such as s, p, and d are related to mechanisms and directional characteristics in the formation of chemical bonds, and it follows that directions and signs of the angular part should be studied carefully.

The s function of the angular part is only one kind, the spherical harmonic function of $Y_{0,0}$, as shown in Table 2.3, which has a constant value, irrespective of the angles θ and ϕ. Namely, s-orbital functions are spherical, and values of s-orbital functions are the same for a constant value of the distance r, irrespective of the directions.

Three types of spherical harmonics $Y_{1,-1}, Y_{1,0}, Y_{1,1}$ correspond to p functions. As shown in Table 1.3 in Section 1.13, $Y_{1,-1}$, and $Y_{1,1}$ are functions of complex numbers, and $Y_{1,0}$ is a real

Table 2.3: s, p, d functions for the angular part

	l	m	definition	functional form
s	0	0	$Y_{0,0}$	$\frac{1}{\sqrt{4\pi}}$
p_x	1	±1	${Y_{1,1}}^+$	$\sqrt{\frac{3}{4\pi}}\frac{x}{r}$
p_y	1	±1	${Y_{1,1}}^-$	$\sqrt{\frac{3}{4\pi}}\frac{y}{r}$
p_z	1	0	$Y_{1,0}$	$\sqrt{\frac{3}{4\pi}}\frac{z}{r}$
d_{xy}	2	±2	${Y_{2,2}}^-$	$\sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$
d_{yz}	2	±1	${Y_{2,1}}^-$	$\sqrt{\frac{15}{4\pi}}\frac{yz}{r^2}$
d_{zx}	2	±1	${Y_{2,1}}^+$	$\sqrt{\frac{15}{4\pi}}\frac{zx}{r^2}$
$\mathrm{d}_{x^2\text{-}y^2}$	2	±2	${Y_{2,2}}^+$	$\sqrt{\frac{15}{16\pi}}\frac{1}{r^2}(x^2-y^2)$
d_{z^2}	2	0	$Y_{2,0}$	$\sqrt{\frac{5}{16\pi}}\frac{1}{r^2}(3z^2-r^2)$

function expressed as follows.

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \tag{2.20}$$

Here, the relation of $z = r\cos\theta$ from the definition of polar coordinates is used. $Y_{1,0}$ depends on the polar angle θ indicating the angle deflected from the z-axis, and the absolute value of $Y_{1,0}$ is at a maximum for the direction of the z-axis. Therefore, the $Y_{1,0}$ function is called p_z function.

$$\mathrm{p}_z = Y_{1,0} = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \tag{2.21}$$

Similar functions depending on the angles deflected from the x-axis and the y-axis can also be defined by the following equations, and they are called the p_x function and the p_y function.

$$\mathrm{p}_x = \frac{Y_{1,1}+Y_{1,-1}}{\sqrt{2}} = \sqrt{\frac{3}{4\pi}}\frac{x}{r} \tag{2.22}$$

$$\mathrm{p}_y = \frac{Y_{1,1}-Y_{1,-1}}{\sqrt{2}i} = \sqrt{\frac{3}{4\pi}}\frac{y}{r} \tag{2.23}$$

Except for some special cases such as under a magnetic field, the three functions of $\mathrm{p}_x, \mathrm{p}_y, \mathrm{p}_z$ are conventionally used as the angular part of p functions. These p functions all satisfy the eigen equation of (2.6) with an azimuthal quantum number of $l = 1$.

In the cases of $m \neq 0$ the spherical harmonics in Table 1.3 are functions of complex numbers in general, and their mathematical treatments are cumbersome. It is convenient to use the following functions with real values, which are denoted as ${Y_{l,m}}^+$ and ${Y_{l,m}}^-$ and are equivalent to $Y_{l,m}, Y_{l,-m}$ to satisfy eq.(2.6).

$${Y_{l,m}}^+ = \frac{Y_{l,m}+Y_{l,-m}}{\sqrt{2}} \tag{2.24}$$

$${Y_{l,m}}^- = \frac{Y_{l,m}-Y_{l,-m}}{\sqrt{2}i} \tag{2.25}$$

These functions are used in Table 2.3 for p and d functions.

The five types of d function shown in Table 2.3 correspond to the angular part for $l = 2$ and their directional characteristics are more complex than p orbitals. The three dimensional characteristics of orbital functions are not easily seen from their mathematical expressions, and it follows that we will introduce several types of typical expression showing their forms.

2.2.3 Angular dependence and figures of polar coordinates

The angular part $Y(\theta, \phi)$ determines the angular dependence of the probability of finding an electron. Taking $|Y|$ in each direction as the length of a vector with the respective direction from the origin, a contour produced with the top point of the vector gives a figure of polar coordinates as the three dimensional surfaces shown in Fig. 2.3. These figures represent the angular dependence of atomic orbitals. Symbols of + and − in Fig. 2.3 indicate the signs for $Y(\theta, \phi)$.

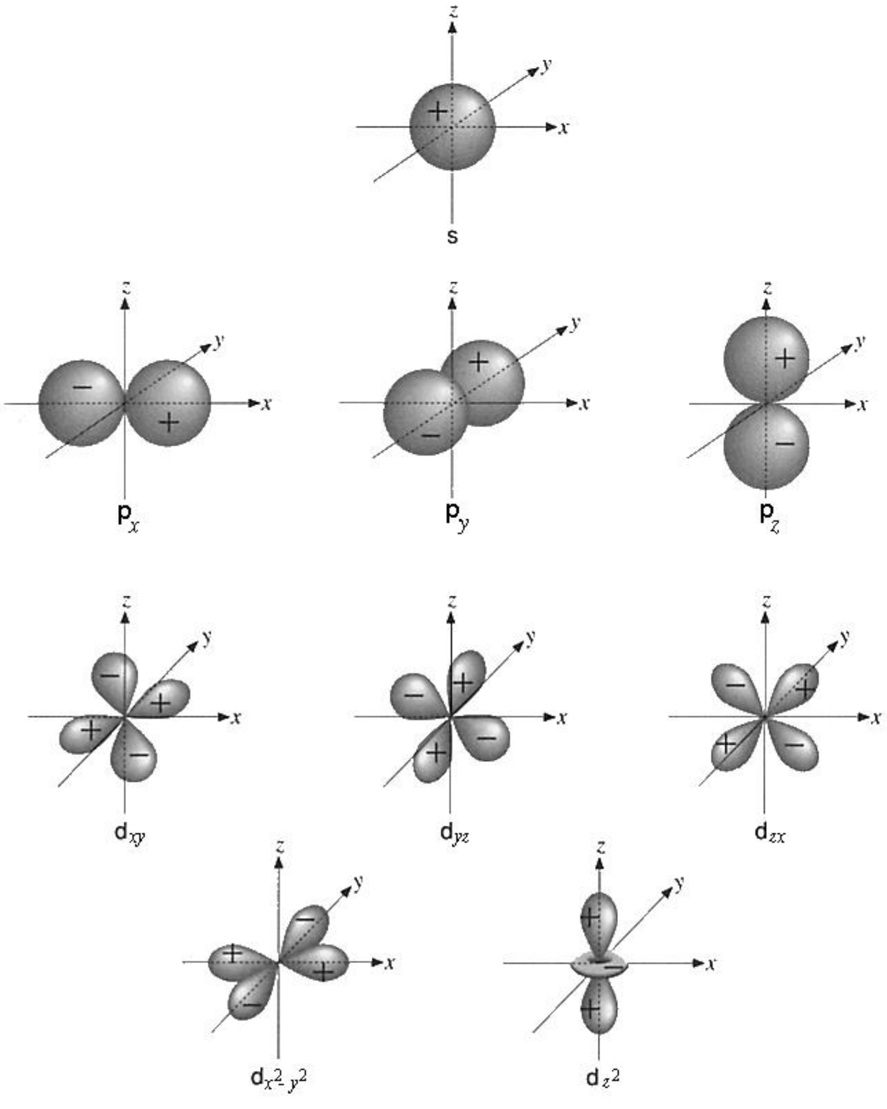


Figure 2.3: Angular dependence of s, p, d orbitals

Example 2.2 Draw the figure of polar coordinates for p_z function $Y_{1,0}$ in the x-z plane.

(Solution) Since $\phi = 0,\ y = 0$ in the x–z plane, x and z coordinates of the top point of the vector $\mathrm{P}(x, 0, z)$ showing the magnitude as its length from the origin are given as follows.

$$x = |Y| \sin\theta$$
$$z = |Y| \cos\theta$$

Here, Y is

$$Y(\theta, 0) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

Noting $|\cos\theta| = \cos\theta$ for $0 \leq \theta \leq \pi/2$ and using a constant a,

$$a = \sqrt{\frac{3}{4\pi}}$$

x and z are expressed as

$$x = a \cos\theta \sin\theta$$
$$z = a \cos\theta \cos\theta = a \cdot \cos^2\theta$$

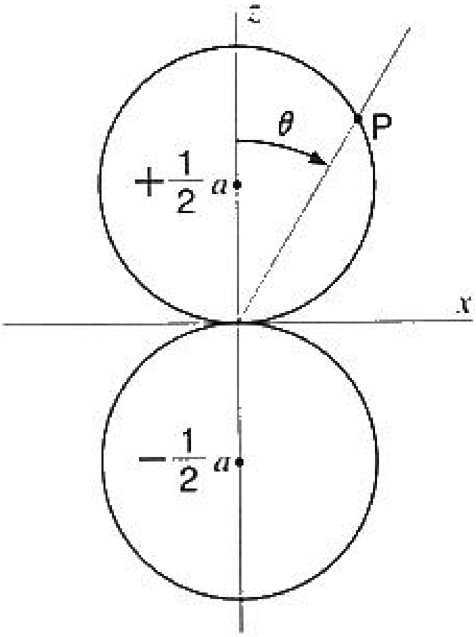
Therefore,

$$\begin{aligned} x^2 &= a^2 \cos^2\theta \sin^2\theta = a^2 \cos^2\theta (1 - \cos^2\theta) = a \cdot z - z^2 \\ &= -\left(z - \frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 \end{aligned}$$

Thus, we obtain

$$x^2 + \left(z - \frac{a}{2}\right)^2 = \left(\frac{a}{2}\right)^2$$

This is a circle with a radius of $a/2$ located at $(x, z) = (0, a/2)$. Another circle with a radius of $a/2$ located at $(x, z) = (0, -a/2)$ also satisfies the required condition, since $|\cos\theta| = -\cos\theta$ for $\pi/2 \leq \theta \leq \pi$. Thus, we obtain two circles of the same radius with centers on the z axis, which make contact with each other at the origin, as shown in the next figure.



As for $\phi \neq 0$, the above figure should be rotated at an angle ϕ around the z axis leading to a three dimensional figure composed of a pair of spheres as shown in Fig. 2.3.

2.2.4 The radial dependence and the radial distribution

The radial dependence of atomic orbitals on the distance r from the nucleus is determined by the radial part $R_{n,l}(r)$. The probability of finding an electron in a region between a pair of spheres with radii r and $r + dr$ is introduced as $D(r)dr$, and this $D(r)$ is defined as the radial distribution function, which is used to understand the radial dependence of the wave function. Fig. 2.4 shows some examples of $D(r)$ for a hydrogen atom. Derivation of the radial distribution function $D(r)$ will be made below. Since $D(r)$ becomes 0 where the radial part R has a node, there are $(n - l)$ maxima which is one more than the number of nodes for R. The largest value of $D(r)$ is located at the outermost maximum. The distance of the largest value r_{max} increases with the increase of n. r_{max} indicates the place where the probability of finding an electron is large, and this distance gives a measure for the size of electron shells as well as for the size of the atom and the bond length.

Let us derive a formula for $D(r)$. Integration of $D(r)$ from 0 to ∞ should be equal to the probability of finding an electron in the total space, which is the integrated value of the square of the wave function Ψ over the whole range of the three dimensional space. This value should be unity because of the normalization condition. Thus,

$$\int_0^\infty D(r)\mathrm{d}r = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z = 1 \tag{2.26}$$

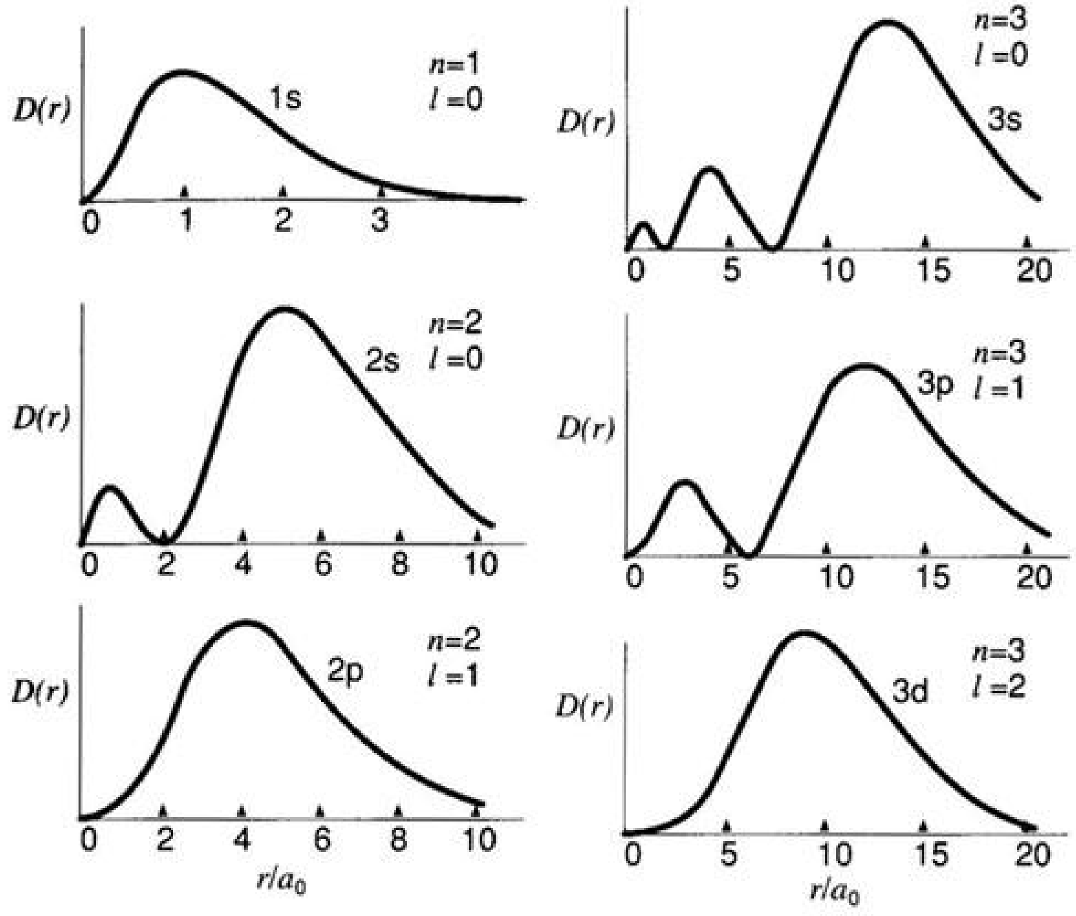


Figure 2.4: The radial distribution function $D(r) = r^2 R_{n,l}^2$

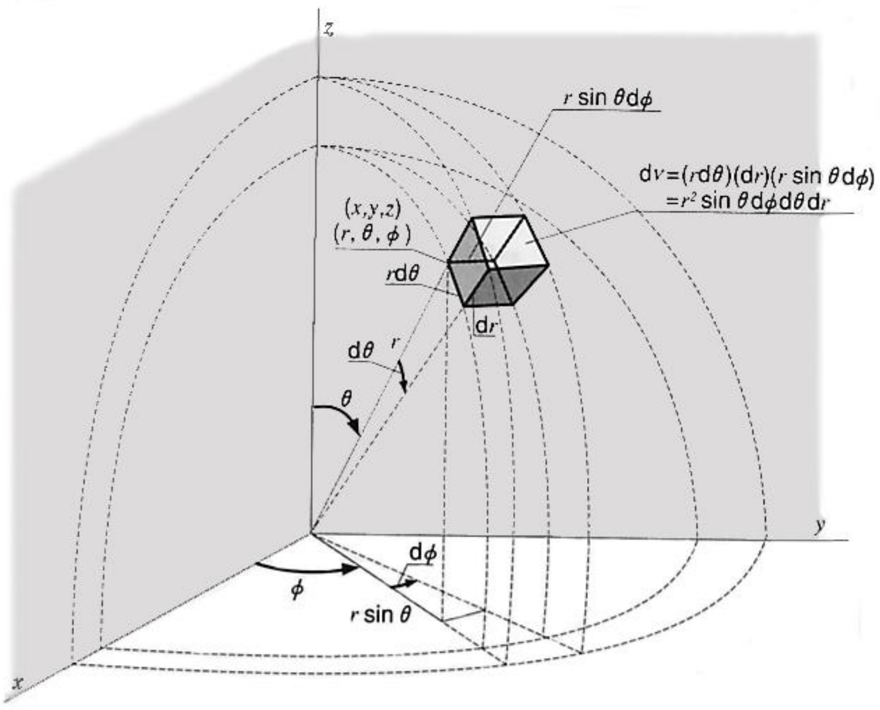


Figure 2.5: The volume element $\mathrm{d}v = r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r$ for polar coordinates

As can be seen in Fig. 2.5, for polar coordinates (r, θ, ϕ), the volume element $\mathrm{d}v = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ can be replaced by the following equation.

$$\mathrm{d}v = \mathrm{d}x\mathrm{d}y\mathrm{d}z = r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r \tag{2.27}$$

It should be noted that the ranges of the integration are from 0 to 2π for ϕ, from 0 to π for θ, and from 0 to ∞ for r. Substituting this replacement into the right side of eq.(2.26) and comparing it with the left side, we obtain the formula for $D(r)$ as the following integrations.

$$D(r) = \int_{0(\theta)}^{\pi} \int_{0(\phi)}^{2\pi} |\Psi|^2 r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \tag{2.28}$$

Next, replacement of Ψ by a product of the radial part R leads to an integration of the angular part Y with respect to the angles θ and ϕ, which is the same as the normalization condition of spherical harmonic functions Y.

$$\int\int |Y|^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta = 1 \tag{2.29}$$

Thus, we obtain a formula for $D(r)$ as follows.

$$D(r) = r^2 R_{n,l}(r)^2 \tag{2.30}$$

Example 2.3 Obtain $D(r)$ for 1s wave function for a hydrogenic atom.

(Solution) The 1s wave function for a hydrogenic atom is given as

$$\Psi_{1\mathrm{s}} = \Psi_{1,0,0} = R_{1,0} Y_{0,0}$$

Using the radial part of this wave function and eq.(2.30), the radial distribution function $D(r)$ is expressed as

$$D_{1\mathrm{s}}(r) = r^2 {R_{1,0}}^2$$

Here,

$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-(Z/a_0)r}$$

and we obtain

$$D_{1\mathrm{s}}(r) = 4\left(\frac{Z}{a_0}\right)^{3} r^2 \mathrm{e}^{-(2Z/a_0)r}$$

It is clear from the differentiation of this equation that the maximum of $D(r)$ is located at $r = a_0/Z$. In the case of a hydrogen atom ($Z = 1$), the distance for the maximum equals a_0, and this is nearly the same as the Bohr radius a_B.

2.2.5 Contour lines

Some devices are required to represent atomic wavefunctions, since they are functions of three-dimensional coordinates. For example, contour lines may be drawn on a certain plane for Ψ or $|\Psi|^2$ with the same value (Fig.2.6).

Since s orbitals have spherical symmetry, concentric circular lines will be drawn for any plane. On the other hand, $\mathrm{p}_x, \mathrm{p}_y$, and p_z orbitals have axial symmetries of the corresponding Cartesian axes, and thus the largest values appear as a pair of points on the axes at symmetric positions. The signs of the p functions for these pairs of points are opposite to each other. Since each p function changes its sign on reflection in the plane including the origin and being vertical to the axis, $\Psi = 0$ in the plane. In other words, each p function has a nodal plane vertical to the axis.

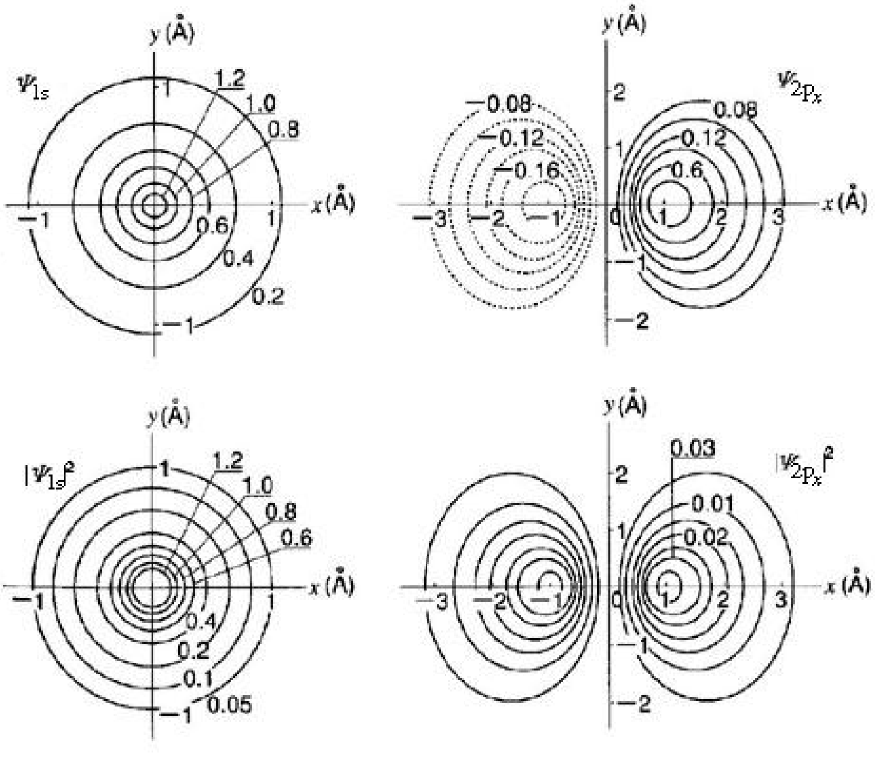


Figure 2.6: Contour lines for Ψ and $|\Psi|^2$

2.3 Many electron atoms

The problem to determining the motion of electrons in general atoms having many electrons is not so easy as the problem of hydrogenic atoms. This is largely due to the following two reasons. One reason is because interactions between electrons do not allow a treatment of independent motion of individual electrons. Another reason is due to the presence of angular momenta of electrons called electron spins which cannot easily be handled. Even for two electron systems such as a helium atom, the wave equation cannot be solved rigorously. Hence, approximate treatments are required. At the birth of the quantum theory, there was no modern computer so that problems of two or more electron systems (many electron systems) were handled with approximation methods such as perturbation or variation methods described in Chapter 3. In these days, variational treatments suitable to modern computers have been developed to enable us to perform calculations rather easily with some conventional program packages. In this section, characteristics of wavefunctions and energy levels for many electron atoms will be compared with those for hydrogenic atoms.

We may conclude here that the motion of individual electrons can be treated similarly to $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x,$
$2\mathrm{p}_y, 2\mathrm{p}_z$ atomic orbitals in hydrogenic atoms. Although energy levels of hydrogenic atoms depend only on the principal quantum number n, energy levels of many electron atoms with the same principal quantum number n may become different as the lower values of the azimuthal quantum number lead to the lower (more stable) energy levels. In the next section, consideration of electron spins will make it possible to understand electron configurations in atomic orbitals and their energy levels, which will be helpful to discuss individual properties of chemical elements.

2.3.1 Independent electron model

As mentioned for hydrogenic atoms, the motion of nucleus can be neglected with respect to the motion of electrons. Thus, nuclei are fixed at the equilibrium positions in dealing with many electron systems. Under this approximation, the Hamiltonian operator $\hat{H}$ for an N electron system is given by the following equation.

$$\hat{H} = \sum_{i=1}^{N} \left[-\left(\frac{\hbar^2}{2m}\right)\Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{2.31}$$

Here, the inside of the parenthesis [ ] of the first term can be denoted as $\hat{h}_i$, which is an operator concerned with the coordinates of the i-th electron. r_{ij} in the right side denotes the distance between the i-th and the j-th electrons, and the terms including r_{ij} represent interactions between electrons. As an exchange of i and j in interactions between electrons also leads to the same pair of electrons, $i > j$ attached to the summation symbol Σ indicates to sum up only once for a pair of i and j. $\hat{h}_i$ is the same as the Hamiltonian operator $\hat{H}$ of a hydrogenic atom with $(\mu = m)$ except for the suffix i attached to Δ and r, and its characteristic equation and solutions are as follows.

$$\hat{h}_i \phi_{nlm} = \varepsilon_n \phi_{nlm} \tag{2.32}$$

$$\varepsilon_n = -\frac{mZ^2e^4}{8{\varepsilon_0}^2 h^2 n^2} \tag{2.33}$$

$$\phi_{n,l,m}(r_i, \theta_i, \phi_i) = R_{n,l}(r_i) \cdot Y_{l,m}(\theta_i, \phi_i) \tag{2.34}$$

$\phi_{n,l,m}$ is an atomic orbital representing the motion of an individual electron, as in the case of hydrogenic atoms. In general, the orbital function representing motion of an electron is called an orbital. The corresponding energy eigen value ε_0 is called an orbital energy.

The omission of interactions between electrons in the second terms of eq.(2.31) yields a Hamiltonian $\hat{H}_0$ of the following form.

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{h}_i \tag{2.35}$$

The eigen equation of this $\hat{H}_0$ is $\hat{H}_0\Phi = E\Phi$, and it can be solved easily from eqs.(2.32)-(2.34) to give the following solutions.

$$\hat{H}_0\Phi_{n_1\cdots n_N} = E_{n_1\cdots n_N}\Phi_{n_1\cdots n_N} \tag{2.36}$$

$$\Phi_{n_1\cdots n_N} = \phi_{n_1}\phi_{n_2}\cdots\phi_{n_N} \tag{2.37}$$

$$E_{n_1\cdots n_N} = \varepsilon_{n_1} + \varepsilon_{n_2} + \cdots + \varepsilon_{n_N} \tag{2.38}$$

Here, the atomic orbital and the orbital energy for the first electron are shown as ϕ_{n_1} and ε_{n_1} rather than written as ϕ_{n_1,l_1,m_1} and $\varepsilon_{n_1,l_1,m_1}$ with three quantum numbers explicitly. This abbreviation is applied to the last ones of $\phi_{n_N}, \varepsilon_{n_N}$.

In hypothetical cases without interactions between electrons, the wave function and the energy for collective motion of electrons can be expressed in terms of orbitals and their energies for independent motion of individual electrons. Characteristic features for the independent electron model are as follows.

[**Characteristic features of the independent electron model**]

(1) The wave function for a many electron system is expressed as a product of wavefunctions for one-electron systems (orbitals).

(2) The energy for a many electron system is given as a simple summation of energies for one-electron systems (orbital energies).

The feature (1) indicates that the probability of finding an electron at a certain position is given as a product of the probabilities of finding individual electrons. The feature (2) suggests that the lowest energy state, the ground state, of a many electron system is realized when individual electrons are in their lowest energy states. Although occupation of all electrons in the 1s orbital is possible for H and He atoms, this is not allowed for all other atoms with the larger atomic numbers $Z \geq 3$. The reason will be given in Section 2.4 in connection with the electron spin.

2.3.2 Screening effect and effective nucleus charge model

Interactions between electrons are omitted in the independent electron model. However, such an approximate treatment is not appropriate for real systems, where interactions between electrons are significant. Let us consider effects of interactions between electrons by using a simple model.

Now, let us estimate the effect of repulsive forces caused by other electrons on an electron moving at a distance of r_0 from the nucleus. The electrostatics gives the following two features for the effects of repulsive interactions between electrons in an atom depending on the regions whether other electrons are located at $r > r_0$ or $r < r_0$, provided that the electron distribution is assumed to be spherical.

(1) There are no forces on average from the outer electrons ($r > r_0$).

(2) Forces to the outward direction are caused on average by the inner electrons, and this effect is equivalent to reducing the attractive force due to the nuclear charge, as if an electron is fixed on the nucleus to decrease the nuclear charge by one.

The effect of the inner electrons reducing the electric attractive forces by the nucleus is called the screening effect. The magnitude of the screening effect is larger for the outer electrons than for the inner electrons. The screening effect is considered to be equivalent to replacing the atomic number Z of the nucleus by the smaller number. The extent of the reduction s is introduced as the screening constant, and the effective nucleus charge $\overline{Z}$ is defined as $\overline{Z} = Z - s$. The screening constant s approximately represents the number of the inner electrons. If an electron is located in the outer most region, the screening constant for this electron will become $s = Z - 1$, and then the corresponding effective nucleus charge becomes $\overline{Z} = Z - (Z - 1) = 1$. This is important when we will discuss the periodicity of ionization energies.

If we replace Z in the first terms in eq.(2.31) by $\overline{Z}$ together with omission of the interactions between electrons, a Hamiltonian $\hat{H}$ of a model in which interactions between electrons are effectively included in the effective nucleus charge defined as $\overline{Z}$, given by

$$\hat{H} = \sum_{i=1}^{N} \left[-\left(\frac{\hbar^2}{2m} \right) \Delta_i - \frac{\overline{Z} e^2}{4\pi\varepsilon_0 r_i} \right] \tag{2.39}$$

This model is called the effective nuclear charge model. Rewriting the inside of [ ] in eq.(2.39) by $\hat{h}_i$, we obtain the same results as eqs.(2.36)-(2.38). It follows that the characteristic features mentioned for the independent electron model may also hold for the effective nuclear charge model. It should be noted that the orbital energies in eq.(2.33) are modified by the replacement of Z by $\overline{Z}$, which depends on the orbital type and especially on the relative order of the inner or the outer location with respect to other electrons. The effective nuclear charge model is useful to discuss electronic configurations of atoms and their periodicity.

2.3.3 Atomic orbitals and energy levels for many electron atoms

Based on the variation method, a theoretical treatment, which is much more rigorous and rational than the effective nuclear charge model, can be established to obtain orbital functions and energies for many electron systems. Characteristic features of such results by the variation method are described below.

The atomic orbital function ϕ is given as a product of the radial part $R'(r)$ and the angular part $Y(\theta, \phi)$ as in the case of the hydrogenic atoms, and these atomic orbitals are classified with a set of three quantum numbers, n, l, and m.

$$\phi_{n,l,m} = R_{n,l}{}'(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.40}$$

$Y_{l,m}$ is the spherical harmonic, and $R'(r)$, which is different from $R(r)$ for hydrogenic atoms, is a function of r, qualitatively very similar to the hydrogenic function $R(r)$ in the aforementioned four respects concerning the asymptotic behavior and the nodes.

It follows that atomic orbitals are classified into $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 2\mathrm{p}_z$, 3s, $3\mathrm{p}_x, 3\mathrm{p}_y, 3\mathrm{p}_z, 3\mathrm{d}_{xy}, 3\mathrm{d}_{yz}$, $3\mathrm{d}_{zx}, 3\mathrm{d}_{x^2-y^2}, 3\mathrm{d}_{z^2}, \cdots$, as in the case of hydrogenic orbitals.

Energy levels with the same principal quantum number n are degenerate for hydrogenic atoms, while for more general many electron atoms, energies for orbitals with the same n may differ when the l values are different; the smaller l leads to the lower energy. For example, the order of 3s, 3p, and 3d orbital energies for many electron atoms are as follows.

$$3\mathrm{s}\,(l = 0) < 3\mathrm{p}\,(l = 1) < 3\mathrm{d}\,(l = 2) \tag{2.41}$$

The reason for this is related to the magnitude of the screening effects. The smaller l becomes, the larger the probability of finding electrons in proximity to the nucleus, where the screening effects are not effective. Hence, the lower l leads to the stronger attractive force from the nucleus on average resulting in the lower energy and becoming more stable. If l is the same, the smaller n gives the lower energy, as in the case of hydrogenic atoms.

2.4 Electron spin

Electron orbitals and energy levels of many electron systems are classified into 1s, 2s, 2p, 3s, 3p, 3d, and so on as in the case of hydrogenic atoms. The problem is how the electrons are distributed into electron orbitals. Are all electrons incorporated into the most stable 1s orbital with the lowest energy ? The conclusion of the quantum theory is such that only two electrons can occupy the same orbital. This rule is related to the special angular momentum of the electron spin.

2.4.1 Experimental grounds for the electron spin

The existence of the electron spin was verified by some experiments.

(1) Atomic beam experiments by Stern and Gerlach

A stream of atoms can be produced in a vacuum through a nozzle after evaporation of silver or alkali metal by heating. Such a stream of atoms in vacuum is called an atomic beam. O. Stern and W. Gerlach discovered in 1922 that atomic beams of silver or sodium atoms, which have one electron in the outermost electron shell, split into two lines in an inhomogeneous magnetic field (Fig.2.7). This experiments suggested that an electron has a magnetic moment, which is a magnetic property associated with a circular electric current.

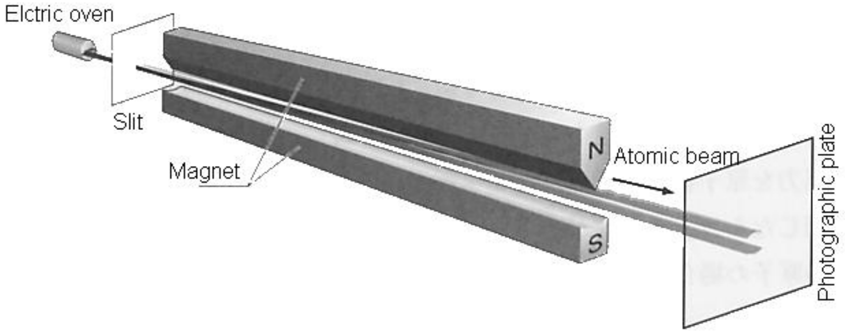


Figure 2.7: Atomic beam experiments by Stern and Gerlach

(2) Double lines (doublets) in the spectrum of an alkali metal atom

An orange light from the flame reaction of sodium is also emitted from a discharge lamp including sodium vapor. The dark lines (Fraunhofer lines) found in the spectrum of the sun light contain the same wavelength lines as the sodium flame spectrum, called D lines. The D lines of sodium originate from transitions between 3s and 3p levels, and they are observed as two adjacent lines (doublets) of 5895.93 Å and 5889.97 Å. Such doublets were also found for other alkali atoms, and intervals of the splitting were found to increase in the order of Li < Na < K < Rb < Cs. S.A.Goudsmit and G.E.Uhlenbeck proposed that the splitting of the spectral lines is due to the magnetic moment of an electron associated with its circular motion. Since an angular momentum is associated with circular motion of an electric charge, this angular momentum is the origin of the magnetic moment of an electron. The angular momentum associated with the circular motion of an electron is called electron spin.

2.4.2 Operators, eigen functions, and quantum numbers for electron spin

In order to consider electron spins in quantum mechanics, operators should be introduced similarly to the orbital angular momentum. Let us denote the spin angular momentum as $\hat{s}$ and its z-component as $\hat{s}_z$. By analogy with the orbital angular momentum, a common eigen function Γ for both $\hat{s}$ and $\hat{s}_z$ is expected to exist and to have the following relations.

$$\hat{s}^2\Gamma = s(s+1)\hbar^2\Gamma \tag{2.42}$$

$$\hat{s}_z\Gamma = m_s\hbar\Gamma \tag{2.43}$$

s is the quantum number for the square of the spin and is called the spin quantum number. m_s is the quantum number for the component and is called the spin magnetic quantum number. General rules for the angular momentum suggest that m_s should have $2s+1$ possible values of $s, s-1, \cdots, -s+1, -s$. By experiments, atomic beams are split into two components in a magnetic field, and spectra of alkali atoms are split into two lines. Based on these findings, m_s is concluded to have only two possible values. It follows that $2s+1 = 2$, and thus we obtain $s = 1/2$, $m_s = \pm 1/2$. It should be noted that the spin quantum number is a half integer with only one value of $s = 1/2$. Allowed values for m_s are limited to be $\pm 1/2$. The spin is a very special angular momentum in comparison with the orbital angular momentum.

Although such special properties of the spin angular momentum are difficult to be understood conceptually, their mathematical treatments are much more simplified. Because of only two allowed states, there are only two eigen functions. Usually, the spin function corresponding to $m_s = 1/2$ is denoted as α, and the other spin function for $m_s = -1/2$ is denoted as β.

$$\hat{s}_z\alpha = \frac{1}{2}\hbar\alpha \tag{2.44}$$

$$\hat{s}_z\beta = -\frac{1}{2}\hbar\beta \tag{2.45}$$

In connection with the orientation of the magnetic moment associated with the spinning motion, the upward one is called the α spin, and the downward one is called the β spin, respectively. The variable σ for spin functions $\alpha(\sigma), \beta(\sigma)$ is called the spin coordinate.

Although the significance of the spin coordinate σ is not clear, we need not to consider what it represents. The spin coordinate is the fourth coordinate following the other three coordinates for the position in the three dimensional space. Formally, allowed values for the spin coordinates are only two cases, the upward orientation of $\sigma = \uparrow$ and the downward orientation of $\sigma = \downarrow$.

$$\begin{array}{ll} \alpha(\uparrow) = 1, & \alpha(\downarrow) = 0 \\ \beta(\uparrow) = 0, & \beta(\downarrow) = 1 \end{array} \tag{2.46}$$

The probability of finding an electron at $\sigma = \uparrow$ is 1 in the upward spin state of α and 0 in the downward spin state β. On the other hand, the probability of finding an electron at $\sigma = \downarrow$ is 0 in the upward spin state of α and 1 in the downward spin state β.

In quantum mechanics, integrals are need to be calculated in connection with probabilities and normalization. As for the spin, a simple summation for the two coordinates $\uparrow$ and $\downarrow$ is only required. For example, eq.(2.46) leads to

$$\begin{aligned} \int |\alpha|^2 \mathrm{d}\sigma &= |\alpha(\uparrow)|^2 + |\alpha(\downarrow)|^2 \\ &= 1 + 0 = 1 \end{aligned} \tag{2.47}$$

and similarly

$$\begin{aligned} \int |\beta|^2 \mathrm{d}\sigma &= |\beta(\uparrow)|^2 + |\beta(\downarrow)|^2 \\ &= 0 + 1 = 1 \end{aligned} \tag{2.48}$$

In addition,

$$\begin{aligned} \int \alpha^*\beta \mathrm{d}\sigma &= \alpha^*(\uparrow)\beta(\uparrow) + \alpha^*(\downarrow)\beta(\downarrow) \\ &= 1 \cdot 0 + 0 \cdot 1 = 0 \end{aligned} \tag{2.49}$$

As can be seen from these calculations, the spin functions α, β in eq.(2.46) satisfy the orthonormality.

For a wave function Ψ of an electron considering the electron spin, the variables are the spatial coordinates x, y, z and the spin coordinate σ. If the component of the electron spin s_z has a certain value, the spin function is either α or β. It follows that the spatial orbital functions for Cartesian coordinates $\phi(x, y, z)$ lead to the following pair of wavefunctions for electrons accommodated in this spatial orbital.

$$\Psi(x, y, z, \sigma) = \phi(x, y, z) \cdot \alpha(\sigma) \tag{2.50}$$

$$\Psi(x, y, z, \sigma) = \phi(x, y, z) \cdot \beta(\sigma) \tag{2.51}$$

These equations are related with a rule that the number of electrons in each spatial orbital (in the case of an atom, $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 3\mathrm{d}_{xy}$ orbitals, etc.) should not exceed two.

2.4.3 Restriction to many-electron wavefunctions and the Pauli principle

The question of how many electrons can occupy an atomic orbital such as the 1s orbital is an important problem in connection with atomic spectra and atomic properties. The solution of this problem was given by Pauli in 1924, and it is a rule called the Pauli principle or The Pauli exclusion principle.

[The Pauli principle (The exclusion principle)]

Each orbital can be occupied by an electron with α spin or β spin, but it cannot be occupied by two or more electrons with the same spin.

This rule is established by Pauli, based on experimental results such as atomic spectra. It is very important that electrons obey this rule, in connection with the construction of many-electron wavefunctions.

Let us consider two electrons. One is located at a coordinate q_1 and the other at q_2. This state is represented by a wave function written as $\Psi(q_1, q_2)$. Similarly, a state of two electrons with their coordinates interchanged may be written as $\Psi(q_2, q_1)$. Although $\Psi(q_1, q_2)$ and $\Psi(q_2, q_1)$ are mathematically different expressions specifying the numbering of the electrons as 1 and 2, we cannot recognize any difference of the numbering when we observe the electrons. It follows that the probability of finding the number 1 electron at q_1 and the number 2 electron at q_2 should be exactly the same as the probability finding the number 1 electron at q_2 and the number 2 electron at q_1. This condition is expressed by the following equation.

$$|\Psi(q_1, q_2)|^2 = |\Psi(q_2, q_1)|^2 \tag{2.52}$$

Noting that wavefunctions are complex numbers in general, we obtain

$$\Psi(q_1, q_2) = \exp(i\theta) \cdot \Psi(q_2, q_1) \tag{2.53}$$

The initial choice of the two electrons as well as their geometries is arbitrary. Thus, it is not reasonable to assume that the constant θ in eq.(2.53) is different depending on the choice of electrons and their geometries. Therefore, the same relationship should hold for an interchange of q_1 and q_2.

$$\Psi(q_2, q_1) = \exp(i\theta) \cdot \Psi(q_1, q_2) \tag{2.54}$$

These two equations lead to

$$\Psi(q_1, q_2) = \exp(i\theta)^2 \cdot \Psi(q_1, q_2) \tag{2.55}$$

Thus,

$$\exp(i\theta)^2 = \exp(2i\theta) = 1 \tag{2.56}$$

This leads to

$$\exp(i\theta) = \pm 1 \tag{2.57}$$

It follows that

$$\Psi(q_2, q_1) = \pm\Psi(q_1, q_2) \tag{2.58}$$

Namely, the sign of a wave function is either unchanged or changed when a pair of identical particles are interchanged with their geometrical coordinates.

The nature of the particles determines which of the two possibilities is the case.

(1) For the sign unchanged with a multiplication of +1, wavefunctions are symmetric with respect to the interchange of coordinates, and this type of particle is called a Bose particle or Boson.

(2) For the sign changed with a multiplication of −1, wavefunctions are antisymmetric with respect to the interchange of coordinates, and this type of particle is called a Fermi particle or Fermion.

The Pauli principle shows that electrons are Fermions and that the wave function changes its sign on the interchange of the coordinates.

If a symmetric wave function were allowed for electrons, it would contradict the Pauli principle. For example, let us assume that there are two electrons occupying the 1s orbital with α spin. The corresponding wave function Ψ for this assumption is expressed with the orbital function $\phi_{1\mathrm{s}}$ as follows.

$$\begin{aligned}&\Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)\\&= \phi_{1\mathrm{s}}(x_1, y_1, z_1)\alpha(\sigma_1)\phi_{1\mathrm{s}}(x_2, y_2, z_2)\alpha(\sigma_2)\end{aligned} \tag{2.59}$$

Now, let us interchange the coordinates of number 1 and number 2, and then we obtain

$$\begin{aligned}&\Psi(x_2, y_2, z_2, \sigma_2, x_1, y_1, z_1, \sigma_1)\\&= \phi_{1\mathrm{s}}(x_2, y_2, z_2)\alpha(\sigma_2)\phi_{1\mathrm{s}}(x_1, y_1, z_1)\alpha(\sigma_1)\\&= \phi_{1\mathrm{s}}(x_1, y_1, z_1)\alpha(\sigma_1)\phi_{1\mathrm{s}}(x_2, y_2, z_2)\alpha(\sigma_2)\\&= \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)\end{aligned} \tag{2.60}$$

This clearly shows the symmetry of wavefunctions for a Boson. In other words, if electrons are Bosons, there would be two or more electrons occupying the same $1s\alpha$ state in an atom. However, this situation contradicts the Pauli principle.

On the other hand for an antisymmetric wave function, no state that contradicts the Pauli principle is acceptable. This feature can be seen easily when a determinant wave function, which is proposed by J. C. Slater and is called a Slater determinant, is used.

Let us introduce two orbital functions ψ_1, and ψ_2 which include spin coordinates in addition to spatial coordinates. We write the wave function Ψ for the system of 2 electrons as the following determinant.

$$\Psi(q_1, q_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) \\ \psi_1(q_2) & \psi_2(q_2) \end{vmatrix} \tag{2.61}$$

After expansion, we obtain the following equations showing the antisymmetric character.

$$\begin{aligned}\Psi(q_1, q_2) &= \frac{1}{\sqrt{2}}\{\psi_1(q_1)\psi_2(q_2) - \psi_1(q_2)\psi_2(q_1)\}\\&= -\frac{1}{\sqrt{2}}\{\psi_1(q_2)\psi_2(q_1) - \psi_1(q_1)\psi_2(q_2)\}\\&= -\Psi(q_2, q_1)\end{aligned} \tag{2.62}$$

It should be noted here that the Hamiltonian $\hat{H}$ is invariant on the interchange of coordinates of identical particles, and that if $\Psi = \psi_1(q_1)\psi_2(q_2)$ is a solution of $\hat{H}\Psi = E\Psi$, then $\Psi = \psi_1(q_2)\psi_2(q_1)$ is also a solution of $\hat{H}\Psi = E\Psi$. It follows that the above determinant satisfies $\hat{H}\Psi = E\Psi$. Using a determinant as proposed by Slater, we can construct an antisymmetric wave function composed of orbital functions.

Now, let us assume again that there are two electrons occupying the 1s orbital with the same α spin. In this case, $\psi_1 = \phi_{1\mathrm{s}} \cdot \alpha$, $\psi_2 = \phi_{1\mathrm{s}} \cdot \alpha$, that is $\psi_1 = \psi_2$. Thus, we may omit the suffixes as $\psi_1 = \psi_2 = \psi$. The determinant wave function for this system becomes

$$\begin{aligned}\Psi(q_1, q_2) &= \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) \\ \psi_1(q_2) & \psi_2(q_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi(q_1) & \psi(q_1) \\ \psi(q_2) & \psi(q_2) \end{vmatrix}\\&= \frac{1}{\sqrt{2}}\{\psi(q_1)\psi(q_2) - \psi(q_2)\psi(q_1)\} = 0\end{aligned} \tag{2.63}$$

The vanishing value of this determinant is a necessary result of a general rule for determinants that a determinant with a pair of the same rows or the same columns becomes vanishing. If this rule is used, the determinant in eq.(2.63) is easily found to be vanishing without expansion. Based on this result, it is easily seen that a configuration of electrons occupying orbitals in contradiction with the Pauli principle leads to a physically unacceptable wave function with a vanishing value indicating no particles at all. Careful and detailed inspections have shown that antisymmetric wavefunctions are compatible with the Pauli principle. It follows that electrons are Fermions with the antisymmetric character.

Hence, it is convenient to express a many-electron wave function as a determinant of a matrix in which orbital functions are arrayed. A determinant wave function composed of normalized orbital functions is also normalized as a many electron function, provided that a factor of $1/\sqrt{N!}$ is attached. In order to express a determinant wave function in a short form, we may write it as $|\psi_1\psi_2 \cdots \psi_N|$ by an array of orbital functions $\{\psi_i\}$ between a pair of vertical bars.

An array of orbital functions in a matrix form is equivalent to making an electron configuration corresponding to occupation of the electrons in respective orbitals. This in other words implies that electrons occupy the respective electron energy levels. Thus, the situation of electrons occupying certain orbitals or levels is called electron configuration or electronic configuration. Determinant wavefunctions are used as the mathematical expressions of electron configuration. The conceptual treatment of making an electron configuration can be understood as the occupation of orbitals by electrons.

The construction of determinant wavefunctions has no physical significance if its value is vanishing in contradiction with the existence of electrons. In order to avoid such a nonsensical situation, care should be taken so that no identical orbital functions may be included in the array of orbitals in the determinant. In other words, we should not use the same combination of a function of spatial coordinates and a spin function more than once in the determinant. The use of determinant wave functions guarantees the satisfaction of the antisymmetric properties of electrons, and hence electron configurations contradicting Pauli principle are automatically avoided, since values of such determinants are vanishing.

2.5 Electron configuration in atoms

Based on spectroscopic experiments and quantum theoretical studies, the electron configurations in the ground states of atoms were determined as shown in Table 2.4.

[Construction principle of electron configurations in atoms]

Electron configurations in the ground states of atoms can be constructed by the following rules.

(1) Electrons occupy preferentially the lower energy orbitals according to the order of the orbital energies.

(2) The order of the orbital energies are as follows.

$$\begin{aligned} &1\mathrm{s} < 2\mathrm{s} < 2\mathrm{p} < 3\mathrm{s} < 3\mathrm{p} < (4\mathrm{s}, 3\mathrm{d}) < 4\mathrm{p} < (5\mathrm{s}, 4\mathrm{d}) \\ &< 5\mathrm{p} < (6\mathrm{s}, 4\mathrm{f}, 5\mathrm{d}) < 6\mathrm{p} < (7\mathrm{s}, 5\mathrm{f}, 6\mathrm{d}) \end{aligned} \tag{2.64}$$

The items on the left are more stable with lower energy than the items on the right. Among orbitals in the same parentheses, the left ones are preferred to be occupied, though the order may be reversed sometimes.

(3) The Pauli principle should be satisfied. Namely, the allowed occupancy of orbitals is one of the following four cases.

(4) ns orbitals are occupied by 0∼2 electrons.
np orbitals is classified into three types, $n\mathrm{p}_x, n\mathrm{p}_y, n\mathrm{p}_z$, and each orbital is occupied by 0∼2 electrons. Altogether, np orbitals can be occupied by 0∼6 electrons.
There are five types for nd orbitals. Each one is occupied by 0∼2 electrons. Altogether, nd orbitals can be occupied by 0∼10 electrons.
There are seven types for nd orbitals. Each one is occupied by 0∼2 electrons. Altogether, nf orbitals can be occupied by 0∼14 electrons.

(5) Configurations in which two or more electrons occupy orbitals with the same energy should follow Hund's rule.
Hund's rule (1) Electrons are separated in different orbitals as far as possible.
Hund's rule (2) Spins are aligned to be parallel as far as possible.

Hund's rule (1) is a rule to reduce the increase of the interaction energy due to repulsion between electrons, for which separation of electrons in different orbitals is effective. Hund's rule 2 is a propensity that spins with the same directions tend to be more stabilized. Consideration of these rules leads to the following order of the total energies for electronic configurations of two-electron systems in a pair of equivalent orbitals.

(2.65)

As an example, let us construct the electron configuration of a Ga atom with the atomic number 31. $1s, 2s, 2p, 3s, 3p, 4s$, and 3d orbitals are occupied by $2+2+6+2+6+2+10=30$ electrons. The remaining $31-30=1$ electron occupies a 4p orbital. Thus, the electron configuration of a Ga atom, [Ga], is expressed as follows.

$$[\mathrm{Ga}] = (1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^6(3\mathrm{s})^2(3\mathrm{p})^6(4\mathrm{s})^2(3\mathrm{d})^{10}(4\mathrm{p})^1$$

The insides of ( ) represent orbitals with the same principal quantum number n and the same azimuthal quantum number l, a part of the electron shells, and thus they are called subshells. The right-hand superscript attached to ( ) denotes the total number of electrons occupying the subshell. When the number of electrons is 1, the figure 1 of the right-hand superscript may be omitted. Among electron shells having electrons, the electron shell of the largest n is called the outermost shell. In the case of Ga, $n \leq 4$, and thus the N shell is the outermost shell.

Typical examples of electron configurations are shown for some atoms.

Examples of electron configurations of atoms

$[\mathrm{He}] = (1\mathrm{s})^2$

$[\mathrm{Li}] = (1\mathrm{s})^2(2\mathrm{s})^1 = [\mathrm{He}](2\mathrm{s})^1$

$[\mathrm{Ne}] = [\mathrm{He}](2\mathrm{s})^2(2\mathrm{p})^6$

$[\mathrm{Ar}] = [\mathrm{Ne}](3\mathrm{s})^2(3\mathrm{p})^6$

$[\mathrm{Cr}] = [\mathrm{Ar}](4\mathrm{s})^1(3\mathrm{d})^5$

$[\mathrm{Fe}] = [\mathrm{Ar}](4\mathrm{s})^2(3\mathrm{d})^6$

$[\mathrm{Cu}] = [\mathrm{Ar}](4\mathrm{s})^1(3\mathrm{d})^{10}$

$[\mathrm{Ge}] = [\mathrm{Ar}](4\mathrm{s})^2(3\mathrm{d})^{10}(4\mathrm{p})^2$

Here, it should be noted that electron configurations for Cr and Cu are exceptions of the order among the inside of ( ) for the rule (2) in the construction principle; the configuration of the (4s) subshell is $(4s)^1$ rather than $(4s)^2$, and one electron occupies a 3d orbital so that the (3d) subshell becomes a half-occupied configuration of $(3d)^5$ or a fully occupied configuration of $(3d)^{10}$.

Exercise 2.4 Show the electron configuration of a carbon atom using electron energy levels.

(Solution) The electron configuration of a C atom is

$[\mathrm{C}] = (1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^2$

Since atomic orbitals up to 2p are occupied by electrons, electron energy levels from 1s to 2p should be shown, and the higher levels may be omitted. According to Hund's rules (1) and (2), the electron configuration for (2p) subshell becomes the following spin parallel configuration.

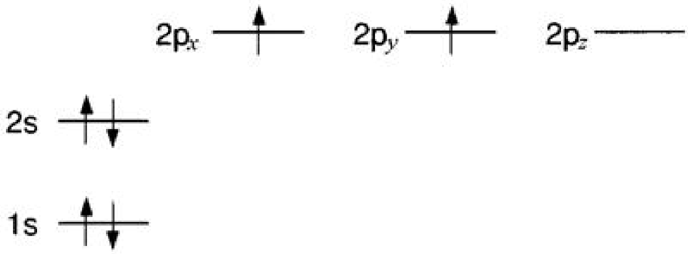


Table 2.4: Electron configurations of atomic ground-states and spectral terms

period	shell	K	L		M			N				O				term
	orbital	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	
1	1 H	1														$^2S_{1/2}$
	2 He	2														$^1S_0$
2	3 Li	2	1													$^2S_{1/2}$
	4 Be	2	2													$^1S_0$
	5 B	2	2	1												$^2P_{1/2}$
	6 C	2	2	2												$^3P_0$
	7 N	2	2	3												$^4S_{3/2}$
	8 O	2	2	4												$^3P_2$
	9 F	2	2	5												$^2P_{3/2}$
	10 Ne	2	2	6												$^1S_0$
3	11 Na	2	2	6	1											$^2S_{1/2}$
	12 Mg	2	2	6	2											$^1S_0$
	13 Al	2	2	6	2	1										$^2P_{1/2}$
	14 Si	2	2	6	2	2										$^3P_0$
	15 P	2	2	6	2	3										$^4S_{3/2}$
	16 S	2	2	6	2	4										$^3P_2$
	17 Cl	2	2	6	2	5										$^2P_{3/2}$
	18 Ar	2	2	6	2	6										$^1S_0$
4	19 K	2	2	6	2	6		1								$^2S_{1/2}$
	20 Ca	2	2	6	2	6		2								$^1S_0$
	21 Sc	2	2	6	2	6	1	2								$^2D_{3/2}$
	22 Ti	2	2	6	2	6	2	2								$^3F_2$
	23 V	2	2	6	2	6	3	2								$^4F_{3/2}$
	24 Cr	2	2	6	2	6	5	1								$^7S_3$
	25 Mn	2	2	6	2	6	5	2								$^6S_{5/2}$
	26 Fe	2	2	6	2	6	6	2								$^5D_4$
	27 Co	2	2	6	2	6	7	2								$^4F_{9/2}$
	28 Ni	2	2	6	2	6	8	2								$^3F_4$
	29 Cu	2	2	6	2	6	10	1								$^2S_{1/2}$
	30 Zn	2	2	6	2	6	10	2								$^1S_0$
	31 Ga	2	2	6	2	6	10	2	1							$^2P_{1/2}$
	32 Ge	2	2	6	2	6	10	2	2							$^3P_0$
	33 As	2	2	6	2	6	10	2	3							$^4S_{3/2}$
	34 Se	2	2	6	2	6	10	2	4							$^3P_2$
	35 Br	2	2	6	2	6	10	2	5							$^2P_{3/2}$
	36 Kr	2	2	6	2	6	10	2	6							$^1S_0$
5	37 Rb	2	2	6	2	6	10	2	6			1				$^2S_{1/2}$
	38 Sr	2	2	6	2	6	10	2	6			2				$^1S_0$
	39 Y	2	2	6	2	6	10	2	6	1		2				$^2D_{3/2}$
	40 Zr	2	2	6	2	6	10	2	6	2		2				$^3F_2$
	41 Nb	2	2	6	2	6	10	2	6	4		1				$^6D_{1/2}$
	42 Mo	2	2	6	2	6	10	2	6	5		1				$^7S_3$
	43 Tc	2	2	6	2	6	10	2	6	5		2				$^6S_{5/2}$
	44 Ru	2	2	6	2	6	10	2	6	7		1				$^5F_5$
	45 Rh	2	2	6	2	6	10	2	6	8		1				$^4F_{9/2}$
	46 Pd	2	2	6	2	6	10	2	6	10						$^1S_0$
	47 Ag	2	2	6	2	6	10	2	6	10		1				$^2S_{1/2}$
	48 Cd	2	2	6	2	6	10	2	6	10		2				$^1S_0$
	49 In	2	2	6	2	6	10	2	6	10		2	1			$^2P_{1/2}$
	50 Sn	2	2	6	2	6	10	2	6	10		2	2			$^3P_0$
	51 Sb	2	2	6	2	6	10	2	6	10		2	3			$^4S_{3/2}$
	52 Te	2	2	6	2	6	10	2	6	10		2	4			$^3P_2$
	53 I	2	2	6	2	6	10	2	6	10		2	5			$^2P_{3/2}$
	54 Xe	2	2	6	2	6	10	2	6	10		2	6			$^1S_0$

period	shell	K	L	M	N				O					P						Q	term
	orbital				4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s···	
6	55 Cs	2	8	18	2	6	10		2	6				1							$^2S_{1/2}$
	56 Ba	2	8	18	2	6	10		2	6				2							$^1S_0$
	57 La	2	8	18	2	6	10		2	6	1			2							$^2D_{3/2}$
	58 Ce	2	8	18	2	6	10	1	2	6	1			2							$^3H_4$
	59 Pr	2	8	18	2	6	10	3	2	6				2							^4I
	60 Nd	2	8	18	2	6	10	4	2	6				2							$^5I_4$
	61 Pm	2	8	18	2	6	10	5	2	6				2							^6H
	62 Sm	2	8	18	2	6	10	6	2	6				2							$^7F_0$
	63 Eu	2	8	18	2	6	10	7	2	6				2							$^8S_{7/2}$
	64 Gd	2	8	18	2	6	10	7	2	6	1			2							$^9D_2$
	65 Tb	2	8	18	2	6	10	9	2	6				2							$^6H_{17/2}$
	66 Dy	2	8	18	2	6	10	10	2	6				2							^5I
	67 Ho	2	8	18	2	6	10	11	2	6				2							^4I
	68 Er	2	8	18	2	6	10	12	2	6				2							^3H
	69 Tm	2	8	18	2	6	10	13	2	6				2							$^2F_{7/2}$
	70 Yb	2	8	18	2	6	10	14	2	6				2							$^1S_0$
	71 Lu	2	8	18	2	6	10	14	2	6	1			2							$^2D_{3/2}$
	72 Hf	2	8	18	2	6	10	14	2	6	2			2							$^3F_2$
	73 Ta	2	8	18	2	6	10	14	2	6	3			2							$^4F_{3/2}$
	74 W	2	8	18	2	6	10	14	2	6	4			2							$^5D_0$
	75 Re	2	8	18	2	6	10	14	2	6	5			2							$^6S_{5/2}$
	76 Os	2	8	18	2	6	10	14	2	6	6			2							$^5D_4$
	77 Ir	2	8	18	2	6	10	14	2	6	7			2							$^4F_{9/2}$
	78 Pt	2	8	18	2	6	10	14	2	6	9			1							$^3D_3$
	79 Au	2	8	18	2	6	10	14	2	6	10			1							$^2S_{1/2}$
	80 Hg	2	8	18	2	6	10	14	2	6	10			2							$^1S_0$
	81 Tl	2	8	18	2	6	10	14	2	6	10			2	1						$^2P_{1/2}$
	82 Pb	2	8	18	2	6	10	14	2	6	10			2	2						$^3P_0$
	83 Bi	2	8	18	2	6	10	14	2	6	10			2	3						$^4S_{3/2}$
	84 Po	2	8	18	2	6	10	14	2	6	10			2	4						$^3P_2$
	85 At	2	8	18	2	6	10	14	2	6	10			2	5						$^2P_{3/2}$
	86 Rn	2	8	18	2	6	10	14	2	6	10			2	6						$^1S_0$
7	87 Fr	2	8	18	2	6	10	14	2	6	10			2	6					1	$^2S_{1/2}$
	88 Ra	2	8	18	2	6	10	14	2	6	10			2	6					2	$^1S_0$
	89 Ac	2	8	18	2	6	10	14	2	6	10			2	6	1				2	$^2D_{3/2}$
	90 Th	2	8	18	2	6	10	14	2	6	10			2	6	2				2	$^3F_2$
	91 Pa	2	8	18	2	6	10	14	2	6	10	2		2	6	1				2	
	92 U	2	8	18	2	6	10	14	2	6	10	3		2	6	1				2	$^5L_4$
	93 Np	2	8	18	2	6	10	14	2	6	10	4		2	6	1				2	
	94 Pu	2	8	18	2	6	10	14	2	6	10	6		2	6					2	
	95 Am	2	8	18	2	6	10	14	2	6	10	7		2	6					2	$^8S_{7/2}$
	96 Cm	2	8	18	2	6	10	14	2	6	10	7		2	6	1				2	
	97 Bk	2	8	18	2	6	10	14	2	6	10	(8)		2	6	(1)				2	
	98 Cf	2	8	18	2	6	10	14	2	6	10	(9)		2	6	(1)				2	

(Note) In the 6-th or 7-th period, the total number of electrons is only shown for K, L, and M shells since they are fully occupied.

2.6 The periodicity

The properties of the elements exhibit a periodicity, which originates from the periodicity in electron configurations. In this section, ionization energies and electron affinities are studied in connection with the periodicity. First, experimental results are surveyed, and then relations with electron configurations are discussed.

2.6.1 Ionization energy and electron affinity

The energy required to make the $n + 1$ valent ionic state by removing an electron from the n valent ionic state of a matter is called the $n + 1$-th ionization energy. This definition may be applied to $n \geq 0$. In the case of $n = 0$, namely the energy required to remove an electron from neutral matter is called the first ionization energy. Usually, the ionization energy denotes the first ionization energy. Figure 2.8. and Table 2.5. show the periodicity of the first ionization energies for atoms, and their main features are as follows.

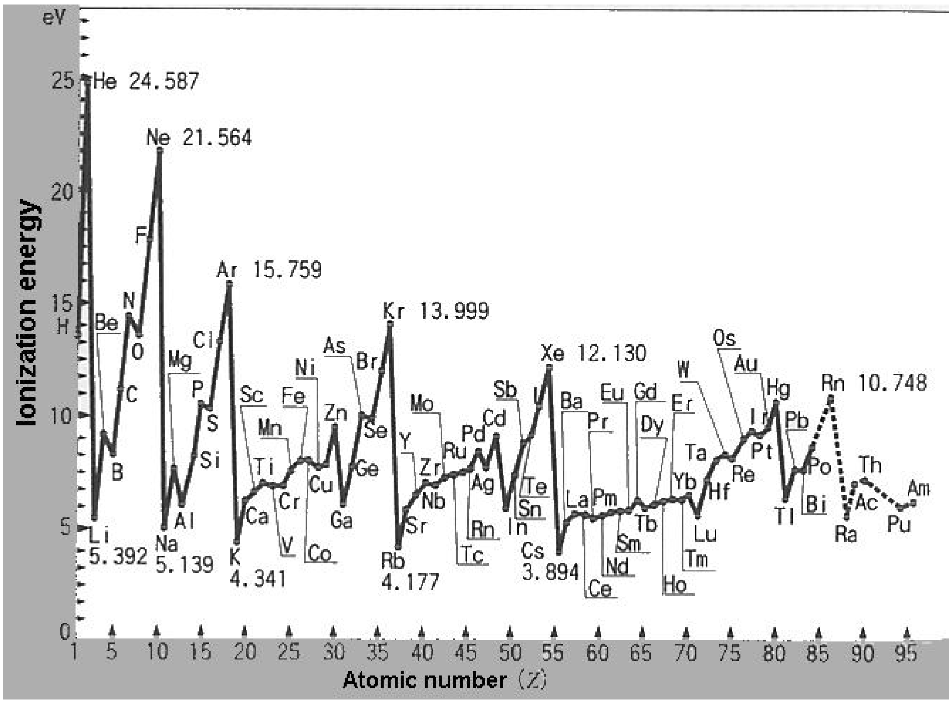


Figure 2.8: The periodicity of ionization energy

Feature (1) Associated with the increase of the atomic number, maxima are found at the rare gas atoms.

Feature (2) Associated with the increase of the atomic number, minima together with sudden drops from rare gas atoms are found at the alkali metal atoms.

Feature (3) Along the same row of the periodic Table, an increasing propensity is found as a whole on going from alkali metal atoms to rare gas atoms.

Feature (4) Fine features along the same row of the periodic Table include small maxima at the second or the fifteenth group together with minima at the next group.

Feature (5) In the same group, a decreasing propensity is found on going downward in the periodic Table.

Table 2.5: Ionization energies of atoms(eV)

H																	He
13.6																	24.6
Li	Be											B	C	N	O	F	Ne
5.4	9.3											8.3	11.3	14.5	13.6	17.4	21.6
Na	Mg											Al	Si	P	S	Cl	Ar
5.1	7.6											6.0	8.1	11.0	10.4	13.0	15.8
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10.0	9.8	11.8	14.0

The energy emitted on attachment of an electron to electrically neutral matter is called the electron affinity, which is equivalent to the energy required to remove an electron from a monovalent negative ion. Electron affinities for atoms also exhibit a periodicity variation as shown in Table 2.6. Although their propensities for variations along vertical and horizontal arrays in the periodic Table are largely similar to those for ionization energies, locations of the outstanding maxima are displaced to halogen atoms from rare gas atoms, and minima are shifted to rare gas atoms.

Table 2.6: Electron affinities of atoms(eV)

H																	He
0.75																	< 0
Li	Be											B	C	N	O	F	Ne
0.62	< 0											0.28	1.27	-0.1	1.46	3.40	< 0
Na	Mg											Al	Si	P	S	Cl	Ar
0.55	< 0											0.46	1.39	0.74	2.08	3.62	< 0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.50	< 0	< 0	0.2	0.5	0.66	< 0	0.25	0.7	1.15	1.23	~ 0	0.30	1.2	0.80	2.02	3.36	< 0

Various methods were devised for measuring the energy W required to remove one electron. For example, based on a method similar to the study of the photoelectric effect, the kinetic energy $\frac{1}{2}mv^2$ of electrons ejected from matter irradiated with a photon of $h\nu$ can be determined, and then W is obtained from the following formula.

$$W = h\nu - \frac{1}{2}mv^2 \tag{2.66}$$

This method is often used for the measurement of ionization energies and electron affinities.

2.6.2 Effective nuclear charge and rules to calculate screening constants

On account of the periodicity in electron configurations, effective nuclear charges of atoms are closely related to the periodicity in ionization energies and electron affinities. Let us study how effective nuclear charges depend on the screening effects mentioned in section 2.3.

In order to obtain the effective nuclear charge $\bar{Z}$, the screening constant s should be determined in addition to the atomic number Z. The screening constant s can be estimated easily based on the following rules.

[Rules to calculate screening constants]

(1) Since screening effects are caused by the repulsive forces of the other electrons against the electron concerned, the screening constant is estimated as a sum of contributions due to individual electrons.

(2) Since screening effects depend crucially on the location of the electrons, whether inside or outside of the electron concerned, as mentioned in section 2.3, relative positions of electron orbitals in atoms are classified into the following groups divided with slashes.

/1s/2s, 2p/3s, 3p/3d/4s, 4p/4d/4f/5s, 5p/5d/5f/

From the left to the right, the orbitals expand from the most inward to the most outward. *ns* and *np* belong to the same group considering the similar location of these orbitals.

(3) Contributions due to electrons of the outer groups are 0, since they do not cause screening effects.

(4) Contributions due to electrons of the same group are considered to be 1/3, because of incomplete screening effects associated with the relative probability of residing in the inward region.

(5) Contributions due to electrons of the inner groups are set equal to 1, since the inner electrons give complete screening effects.

The above rules are simplified versions of Slater's rules in 1930, from which the essential parts are only retained. The rules (1)-(3) are the same. As for (4), Slater introduced a subtle difference between 1s and other orbitals, 0.30 for 1s and 0.35 for others. Though (5) is the same except for electrons in ns or np, Slater considered that electrons in $(n-1)$s or $(n-1)$p have contributions of 0.85 for the screening with respect to the selected electron in the n-th shell, since the screening effects may be incomplete for the nearly overlapping electron shells. Slater's rules have been used to construct atomic orbital functions by simple treatments for various atoms, and they played important roles especially in early days of quantum chemistry. Atomic orbital functions with a form proposed by J. C. Slater are called Slater type orbital(STO), and they have been used even in recent program packages for quantum chemistry.

2.6.3 Effective nuclear charge and ionization energies

Loosely bound electrons in the outermost electron shell are the most important to be considered for ionization energies of atoms. Now, let us estimate the effective nuclear charge for an electron in the outermost electron shell, using the above rules for screening constants. For example, we consider a 2p electron of a fluorine atom F (Z=9). The electron configuration of a F atom is as follows.

$$(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^5$$

On the inner side of the noted 2p electron, there are two 1s electrons, which yield a contribution of 1×2 from the rule (5). In the same region as 2p, there are six electrons altogether, two 2s electrons and 5-1=4 electrons in 2p, which give a contribution of $\frac{1}{3} \times 6$ from the rule (4). Thus, $s = 1\times 2+\frac{1}{6} = 4$, and it follows that the effective nucleus charge $\bar{Z}$ becomes $\bar{Z} = Z - s = 9 - 4 = 5$.

Table 2.7 lists the effective nuclear charges for an electron in the outermost shell of atoms from hydrogen H to argon Ar, which are estimated on the basis of the above rules for screening constants. Features (1) $\sim$ (5) found for the periodicity in ionization energies can now be discussed in terms of the effective nuclear charges listed in the Table. Since ionization energies increase, associated with the increase of the attractive force by the nucleus, there should be the following two tendencies.

(Tendency 1): Ionization energies increase with the increase of the effective nuclear charge, because of the dependence of the Coulomb force on the electric charge.

(Tendency 2): Ionization energies decrease with the electron shell becoming more outer, because of the dependence of the Coulomb force on the distance.

Within a row in the periodic Table, valence electrons belong to the same electron shell, and effective nucleus charges increase on going from the left to the right. It follows that Tendency 1 explains the Feature 3 that along the same row ionization energies increase from the left to the right. On going from the right end to the top of the next row, the electron shell changes to the outer one(Tendency 2) associated with the sudden drop of the effective nuclear charge(Tendency 1), and therefore these tendencies explain the maximum at the right end(Feature 1) and the minimum at the left end(Feature 2). Among the same group effective nuclear charges are the same except for a change between He and Ne in the rare gas atoms, and the outer electron shell contributes to the lower elements. It follows that the lower rows give the lower ionization energies(Feature 5). In the change between He and Ne, it is difficult to guess the relative order since Tendency 1 and Tendency 2 work oppositely. Experimental values show a distinct decrease from He to Ne, and this indicates that Tendency 2, the effect of the distances from K shell to L shell, is much more important to the magnitude of the ionization energies. This effect can also be understood for a large drop of the ionization energies from 13.6 eV (H) to 5.4 eV (Li) in spite of the same effective nuclear charge of the unity.

Feature 4 for experimental values of ionization energies includes rather fine changes, and it cannot be explained only from Tendency 1 and Tendency 2. The change from the group 2 to the group 13 is due to the change of electron subshells from ns to np. An electron in an s orbital has the higher probability of approaching to the nucleus than an electron in a p orbital. Since the potential energy of Coulombic interactions is proportional to the inverse of the distance, behavior around the nucleus is most effective. Thus, the screening effects of s electrons are much smaller than those of p electrons. It follows that the effective nuclear charge for s electrons become larger than those for p electrons. This effect explains the difference of the ionization energies on going from the

Table 2.7: Effective nuclear charges for an electron in the outermost electron shell

H 1.00							He 1.67
Li 1.00	Be 1.67	B 2.33	C 3.00	N 3.67	O 4.33	F 5.00	Ne 5.67
Na 1.00	Mg 1.67	Al 2.33	Si 3.00	P 3.67	S 4.33	Cl 5.00	Ar 5.67

group 2 to the group 13. The change from the group 15 to the group 16 can be understood clearly when electron configurations of N and O atoms are compared in detail. N has a configuration of $[\mathrm{He}](2\mathrm{s})^2(2\mathrm{p}_x)^1(2\mathrm{p}_y)^1(2\mathrm{p}_z)^1$, while O has a configuration of $[\mathrm{He}](2\mathrm{s})^2(2\mathrm{p}_x)^2(2\mathrm{p}_y)^1(2\mathrm{p}_z)^1$. In an O atom, an electron is added to the same 2p orbital, which causes the larger electron repulsion to increase the energy of the electron in the outermost electron shell, and hence the ionization energy decreases.

2.6.4 Effective nuclear charge and electron affinity

Let us study the periodicity in electron affinities of atoms on the basis of the effective nuclear charges. Since the electron affinity equals the energy to remove an additional electron, we consider the effective nuclear charge for an electron in the outermost electron shell in the mononegative ion. For a 2p electron of the F^- ion ($Z = 9$) as an example, the electron configuration of the F^- ion is given by

$$(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^6$$

There are two 1s electrons in the inner side of the selected 2p electron, and thus their screening effects amount to 1×2 from the rule (5). Electrons in the same group of the selected 2p electron are seven altogether, two 2s electrons and 6-1=5 2p electrons, which leads to a contribution of $\frac{1}{3} \times 7$ as a whole from the rule (4). It follows that the screening constant s becomes $s = 1 \times 2 + \frac{1}{3} \times 7 = \frac{13}{3} = 4.33$. Thus, the effective nucleus charge $\overline{Z}$ is estimated as $\overline{Z} = Z - s = 9 - \frac{13}{3} = \frac{14}{3} = 4.67$. If a negative ion is formed for a Ne atom with an atomic number of $Z = 10$, the outermost electron of Ne^- is in a 3s orbital. The screening constant for this 3s electron becomes $s = 10$, since the number of the inner electrons are ten. Therefore, the effective nuclear charge becomes $\overline{Z} = 10 - 10 = 0$.

Table 2.8 lists effective nuclear charges for an electron in the outermost shell of mononegative ion from hydrogen H to argon Ar.

Table 2.8: Effective nuclear charges for an electron in the outermost electron shell in the mononegative ion

H 0.67							He 0.00
Li 0.67	Be 1.33	B 2.00	C 2.67	N 3.33	O 4.00	F 4.67	Ne 0.00
Na 0.67	Mg 1.33	Al 2.00	Si 2.67	P 3.33	S 4.00	Cl 4.67	Ar 0.00

Although the periodicity of the effective nuclear charges for mononegative ions are similar to those for neutral atoms, positions of the minima and maxima are displaced to the lower atomic numbers by one, respectively. It follows that electron affinities give their maxima at halogen atoms and their minima at rare gas atoms. Small maxima and minima as Feature 4 in ionization energies are also found at displaced positions to the left by one; at the groups 2 and 15, the values become smaller with respect to the atoms on their left.

2.7 Excited atoms and spectral terms

In a hydrogenic atom, states of $n \geq 2$ are called excited states. Atoms in excited states with excess energies larger than the energy of the ground state($n = 1$) are called excited atoms. Excited atoms may be formed by excess energies of chemical reactions in a flame or discharge. Contrary to hydrogenic atoms, electron configurations of excited atoms are complicated in general, since there are two or more electrons. Now, let us study the excited-state wavefunctions of a helium atom as a typical example for systems with many electrons. Then, we will also study spectral terms which are very important in spectroscopic classification of energy levels as well as their relationship with various angular momenta.

2.7.1 The ground state of a helium atom

As has been already studied, the electron configuration of the ground-state helium atom is $(1\mathrm{s})^2$. The corresponding determinant wave function of this configuration is given by

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) \\ \psi_1(2) & \psi_2(2) \end{vmatrix} \tag{2.67}$$

Here, electron coordinates are denoted simply by their number 1 or 2 in place of writing q_1 or q_2. ψ_1 and ψ_2 are orbital functions of electrons including their spins, and they are constructed from a combination of orbital functions of spatial coordinates $\phi_{1\mathrm{s}}$ and spin functions α or β.

$$\psi_1 = \phi_{1\mathrm{s}} \cdot \alpha \tag{2.68}$$

$$\psi_2 = \phi_{1\mathrm{s}} \cdot \beta \tag{2.69}$$

Using these equations and expanding the above determinant, we obtain the following formula.

$$\Psi(1,2) = \phi_{1\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)\frac{\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}}{\sqrt{2}} \tag{2.70}$$

$\phi_{1\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)$ in this formula is symmetric with respect to the permutation of the electrons, while the inside of { } depending on the spins is antisymmetric with respect to the permutation of the electrons. It follows that as a whole this formula is symmetric(+1) × antisymmetric(−1) = antisymmetric(−1).

2.7.2 Excited states of a helium atom

Now let us consider an electron configuration $(1\mathrm{s})^1(2\mathrm{s})^1$, in which an electron is excited to the 2s orbital from the 1s orbital. Including electron spins, we obtain the following four configurations of (a)-(d) as shown in Fig.2.9.

Using spatial orbital functions $\phi_{1\mathrm{s}}$ and $\phi_{2\mathrm{s}}$ together with spin functions α, β, let us construct the functions for two-electron systems. We obtain symmetric and antisymmetric functions as follows.

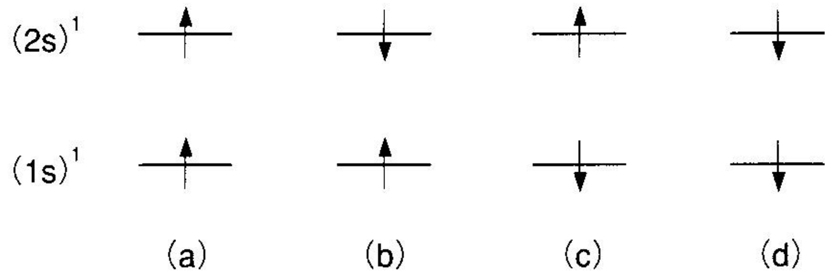


Figure 2.9: Electron configurations for $(1\mathrm{s})^1(2\mathrm{s})^1$

The symmetric function for the spatial part is given by

$$\Phi^{+} = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) + \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \tag{2.71}$$

and the antisymmetric function for the spatial part is given by

$$\Phi^{-} = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \tag{2.72}$$

There are three symmetric functions for the spin part as follows,

$$\Gamma_1 = \alpha(1)\alpha(2) \tag{2.73}$$

$$\Gamma_2 = \beta(1)\beta(2) \tag{2.74}$$

$$\Gamma_3 = \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.75}$$

and the antisymmetric spin function is given by

$$\Gamma_4 = \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.76}$$

Combinations of these functions lead to the following antisymmetric functions.

For the symmetric spatial function, there is only one antisymmetric spin function, ant thus we obtain

$$\Phi_1 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) + \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.77}$$

The excited state represented by this equation is called a singlet state.

For the antisymmetric spatial function, there are three symmetric spin functions to yield the following three combinations of antisymmetric functions.

$$\Phi_2 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \alpha(1)\alpha(2) \tag{2.78}$$

$$\Phi_3 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \beta(1)\beta(2) \tag{2.79}$$

$$\Phi_4 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.80}$$

Excited states represented by these functions are called triplet states. Experiments show that the triplet sates are more stable with the lower energies than the singlet state. This can be confirmed by theoretical calculations of expectation values. Energies for Φ_2, Φ_3, Φ_4 are the same, and they are triply degenerate states.

2.7.3 Angular momenta and spectral terms for many electron systems

In order to understand the excited states of atoms, angular momenta need to be studied in detail. As studied in section 1.13, the angular momentum is a vector with a magnitude and direction. The angular momentum of a many-electron system is given as a vector summation of individual angular momenta of the electrons and called the resultant angular momentum. Construction of such summations can be made for the orbital angular momentum $\hat{l}_i$, the spin angular momentum $\hat{s}_i$, and the total angular momentum of their sum $\hat{j}_i = \hat{l}_i + \hat{s}_i$. Thus, the resultant orbital angular momentum $\hat{L}$, the resultant spin angular momentum $\hat{S}$, and the resultant total angular momentum $\hat{J}$ are defined by the following equations.

$$\hat{L} = \sum_i \hat{l}_i \tag{2.81}$$

$$\hat{S} = \sum_i \hat{s}_i \tag{2.82}$$

$$\hat{J} = \sum_i \hat{j}_i \tag{2.83}$$

Since $\hat{j}_i = \hat{l}_i + \hat{s}_i$, we obtain $\hat{J} = \hat{L} + \hat{S}$.

The three types of angular momenta for an electron satisfy the respective eigen equations as follows.

$$\hat{l}^2\Gamma = l(l+1)\hbar^2\Gamma \tag{2.84}$$
$$\hat{l}_z\Gamma = m_l\hbar\Gamma \tag{2.85}$$
$$\hat{s}^2\Gamma = s(s+1)\hbar^2\Gamma \tag{2.86}$$
$$\hat{s}_z\Gamma = m_s\hbar\Gamma \tag{2.87}$$
$$\hat{j}^2\Gamma = j(j+1)\hbar^2\Gamma \tag{2.88}$$
$$\hat{j}_z\Gamma = m_j\hbar\Gamma \tag{2.89}$$

The subscript i should be attached to both of the operators and the quantum numbers in order to denote the i-th electron. The quantum number m for the component should have respective subscripts specifying l, s, j.

The resultant angular momenta introduced above should also satisfy similar eigen equations as follows.

$$\hat{L}^2\Gamma = L(L+1)\hbar^2\Gamma \tag{2.90}$$
$$\hat{L}_z\Gamma = M_L\hbar\Gamma \tag{2.91}$$
$$\hat{S}^2\Gamma = S(S+1)\hbar^2\Gamma \tag{2.92}$$
$$\hat{S}_z\Gamma = M_S\hbar\Gamma \tag{2.93}$$
$$\hat{J}^2\Gamma = J(J+1)\hbar^2\Gamma \tag{2.94}$$
$$\hat{J}_z\Gamma = M_J\hbar\Gamma \tag{2.95}$$

L, S, J are quantum numbers corresponding to the operators of the squares, and M_L, M_S, M_J are quantum numbers corresponding to their components. M_L, M_S, M_J are equal to summations of the contributions due to individual electrons.

$$M_L = \sum_i (m_l)_i \tag{2.96}$$
$$M_S = \sum_i (m_s)_i \tag{2.97}$$
$$M_J = \sum_i (m_j)_i \tag{2.98}$$

Using quantum numbers for the resultant angular momenta L, S, J and the principal quantum number n, atomic energy levels are represented by the following symbol.

$$n^{2S+1}\{L\}_J \tag{2.99}$$

This symbol is useful and important, especially in atomic spectroscopy, and is called a spectral term. n is the maximum value among the principal quantum numbers of the electrons, and this value is placed on the top. For the symbol $\{L\}$, capital letters of S,P,D,F,G,H are assigned with respect to the value of L=0,1,2,3,4,5, respectively. $2S+1$ is called the spin multiplicity, and its value calculated from the value of S is attached to the left shoulder of a letter such as S and P corresponding to the symbol $\{L\}$; the superscript for the letter of $\{L\}$ becomes 3 for triplet and 1 for singlet. The value of J is attached as a subscript to the right side of the letter of $\{L\}$. n and J are often omitted for abbreviation unless they are necessary.

L	0	1	2	3	4	5
$\{L\}$	S	P	D	F	G	H

$\hat{L}$ and $\hat{S}$ are commutable with $\hat{H}$, the Hamiltonian operator for a many electron atom given by eq.(2.31). Therefore, energy levels corresponding to spectral terms with the same combinations of L and S and the same electron configurations, which are called LS terms, are identical and degenerate. For such degenerate cases, the right subscript J may be omitted, since they are not important. However, experiments sometimes shows plitting of LS terms. One of the causes is spin-orbit interactions, which yield splitting proportional to the fourth power of the atomic number Z. Thus, the effect becomes significant for heavy atoms. On the other hand, splitting due to external magnetic fields is called the Zeeman effect.

In the case of hydrogenic atoms, it is easy to obtain spectral terms, since the system has only one electron. For example, let us consider a state of one 2p electron. Because of a 2p electron, $n = 2$, and $s = \frac{1}{2}$ with $m_s = \pm\frac{1}{2}$. For a single electron system, $M_s = m_s$, and thus $S = \frac{1}{2}$ leading to the spin multiplicity $2S + 1 = 2 \times (1/2) + 1 = 2$, which is called a doublet. Similarly, $M_l = m_l$, and thus $L = 1$ corresponding to the letter P for the symbol $\{L\}$. In order to determine the quantity of J, we need to know the rule for the permitted values of coupled angular momenta.

[The rule for permitted values of coupled angular momenta]

We introduce a coupled angular momentum of $\hat{J} = \hat{J}_1 + \hat{J}_2$, where $\hat{J}_1$ and $\hat{J}_2$ are both angular momenta commutable with each other. Using quantum numbers J_1 and J_2 for $\hat{J}_1$ and $\hat{J}_2$, permitted values of the quantum number J for the square of $\hat{J}$ are as follows.

$$J = J_1 + J_2,\ J_1 + J_2 - 1,\ \cdots,\ |J_1 - J_2| \tag{2.100}$$

Since $\hat{J}$ is a coupled vector of $\hat{L}$ and $\hat{S}$, the magnitude of the coupled angular momentum $\hat{J}$ has a value between the maximum of $L+S$ and the minimum of $|L-S|$. In the case of one 2p electron, $L = 1$ and $S = \frac{1}{2}$, and thus the possible cases are $J = 1 + 1/2 = 3/2$ or $J = 1 - 1/2 = 1/2$. It follows that the spectral term for $(2p)^1$ are given by

$$2^2\mathrm{P}_{3/2} \text{ and } 2^2\mathrm{P}_{1/2}$$

These two terms have the same combination of L and S, and they are degenerate, if the spin orbit interactions are negligible. In the case of a hydrogen atom, the splitting due to the spin orbit interactions are very small, and $^2\mathrm{P}_{1/2}$ is only 0.365 cm^{-1} lower than the other term.

Example 2.5 Verify that spin functions $\Gamma_1 \sim \Gamma_4$ for a two-electron system(equations(2.73)-(2.76)) are eigen functions of the z-component operator of the resultant spin angular momentum $\hat{S}_z$, and obtain individual values of M_s.

(Solution) First derive equations in the form of $\hat{S}_z\Gamma = M_S\hbar\Gamma$, and second obtain values of M_s.

(1) $\Gamma_1 = \alpha(1)\alpha(2)$

$$\begin{aligned} \hat{S}_z\Gamma_1 &= (\hat{s}_{z_1} + \hat{s}_{z_2})\alpha(1)\alpha(2) = \hat{s}_{z_1}\alpha(1)\alpha(2) + \hat{s}_{z_2}\alpha(1)\alpha(2) \\ &= \{\hat{s}_{z_1}\alpha(1)\}\alpha(2) + \alpha(1)\{\hat{s}_{z_2}\alpha(2)\} = \frac{1}{2}\hbar\alpha(1)\alpha(2) + \alpha(1)\frac{1}{2}\hbar\alpha(2) \\ &= \left(\frac{1}{2} + \frac{1}{2}\right)\hbar\alpha(1)\alpha(2) = \hbar\Gamma_1 \end{aligned}$$

Thus, Γ_1 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 1$.

(2) $\Gamma_2 = \beta(1)\beta(2)$

$$\begin{aligned} \hat{S}_z\Gamma_2 &= (\hat{s}_{z_1} + \hat{s}_{z_2})\beta(1)\beta(2) = \{\hat{s}_{z_1}\beta(1)\}\beta(2) + \beta(1)\{\hat{s}_{z_2}\beta(2)\} \\ &= -\frac{1}{2}\hbar\beta(1)\beta(2) + \beta(1)\left(-\frac{1}{2}\right)\hbar\beta(2) = \left(-\frac{1}{2} - \frac{1}{2}\right)\hbar\beta(1)\beta(2) = -\hbar\Gamma_2 \end{aligned}$$

Thus, Γ_2 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = -1$.

(3) $\Gamma_3 = \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/\sqrt{2}$

$$\hat{S}_z\Gamma_3 = \left(\frac{1}{2} - \frac{1}{2}\right)\hbar\Gamma_3 = 0\hbar\Gamma_3$$

Thus, Γ_3 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 0$.

(4) $\Gamma_4 = \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}$

$$\hat{S}_z\Gamma_4 = \left(\frac{1}{2} - \frac{1}{2}\right)\hbar\Gamma_4 = 0\hbar\Gamma_4$$

Thus, Γ_4 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 0$.

Next, let us study the spectral terms of excited states $(1s)^1(2s)^1$ for a He atom. The largest principal quantum number is for a 2s electron, and thus $n = 2$.Since all electrons are in s orbitals with $m_l = 0$, then $L = 0 + 0 = 0$. The value of S depends on the spin multiplicity, singlet or triplet. From Example 2.5, the only possible value for M_S is 0, and this leads to $S = 0$ and $2S + 1 = 0 + 1 = 1$. From $S = 0$ and $L = 0$, $J = 0 + 0 = 0$. It follows that the spectral term for the singlet excited-state is given by 2^1S_0.

For triplet excited-states, there are three values of M_S, 1 for Γ_1, 0 for Γ_3, and -1 for Γ_2, and thus $S = 1$. Noting $L = 0$, we find $J = 1 + 0 = 1 - 0 = 1$. It follows that the spectral term of the triplet excited states is given by 2^3S_1.

The following rules are very useful for obtaining spectral terms.

[How to obtain spectral terms]

(1) When a subshell is fully occupied by electrons, those electrons in the subshell may be disregarded, since contributions of the subshell to M_S and M_L are vanishing. For example, in order to obtain the spectral term for the ground-state of Li $(1s)^2(2s)^1$, we may only deal with $(2s)^1$ neglecting $(1s)^2$.

(2) When a subshell with an azimuthal quantum number of l is fully occupied by electrons, the configuration can be expressed as $(n\{l\})^{(4l+2)}$, where $l = 0, 1, 2$ correspond to s, p, d, respectively. A pair of incompletely occupied subshells, $(n\{l\})^{(4l+2-k)}$ and $(n\{l\})^{(k)}$, give the same spectral terms. For example, $(2p)^5$ and $(2p)^1$ give the same set of spectral terms, $2^2P_{3/2}$ and $2^2P_{1/2}$.

Exercises

2.1 Calculate the energy of a photon emitted in a transition of an electron in the monopositive helium ion from an excited state of principal quantum number $n = 2$ to the ground state $n = 1$.

2.2 Show that an anticlockwise rotation of the $d_{x^2-y^2}$ orbital by 45 degrees in the x–y plane leads to a d_{xy} orbital. Verify that the d_{z^2} orbital is made of a linear combination of $d_{y^2-z^2}$ and $d_{z^2-x^2}$ orbitals, which are equivalent to $d_{x^2-y^2}$ orbital.

2.3 Calculate the distances where the radial distribution functions for the 1s and 2p orbitals of a hydrogen atom are maxima, and compare the results with the Bohr radius.

2.4 Construct the wave function with a Slater determinant for an electron configuration of He in which one electron occupies the 1s orbital with α spin and the other electron occupies the 2s orbital with α spin. Show that for this wave function the probability of finding two electrons at identical spatial coordinates is vanishing (the probability of finding electrons occupying different spatial orbitals with the same spin at the same place is vanishing).

2.5 Construct the electron configuration of an iodide ion (I^-).

2.6 Which group in the periodic table gives the maximum for the energies (the second ionization energy) required for producing a dipositive ion from a monopositive ion, when the energies are compared as functions of the atomic numbers? Which group gives the minimum? Answer these questions by considering the effective nuclear charges in the range of atomic numbers from 2 to 18.

2.7 Determine all wavefunctions for excited states of He in which one of 1s electrons is excited to a 2p orbital. Determine their spectral terms.

Chapter 3

Basic methods of approximation

Except for a very simple case such as a hydrogen atom, the fundamental equation of quantum mechanics cannot be solved rigorously. It follows that approximation mathods should be used to apply quantum mechanics to various problems. Methods to be used as well as the accuracies to be required depend on the problems to be solved.

In this chapter, we will study most imortant and useful methods for approximation.

3.1 Perturbation theory

Even if an equation is difficult to solve directly, true solutions can be deduced from approximate solutions of a slightly simplified equation, provided that the approximate solutions are known or can be obtained easily. Such a technique, based on perturbation theory, is often used for calculations in quantum theory. Perturbation theory is applied to many problems for estimating changes of energy levels and wave functions associated with additional variations due to interparticle interaction as well as magnetic or electric fields.

3.1.1 Perturbation theory

In the equation of quantum mechanics, an additional term $\hat{H}'$ included in the Hamiltonian operator $\hat{H}$ is called a perturbation. A system without perturbation is called the unperturbed system. Assuming that solutions $\{E_i{}^\circ,\ \Psi_i{}^\circ\}$ of the eigen equation $\hat{H}_0\Psi^\circ = E\Psi^\circ$ for the unperturbed Hamiltonian $\hat{H}_0 = \hat{H} - \hat{H}'$ are known, let us try to obtain solutions $\{E_n,\ \Psi_n\}$ of the eigen equation $\hat{H}\Psi = E\Psi$ for the Hamiltonian including the perturbation $\hat{H} = \hat{H}_0 + \hat{H}'$.

First, we introduce a perturbation $\hat{H}' = \lambda\hat{V}$ with a parameter λ indicating the magnitude of the perturbation. Next, we expand Ψ_n in terms of solutions for the unperturbed system $\{\Psi_i{}^\circ\}$.

$$\Psi_n = \sum_i c_{in}\Psi_i{}^\circ \tag{3.1}$$

Insertion of $\hat{H} = \hat{H}_0 + \lambda\hat{V}$ into the eigen equation of $\hat{H}$, followed by using the above expanded equation for Ψ_n and the eigen equation of $\hat{H}_0$, then results in

$$\sum_i c_{in}\{E_i{}^\circ + \lambda\hat{V}\}\Psi_i{}^\circ = E_n \sum_i c_{in}\Psi_i{}^\circ \tag{3.2}$$

Noting that an orthonormal system can be used in general for $\{\Psi_i{}^\circ\}$, multiplication through from the left by $\Psi_j{}^{\circ *}$ and integration yield the following equation.

$$c_{jn}E_j{}^\circ + \lambda\sum_i c_{in}V_{ji} = c_{jn}E_n \tag{3.3}$$

V_{ji} is an integral for all coordinates represented by q, which is give by the following equation.

$$V_{ji} = \int \Psi_j{}^{\circ *} \hat{V} \Psi_i{}^{\circ} \mathrm{d}q \tag{3.4}$$

This quantity V_{ji} can be evaluated when $\{\Psi_i{}^{\circ}\}$ as well as the operator representing the perturbation $\hat{V}$ are given. λV_{ji} is denoted by $H_{ji}{}'$ and is called the ji-matrix element of the perturbation.

$$\begin{aligned} H_{ji}{}' &= \int \Psi_j{}^{\circ *} \hat{H}' \Psi_i{}^{\circ} \mathrm{d}q \\ &= \int \Psi_j{}^{\circ *} \lambda \hat{V} \Psi_i{}^{\circ} \mathrm{d}q \\ &= \lambda V_{ji} \end{aligned} \tag{3.5}$$

This equation will be used for the formula of perturbation theory.

The equation (3.3) is an equation for obtaining energy eigen values E_n and $\{c_{in}\}$ determining the wave functions Ψ_n. In order to solve this equation approximately, let us expand c_{in} and E_n into power series of λ.

$$c_{in} = c_{in}{}^{\circ} + \lambda c_{in}{}' + \lambda^2 c_{in}{}'' + \cdots \tag{3.6}$$

$$E_n = E_n{}^{\circ} + \lambda E_n{}' + \lambda^2 E_n{}'' + \cdots \tag{3.7}$$

When $E_n{}^{\circ}$ has no degeneracy, we obtain $c_{in}{}^{\circ} = \delta_{in}$(1 for $i = n$, 0 for $i \neq n$), since for $\lambda \to 0$ $\Psi_n \to \Psi_n{}^{\circ}$ associated with $E_n \to E_n{}^{\circ}$. Therefore, the first terms in the expansion correspond to the unperturbed system, and the second terms are corrections to the perturbation. Inserting the above expansions eqs.(3.6)(3.7) into eq.(3.3), followed by arranging the lower order terms of λ from the left, we obtain

$$\lambda(V_{nn} - E_n{}') + \lambda^2 \left(\sum_i V_{ni} c_{in}{}' - c_{nn}{}' E_n{}' - E_n{}'' \right) + \cdots = 0 \tag{3.8}$$

By neglecting the second and the higher order terms, we obtain the following result for the first order correction of the energy.

$$E_n{}' = V_{nn} \tag{3.9}$$

It follows that the formula for the energy to the first order of the perturbation is given by

$$\begin{aligned} E_n \fallingdotseq E_n{}^{\circ} + \lambda V_{nn} &= E_n{}^{\circ} + H'_{nn} \\ &= \int \Psi_n{}^{\circ *} \{\hat{H}_0 + \hat{H}'\} \Psi_n{}^{\circ} \mathrm{d}q \\ &= \int \Psi_n{}^{\circ *} \hat{H} \Psi_n{}^{\circ} \mathrm{d}q \end{aligned} \tag{3.10}$$

The last equation indicates that the expectation value of the Hamiltonian operator including the perturbation in terms of unperturbed wave functions $\Psi_n{}^{\circ}$ yields the energy to the first order of the perturbation.

By considering the second order contributions of λ, we obtain the following equation.

$$E_n{}'' = \sum_{i\,(i \neq n)} V_{ni} c_{in}{}' \tag{3.11}$$

From the first order terms of λ in eq.(3.3) with insertion of expanded expressions, $c_{in}{}'$ $(i \neq n)$ can be written as follows.

$$c_{in}{}' = \frac{V_{in}}{E_n{}^{\circ} - E_i{}^{\circ}} \qquad (i \neq n) \tag{3.12}$$

Using this expression for eq.(3.11) we write

$$E_n{}'' = \sum_{i\,(i \neq n)} \frac{V_{ni} V_{in}}{E_n{}^{\circ} - E_i{}^{\circ}} \tag{3.13}$$

Using the above results, we obtain the following formulas for approximations of $\{E_n, \Psi_n\}$ to the second order of the perturbation.

$$E_n \fallingdotseq E_n{}^\circ + H_{nn}{}' + \sum_{i\,(i\neq n)} \frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} \tag{3.14}$$

$$\Psi_n \fallingdotseq \Psi_n{}^\circ + \sum_{i\,(i\neq n)} \left(\frac{H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} \right) \Psi_i{}^\circ \tag{3.15}$$

Example 3.1 Verify that second-order perturbation corrections of the energy due to the lower energy states are always positive, whereas those due to the higher energy states are always negative. It should be noted that $H_{ni}{}' = H_{in}{}'^*$, where * denotes the complex conjugate (eq.(1.37)).

(Solution) The second-order perturbation corrections for the energy of the n-th state is expressed by

$$E_n(2) = \sum_{i\,(i\neq n)} \frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ}$$

Using $H_{ni}{}' = H_{in}{}'^*$ and noting $|H_{in}{}'|^2 > 0$, we obtain

$$H_{ni}{}' H_{in}{}' = H_{in}{}'^* H_{in}{}' = |H_{in}{}'|^2 > 0$$

This means that the numerators in the expression for $E_n(2)$ are always positive. It follows that contributions due to the lower energy states $i(E_i{}^\circ < E_n{}^\circ)$ are always positive.

$$\frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} > 0$$

Also, contributions due to the higher energy states $i(E_i{}^\circ > E_n{}^\circ)$ are always negative.

$$\frac{H_{ni}{}' H_{in}{}'}{E_n{}^\circ - E_i{}^\circ} < 0$$

3.1.2 Perturbation theory for degenerate states

Now let us consider a system with f-fold degeneracy in the energy E°. The degenerate states are numbered from 1 to f , and energies of these degenerate states are denoted as $E_1{}^\circ = E_2{}^\circ = \cdots = E_f{}^\circ$. For any other state a number n larger than f is assigned. For the energy levels of $n > f$, $\{E_n, \Psi_n\}$ are obtained by the method studied above. The energy levels from 1 to f should be treated differently, noting that $E_n \to E_n{}^\circ$ and $\Psi_n \to \sum_{i=1}^{f} c_{in}{}^\circ \Psi_i{}^\circ$, associated with $\lambda \to 0$. Insertion of equations (3.6) and (3.7) into eq.(3.3), followed by neglecting higher order terms than the second order of λ, results in the following a set of simultaneous equations.

$$\sum_{i=1}^{f} (V_{ji} - \delta_{ji} E_n{}') c_{in}{}^\circ = 0 \tag{3.16}$$

where j and n are arbitrary numbers from 1 to f.

According to linear algebra, the necessary and sufficient condition for the existence of nontrivial solutions other than all $\{c_{in}{}^\circ\}$ to be vanishing is that the determinant of the matrix with ji element corresponding to the inside of ( ) in eq.(3.16) should be zero.

$$\begin{vmatrix} V_{11} - E_n{}' & V_{12} & V_{13} & \cdots & V_{1f} \\ V_{21} & V_{22} - E_n{}' & V_{23} & \cdots & V_{2f} \\ V_{31} & V_{32} & V_{33} - E_n{}' & \cdots & V_{3f} \\ \vdots & \vdots & \vdots & & \vdots \\ V_{f1} & V_{f2} & V_{f3} & \cdots & V_{ff} - E_n{}' \end{vmatrix} = 0 \tag{3.17}$$

By solving this algebraic equation of the order f with respect to $E_n{}'$, f solutions of $E_1{}', E_2{}', \cdots, E_f{}'$ can be obtained. Thus, the energy levels shifted by the perturbation can be determined as follows.

$$E_n \fallingdotseq E_n{}^{\circ} + \lambda E_n{}' \qquad (1 \leqq n \leqq f) \tag{3.18}$$

$\{c_{in}{}^{\circ}\}$ can also be obtained from solutions of the simultaneous equations of (3.16), provided that a value of $\{E_n{}'\}$ from eq.(3.17) is inserted in place of $E_n{}'$ in ( ). It should be noted that the following equation for the normalization condition for $\{\Psi_n\}$.

$$\sum_{i=1}^{f} |c_{in}{}^{\circ}|^2 = 1 \qquad (1 \leqq n \leqq f) \tag{3.19}$$

3.1.3 Modification of states by perturbation

Modification of energy levels due to additional actions can be observed as spectral changes for transitions related to the levels. We will see some typical examples below.

[The Zeeman effect]

When magnetic fields are applied, doublet or triplet states may exhibit the splitting of degenerate energy levels. Phenomena of the splitting in spectral lines under magnetic fields are called the Zeeman effect. The extent of the splitting of spectral lines depends on the strength of the applied field. Fig.3.1 shows an example of the Zeeman effect on the $^1D_2$–$^1P_1$ transition giving red emission (6438.47 Å) from a cadmium atom. One line without a field splits into three lines under the magnetic field.

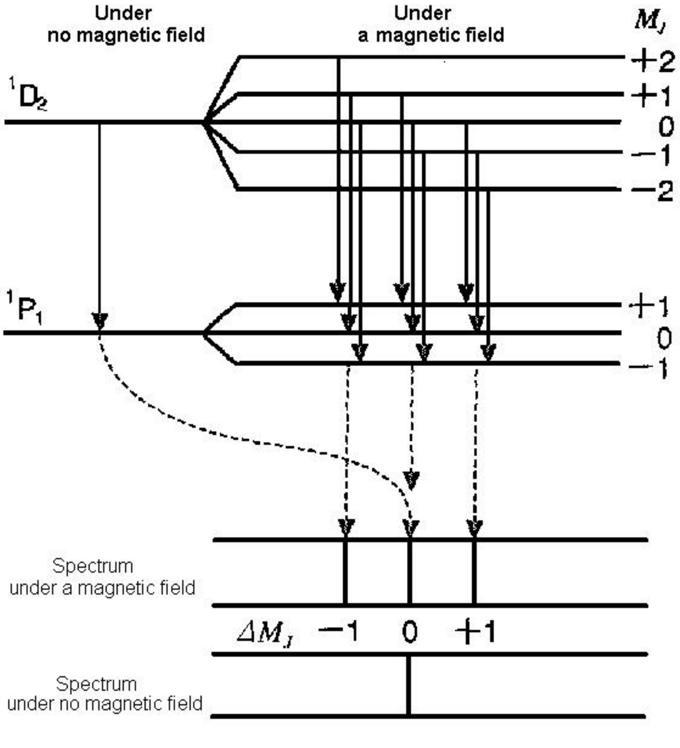


Figure 3.1: An example of the Zeeman effect. The splitting of spectral terms under a magnetic field

[The Stark effect]

Emission spectra from a hydrogen atom in a strong electric field give splitting of spectral lines. The splitting of spectral lines under an electric field is called the Stark effect. The Stark effect is observed for the following cases.

(1) At least one of the energy levels related to the transition is degenerate, and the degeneracy is lifted by the action of the electric field.

(2) Polar molecules with various orientation may have different energies under a strong electric field, and transition energies may also be modified depending on the molecular orientation.

The latter type of the Stark effect does not require the degeneracy of the levels. The extent of the splitting in the Stark effect depends on the strength of the applied electric field.

[The splitting of d levels]

Levels of d electrons in a metal atom or its ion (M) exhibit varieties of split patterns under the field (ligand field or crystal field) of the surrounding ligands (L), depending on the symmetry and the field strengths (Fig.3.2). Subtle changes in color for transition metal ions and their compounds are related to the variations of split patterns of d levels.

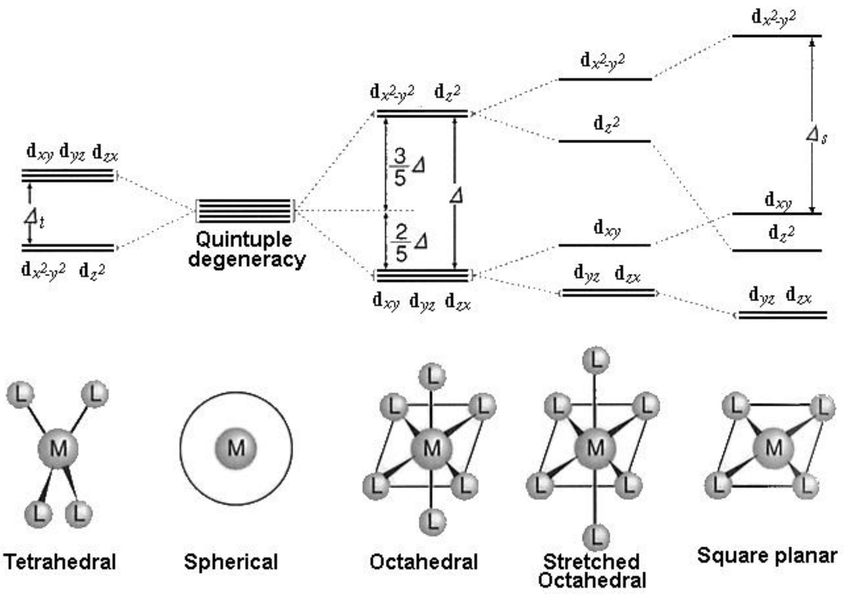


Figure 3.2: The ligand field splitting of d levels. M: central metal, L: ligand.

[Spin-orbit coupling effects]

As studied in section 2.7, levels with the same set of L and S are degenerate, when the spin-orbit coupling can be disregarded. If the spin-orbit coupling is significant, especially for atoms with large atomic numbers to which relativistic effects cannot be neglected, the degeneracy is lifted to give splitting of spectral lines. Multiplet states such as doublets and triplets can be observed as split states even without external fields, and such a phenomenon is called the zero-field splitting in contrast to the Zeeman effect.

[The transition probability and spectral selection rules]

In addition to the above examples, rapid variations such as actions due to electromagnetic waves can also be treated as a perturbation. Since systems under actions of electromagnetic waves are not in stationary states, theoretical treatments of unstationary states need to be made. Although details will not be mentioned in this book, an extension of perturbation theory to unstationary states makes it possible to evaluate the transition probabilities between stationary states. Looking into the transition probabilities reveals that transitions do not necessarily occur between any pair of states. There are certain rules which lead to either allowed transitions or forbidden transitions.

For example, the following selection rules are well known as conditions in order to observe light absorption or emission by atoms.

$$\begin{aligned}
&\Delta L = 0\,\text{or}\ \pm 1 && \text{(The selection rule for orbital angular momenta)}\\
&\Delta J = 0\,\text{or}\ \pm 1 && \text{(The selection rule for total angular momenta)} \qquad (3.20)\\
&\Delta S = 0 && \text{(The selection rule for spin angular momenta)}
\end{aligned}$$

Exceptionally, $\Delta L = 0$ should be omitted between a pair of states with $L = 0$, and also $\Delta J = 0$ should be omitted between a pair of states with $J = 0$. When transitions do not satisfy the conditions in eq.(3.20), the corresponding spectral lines cannot be observed or appear with extremely weak intensities, even if they could be observed. The last rule of $\Delta S = 0$, forbidding transitions between levels with different spin-multiplicity becomes to be less effective with the increase of the atomic number, since the spin-orbit coupling becomes to be strong for heavy atoms.

As can be seen from Fig.3.1, among transitions between split sublevels due to the difference of the M_J values, transitions of $\Delta M_J = 0$ or ± 1 are only allowed.

3.2 The variation method

Besides the perturbation method studied in the previous section, another approach called the variation method has been used for applying quantum mechanics to various problems. Especially in recent years, development of modern computers has facilitated valuable usage of calculation methods based on the variation method. In this section we will study the variation method. Now, let us start with the variation principle.

3.2.1 The variation principle

A trial expectation value with an arbitrary function Φ is introduced by the following equation.

$$\varepsilon[\Phi] = \frac{\int \Phi^* \hat{H} \Phi \mathrm{d}q}{\int \Phi^* \Phi \mathrm{d}q}. \tag{3.21}$$

The value of $\varepsilon[\Phi]$ which depends on the choice of Φ is not smaller than the lowest eigen value E_0 for the eigen equation $\hat{H}\Psi = E\Psi$.

$$\varepsilon[\Phi] \geqq E_0 \qquad \text{(The equality holds only if } \hat{H}\Phi = E_0\Phi) \tag{3.22}$$

The equality of this formula holds only for a special case where $\varepsilon[\Phi]$ is an eigen function belonging to E_0. This formula of eq.(3.22) is called the variation principle.

[Proof]

Φ can be expanded in terms of eigen functions $\{\Psi_i\}$ for $\hat{H}$ as $\Phi = \sum\limits_i c_i \Psi_i$. Calculating $\varepsilon[\Phi] - E_0$ with the expansion of Φ and using $\hat{H}\Psi_i = E_i\Psi_i$ as well as the normality of $\{\Psi_i\}$, we obtain

$$\varepsilon[\Phi] - E_0 = \frac{\sum\limits_i (E_i - E_0)|c_i|^2 \int |\Psi_i|^2 \mathrm{d}q}{\sum\limits_i |c_i|^2 \int |\Psi_i|^2 \mathrm{d}q} \geqq 0.$$

The last inequality is derived from the followings; E_0 is the lowest eigen value, and an absolute value cannot be negative. Since $\{\Psi_i\}$ cannot be zero for all possible cases of the variables, the equality requires $c_i = 0$ for all $\{\Psi_i\}$ having an energy E_i larger than E_0. It follows that a nonzero value for the coefficient c_i in the expansion of Φ in terms of $\{\Psi_i\}$ is allowed only if $E_i = E_0$. Only in this case, $\hat{H}\Phi = E_0\Phi$ holds, and Φ becomes the eigen function belonging to the eigen value E_0. Conversely, if Φ is an eigen function of E_0 satisfying $\hat{H}\Phi = E_0\Phi$, the numerator of eq.(3.21) becomes $\int \Phi^* E_0 \Phi \mathrm{d}q = E_0 \int \Phi^* \Phi \mathrm{d}q$, which leads to $\varepsilon[\Phi] = E_0$. Therefore, the equality holds only if $\hat{H}\Phi = E_0\Phi$, which is the case that Φ is the eigen function of the lowest eigen value E_0.

The variation principle gives a guide to obtain the wave function and the eigen value of the ground-state. For this purpose, Φ should be determined so that the value of $\varepsilon[\Phi]$ using Φ may become the minimum. The resultant Φ is the eigen function of the lowest eigen value E_0, the wave function of the ground-state. It follows that this Φ yields $\varepsilon[\Phi]$ corresponding to the ground-state energy value of E_0.

3.2.2 The variation method using a linear-combination approximation (Ritz's variation method)

It is difficult to find out Φ minimizing $\varepsilon[\Phi]$ on the basis of the above variation principle. For various functions ϕ_1, ϕ_2, ϕ_3, $\cdots$, we need to calculate the respective value of $\varepsilon[\phi_i]$, and we should find out a function giving the minimum. It is however impossible to test all functions. Even if several combinations of E and Ψ satisfying $\hat{H}\Psi = E\Psi$, the lowest eigen value among them is not necessarily the true minimum eigen value. Therefore, a compromise of finite numbers of trials giving up infinite repetitions would lead to unsuccessful results unless fortunate choices happened to be made.

Now, let us try to test a wide range of functions more efficiently. A linear combination of n functions ϕ_1, ϕ_2, ϕ_3, $\cdots$, ϕ_n

$$\Phi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n \tag{3.23}$$

can be used to test infinite numbers of trial functions expressed by eq.(3.23), provided that expansion coefficients $\{c_i\}$ as adjustable variables are continuously varied. Although there is a restriction due to the selection of $\{\phi_i\}$, we can obtain the best result for testing all of arbitrary linear combinations of $\{\phi_i\}$ as well as individual functions from ϕ_1 to ϕ_n. In this way, the variation principle is used to determine a series of $\{c_i\}$ so that $\{c_i\}$ may lead to the minimum of $\varepsilon[\Phi]$. This procedure is called the variation method using a linear-combination approximation (Ritz's variation method).

Insertion of eq.(3.23) into the definition of $\varepsilon[\Phi]$ leads to the following equation.

$$\varepsilon[\Phi] = \frac{\sum\limits_i \sum\limits_j c_i{}^* H_{ij} c_j}{\sum\limits_i \sum\limits_j c_i{}^* S_{ij} c_j} \tag{3.24}$$

In this expression summations for i and j should be taken from 1 to n. H_{ij} and S_{ij} are elements of $n \times n$ matrices and defined by the following integrals.

$$H_{ij} = \int \phi_i{}^* \hat{H} \phi_j \mathrm{d}q \tag{3.25}$$

$$S_{ij} = \int \phi_i{}^* \phi_j \mathrm{d}q \tag{3.26}$$

S_{ij} is called an overlap integral between ϕ_i and ϕ_j.

Based on the variation principle, $\varepsilon[\Phi]$ should be minimized by changing $\{c_i\}$, which are the coefficients introduced in the definition of Φ. Since c_i and c_i^* are complex conjugates with each other, we may take one of them as an independent variable. Hence, let us obtain the condition for $\partial\varepsilon/\partial c_i{}^* = 0$. For convenience, we rewrite eq.(3.24) as

$$\varepsilon[\Phi] \sum_i \sum_j c_i{}^* S_{ij} c_j = \sum_i \sum_j c_i{}^* H_{ij} c_j \tag{3.27}$$

Differentiation of the both sides of this equation with respect to $c_i{}^*$ gives

$$\frac{\partial\varepsilon}{\partial c_i{}^*} \sum_i \sum_j c_i{}^* S_{ij} c_j + \varepsilon \sum_j S_{ij} c_j = \sum_j H_{ij} c_j \tag{3.28}$$

Using the condition of $\partial\varepsilon/\partial c_i{}^* = 0$, we obtain

$$\sum_j (H_{ij} - \varepsilon S_{ij}) c_j = 0 \qquad (i = 1, 2, \cdots, n) \tag{3.29}$$

This expression is a set of simultaneous equations for $\{c_j\}$, which is similar to eq.(3.16) in the previous section.

If all coefficients from c_1 to c_n are zero, then they satisfy eq.(3.29). However, this set of solutions leads to an identity of $\Phi = 0$, which is physically of no meaning. In order to obtain nontrivial solutions other than all $\{c_j\}$ to be vanishing, the following determinant should be zero.

$$\begin{vmatrix} H_{11}-\varepsilon S_{11} & H_{12}-\varepsilon S_{12} & \cdots & H_{1n}-\varepsilon S_{1n} \\ H_{21}-\varepsilon S_{21} & H_{22}-\varepsilon S_{22} & \cdots & H_{2n}-\varepsilon S_{2n} \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ H_{n1}-\varepsilon S_{n1} & H_{n2}-\varepsilon S_{n2} & \cdots & H_{nn}-\varepsilon S_{nn} \end{vmatrix} = 0 \tag{3.30}$$

The ij elements A_{ij} of this determinant is derived from the coefficients of $(H_{ij} - \varepsilon S_{ij}) = A_{ij}$ in the simultaneous equations (3.29). Eq.(3.30) is an algebraic equation of the order n for ε, and it is called the secular equation. The secular equation is simply expression as $|H_{ij} - \varepsilon S_{ij}| = 0$, in which only the ij element is written between a pair of vertical bars. $\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_n (\varepsilon_i \leqq \varepsilon_{i+1})$ are n solutions of this equation and approximate energy eigen values. The lowest eigen value ε_1 is the best approximation of the true ground-state energy within all possible ranges of the linear combination for Φ in eq.(3.23). In comparison with true eigen values from the lower ones, $E_1, E_2, E_3, \cdots$, the eigen values obtained by Ritz's variation method satisfy the following relation.

$$E_k \leqq \varepsilon_k \qquad (k = 1, 2, \cdots, n) \tag{3.31}$$

Therefore, ε_k $(k \geqq 2)$ is an approximate energy value for the k-th excited state.

Wave functions $\{\Phi_k\}$ corresponding to the approximate energy eigen values $\{\varepsilon_k\}$ can be determined by insertion of ε_k into the simultaneous equations (3.29), followed by obtaining $\{c_j\}$. It should be noted here that the normalization condition leads to the following equation to be satisfied for $\{c_j\}$.

$$\int \Phi_k{}^* \Phi_k \mathrm{d}q = \sum_i \sum_j c_i{}^* c_j S_{ij} = 1 \tag{3.32}$$

Example 3.2 Calculate approximate energies and wave functions by applying Ritz' variation method to $\Phi = c_1\phi_1 + c_2\phi_2$, provided that $H_{11} = -12\,\mathrm{eV}$, $H_{22} = -6\,\mathrm{eV}$, $H_{12} = H_{21} = -4\,\mathrm{eV}$, $S_{11} = S_{22} = 1$, $S_{12} = S_{21} = 0$.

(Solution) Using the given conditions, the secular equation is expressed by

$$\begin{vmatrix} -12-\varepsilon & -4 \\ -4 & -6-\varepsilon \end{vmatrix} = \varepsilon^2 + 18\varepsilon + 56 = (\varepsilon + 14)(\varepsilon + 4) = 0$$

The lower solution gives the ground-state energy of $\varepsilon_1 = -14\,\mathrm{eV}$, and the higher one corresponds to the excited-state energy of $\varepsilon_2 = -4\,\mathrm{eV}$.

The wave function Φ can be obtained in the following way. Applying the given conditions to the normalization condition of eq.(3.32),

$$|c_1|^2 + |c_2|^2 = 1 \tag{1}$$

Simultaneous equations (3.29) for coefficients c_1, c_2 give

$$(H_{11} - \varepsilon)c_1 + H_{12}c_2 = 0 \tag{2}$$

Insertion of values for H_{11}, H_{12} and ε_1 into this equation (2) leads to

$$(-12 + 14)c_1 + (-4)c_2 = 0$$

This yields $c_1 = 2c_2$, and then eq.(1) gives $c_1 = 2/\sqrt{5},\ c_2 = 1/\sqrt{5}$. Thus, we obtain the ground-state wave function.

$$\Phi_1 = \frac{1}{\sqrt{5}}(2\phi_1 + \phi_2)$$

Next, insertion of ε_2 into ε in eq.(2) leads to

$$(-12 + 4)c_1 + (-4)c_2 = 0$$

This yields $2c_1 = -c_2$, and then eq.(1) gives $c_1 = 1/\sqrt{5},\ c_2 = -2/\sqrt{5}$. Thus we obtain the excited-state wave function.

$$\Phi_2 = \frac{1}{\sqrt{5}}(\phi_1 - 2\phi_2)$$

3.3 The SCF method

As studied in section 2.4, wave functions for many electrons systems can be constructed with orbital functions. The problem is how to determine orbital function for many electron systems. In this section, we study a fundamental approach obtaining orbital functions on the basis of the variation method.

The Hamiltonian operator for an n electron system is given by the following expression.

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i>j}^{n} \hat{g}(i,j) \tag{3.33}$$

Here, $\hat{h}(i)$ and $\hat{g}(i,j)$ are one and two electron operators, respectively. The indices i and j refer to the respective electrons. A comparison of this equation with the formula (2.31) for many electron system in section 2.3 leads to the following expressions for the above operators.

$$\hat{h}(i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \tag{3.34}$$

$$\hat{g}(i,j) = \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{3.35}$$

Orthonormal orbital functions including spins $\{\psi_i\}$ can be determined from the following simultaneous equations derived from the minimization conditions for the expectation value of $\hat{H}$ by a determinant wave function $\Psi = |\psi_1\psi_2\cdots\psi_n|$ composed of the orbital functions.

$$\begin{aligned}&\left[\hat{h}(i) + \sum_k \int \hat{g}(i,j)|\psi_k(j)|^2 \mathrm{d}q_j\right]\psi_i(i) - \sum_k \left[\int \hat{g}(i,j)\psi_k{}^*(j)\psi_i(j)\mathrm{d}q_j\right]\psi_k(i)\\ &= \varepsilon_i\psi_i(i) \qquad (i = 1, 2, \cdots, n)\end{aligned} \tag{3.36}$$

The summation should be taken from 1 to n except for $k = i$. Eq.(3.36) is called the Hartree-Fock equation, and solutions of this equation yield the orbital functions $\{\psi_i\}$ and the orbital energies $\{\varepsilon_i\}$.

A sophisticated approach needs to be used for solving eq.(3.36). First, we assume that an approximate set of solutions (the 0-th approximation) for $\{\psi_i\}$ is given. Replacement of ψ_k in the left of eq.(3.36) by the 0-th approximation leads to a simple equation to be solved as follows.

$$\hat{F}\psi = \varepsilon\psi \tag{3.37}$$

Although the approximate solutions of $\{\psi_i\}$ are included in the operator $\hat{F}$, $\{\psi_i\}$ to be determined are not included. It follows that eq.(3.37) can be solved as a normal eigen value equation. Although the first solutions so obtained for $\{\psi_i\}$ and $\{\varepsilon_i\}$, are approximate ones, they are expected to be better than those of the initial guess. Next, we estimate the operator $\hat{F}$ with the first solutions, and then we solve eq.(3.37) again to obtain the second solutions. In such procedures, we improve the solutions iteratively until discrepancies between the results and the assumptions will become negligibly small. It is called self-consistent when the assumed ψ as an approximation becomes consistent with the obtained ψ as a solution. In the convergent solutions, interactions between electrons included in $\hat{F}$ are the self-consistent field. Such a procedure obtaining solutions in an iterative way is the SCF method, and the solutions are called SCF solutions. Orbital functions determined by the SCF method are called SCF orbitals.

Construction of the determinant wave function with the lower-energy SCF orbitals, followed by calculation of the expectation value of the Hamiltonian operator of eq.(3.33), yields an approximation of the ground-state energy, which is called the SCF energy. The SCF energy E_{SCF} is expressed in terms of some integrals by the following equation.

$$E_{\mathrm{SCF}} = \sum_i (h)_i + \frac{1}{2}\sum_{i,j}\{(J)_{ij} - (K)_{ij}\} \tag{3.38}$$

The summation should be taken for all occupied orbitals. The integrals for the SCF orbitals including spins are defined as follows.

$$(h)_i = \int \psi_i{}^* \hat{h}(i)\psi_i \mathrm{d}q$$

$$(J)_{ij} = \int \psi_i{}^*(1)\psi_j{}^*(2)\hat{g}(1,2)\psi_i(1)\psi_j(2)\mathrm{d}q_1\mathrm{d}q_2$$

$$(K)_{ij} = \int \psi_i{}^*(1)\psi_j{}^*(2)\hat{g}(1,2)\psi_j(1)\psi_i(2)\mathrm{d}q_1\mathrm{d}q_2$$

The SCF energy is expressed in terms of individual orbital energies $\{\varepsilon_i\}$ as follows.

$$E_{\mathrm{SCF}} = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i,j}\{(J)_{ij} - (K)_{ij}\} \tag{3.39}$$

This indicates that the SCF energy is not equal to the summation of the orbital energies. The additional term is identical with the second term in eq.(3.38) except for the opposite signs. This term is due to the interactions between electrons. The sum of orbital energies includes duplicated contributions of interactions between electrons, since an interaction between a particular couple of two electrons appears in both of the respective orbital energies of the pair of the electrons. It follows that in eq.(3.39) the interactions between electrons multiplied by -1 are added to the sum of the orbital energies. If the interactions between electrons can be neglected, the total energy becomes the sum of individual orbital energies, and the situation is the same as the independent particle model studied in section2.3.

A comparison of the SCF energy with the ground-state energy E_{G} without including relativistic effects such as the spin-orbit coupling leads to the following inequality.

$$E_{\mathrm{G}} \leqq E_{\mathrm{SCF}}$$

The equality is only for one-electron systems such as hydrogenic atoms. The equality does not hold for many electron systems. The difference of $E_{\mathrm{SCF}} - E_{\mathrm{G}} = E_{\mathrm{CORR}}$ for many electron systems are always positive. Its magnitude $E_{\mathrm{CORR}}$is called the electron correlation energy. Such a discrepancy is due to the construction of the many-electron wave function from orbitals for independent motion of electrons, which excludes effects of the electron correlation. The variation method as well as the perturbation method may be used to consider electron correlation effects (see section 4.3). In conclusion of this chapter, characteristic features for the perturbation method and the variation method are listed in Table 3.1.

Table 3.1: Characteristic features for the perturbation method and the variation method

	Perturbation method	Variation method
Approach	True solutions are guessed as series expansions with unperturbed solutions, if they are known.	Trial wave functions with adjustable parameters are assumed and optimized to minimize the expectation value.
Feature	If the perturbation is weak, even the lower order expansions give successful results. When the perturbation is strong, slow convergence makes calculations of higher order terms formidable.	Trial functions similar to the true solution give excellent results. If the adjustable range of trail functions is too large, calculations become formidable.

Exercises

3.1 Based on the variation principle, verify that the energy up to the first order of a perturbation $E(1)$ is higher than the true ground-state energy E_{G}.

3.2 For a system of two levels, verify that the higher state goes up and that the lower state comes down, by considering energy corrections due to the second order perturbation.

3.3 Applying Ritz's variation method to $\Phi = c_1\phi_1 + c_2\phi_2$, obtain approximate solutions for the energies and the wave functions, using $H_{11} = H_{22} = -6\,\mathrm{eV},\ H_{12} = H_{21} = -3\,\mathrm{eV},\ S_{11} = S_{22} = 1,\ S_{12} = S_{21} = 0$.

Chapter 4

Methods for many-atom systems and their applications

If atoms are solid balls, they do not bind with each other. Real atoms can produce chemical bonds, and they can transfer electrons to yield ions. Ions can also bind with atoms. These binding processes give complexes, clusters, polymers, and crystals. Combined systems of atoms and ions are composed of nuclei and electrons, which interacts with each other by Coulomb forces.

In this chapter, we will study how nuclei and electrons form molecules, on the basis of quantum mechanical treatments for diatomic and polyatomic systems.

4.1 Motion of electrons and nuclei

4.1.1 The Hamitonian operator for nuclei and electrons

Let us consider systems of nuclei and electrons. Such systems include molecules, ions, complexes, polymers, and crystals, and all materials. In order to make quantum mechanical treatments, some symbols need to be introduced. For systematic treatments, Z_A and Z_B denote atomic numbers for the atoms A and B, and their distance is denoted by R_AB, as shown in Fig.4.1. r_ij denotes the distance between the electrons i and j, and $R_{\mathrm{A}i}$ denotes the distance between the atom A and the electron i. The Laplacian operators and masses for the atom A and the electron i are expressed by Δ_A, Δ_i, M_A, and m, respectively. Using these notations, the Hamiltonian operator can be expressed as a summation of the following five terms.

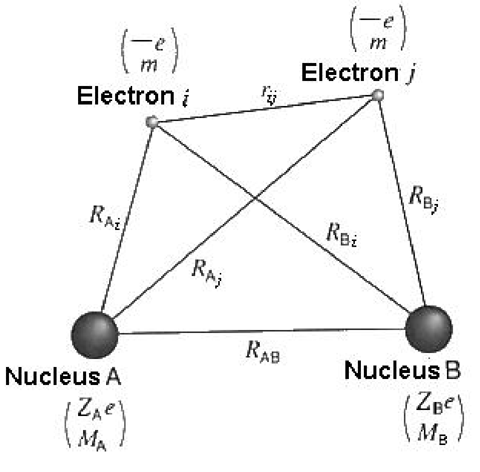


Figure 4.1: A system of nuclei and electrons

$$\hat{H} = K_{\mathrm{n}} + K_{\mathrm{e}} + U_{\mathrm{nn}} + U_{\mathrm{ne}} + U_{\mathrm{ee}} \tag{4.1}$$

(Kinetic energies of the nuclei) $K_{\mathrm{n}} = \sum\limits_{\mathrm{A}} \left(-\frac{\hbar^2}{2M_{\mathrm{A}}} \right) \Delta_{\mathrm{A}}$ (4.2)

(Kinetic energies of the electrons) $K_{\mathrm{e}} = \sum\limits_{i} \left(-\frac{\hbar^2}{2m} \right) \Delta_i$ (4.3)

(Potential energies of interactions between the nuclei)

$$U_{\mathrm{nn}} = \sum_{\mathrm{A}>\mathrm{B}} \left(\frac{Z_{\mathrm{A}} Z_{\mathrm{B}} e^2}{4\pi\varepsilon_0 R_{\mathrm{AB}}} \right) \tag{4.4}$$

(Potential energies of interactions between the nuclei and the electrons)

$$U_{\mathrm{ne}} = \sum_{\mathrm{A}} \sum\nolimits_i \left(-\frac{Z_{\mathrm{A}} e^2}{4\pi\varepsilon_0 R_{\mathrm{A}i}} \right) \tag{4.5}$$

(Potential energies of interaction between the electrons)

$$U_{\mathrm{ee}} = \sum_{i>j} \left(\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right) \tag{4.6}$$

The symbols A and i under Σ indicate that the summation should be taken for all atoms or all electrons, respectively. The symbols $\mathrm{A} > \mathrm{B}$ and $i > j$ under Σ denote that the summations should be taken for only one pair of nuclei or electrons without duplication.

The Hamiltonian operator given above can be applied to special systems such as a system of only one nucleus as well as a system of only one electron. If there is only one nucleus, U_{nn} is omitted, and the summation for A has only one contribution of the nucleus. For only one electron, U_{ee} is omitted, and summations for i includes only one contribution due to the electron. Furthermore, for no electrons $K_{\mathrm{e}}, U_{\mathrm{ne}}, U_{\mathrm{ee}}$ are omitted, and for no nuclei $K_{\mathrm{e}}, U_{\mathrm{ne}}, U_{\mathrm{ee}}$ are omitted. It follows that $\hat{H}$ given above in eq.(4.1) can be applied to any system composed of arbitrary numbers of nuclei and electrons.

When we do not care for the difference between nuclei and electrons, the Hamiltonian operator $\hat{H}$ for a system including particles with masses M_I, M_J and electric charges Q_I, Q_J can be expressed much more simply by the following formula.

$$\hat{H} = \sum_{I} \left(-\frac{\hbar^2}{2M_I} \right) \Delta_I + \sum_{I>J} \left(\frac{Q_I Q_J}{4\pi\varepsilon_0 R_{IJ}} \right) \tag{4.7}$$

There are some reasons why in the above treatments we note the difference between nuclei and electrons, as discussed below.

4.1.2 Separation of nuclear and electronic motions

When a force F acts on a body with a mass of M, the body undergoes an acceleration of $a = F/M$. This is clear from Newton's equation of motion, $F = Ma$. Now let us suppose that forces of F act independently on two bodies with different masses of M and m. Magnitudes of accelerations on these bodies are F/M and F/m, and their ratio becomes $(F/M)/(F/m) = m/M$. If M is very large in comparison with m, this ratio becomes to be vanishing. Thus, the acceleration on the heavy body (M) can be neglected with respect to that for the light body (m). When owing to the law of action and reaction a pair of forces of the same magnitude act on each of two bodies with a very large mass ratio, the heavy body scarcely moves, whereas the light body significantly moves. Thus, the motion of a heavy particle can be neglected in comparison with the motion of a light particle. In other words, as long as the motion of light particles is concerned, heavy particles can be fixed to the rest positions.

M. Born and J.B. Oppenheimer applied such an idea based on large mass ratios to systems of nuclei and electrons, and in 1927 they introduced the adiabatic approximation or the Born-Oppenheimer approximation in which nuclei are fixed when the electronic motion is considered.

Under this approximation, we omit K_{n} from the complete $\hat{H}$ in the above expression, and the following Hamiltonian $\hat{H}_{\mathrm{e}}$, called electronic Hamiltonian, is used instead.

$$\hat{H}_{\mathrm{e}} = K_{\mathrm{e}} + U_{\mathrm{nn}} + U_{\mathrm{ne}} + U_{\mathrm{ee}} \tag{4.8}$$

Here, U_{nn} may be omitted for problems dealing with the electronic motion, since it does not contain electron coordinates. In order to discuss the stability of the system or forces acting on nuclei, however, U_{nn} would better be included in $\hat{H}_{\mathrm{e}}$.

Let us suppose that the eigen equation of $\hat{H}_{\mathrm{e}}$, that is the eigen equation for electrons $\hat{H}_{\mathrm{e}}\psi = u\psi$, has been solved. In order to specify meanings of the coordinates clearly, nuclear and electronic coordinates are represented by R and r, respectively. With these notations, the eigen equation for electrons is expressed by

$$\hat{H}_{\mathrm{e}}(R, r)\psi(R, r) = u(R)\psi(R, r) \tag{4.9}$$

We should note here that R represents parameters of the fixed nuclear coordinates. If R is displaced, then $\hat{H}_{\mathrm{e}}$ changes accordingly to yield modified eigen functions ψ and eigen values u. Once $\psi(R, r)$ is obtained, then we know probability distributions of finding electrons around the fixed nuclei. Once $u(R)$ is determined, we know the energy at the fixed nuclear configuration. The functional values of $u(R)$ depend on R. A decrease of u results in an energetically more stable situation, and an increase of u brings the system unstable. It follows that $u(R)$ is the potential energy of nuclear motion, which changes depending on the relative positions of nuclei. This can be seen from the meaning of the complete Hamiltonian $\hat{H}$, which is expressed by $\hat{H} = K_{\mathrm{n}} + \hat{H}_{\mathrm{e}}$, and also from the meaning of the following Hamiltonian $\hat{H}_{\mathrm{n}}$, which can be derived from $\hat{H}$ with an replacement of $\hat{H}_{\mathrm{e}}$ by its eigen value $u(R)$.

$$\hat{H}_{\mathrm{n}} = K_{\mathrm{n}} + u(R) \tag{4.10}$$

$\hat{H}_{\mathrm{n}}$ is the Hamiltonian for nuclear motion in the adiabatic approximation, K_{n} is the kinetic energy, and $u(R)$ represents the potential energy. In this sense, $u(R)$ is called the adiabatic potential. As discussed below, from $u(R)$ we can obtain information on stable nuclear configurations (molecular structures for molecules), heats of reactions (binding energies for diatomic molecules), and strengths of chemical bonds.

Let us solve the eigen equation of $\hat{H}$ in eq.(4.1).

$$\hat{H}\Psi = E\Psi \tag{4.11}$$

The eigen value E is for the total energy including both nuclear and electronic motion. Noting that the eigen function $\psi(R, r)$ in eq.(4.9) for electronic motion describes electronic behavior with nuclei almost resting, we assume the following form of the wave function Ψ.

$$\Psi(R, r) = \phi(R)\psi(R, r) \tag{4.12}$$

Insertion of eq.(4.12) into eq.(4.11) followed by use of eq.(4.9) as well as an approximation of $\Delta_{\mathrm{A}}\psi(R, r) = 0$ based on consideration of slowly changing $\psi(R, r)$ with respect to R leads to the following equation.

$$\hat{H}_{\mathrm{n}}\phi(R) = E\phi(R) \tag{4.13}$$

By solving this equation, we obtain energy levels including both nuclear and electronic motion. Namely, energies obtained from eq.(4.13) contain energies for translational, rotational, and vibrational motion in addition to electronic motion. Methods for separating translational, rotational, and vibrational motions have been studied in Section 1.12 for two-particle systems (diatomic molecules).

4.1.3 The adiabatic potentials for diatomic molecules

When the adiabatic potential is given for a polyatomic system, various properties can be determined. Let us study these characteristics of diatomic systems as examples. $u(R)$ for a diatomic molecule is in general a curve as shown in Fig.4.2. R is the distance between the nuclei, and two separated atoms correspond to the dissociation limit of $R \to \infty$. In the figure, $u(R)$ decreases on going from $R = \infty$ to the shorter distance between the two nuclei. The nuclei mutually undergo

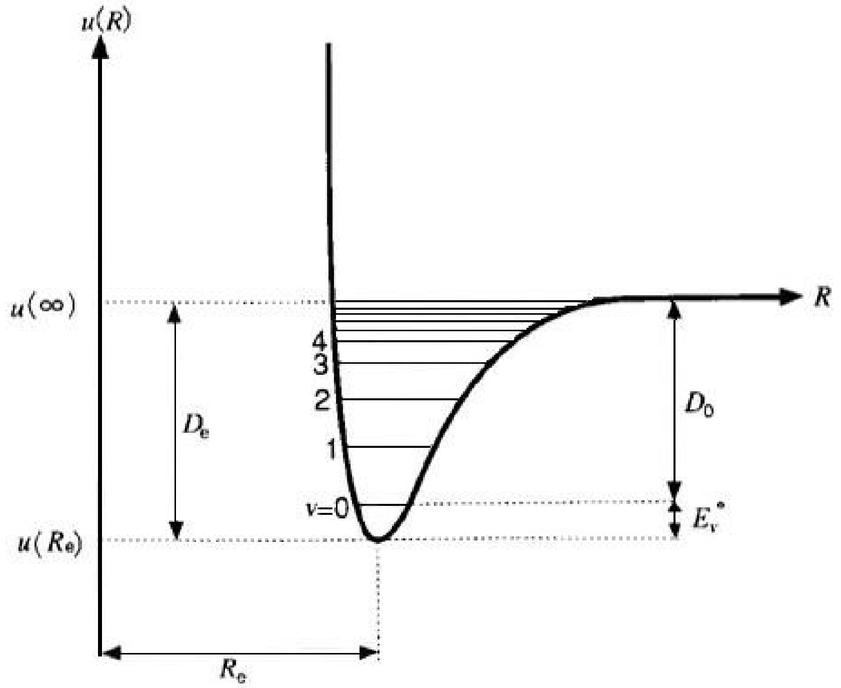


Figure 4.2: The potential energy curve for a diatomic molecule

attractive forces associated with the decrease of the energy. This means that binding forces exist. The further decrease of R leads to the minimum of $u(R)$ at a distance of R_e, and for the shorter distances $u(R)$ increases rapidly. This indicates that for $R < R_\mathrm{e}$ atoms strongly repel each other. The force F may be defined as $F = -\mathrm{d}u/\mathrm{d}R$, which formally represents a force expanding the interatomic distance R. For $R < R_\mathrm{e}$ F becomes positive, which leads to a repulsion between the nuclei. For $R > R_\mathrm{e}$ F becomes negative, which leads to an attraction between the nuclei. R_e is called the equilibrium internuclear distance, which means the bond-length or the interatomic distance, one of the most important constant determining the molecular structure.

The magnitude of the stabilization energy associated with the formation of a molecule is called the bond energy and is defined by the following quantity D_e.

$$D_\mathrm{e} = u(\infty) - u(R_\mathrm{e}) \tag{4.14}$$

The bond energy is roughly equal to the dissociation energy, though some corrections for thermal energies and zero-point energies need to be made for a rigorous comparison with the heat of reaction actually measured. If the bond energy is small, corrections of thermal energies are especially important. When temperature is so high that the thermal energy exeeds the bond energy, molecules tend to dissociate and become unstable.

Around the equilibrium point of $R = R_\mathrm{e}$ in the adiabatic potential curve $u(R)$, a restoring force arises with a magnitude proportional to $\Delta R = R - R_\mathrm{e}$. According to Hooke's law ($F = -k\Delta R$), stretched bonds tend to shrink, and conversely shrunk bonds tend to stretch. The force constant indicating the magnitude of the spring can be obtained from the second derivative of $u(R)$ as follows.

$$k = \frac{\mathrm{d}^2 u}{\mathrm{d}R^2} \qquad \text{(differentiation should be made at } R = R_\mathrm{e}\text{)} \tag{4.15}$$

This formula can be derived from a power series expansion of $u(R)$ in terms of $\Delta R = R - R_\mathrm{e}$ around $R = R_\mathrm{e}$. A differentiation yielding the force F followed by a comparison with Hooke's law, neglecting the higher order terms, leads to the expression for k.

When the force constant k for the bond spring together with the reduced mass are given, the vibrational frequency in the harmonic approximation is given by the following equation.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{4.16}$$

The zero-point energy ${E_v}^\circ$ of the harmonic oscillator is given by

$${E_v}^\circ = \frac{1}{2}h\nu = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}} \tag{4.17}$$

The ground-state energy of a diatomic molecule cannot become the minimum energy of the adiabatic potential. This is clearly related with the explanation of the zero-point energy in section 1.10. Therefore, the net energy required for dissociation (the dissociation energy) D_0 is smaller than the bond energy D_e by the zero-point vibration energy ${E_v}^\circ$ (see Fig.4.2).

$$D_0 = D_\mathrm{e} - {E_v}^\circ \tag{4.18}$$

As can be seen from the above, the adiabatic potential energy curve leads to the following very important quantities.

(1) The bond length (The equilibrium internuclear distance) R_e

(2) The bond energy D_e

(3) The spring constant of the bond (The force constant) k

(4) The vibrational frequency ν

(5) The zero-point vibration energy ${E_v}^\circ$

(6) The dissociation energy D_0

Example 4.1 P. M. Morse proposed an experimental formula of the adiabatic potential curve for diatomic molecules, which is given by

$$M(R) = D[\mathrm{e}^{-2(R-R_0)/a} - 2\mathrm{e}^{-(R-R_0)/a}]$$

This is called the Morse potential. Using this potential, obtain (1) The equilibrium internuclear distance R_e, (2) The bond energy D_e, (3) The force constant k, and (4) The vibrational frequency ν. In the calculation of ν, assume a harmonic oscillator with a reduced mass of μ.

(Solution) In this problem we may write $u(R) = M(R)$, and we obtain

$$\begin{aligned}\frac{\mathrm{d}u}{\mathrm{d}R} &= D\left[-\frac{2}{a}\mathrm{e}^{-2(R-R_0)/a} - 2\left(-\frac{1}{a}\right)\mathrm{e}^{-(R-R_0)/a}\right] \\ &= D\left(-\frac{2}{a}\right)\left[\mathrm{e}^{-(R-R_0)/a} - 1\right]\mathrm{e}^{-(R-R_0)/a}\end{aligned}$$

In order to satisfy the equilibrium condition, the value of this equation should be vanishing. Thus the parenthesis in the right side needs to be zero, and we obtain the condition to be $R = R_0$. Therefore,

$$R_\mathrm{e} = R_0 \tag{1}$$

Next, we calculate $D_\mathrm{e} = u(\infty) - u(R_\mathrm{e})$.

$$D_\mathrm{e} = M(\infty) - M(R_0) = 0 - D[1-2] = D \tag{2}$$

Then, we calculate $k = \mathrm{d}^2u/\mathrm{d}R^2$.

$$\begin{aligned}k &= \frac{\mathrm{d}^2M}{\mathrm{d}R^2} \\ &= D\left[\left(-\frac{2}{a}\right)^2\mathrm{e}^{-2(R-R_0)/a} - 2\left(-\frac{1}{a}\right)^2\mathrm{e}^{-(R-R_0)/a}\right]\end{aligned}$$

Inserting the equilibrium condition $R = R_\mathrm{e} = R_0$, we obtain

$$k = D\left[\left(\frac{2}{a}\right)^2 - 2\left(\frac{1}{a}\right)^2\right] = \frac{2D}{a^2} \tag{3}$$

Assuming a harmonic oscillator,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Inserting the above equation (3) for k into this expression, we obtain

$$\nu = \frac{1}{2\pi a}\sqrt{\frac{2D}{\mu}} \tag{4}$$

4.2 The binding force and the electron density

In the previous section we studied the relationship between the slope of the adiabatic potential and the binding force. In this section we will study how the binding forces connecting nuclei are related with the quantum mechanical behavior of electrons and elucidate the causes of chemical bonds.

4.2.1 Forces acting on nuclei and Feynman's electrostatic theorem

Forces acting on individual atoms can be calculated by differentiation of the adiabatic potential u with respect to the respective nuclear coordinates. For example, the force acting on the nucleus A $(F_\mathrm{A})_x$ along the x-coordinate (x_A) is given by the following equation.

$$(F_\mathrm{A})_x = -\frac{\mathrm{d}u}{\mathrm{d}x_\mathrm{A}} \tag{4.19}$$

R. P. Feynman presented a theory in 1939 that the right side of eq.(4.19) is related to the spatial distribution of electrons based on the adiabatic approximation. $\rho(x, y, z)\mathrm{d}x\mathrm{d}y\mathrm{d}z$ is introduced as a quantity indicating how many electrons are contained in the volume element of $\mathrm{d}x\mathrm{d}y\mathrm{d}z$. ρ is a quantity depending on the spatial coordinates and is called the electron density. This density is related with all electrons involved in the system, and thus it is sometimes called the total electron density. It should be noted that ρ is the number density rather than the probability density. It follows that the integration of ρ over the whole space gives the total number of electrons N.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho(x, y, z)\mathrm{d}x\mathrm{d}y\mathrm{d}z = N \tag{4.20}$$

The electron density ρ can be calculated from the following equation, provided that functions of occupied orbitals ϕ_i as well as their occupation numbers n_i are known.

$$\rho = \sum_i n_i|\phi_i|^2 \tag{4.21}$$

From the Pauli principle occupation numbers n_i are either 0, 1, or 2, depending on the electron configuration. When ρ is obtained by quantum mechanics, the spatial distribution of negative charges due to electrons is given by $-e\rho(x, y, z)\mathrm{d}x\mathrm{d}y\mathrm{d}z$.

Forces acting on nuclei are expressed with the electron density as follows.

> **[Feynman's electrostatic theorem]**
>
> The force acting on a nucleus is a resultant force of all sums of the electrostatic repulsion due to all other nuclei and the electrostatic attraction due to the whole electron densities.

This is called Feynman's electrostatic theorem. Since the resultant force is a vector quantity, the summation should be made, considering the directions. As studied in chapter 1, the electrostatic force on atom A at a position vector $\boldsymbol{R}_{\mathrm{A}}$ with an atomic number Z_{A} and an electric charge $Q_{\mathrm{A}} = Z_{\mathrm{A}}e$ caused by an electric charge Q placed at a position vector $\boldsymbol{r}$ is given by

$$F = \frac{QQ_{\mathrm{A}}}{4\pi\varepsilon_0|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}|^2} \qquad (\ F < 0 \text{ for attraction, } F > 0 \text{ for repulsion }\ )$$

In this expression, the direction of the vector is not specified. The force vector is in the opposite direction against the position of the other charge, when the force is repulsive between charges with the same sign. The unit vector of this direction is expressed as $-(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}})/|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}|$. Using this relation, the force vector $\boldsymbol{F}$ on the atom A caused by an electric charge Q placed at $\boldsymbol{r}$ is given by

$$\boldsymbol{F} = -\frac{QQ_{\mathrm{A}}(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}})}{4\pi\varepsilon_0|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}|^3} = -Q\boldsymbol{E}_{\mathrm{A}}(\boldsymbol{r}) \tag{4.22}$$

Here,

$$\boldsymbol{E}_{\mathrm{A}}(\boldsymbol{r}) = \frac{Q_{\mathrm{A}}(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}})}{4\pi\varepsilon_0|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}|^3} \tag{4.23}$$

$\boldsymbol{E}_{\mathrm{A}}$ represents the force on a unit charge at $\boldsymbol{r}$ caused by the charge of the nucleus A, and this is called the electric field. It follows that eq.(4.22) stands for the reaction, that is the same magnitude force to the opposite direction with respect to the force on an electric charge Q at $\boldsymbol{r}$ under the electric field caused by the nucleus A.

The above arguments lead to the following theorem.

[Theorem] The electrostatic force acting on a charged particle is equal to the resultant force of all reactions against the forces to other charged particles caused by the particle itself.

Using this theorem together with the formula for the electric field, a mathematical expression for the force vector $\boldsymbol{F}_{\mathrm{A}}$ acting on the nucleus A is given as Feynman's electrostatic theorem as follows.

$$\boldsymbol{F}_{\mathrm{A}} = \int e\rho(\boldsymbol{r})\boldsymbol{E}_{\mathrm{A}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} - \sum_{\mathrm{B}\,(\mathrm{B}\neq\mathrm{A})} eZ_{\mathrm{B}}\boldsymbol{E}_{\mathrm{A}}(\boldsymbol{R}_{\mathrm{B}}) \tag{4.24}$$

In this formula, the three dimensional volume element $\mathrm{d}x\mathrm{d}y\mathrm{d}z$ is written as $\mathrm{d}\boldsymbol{r}$. The integral of the first term in the right side of eq.(4.24) is the resultant force of attraction due to electron densities distributed spatially, and the second terms are the resultant force of repulsion due to other nuclei of the atomic number Z_{B}. Since the direction of $\boldsymbol{E}_{\mathrm{A}}$ is defined toward the other charge, the attraction is positive and the repulsion is negative in eq.(2.24).

4.2.2 The binding region and the antibinding region

Whether electron densities give attraction or repulsion between nuclei depends simply on where electron densities are placed spatially. In order to understand this, let us study two cases shown in Fig.4.3, (a) an electron inserted in the midpoint of two protons, and (b) an electron is placed outside at a half of the distance between the protons.

In the case of (a), the distance between the electron in the midpoint and a proton is a half of the distance between the protons, and thus attractive forces on the protons caused by the electron is four times larger than the repulsion between the protons (cf. Example 1.2). In the situation of (a), the two protons approach each other, since the attractive forces due to the electron exceeds the repulsion between the protons. In the case of (b), the proton near the electron attracted outward by the electron with the same magnitude of a force of the case (a), whereas another proton in the long distance is pulled to the same direction but very weakly with a magnitude of $(1/3)^2$ times of the force acting on the proton in the short distance. Although in this case the electron attracts both of the protons to the right side, the nearer proton is attracted much more strongly to cause a relative separation of the protons. This effect in (b) accelerate the repulsion between the protons.

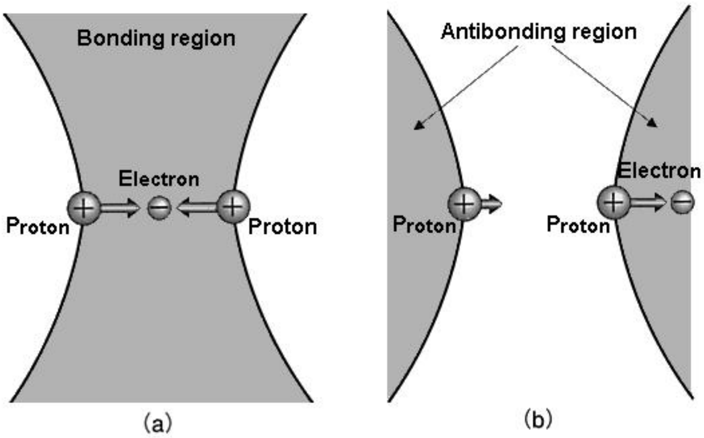


Figure 4.3: The binding region and the antibinding region

Based on the features in Fig.4.3, forces on a pair of unit positive charges by a unit negative charge can be classified into the following cases.

(1) The force due to the unit negative charge binds two nuclei relatively.

(2) The force due to the unit negative charge repels two nuclei relatively.

This classification divides each spatial point into either the binding region (the bonding region) , the antibinding region (the antibonding region), or the boundary between the binding and antibinding regions.

When a pair of nuclei are attracted by forces due to electron densities in the binding region which cancels out the repulsion between them, the nuclei are mutually bound to make a bond. This is the mechanism of producing a chemical bond by the action of electron densities. When a chemical bond is already produced, donation-reception by oxidation-reduction, light absorption, or variation of electron distributions on the access of other atoms or molecules may cause a change of the balance between the binding force and the antibinding force. Depending on the situations, the bond may be strengthened to become short, and conversely the bond may be weakened to become lengthened or even to dissociate. In this way, depending on how electron densities distribute over the bonding and antibonding regions, chemical bonds are produced or broken.

4.2.3 The virial theorem

We have studied that binding forces originate from the action due to electron densities. The Feynman's electrostatic theorem, however, lose its significance if the electron densities are not accurately obtained. Accurate electron densities need accurate wave functions. In order to test the accuracy of wave functions, the following virial theorem is often used.

The virial theorem is expressed with using the internuclear distance R as follows.

$$2\langle K\rangle + \langle U\rangle + R\frac{\mathrm{d}u(R)}{\mathrm{d}R} = 0 \tag{4.25}$$

$u(R)$ is the adiabatic potential in the Born-Oppenheimer approximation, and $\langle K\rangle$ and $\langle U\rangle$ are the expectation values for the kinetic energy and the potential energy, respectively. At the equilibrium internuclear distance, the last term in eq.(4.25) is vanishing, and thus the following quantity becomes equal to 2.

$$-\frac{\langle U\rangle}{\langle K\rangle} = 2 \tag{4.26}$$

A calculated value of the left side becomes different from 2, if the wave function is not accurate, and this ratio called the virial ratio in eq.(4.26) has a significance to test the quality of wave functions. The eq.(4.26) can also be applied to an atom. The relation in eq.(4.26) generally holds for a system of a potential energy with an inverse power of the distance as the Coulombic force.

4.3 The molecular orbital method

An orbital function representing the electronic motion is called an atomic orbital (AO) for an atom and a molecular orbital (MO) for a molecule. An approch using molcular orbitals for various problems in chemistry is called the molecular orbital method. A fundamental technique to obtain molecular orbitals is the SCF method based on the Hartree-Fock equation studied in Section 3.3. In this section, we will study an SCF method using linear combinations as a most powerful technique in quantum chemistry as well as its application to the molecular orbital metohd.

Until ca. 1980 this field has been a holy ground limited to specialists of quantum chemistry. However, recent developments of both hardwares and softwares for computers made it possible for many people even with no special trainings in chemistry to use the molecular orbital method easily. After 1990, this tendency has been accelerated. Thus we will study some basic ideas and techniques for actual calculations in quantum chemistry.

4.3.1 The SCF method using linear combinations

Although the Hartree-Fock method studied in Section 3.3 is a general method determining orbital functions based on the variation principle, its direct application is almost impossible except for atoms or simple diatomic molecules. If we use linear combinations of some known functions called basis functions or the basis set, problems to determine orbital functions reduce to feasible numerical calculations, as studied for Ritz's variation method in Section 3.2(b). It follows that we can obtain the best orbital functions that can be expressed in terms of linear combinations of the basis set.

Orbital functions $\{\phi_i\}$ to be determined are expanded in terms of linear combinations of basis functions $\chi_1, \chi_2, \cdots, \chi_N$.

$$\phi_i = \sum_{p=1}^{N} C_{pi}\chi_p \tag{4.27}$$

C. C. Roothaan derived a set of simultaneous equations to determine the best orbital functions within the limitation of the basis set by adjusting the coefficients $\{C_{pi}\}$ in 1951. We will not describe details of the equations. The important features are as follows. For a basis set composed of N linearly independent functions, the problem reduces to solving the secular equations with the order N, as in the case of Ritz's variation method. The SCF technique is used for solving the secular equation in an iterative way until a set of SCF solutions are obtained, as in the Hartree-Fock method. Consequently, we can obtain coefficients $\{C_{pi}\}$ determining shapes of orbitals as well as their orbital energies $\{\varepsilon_i\}$. In addition, the total energy of the system, which may be called as the SCF energy, can be obtained as an approximation of the ground-state energy. For molecules, some special structures with fixed nuclear positions are assumed in the adiabatic approximation. Consecutive SCF procedures changing the molecular structures will yield approximate adiabatic potentials. The SCF method using linear combinations proposed by Roothaan crucially depends on the choice of basis functions $\{\chi_p\}$.

The following inequalities hold among the Hartree-Fock SCF energy E_{HF}, the SCF energy in the linear combination approximation E_{LC}, and the true ground-state energy E_{G}.

$$E_{\mathrm{G}} \leq E_{\mathrm{HF}} \leq E_{\mathrm{LC}} \tag{4.28}$$

The equality is only possible for one electron system. For many electron systems, the equality does not hold, and the electron correlation energy, $E_{\mathrm{HF}} - E_{\mathrm{G}} = E_{\mathrm{CORR}}$, is always positive. In addition, $E_{\mathrm{LC}} - E_{\mathrm{HF}}$ is also positive for many electron systems, which is due to the incompleteness of the basis set, since finite numbers of basis functions do not constitute a complete system.

4.3.2 The basis functions

In order to obtain molecular orbitals in the linear combination approximation, atomic orbital functions such as $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 2\mathrm{p}_z$ for atoms composing a molecule are used as basis functions. This idea comes from the traditional chemical concept that a molecule is composed of atoms. From a physical point of view, molecular orbitals are considered as a superposition of electron waves of atomic orbitals, since an electron in the proximity of a particular atom is expected to behave very similarly with the respective atomic orbitals.

Although various ways of constructing a basis set are proposed, one of the standard choice for an individual atom is to use all atomic orbitals from the inner shell to the valence electrons, which are concerned with the atomic ground-state. For example for a nitrogen atom, five types of orbitals, $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 2\mathrm{p}_z$, are used for atomic orbital functions. For an alkali atom or an alkaline earth atom, np orbitals are included in addition to the ns orbitals. Such a basis set is called the minimal basis. The minimal basis is the standard basis for obtaining molecular orbitals, and we may assume this basis set if no special explanation is made.

For detailed quantum chemical calculations, we need to care for the choice of basis functions. If we use a number of basis functions to improve accuracies of calculations, the size of the computation (the computation time and the memory size) inevitably increases. In order to avoid unnecessary expansion of the computation size, carefully selected basis functions should be supplemented depending on the required accuracy of the calculations. For the better description of valence electrons, valence atomic orbital functions with different spatial expansion are used doubly or triply in addition to the standard functions. This kind of basis set is called the split valence basis. Atomic orbital functions with the higher azimuthal quantum number are often augmented for adjusting the shape of electron waves of individual atoms under the circumstance in the molecule. This type of augmented functions are called the polarization functions. For example, a basis set including only s and p type functions is augmented by d type functions as polarization functions. Furthermore, loosely bound electrons such as the additional electron in a negative ion require diffuse functions which supplement the remote area to which the additional electron may be distributed.

Atomic orbital functions for basis functions need not necessarily to be exact atomic orbital functions. In actual computations, approximate forms of atomic orbital functions have been used in general owing to the convenience dealing with various types of integrals. For such approximate functions, orbital functions proportional to $\mathrm{e}^{-\zeta r}$, which are proposed by Slater and are called the Slater type orbitals (STO), have been used, and in recent years their analogues expanded in terms of several numbers of Gaussian functions (Gaussian) with a factor of $\mathrm{e}^{-\alpha r^2}$, called STO-nG if the number of Gaussians is n, are widely employed. Some other basis sets composed of several Gaussians such as 4-31G and 6-31G developed by J. A. Pople and his colleagues are extensively used. The detailed descriptions of basis functions should be referred to books for the molecular orbital method and quantum chemical calculations. The SCF method with the linear combination approximation is used not only for molecular orbital calculations but also for obtaining precise atomic orbitals.

Conventions for signs and directions of atomic orbitals should be noted for practical use. In principle, any atomic orbital function can be multiplied by -1 or varied its sign, and the sign may be chosen arbitrarily for each atom within the mathematical freedom. However, in order to understand calculated results the arbitrariness of the choice of signs for employed atomic orbitals would result in confusion. For orbitals with directions such as p orbitals, coordinate axes may be chosen arbitrarily for each atom, though analyses and interpretation would become difficult. It follows that a systematic choice of signs and directions is recommended; usually, the same coordinate axes are assumed for all atoms, and signs for the same types of orbitals such as $1\mathrm{s}, 2\mathrm{p}$ are commonly chosen. For example, the sign for an $2\mathrm{p}_x$ orbital is set positive at the outer region along the commonly chosen x-axis. In many programs for quantum chemical calculations, such a systematic choice has been utilized. However, usually no descriptions have been made in computation programs or their manuals, and no explanations have been included in textbooks. Thus, for students conventions for atomic orbitals are often the cause of confusion. We should also be careful about the choice of the coordinate system and signs, since a different convention may be used for a necessity such as symmetry. A different choice may be encountered when looking up some references.

Example 4.2 Write down all members of the minimal basis for a water molecule, and answer the total number of basis functions.

(Solution) Five basis functions $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 2\mathrm{p}_z$ are used for an oxygen atom. There are two hydrogen atoms, and each of them uses a 1s orbital. Thus, the total numbers of basis functions are $5 + 1 + 1 = 7$. It follows that molecular orbitals of a water molecule in the minimal basis are obtained as linear combinations of these seven basis functions.

4.3.3 The non-empirical method and the semi-empirical method

A theoretical approach with no empirical information except for the atomic numbers, geometrical coordinates of the nuclei, and numbers of electrons in the system to be studied is called the ab initio (from the beginning) method or the nonempirical method. In the ab initio method, orbital functions and their energies are determined by the SCF method in the linear combination approximation, and then the total energy of the system, the wave function, electron densities, and other properties are calculated. The nonempirical molecular orbital method in general requires calculations of a huge numbers of integrals, which amount to the fourth power of the number of basis functions. From this reason, nonempirical calculations of large molecules often encounter considerable difficulties on account of the limited system of the computation facilities.

An approach considerably reducing the computation time and the amount of the data to be disposed by estimating integral values with some equations involving empirical parameters is called the semiempirical method. Empirical parameters in the semiempirical method are adjusted so as to produce better results as far as possible. In the semiempirical molecular method, only valence electrons are treated, and the nucleus charge are often combined with the inner shell electrons to be handled as the effective core with a positive charge of (atomic number)-(the number of the inner electrons). As for planar molecules with unsaturated bonds such as benzene, electrons (π electrons) in p orbitals with a direction vertical to the molecular plane are often only dealt with, and such an approach is called the π electron approximation. In a simple molecular orbital method by E. Hückel, which will be introduced in the following Chapter, the eigen equation to obtain molecular orbitals is simplified, and only one procedure solving the secular equation gives molecular orbital functions and their orbital energies, provided that required integrals are evaluated beforehand by a given procedure.

4.3.4 Electron configuration and HOMO/LUMO

After orbital functions $\{\phi_i\}$ and orbital energies $\{\varepsilon_i\}$ are obtained by SCF methods or some other methods, we can construct determinant wave functions Φ corresponding to various electron configurations such as those shown in Fig.4.4 (cf. Ground-state and excited states of a helium atom in Section2.7).

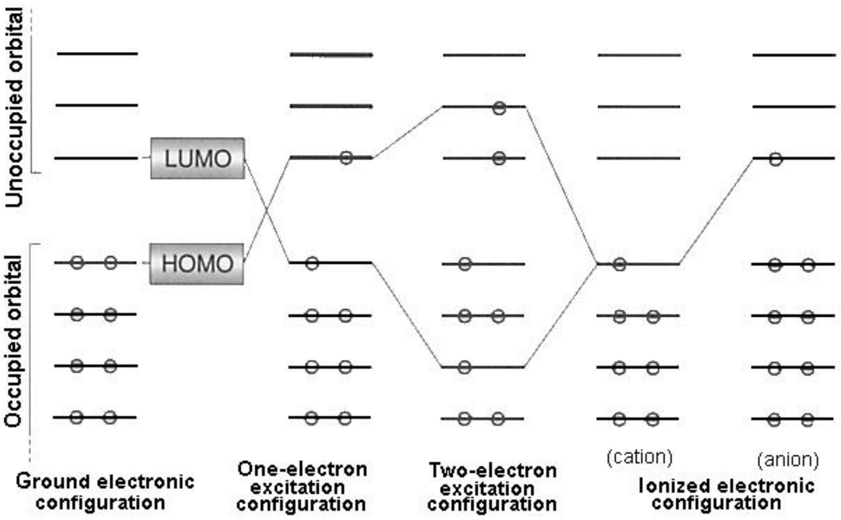


Figure 4.4: HOMO/LUMO and various electron configurations

The occupation number of electrons n_i for an orbital ϕ_i without spin is either 0, 1, or 2 owing to Pauli principle. An orbital containing one or two electrons is called an occupied orbital. An orbital of $n_i = 0$ is called a vacant orbital. An occupied orbital of $n_i = 1$ is called a singly occupied molecular orbital (SOMO) or an unpaired electron. An occupied orbital of $n_i = 2$ is called a fully occupied orbital, a pair of electrons, or an electron-pair. Among occupied orbitals, the highest occupied molecular orbital is called HOMO, and the lowest unoccupied molecular orbital is called LUMO. HOMO, LUMO, and SOMO are called the frontier orbitals, because these orbitals are especially related with the chemical reactivity as will be studied in Chapter 6.

An electron configuration with no unpaired electrons is called a closed shell, whereas an electron configuration with some unpaired electrons is called an open shell. Among all electron configurations produced with the same number of orbital functions from $\{\phi\}$, a special electron configuration with the lowest expectation value by the determinant wave function Φ is called the ground electronic configuration. The ground electronic configuration, which usually gives the minimum sum of the orbital energies, $\sum_i n_i \varepsilon_i$, may be considered to represent the ground state. In the ground electronic configuration for an even-number electron system, orbitals from the lowest to HOMO are occupied by a pair of electrons. Exceptionally, some systems with degenerate or nearly degenerate HOMO and LUMO prefer to have a configuration of two unpaired electrons with parallel spins, which can be deduced from Hund's rule. Electron configurations produced by electron excitation to unoccupied orbitals are called excited electronic configurations. Excited electronic configurations are classified into one-electron excitation configurations, two-electron excitation configurations and so forth depending on the number of excited electrons.

When addition or extraction of some electrons is made for an electrically neutral N-electron system, we can construct a configuration of an $N + z$ electron system. The system becomes a negative ion if $z > 0$, and it becomes a positive ion if $z < 0$. Electron configurations for ions are called ionic (or ionized) configurations.

4.3.5 Orbital energies and ionization energies

In connection with a mono positive ion, the difference between the energy E_i of an ionic configuration Φ_i constructed with the SCF orbitals of the neutral system and the energy E_g of the ground electronic configuration Φ_g, $E_i - E_\mathrm{g}$, is simply equated with a -1 times value of the orbital energy ε_i for the orbital ϕ_i from which an electron is removed.

$$E_i - E_\mathrm{g} = -\varepsilon_i \tag{4.29}$$

This equation presented in 1934 is called Koopmans' theorem. If we assume that $E_i - E_\mathrm{g}$ equals to the ionization energy, we may suppose that -1 times of SCF occupied orbital energies correspond to ionization energies for removing an electron from the respective orbitals. Thus the following equation holds.

$$I_i = -\varepsilon_i \tag{4.30}$$

This is called Koopmans' formula. Similar treatment for a mono negative ion leads to an analogous equation including the orbital energy ε_k for the additional electron and the energy E_k for the configuration of the negative ion.

$$E_\mathrm{g} - E_k = -\varepsilon_k \tag{4.31}$$

If we assume that the left side of this equation represents the electron affinity A_k, we obtain

$$A_k = -\varepsilon_k \tag{4.32}$$

As clearly be seen from definitions of HOMO and LUMO, the electron affinity becomes the maximum at LUMO, and the ionization energy becomes the minimum at HOMO, provided that the electronic configuration represents to the ground state.

$$A_k \leq A_\mathrm{LUMO} \leq I_\mathrm{HOMO} \leq I_i \tag{4.33}$$

The middle equation is limited to a special system in which an orbital is HOMO as well as LUMO.

4.3.6 Methods including the electron correlation

As mentioned in Section 3.3, the SCF method does not include the electron correlation. In order to include electron correlation effects, the configuration interaction (CI) method based on the variation approach and Mϕller-Plesset's (MP) method based on the perturbation approach are extensively used.

In the CI method, linear combinations of various electron configurations $\{\Phi_i\}$ as many as possible are used to solve $\hat{H}\Psi = E\Psi$.

$$\Psi = \sum_j C_j \Phi_j \tag{4.34}$$

Mathematical treatments for this problem is the same as mentioned for Ritz's variation method. Inclusion of electron configurations as many as possible for obtaining the better accuracy and reliability is incompatible with saving the computation time and the computer memory for reducing the cost of calculations. A compromise between the conflicting demands needs to be made. The CI method often requires special knowledge to choose reasonable selections of electron configurations to be included. The CI method has an advantage to obtain excited-state energies and wave functions in addition to the ground-state properties owing to the characteristics of Ritz's variation method.

In the MP method, an unperturbed Hamiltonian operator $\hat{H}_0$ is defined so that it may have eigen functions constructed as determinant wave functions $\{\Phi_j\}$using the SCF orbitals. Thus the perturbation for the MP method $\hat{H}'$ is introduced as $\hat{H}' = \hat{H} - \hat{H}_0$, which is the difference between the exact Hamiltonian $\hat{H}$ and $\hat{H}_0$. Treatments to the second order have already been mentioned in Section 3.1. Energy corrections by the MP method starts from the second order, which is denoted as MP2. In general the n-th order treatment in the MP method is denoted as MPn. Although it is possible to include the higher order terms such as MP3 or MP4, the higher terms need considerably long computation time. Since there is no difficulties except for the choice of the order n, the MP method is conveniently used for the correction of the ground-state energy.

4.4 Quantum chemical calculations

In this section quantum chemical calculations by the nonempirical molecular orbital method are compared with the experiments.

4.4.1 Molecular structures

By finding out the minimum point on the potential energy surface depending on the nuclear coordinates (geometry optimization), we can determine the molecular structure. Table 4.1 lists calculated molecular structures in comparison with the experiments. Molecular structures are determined by experimental methods, such as electron diffraction and microwave spectroscopy. Theoretically obtained molecular structures can be used to predict microwave spectra and other experiments.

4.4.2 Molecular vibrations

Vibrational frequencies ν can be calculated with the curvatures (the second derivatives) around the minimum of the potential energy surface. Table 4.2 lists calculated vibrational frequencies in the harmonic approximation in comparison with experimental harmonic frequencies deduced from the experiments assuming the Morse potential with unit of the wave number (cm^{-1}). Although we will not describe details to avoid stepping outside the range of this book, calculations of molecular vibrations are useful for prediction of infrared (IR) absorption spectra as well as Raman scattering spectra. Furthermore, knowledge of molecular vibrations can be used to obtain important thermodynamic quantities such as heat capacities and entropies.

Table 4.1: Molecular structure (Bond length R/Å and bond angle θ/°)

Molecule	Structure constant	SCF method	MP2 method	CI method	Experiment
H_2	$R(\mathrm{H}-\mathrm{H})$	0.730	0.738	0.746	0.742
CH_4	$R(\mathrm{C}-\mathrm{H})$	1.084	1.090	1.091	1.092
	$\theta\,(\mathrm{HCH})$	109.47	109.47	109.47	109.47
H_2O	$R(\mathrm{O}-\mathrm{H})$	0.947	0.969	0.966	0.958
	$\theta\,(\mathrm{HOH})$	105.5	104.0	104.3	104.5
HCN	$R(\mathrm{C}-\mathrm{N})$	1.133	1.177	1.154	1.153
	$R(\mathrm{C}-\mathrm{H})$	1.509	1.070	1.067	1.065
HNC	$R(\mathrm{C}-\mathrm{N})$	1.154	1.187	1.171	1.169
	$R(\mathrm{N}-\mathrm{H})$	0.985	1.002	0.997	0.994
HCHO	$R(\mathrm{C}-\mathrm{O})$	1.184	1.221	1.205	1.208
	$R(\mathrm{C}-\mathrm{H})$	1.092	1.104	1.101	1.116
	$\theta\,(\mathrm{HCH})$	115.7	115.6	115.8	116.5

Table 4.2: Molecular vibration of diatomic molecules in harmonic approximation/cm^{-1}. Experimental harmonic frequencies are obtained from observed data assuming the Morse potential.

Molecule	SCF method	MP2 method	Experiment
H_2	4647	4528	4401
HF	4358	4038	4139
LiH	1415	1393	1406
LiF	1033	998	914
Li_2	339	368	351
CO	2438	2113	2170
N_2	2763	2173	2360

4.4.3 Heats of reaction

Quantum chemical calculations of reactants and products lead to the heat of reaction, which can be obtained from the energy change on the reaction. For a reaction of $\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{C}$, we need to calculate the energies $E(A)$, $E(B)$, $E(C)$ by a molecular orbital method, and the heat of reaction can be obtained as $\Delta E = 2E(\mathrm{C}) - E(\mathrm{A}) - E(\mathrm{B})$. For endothermic reactions $\Delta E > 0$, and for exothermic reactions $\Delta E < 0$. Table 4.3 shows calculated results for heats of reaction in comparison with the experiments. Although experimental values of heats of reaction are conventionally shown for the standard state at a pressure of 1 atm and a temperature of 298 K, listed values in Table 4.3 are those at 0 K corrected with zero-point energies so that they may correspond to theoretically obtained values.

4.4.4 Electron distribution and the electric dipole moment

We can obtain the electron density distribution by molecular orbital calculations. Figure 4.5 demonstrates electron densities in some molecules. Contour lines in the figure are shown in a geometric series with a ratio of 2. HC≡CH, HC≡N, and N≡N are called an isoelectronic series, since they have the same number of electrons, similar electron configurations, and similar orbital shapes. The third and the fourth orbitals from the bottom are inner shell orbitals, whose electron densities are concentrated around the nuclei with extremely narrow spacings. The bottom maps are contours of the total electron densities, and these maps represent the shapes of the molecules.

The electron distribution of a molecule is related to its electric polarization. The electric polarization of a molecule is represented by the electric dipole moment. When an electric charge Q_i is located at $\boldsymbol{R}_i$ in a group of electric charges, the electric dipole moment μ of this system is given

Table 4.3: Heats of reaction including zero-point energies at 0 K (the unit is $\mathrm{kJ\,mol^{-1}}$)

Reaction	SCF method	Experiment
$Li_2 + H_2 \longrightarrow 2LiH$	92	84
$F_2 + H_2 \longrightarrow 2HF$	−561	−556
$Cl_2 + H_2 \longrightarrow 2HCl$	−230	−192
$O_2 + 2H_2 \longrightarrow 2H_2O$	−439	−523
$N_2 + 3H_2 \longrightarrow 2NH_3$	−138	−155
$HC \equiv CH + H_2 \longrightarrow CH_2 = CH_2$	−226	−201
$CH_2 = CH_2 + 2H_2 \longrightarrow 2CH_4$	−268	−238
$CO + 3H_2 \longrightarrow CH_4 + H_2O$	−247	−264
$HOOH + H_2 \longrightarrow 2H_2O$	−364	−360
$HCN \longrightarrow HNC$	52	61
$CH_3CN \longrightarrow CH_3NC$	87	87

Table 4.4: Molecular electric dipole moments (in the unit of 10^{-30} C m)

Molecule	SCF method	Experiment
H_2	0.0	0.0
HF	6.6	6.1
HCl	5.0	3.6
LiH	19.3	19.4
LiF	20.2	21.0
LiCl	24.8	23.8
NaF	26.7	27.2
NaCl	31.3	30.0
HCN	10.8	10.0
C_2H_2	0.0	0.0
NH_3	6.5	4.9
PH_3	2.6	1.9
H_2O	7.4	6.2
H_2S	4.6	3.2
HCHO	9.2	7.8

by the following formula.

$$\boldsymbol{\mu} = \sum_i Q_i \boldsymbol{R}_i \tag{4.35}$$

Within the adiabatic approximation, we may treat electrons as electron densities and nuclei resting, and it follows that the electric dipole moment based on the quantum theory is given by the following equation.

$$\boldsymbol{\mu} = -\int e\rho(\boldsymbol{r})\boldsymbol{r}\mathrm{d}\boldsymbol{r} + \sum_{\mathrm{A}} eZ_{\mathrm{A}}\boldsymbol{R}_{\mathrm{A}} \tag{4.36}$$

Table 4.4 lists some examples of theoretically calculated electric dipole moments in comparison with the experiments. Experimental values of molecular electric dipole moments are obtained by the following experiments.

(1) Measurements of dielectric constants or refractive indexes for gases and solutions.

(2) Measurements of changes of microwave spectra under the applied electric fields (the Stark effect).

(3) Measurements of changes in directions under the action of the applied electric fields for molecular beams ejected through a nozzle into vacuum.

As unit for dipole moments, 1 D(debye) = 3.3356×10^{-30} Cm is sometimes used.

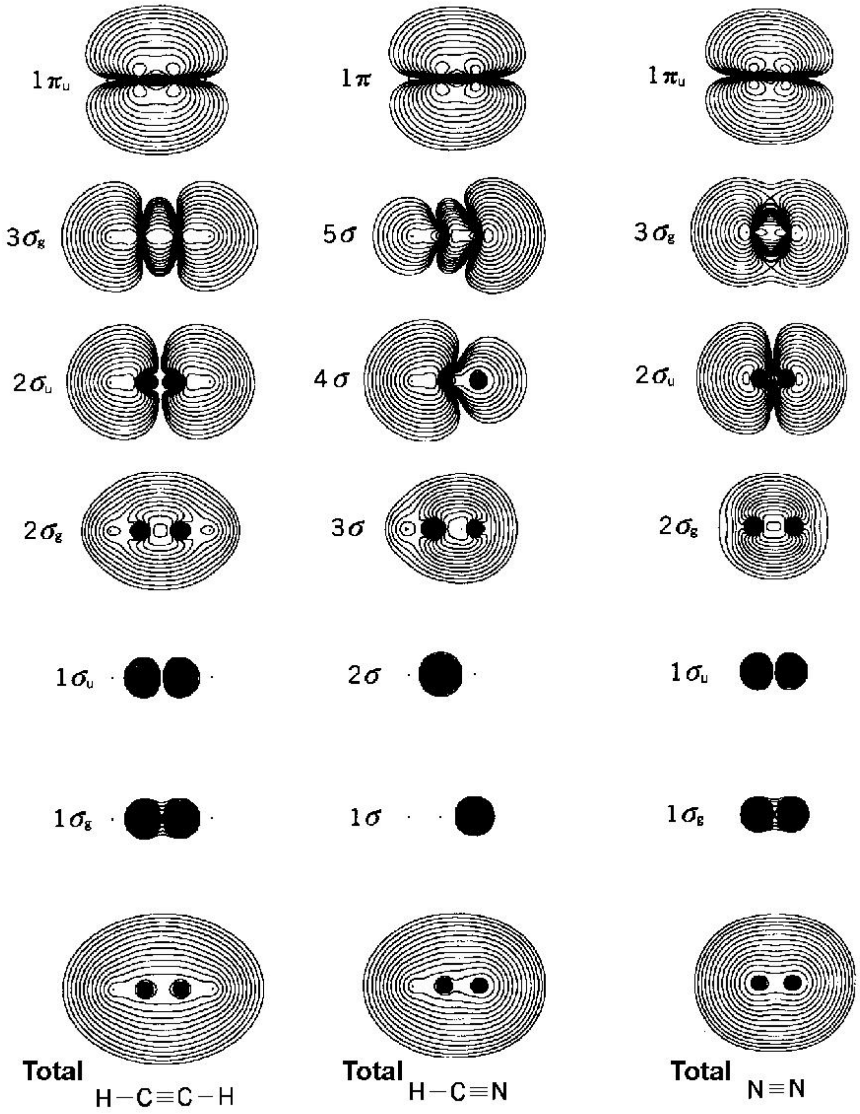


Figure 4.5: Contour maps of electron densities

4.4.5 Ionization energy

Ionization energies can easily be obtained from molecular orbital energies via Koopmans' formula (4.30). Table 4.5 lists examples of calculated ionization energies via Koopmans' formula in comparison with experimental values. This table only shows the lowest ionization energies corresponding to the energy required to remove an electron from HOMO. Improved results by the configuration interaction (CI) method are also listed for some molecules. Ionization energies can be measured by the following experiments.

(1) Measurements of photoelectron spectra.

(2) Measurements of the minimum energies required to ionize the sample molecule by impact of electron beams, which can be made by means of a mass spectrometer.

(3) Observation and analysis of spectral line series called Rydberg series which is similar to spectral line series of the hydrogen atom.

Photoelectron spectroscopy gives not only the lowest ionization energy but also other ionization energies, corresponding to removal of an electron from various molecular orbitals (cf. Section 5.8).

Table 4.5: The lowest ionization energies for molecules (eV)

Molecule	SCF method	CI method	Experiment
F_2	18.20	15.48	15.83
N_2	17.13	16.62	15.60
H_2O	13.64	11.70	12.62
H_2S	10.43	9.61	10.48
NH_3	11.29	9.68	10.85
HF	17.09	15.14	16.05
HCN	13.56	13.28	13.60
HCHO	11.96	10.32	10.88
CO_2	14.63	13.01	13.78
CS_2	9.94	9.23	10.06
$CH_2 = CH_2$	12.12	10.22	10.51
$CH{\equiv}CH$	11.02	10.75	11.40
CH_3CN	12.56	12.10	12.21
CH_3Cl	11.68	10.70	11.29
CH_3OCH_3	11.38	9.62	10.04
CH_3OH	12.16	10.37	10.94
C_2H_5OH	11.89		10.64
C_2H_5SH	9.58		9.36
$C_2H_5NH_2$	10.19		9.50
C_2H_5Cl	11.54		11.06
C_6H_6	9.03		9.25
$C_6H_5NH_2$	7.95		8.00
C_6H_5OH	8.55		8.70
B_2H_6	12.75	11.86	11.89

Exercises

4.1 J. E. Lennard-Jones proposed an experimental formula representing intermolecular potential energy curves, which includes integers n and m (usually $n = 12,\ m = 6$) and constants D and σ.

$$U(R) = D\left[\frac{m}{n-m}\left(\frac{\sigma}{R}\right)^n - \frac{n}{n-m}\left(\frac{\sigma}{R}\right)^m\right]$$

Using this equation, obtain the equilibrium internuclear distance R_e and the bond energy D_e.

4.2 Calculate expectation values of the potential energy $\langle U\rangle$, the kinetic energy $\langle K\rangle$, and their ratio (the virial ratio)$= -\langle U\rangle/\langle K\rangle$ for the 1s wave function of the hydrogen atom.

4.3 List up the minimal basis set for molecular orbital calculations of a formaldehyde molecule, and answer the number of basis functions.

Chapter 5

Molecular orbital and molecular structure

Various problems in chemistry can be investigated theoretically based on the molecular orbital method. Theoretical approaches can be grouped into two types; one is the quantitative approach yielding calculated values which can be compared with experimental values, and the other is the qualitative approach giving explanation and expectation of experiments. Basic descriptions for the quantitative approach have been given in the preceding chapter. In this chapter, basic methods of qualitative treatments and applications to molecular structures and molecular electronic states will be studied. In the last section of this chapter, relationships among energy levels of molecular orbitals, ionization energies, and dissociation energies will also be studied in connection with observed photoelectron spectra.

5.1 Hydrogen molecule ion and hydrogen molecule

5.1.1 Hydrogen molecule ion

A hydrogen molecule ion is composed of two protons and an electron. In Figure 5.1 $\boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}}$, and $\boldsymbol{r}$ denote positions of two protons A, B, and the electron, respectively. Fixing the protons at the distance R, we consider the motion of the electron using the following Hamiltonian operator $\hat{H}$.

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{4\pi\varepsilon_0 r_{\mathrm{A}}} - \frac{e^2}{4\pi\varepsilon_0 r_{\mathrm{B}}} + \frac{e^2}{4\pi\varepsilon_0 R} \tag{5.1}$$

r_{A} and r_{B} denote distances between the electron and the protons A and B, respectively. The wave function ψ representing the motion of the electron is a function of the position of the electron $\boldsymbol{r}$, and ψ changes together with the change of the distance R between the protons.

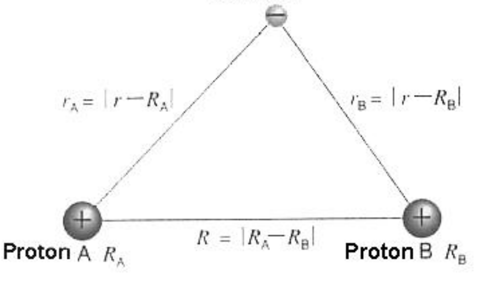


Figure 5.1: The Hydrogen molecule ion $\mathrm{H_2}^+$

Since ψ represents the behavior of the electron wave of a hydrogen molecule ion, it can be expressed as a superposition of electron waves for isolated hydrogen atoms, which correspond to electron waves moving around respective protons separately. Thus, ψ of the hydrogen molecule ion can be expanded as a linear combination of atomic orbitals χ_A and χ_B for the hydrogen atoms.

$$\psi(\boldsymbol{r}) = C_\mathrm{A}\chi_\mathrm{A}(\boldsymbol{r}) + C_\mathrm{B}\chi_\mathrm{B}(\boldsymbol{r}) \tag{5.2}$$

C_A, C_B are coefficients representing the weights of the superposition of χ_A and χ_B. As χ_A, χ_B, the valence 1s orbital function ϕ_1s for the hydrogen atom is used.

$$\phi_\mathrm{1s}(r) = \pi^{-1/2}{a_\mathrm{B}}^{-3/2}\mathrm{e}^{-r/a_\mathrm{B}} \tag{5.3}$$

For χ_A and χ_B, distances r_A, r_B between the electron and the respective proton A,B should be used for the variables of ϕ_1s.

$$\begin{aligned} \chi_\mathrm{A} &= \phi_\mathrm{1s}(r_\mathrm{A}) \\ \chi_\mathrm{B} &= \phi_\mathrm{1s}(r_\mathrm{B}) \end{aligned} \tag{5.4}$$

Now, let us consider the following expectation value u of $\hat{H}$ by ψ in eq.(5.2).

$$u = \frac{\int \psi^* \hat{H} \psi \mathrm{d}\boldsymbol{r}}{\int \psi^* \psi \mathrm{d}\boldsymbol{r}} \tag{5.5}$$

Conditions minimizing this u based on Ritz's variation method yield the following simultaneous equations (cf. Section 3.2).

$$\begin{aligned} (\alpha - u)C_\mathrm{A} + (\beta - uS)C_\mathrm{B} = 0 \\ (\beta - uS)C_\mathrm{A} + (\alpha - u)C_\mathrm{B} = 0 \end{aligned} \tag{5.6}$$

In place of the following integrals including atomic orbital functions χ_A and χ_B, symbols α, β and S are used in the above equations.

$$\int {\chi_i}^* \hat{H} \chi_j \mathrm{d}\boldsymbol{r} = \begin{cases} \alpha & (i = j) \\ \beta & (i \neq j) \end{cases} \tag{5.7}$$

$$\int {\chi_i}^* \chi_j \mathrm{d}\boldsymbol{r} = \begin{cases} 1 & (i = j) \\ S & (i \neq j) \end{cases} \tag{5.8}$$

In the above equations, i and j refer to protons A and B, but no specification of A and B need to be made for α, since two protons are the same particle.

Among the integrals in eqs. (5.7) and (5.8), integrated values depend on the distance R between the protons, except for the integral of the normalization condition of the 1s function. α, β and S are integrals including exponential functions, which can be calculated based on mathematical knowledge in the college level. Although the details will not be mentioned, qualitative features of these integrals are summarized as follows.

The overlap integral S satisfies the following inequalities.

$$0 < S < 1 \tag{5.9}$$

As shown in Fig.5.2, $S \to 1$ in the limit of $R \to 0$, and $S \to 0$ in the limit of $R \to \infty$. α and β approach $+\infty$ in the limit of $R \to 0$. Although the potential energy due to attractive forces between the electron and the protons becomes just twice of the case of a hydrogen atom in the limit of $R \to 0$, the potential energy for the repulsion between the protons corresponding to the last term of eq.(5.1) diverges to $+\infty$ for $R \to 0$. The value of α for $R \to \infty$ agrees with the 1s orbital energy E_1s of a hydrogen atom, since the interaction with the other proton may be neglected. The value of β for $R \to \infty$ results in $\beta \to 0$, because at least one of the orbital functions becomes to vanish irrespective of the location of the electron. Figure 5.2 also shows the R-dependence of $u_\mathrm{a}, u_\mathrm{b}$.

In order to obtain nontrivial solutions for the simultaneous equations (5.6) other than $C_\mathrm{A} = C_\mathrm{B} = 0$, the following secular equation should be satisfied.

$$\begin{vmatrix} \alpha - u & \beta - uS \\ \beta - uS & \alpha - u \end{vmatrix} = 0 \tag{5.10}$$

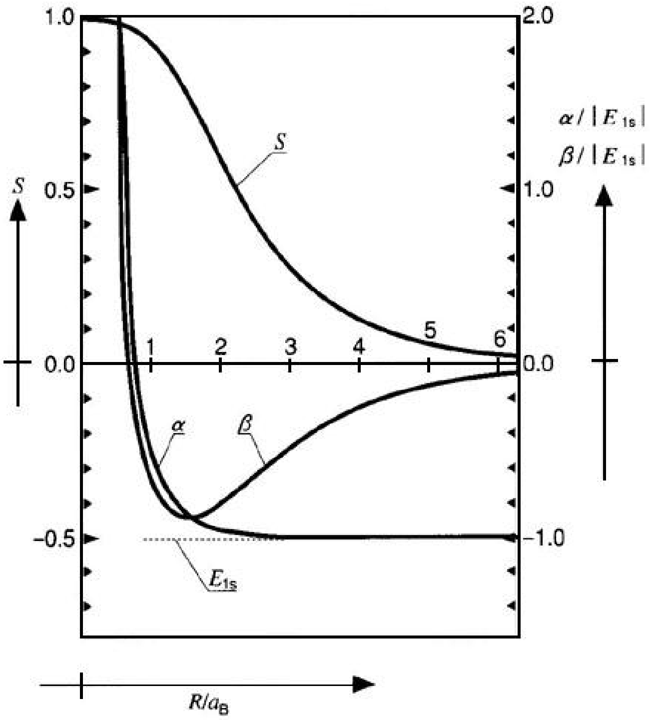


Figure 5.2: The R -dependence of α, β and S

We expand this equation to obtain

$$(\alpha - u)^2 - (\beta - uS)^2 = 0$$

This is a quadratic equation of u, and two solutions $u_\mathrm{a}, u_\mathrm{b}$ (let $u_\mathrm{a} > u_\mathrm{b}$ for convenience) are given as follows.

$$\begin{aligned} u_\mathrm{a} &= \tfrac{\alpha-\beta}{1-S} \\ u_\mathrm{b} &= \tfrac{\alpha+\beta}{1+S} \end{aligned} \tag{5.11}$$

These two solutions are approximate energy levels of $H_2{}^+$. u_a and u_b correspond to the excited state and the ground-state, respectively. Figure 5.3 shows variations of $u_\mathrm{a}, u_\mathrm{b}$ as functions of the internuclear distance R.

The curve for u_b has a minimum giving an internuclear distance $R_\mathrm{e} = 1.32\,\text{Å}$ and a binding energy $D_\mathrm{e} = 1.77\,\mathrm{eV}$, which means a production of a stable bond. Corresponding observed values are $R_\mathrm{e} = 1.06$ Å and $D_\mathrm{e} = 2.78\,\mathrm{eV}$. These results are not disappointing, since the restriction of the wave function ψ in the form of eq.(5.2) is a very crude approximation. It is significant that a brief description of the chemical bonding with R_e of 1 Å and D_e of a few eV is given. The curve for u_a decreases with the increase of R, which gives repulsion between nuclei to lead to dissociation.

Wave functions $\psi_\mathrm{a}, \psi_\mathrm{b}$ corresponding to the respective states are obtained by using relations for C_A and C_B, which are derived from insertion of $u_\mathrm{a}, u_\mathrm{b}$ into eq.(5.6). The following normalization condition should also be used.

$$\int |\psi|^2 \mathrm{d}\boldsymbol{r} = C_\mathrm{A}{}^2 + C_\mathrm{B}{}^2 + 2C_\mathrm{A}C_\mathrm{B}S = 1 \tag{5.12}$$

Insertion of u_a into eq.(5.6) gives

$$(C_\mathrm{A} + C_\mathrm{B})\frac{\beta - \alpha S}{1 - S} = 0$$

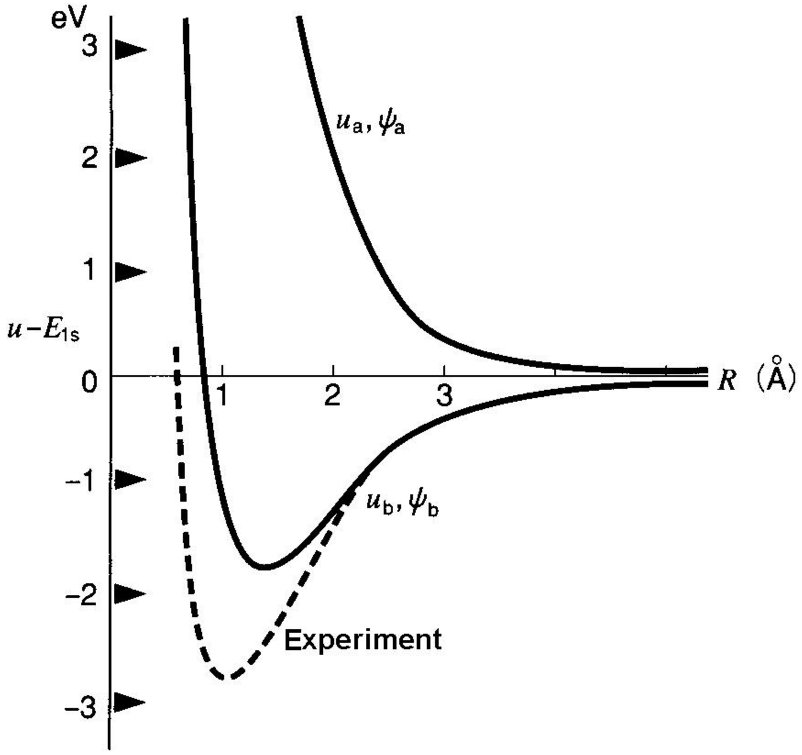


Figure 5.3: Potential energies for $H_2{}^+$

This equation leads to $C_A = -C_B$, and by using the normalization condition we obtain for ψ_a

$$\psi_a = \frac{\chi_A - \chi_B}{\sqrt{2(1-S)}} \tag{5.13}$$

Next, using u_b similarly we obtain

$$\psi_b = \frac{\chi_A + \chi_B}{\sqrt{2(1+S)}} \tag{5.14}$$

Now, let us consider physical significance of these wave functions ψ_a and ψ_b. As can be seen from eq.(5.2), ψ is a new electron wave produced by interference of electron waves of atomic orbitals χ_A and χ_B with weighting factors of coefficients C_A and C_B. In ψ_a signs of two components $C_A\chi_A$ and $C_B\chi_B$ are opposite to cancel out each other (Fig.5.4). Such an orbital is called an antibonding orbital. Interference of electron waves of atomic orbitals effectively occurs at spatial regions between two nuclei where the orbitals overlap each other. For ψ_a, electron densities in the binding region decrease by interference in comparison with the case of no interference, and electron densities in the antibinding region increase to result in strong repulsion between the nuclei. On the other hand for ψ_b, two components are constructive with the same sign. Such an orbital is called a bonding orbital. In the case of ψ_b, electron densities in the binding region increase to produce binding forces between the nuclei (Fig. 5.4). The bonding in the hydrogen molecule ion is due to an electron shared in the binding region between two nuclei, and thus this kind of bond is called the one-electron bond. Although treatments here are approximate, the following two findings are important; (1) electron distribution determined by interference between electron waves lead to binding or anti binding forces, and (2) only one electron can produce a bond.

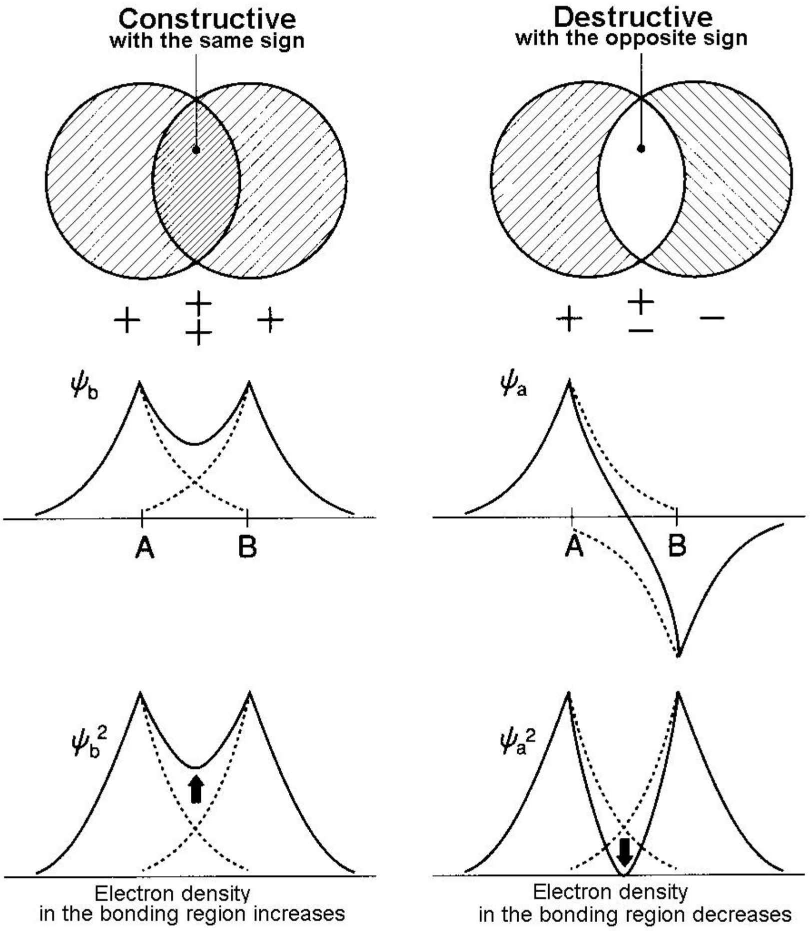


Figure 5.4: Interference of electron wave of atomic orbitals

5.1.2 The hydrogen molecule

The first explanation based on quantum mechanics was made for the mechanism of the chemical bond in a hydrogen molecule by W. Heitler and F. London in 1927. According to their valence bond method, a bond is formed by interactions between atoms approaching each other. This method is thereafter a standard version of the theory of the chemical bond in many textbooks. Long after in 1962 J. R. Reudenberg made a careful analysis of the binding energy in the valence bond method, and he disclosed that the balance of potential and kinetic energies, which is related with the virial ratio studied in Section 4.2, is incorrect in the method by Heitler and London. Recent developments of computers have considerably increased the advantage of the molecular orbital method, and thus we do not deal with the valence bond method.

The molecular orbital method mentioned in Section 4.3 gives potential energy curves for a hydrogen molecule as shown in Fig.5.5. $E(\mathrm{H}_2)$ and $E(\mathrm{H})$ denote energies of a hydrogen molecule and a hydrogen atom, respectively. R and a_B are the internuclear distance and the Bohr radius, and both of the ordinate and the abscissa are normalized to the atomic unit. Even in the SCF level a stable chemical bond is formed, and the configuration interaction method (CI) considering the electron correlation effects gives a much better result in comparison with the experiments. The molecular orbital method and its application to many molecules including the hydrogen molecule will be described in detail in the following Sections.

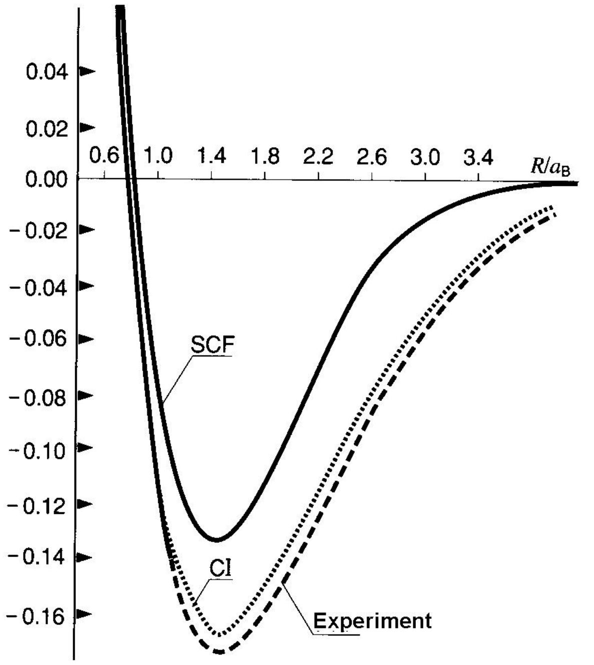


Figure 5.5: The potential energy of the hydrogen molecule H_2. The ordinate shows $\frac{E(H_2)-2E(H)}{2|E(H)|}$

5.2 The Hückel molecular orbital method

Precise calculations by the *ab initio* molecular orbital method produce considerable amounts of computed results due to the huge size of the calculations, which often leads to confusions in the interpretation. In general, the larger basis set in the linear combination method yields the better accuracy at the expense of the simplicity. Many basis functions inevitably make it difficult to understand obtained wave functions in terms of interference of electron waves. These difficulties in interpretation and understanding also lead to difficulties in scientific analyses and prediction without calculations.

In order to avoid such difficulties in interpretation and understanding, even specialists of molecular orbital calculations dare to perform simple calculations with the minimal basis (cf. Section 4.3) for the basis functions and carefully investigate constructions of molecular orbitals. Without numerical calculations, shape of orbitals as well as energy levels can be briefly anticipated on the basis of drastically simplified molecular orbital methods. In this section, we study the Hückel molecular orbital method, since it has been used as the most suitable method to discuss the qualitative nature of molecular orbitals.

5.2.1 Fundamental treatments in the Hückel method

In the Hückel molecular orbital method, which is sometimes called the Hückel method or the HMO method, shape and energies of orbitals are obtained without numerical integrations as far as possible. Although there are many integrals in the basic equations, various quantities included in the secular equation are replaced by parameters with characteristic values depending on the elements or bonding types.

Molecular orbitals $\{\phi_i\}$ in the Hückel method are expressed as linear combinations of atomic orbitals $\{\chi_q\}$.

$$\phi_i = \sum_q C_{qi}\chi_q \tag{5.15}$$

Here, $\{\chi_q\}$ are assumed to be normalized atomic orbital functions. Unless necessary, real functions are used for $\{\chi_q\}$, and coefficients of the linear combinations are also treated as real numbers. In some special cases such as ring molecules with periodicity, complex numbers should be used for $\{C_{qi}\}$ exceptionally. Molecular orbitals $\{\phi_i\}$ should be normalized by the following condition.

$$\int {\phi_i}^2 \mathrm{d}\boldsymbol{r} = \sum_p \sum_q C_{pi} C_{qi} S_{pq} = 1 \tag{5.16}$$

S_{pq} is the overlap integral between χ_p and χ_q given by the following equation.

$$S_{pq} = \int \chi_p \chi_q \mathrm{d}\boldsymbol{r} \tag{5.17}$$

Since $\{\chi_q\}$ are assumed to be normalized, $\{S_{pp}\}$ are all equal to the unity. The absolute value of $\{S_{pq}\}$ for $p \neq q$, which is in general smaller than 1, becomes very small to be neglected, if the distance between p and q is very large. $\{S_{pq}\}$ represent how much extent electron waves of the atomic orbitals are overlapping, and thus they are called overlap integrals.

Molecular orbitals $\{\phi_i\}$ are determined from the following one electron eigen equation.

$$\hat{h}\phi_i = \varepsilon_i \phi_i \tag{5.18}$$

Here, $\hat{h}$ is the one-electron Hamiltonian operator determining the electron motion. This $\hat{h}$ includes an operator corresponding to the kinetic energy of an electron and average potentials of interactions between electrons as well as attractive potentials from nuclei. The problem to obtain $\{\phi_i\}$ and $\{\varepsilon_i\}$ begins with the condition minimizing the expectation value ε_i of $\hat{h}$ with $\{\phi_i\}$ by changing $\{C_{qi}\}$. This is a variational problem in terms of linear combinations, which leads to the following simultaneous equations.

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0 \tag{5.19}$$

Here, H_{pq} is given by the following equation.

$$H_{pq} = \int \chi_p \hat{h} \chi_q \mathrm{d}\boldsymbol{r} \tag{5.20}$$

H_{pq} is called the Coulomb integral for $p = q$ with writing $H_{pp} = \alpha_p$ and called the resonance integral for $p \neq q$ with writing $H_{pq} = \beta_{pq}$. Resonance integrals as well as overlap integrals can be neglected, since they become very small when p and q are in a long distance.

Orbital energies ε_i are obtained from the following secular equations (cf. Section 3.2).

$$|H_{pq} - \varepsilon_i S_{pq}| = 0 \tag{5.21}$$

Inserting orbital energies ε_i from the solutions of eq.(5.21) into eq.(5.19) and using normalization conditions of eq.(5.16), $\{C_{qi}\}$ are obtained.

5.2.2 The simple Hückel method

According to the policy of the Hückel method that numerical calculations of integrals should be avoided as long as possible, the simple Hückel method adopts further simplifications with the following approximations. The traditional Hückel method is this method, which can be compared with the extended Hückel method mentioned in the next subsection and is called as the simple Hückel method. In the conventional Hückel method, the π electron approximation is usually adopted. If α and β are carefully estimated, the Hückel method can be applied to the more general cases.

(1) Neglect of overlap integrals S_{pq} $(p \neq q)$

Overlap integrals S_{pq} for $p \neq q$ are much smaller than the case of $S_{pp} = 1$, and thus they can be neglected.

$$S_{pq} = \delta_{pq} = \begin{cases} 1 & \text{for } p = q \\ 0 & \text{for } p \neq q \end{cases} \tag{5.22}$$

This approximation leads to the following equations much more simplified than eqs. (5.19) and (5.21).

$$\sum_q (H_{pq} - \varepsilon_i \delta_{pq}) C_{qi} = 0 \tag{5.23}$$

$$|H_{pq} - \varepsilon_i \delta_{pq}| = 0 \tag{5.24}$$

In addition, the normalization condition for molecular orbitals is also simplified as follows.

$$\sum_q {C_{qi}}^2 = 1 \qquad \text{(the summation should be taken for all atomic orbitals } \chi_q\text{)} \tag{5.25}$$

Since the assumption of eq.(5.22) corresponds to the expansion in terms of the orthonormal set $\{\chi_q\}$ by eq.(5.15), the summation of coefficients of all molecular orbitals $\{\phi_i\}$ satisfys the following formula.

$$\sum_i {C_{qi}}^2 = 1 \qquad \text{(the summation should be taken for all molecular orbitals } \phi_i\text{)} \tag{5.26}$$

(2) Neglect of resonance integrals β for non-bonded atomic pairs

β_{pq} as well as S_{pq} become very small when χ_p and χ_q become spatially far apart. However, for bonded atomic pairs β_{pq} are considered, since they are very important. β_{pq} for non-bonded atomic pairs are disregarded.

(3) Parameterization of resonance integrals β for bonded atomic pairs

Depending on combinations of atomic orbitals, β_{pq} is treated as a parameter. In many cases, numerical values for β are not necessarily given. Sometimes β is determined by experiments. Although the sign of β is important, it depends on the type of bonds (cf. Section 5.3).

(4) Parameterization of Coulomb integrals α

Depending on the type of atomic orbitals, Coulomb integrals are treated as parameters. α equals approximately to the atomic orbital energy, and its sign is always negative. $|\alpha|$ is equal to the energy required to remove an electron from the atomic orbital, which is approximately the ionization energy. Although α can often be used with no value, the relative magnitude as well as its sign are very important.

5.2.3 The Extended Hückel method

Although the simple Hückel method is a convenient method, it cannot be applied to a system in which positions of chemical bonds are not clear. For example, metal complexes as well as organic compounds having complex structures are not suitable for the simple Hückel method method. Thus, the extended Hückel method exceptionally evaluating overlap integrals was proposed, and it has been extensively used as an improved approach, though such a treatment is clearly against the policy avoiding numerical integrations as far as possible. The extended Hückel method is based on the fundamental formula of eqs. (5.15)∼(5.21) as well, and some further approximations used are summarized as follows.

(1) Overlap integrals S_{pq} are evaluated by direct integration using atomic orbitals functions $\{\chi_q\}$. In many cases, STOs mentioned in Section 4.3 are used.

(2) Resonance integrals $H_{pq} = \beta_{pq}\,(p \neq q)$ are estimated by the following approximate formula.

$$\beta_{pq} = K S_{pq} \frac{\alpha_p + \alpha_q}{2} \tag{5.27}$$

Here, α_q is a Coulomb integral involving an atomic orbital χ_q, and the constant K is set as $K = 1.75$. This formula can be deduced as follows. In the eq.(5.20) defining the resonance integral, replacement of the operator $\hat{h}$ by an assumed constant value of a leads to $\beta_{pq} = aS_{pq}$, and also in eq.(5.20) assumption of a simple average of the integrals for $p = q$ in place of the integral for $p \neq q$ yields $\beta_{pq} = (\alpha_p + \alpha_q)/2$. These characteristics are combined into the formula (5.27). This formula (5.27) leads to an important relationship that the resonance integral β_{pq} and the overlap integral S_{pq} have opposite signs, because $K > 0$ and $\alpha_p < 0$, $\alpha_q < 0$ based on the reasons given below. Also in the simple Hückel method, the resonance integral β_{pq} and the overlap integral S_{pq} have opposite signs.

(3) Coulomb integral $H_{qq} = \alpha_q$ is nearly equal to the energy of the atomic orbital χ_q, and thus α_q is estimated by the following formula using the ionization energy I_q of the electron in χ_q.

$$\alpha_q = -I_q \tag{5.28}$$

Here, I_q is positive, and α_q is negative. An atom with strong negativity has a large ionization energy I_q, which leads to a large value of $|\alpha_q|$. Oppositely, $|\alpha_q|$ for an atom with weak negativity becomes small. Magnitudes of $|\alpha_q|$ for orbitals of valence electrons are usually in the range of 5 eV - 30 eV. On the other hand, magnitudes of $|\alpha_q|$ for atomic orbitals of inner shell electrons have much larger values in the range of several hundreds or thousands eV.

5.3 Overlap between orbitals and orbital interactions

Molecular orbitals (MO) are composed of atomic orbitals (AO), (1) mathematically linear combinations of functions, and (2) physically superposition of electron waves, and (3) chemically mixture of ingredients. Composition of molecular orbitals made of some atomic orbitals is in general governed by interactions between orbitals. Overlap of orbitals leads to interactions and mixing of orbitals, which results in formation of new orbitals. In this section, the mechanisms involved in the formation of new orbitals associated with overlap between orbitals are studied on the basis of Hückel molecular orbital method.

5.3.1 Overlap between orbitals

In the Hückel method, the magnitude of the resonance integral $|\beta|$ is most important for the formation mechanisms of molecular orbitals from atomic orbitals via interference of electron waves. The detail of the reason will be discussed below. Here, we will study characteristics of overlap integrals, since there is a relationship of eq.(5.27) that β is proportional to the overlap integral S.

Overlap integrals depend on types and combinations of atomic orbitals as well as on the distance between the nuclei at which the atomic orbitals are placed. Typical cases are illustrated in Fig.5.6.

In this figure, as an s orbital and a p orbital, 1s and 2p orbital functions are used, respectively. In order to represent the spatial distribution of each orbital, a circle is used for an s orbital, and a pair of ellipses are used for a p orbital. Signs of the functions are specified by $+$ and $-$ in the figures. Absolute values of atomic orbital functions are generally decreasing to vanish with the distance becoming very large. It should be noted that the same sign of electron distributions extending outside of the circles and the ellipses.

Fig.5.6(a) shows the R dependence of an overlap integral between two p orbitals having parallel directions, which decreases monotonically. Such an overlap between parallel p orbitals is called the π type orbital, and chemical bonds originating from this type of overlaps are called the π bonds. In π type overlaps, the axis connecting the atoms is included in a common nodal plane of the atomic orbitals. In a π orbital produced by the π type overlap, probabilities of finding an electron on the nodal plane containing the bond axis are vanishing. Fig.5.6(b),(c),(d) show the R dependence of overlap integrals between orbitals with no common nodal plane including the bond axis. These types of overlaps are called the σ type overlap, and chemical bonds originating from this type of overlaps are called the σ bonds. Although the overlap integral is not necessarily monotonous in the σ type, the overlaps become decreasing until vanishing on going to a large distance in R as in the case of the π type overlap. This is related to the general tendency that, associated with the increase of the overlap between orbitals approaching each other, the interference between electron waves becomes to be more significant.

In Fig.5.6(e)(f), overlap integrals are shown for combination of orbitals with and without a nodal plane including the bond axis, contrary to other cases. Although the absolute values of the orbital functions are the same at a pair of symmetrical points with respect to the plane including the bond axis, their signs are opposite for one orbital and the same for the other orbital. It follows that overlap integrals of these orbital functions are always vanishing irrespective of the distance R, because the lower and the upper contributions cancel out mutually. This type of overlaps is called the overlap without symmetry matching. When overlaps are vanishing, necessarily no interference occurs, and hence no bonds are formed.

As will be studied in detail below, the formation of a chemical bond is governed by the overlap between orbitals. This is called the principle of overlap, and interactions between orbitals are called orbital interactions. The magnitude of interorbital interactions depend on the magnitude of $|\beta|$ or $|S|$. According to the principle of overlap, the orbital interaction is forbidden for $\beta = 0 (S = 0)$ and allowed for $\beta \neq 0 (S \neq 0)$. The relationship of orbital interactions with overlaps between orbitals can be summarized as follows. [**Orbital interactions and overlap between orbitals**]

1. Orbitals without symmetry matching ($S = 0$) do not interact with each other.
2. Orbitals with overlaps ($S \neq$) interact with each other.
3. The magnitude of an orbital interaction increases with the increase of the overlap ($|S|$).
4. Orbital interactions become negligibly small for long distances (large R) and become large when the overlap increases for short distances.

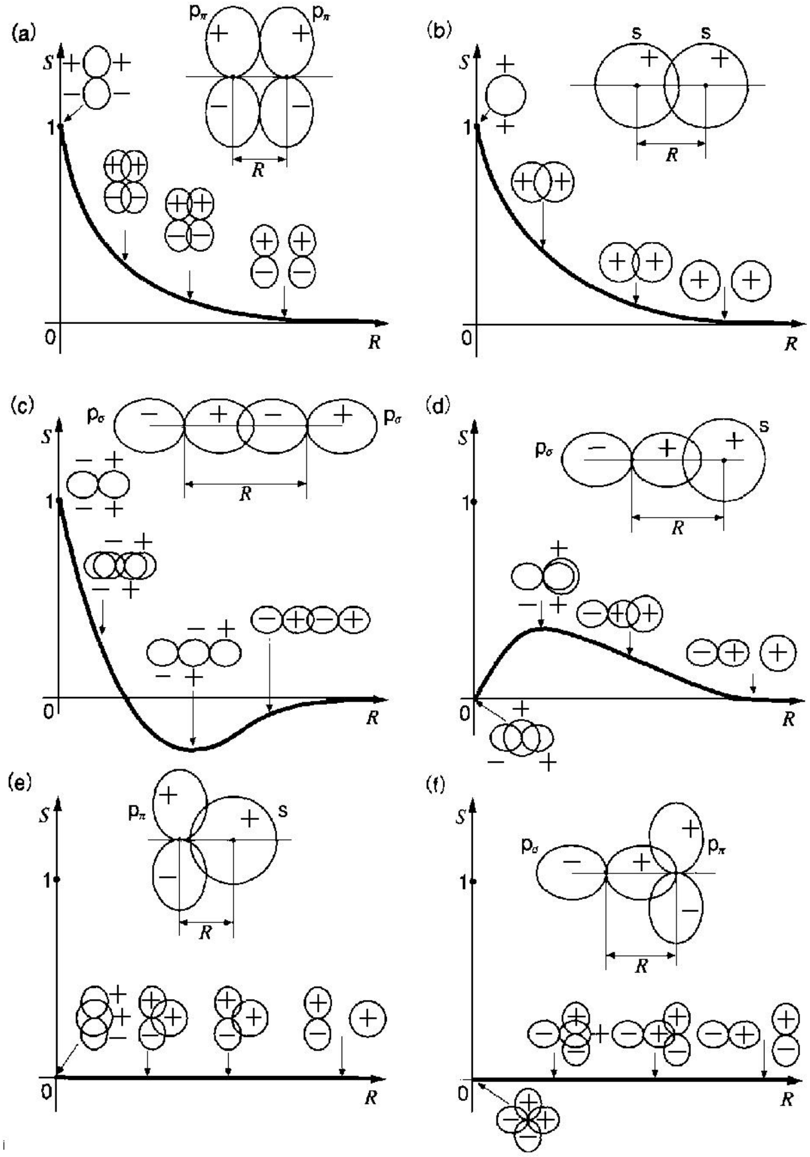


Figure 5.6: Overlap (overlap integrals S) between various atomic orbitals

5.3.2 The principles of orbital interactions

Let us study by the simple Hückel method the mechanism of orbital interactions between a pair of atomic orbitals $\chi_{\rm A}$ and $\chi_{\rm B}$ with orbital energies of $\alpha_{\rm A}$ and $\alpha_{\rm B}$ and their mutual resonance integral of β, yielding a molecular orbital of $\phi = C_{\rm A}\chi_{\rm A} + C_{\rm B}\chi_{\rm B}$ with an orbital energy of ε. First, we obtain ε by solving the secular equation (5.24). In this case, $H_{\rm AA} = \alpha_{\rm A}$, $H_{\rm BB} = \alpha_{\rm B}$, $H_{\rm AB} = H_{\rm BA} = \beta$, and thus the secular equation becomes

$$\begin{vmatrix} \alpha_{\rm A} - \varepsilon & \beta \\ \beta & \alpha_{\rm B} - \varepsilon \end{vmatrix} = 0 \tag{5.29}$$

Denoting the left-hand side as $f(\varepsilon)$ and expanding the determinant, we obtain a quadratic equation of ε.

$$f(\varepsilon) = \varepsilon^2 - (\alpha_{\rm A} + \alpha_{\rm B})\varepsilon + \alpha_{\rm A}\alpha_{\rm B} - \beta^2 = 0 \tag{5.30}$$

Let us consider the following two cases depending on whether β is equal to zero or not.

For $\beta = 0$, factorization can easily be made to give $f(\varepsilon) = (\varepsilon - \alpha_{\rm A})(\varepsilon - \alpha_{\rm B}) = 0$, and two solutions become $\alpha_{\rm A}$ and $\alpha_{\rm B}$, which results in no changes from the original orbital energies and orbital functions. Such simple solutions of ($\varepsilon_{\rm A} = \alpha_{\rm A}$, $\phi_{\rm A} = \chi_{\rm A}$) and ($\varepsilon_{\rm B} = \alpha_{\rm B}$, $\phi_{\rm B} = \chi_{\rm B}$) satisfy the eq.(5.18), $\hat{h}\phi_{\rm A} = \varepsilon_{\rm A}\phi_{\rm A}$ and $\hat{h}\phi_{\rm B} = \varepsilon_{\rm B}\phi_{\rm B}$, to give no orbital mixing. It follows that for $\beta = 0$ there are no interactions between the orbitals to keep the orbital functions unchanged in their original forms.

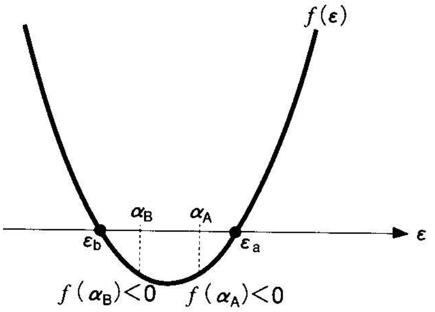
Next, let us consider variations of orbital energies for $\beta \neq 0$. We may use a convenience to set $\alpha_{\rm A} \geq \alpha_{\rm B}$ without losing the generality. Calculations of $f(\alpha_{\rm A})$ and $f(\alpha_{\rm B})$ lead to the following equation.

$$f(\alpha_{\rm A}) = f(\alpha_{\rm B}) = -\beta^2 < 0 \tag{5.31}$$

Since $f(\varepsilon)$ is a quadratic function with a concave in a parabolic form, there exist two solutions of $\varepsilon_{\rm a}$, $\varepsilon_{\rm b}(\varepsilon_{\rm a} \geq \varepsilon_{\rm b})$, and we obtain the following inequality.

$$\varepsilon_{\rm a} > \alpha_{\rm A} \geq \alpha_{\rm B} > \varepsilon_{\rm b} \tag{5.32}$$

As verified later, the higher orbital energy ε_a corresponds to the energy level of the antibonding orbital, and the lower one ε_b corresponds to that of the bonding orbital.



These results can be summarized as the rules for orbital-energy changes.

Rules for orbital-energy changes

For a non-vanishing resonance integral ($\beta \neq 0$) orbital interactions give new orbital energies ($\varepsilon_{\rm a} > \varepsilon_{\rm b}$) which are different from the initial energies; the higher one (ε_a) is higher than the higher initial orbital energy of α_A, and the lower one (ε_b) is lower than the lower initial orbital energy of α_B.

Such changes of orbital energies are illustrated in Fig.5.7 for easy understanding; A and B at a long distance in the initial state are placed on both ends, while the new state for A and B in a short distance is shown in the middle of the figure.

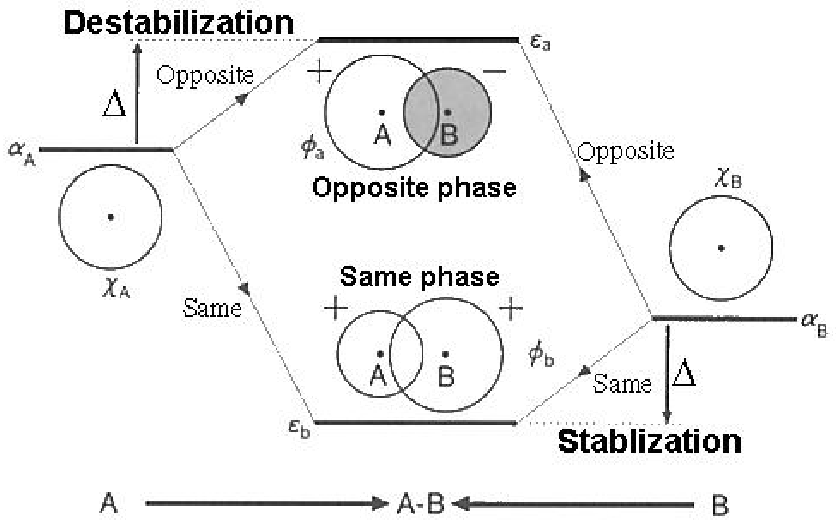


Figure 5.7: Orbital interactions

Amounts of the stabilization energy of $(\alpha_B - \varepsilon_b)$ and the destabilization energy of $(\varepsilon_a - \alpha_A)$ are found to be the same and are denoted as Δ.

$$\alpha_B - \varepsilon_b = \varepsilon_a - \alpha_A = \Delta = \frac{\sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2} - (\alpha_A - \alpha_B)}{2} \tag{5.33}$$

This quantity Δ is an index indicating how much extent the stabilization and the destabilization occur by interactions between orbitals.

In order to see what governs the extent of stabilization and destabilization Δ, let us study the possible range of Δ. Noting the convention of $\alpha_A \geq \alpha_B$, introducing a quantity $t\,(t \geq 0)$ defined as $t = (\alpha_A - \alpha_B)/2|\beta|$, and further defining a function $F(t) = \sqrt{t^2+1} - t$, we obtain

$$\Delta = F(t)|\beta| \tag{5.34}$$

The function $F(t)$ decreases from $F(0) = 1$ monotonously with the increase of t for $t \geq 0$ and approaches 0 in the limit of $t \to \infty$, which results in $1 \geq F(t) > 0$. Thus we obtain the following inequalities.

$$|\beta| \geq \Delta > 0 \tag{5.35}$$

The equality in the left holds for $t = 0$, that is $\alpha_A = \alpha_B$, which gives the maximum of Δ. The magnitude of Δ is governed by the following two factors.

(1) **The principle of the energy difference**
One of the factors is the energy difference between α_A and α_B. The smaller it becomes, the smaller t becomes to yield the larger $F(t)$ resulting in the larger Δ. This indicates that the smaller energy difference between orbitals leads to the larger interactions between these orbitals. Conversely, a very large energy difference between orbitals such as one of valence orbitals and one of the inner shell orbitals leads to negligibly small interactions. Such an effect by the energy difference of $|\alpha_A - \alpha_B|$ on orbital interactions is called the principle of the energy difference.

(2) **The principle of the overlap**
Another factor is $|\beta|$. When it becomes large, t becomes small to lead to a large $F(t)$. In eq.(5.34), Δ is expressed as a product of $F(t)$ and $|\beta|$. Thus, the larger $|\beta|$, the larger Δ. Since $|\beta|$ can be considered to be proportional to $|S|$, the larger the overlap between orbitals becomes, the larger interactions between orbitals become. Conversely, the smaller the overlap as well as $|\beta|$, the smaller the orbital interactions. Such an effect of $|\beta|$ or $|S|$ on the extent of orbital interactions is called the principle of the overlap.

Next, let us consider forms of new orbitals produced by orbital interactions. From simultaneous equations of eq.(5.23), the following equation is obtained for C_{A} and C_{B}.

$$\frac{C_{\mathrm{B}}}{C_{\mathrm{A}}} = \frac{\varepsilon - \alpha_{\mathrm{A}}}{\beta} \tag{5.36}$$

Substituting ε_{a} or ε_{b} into this equation and using $t = (\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})/2|\beta|$ $(t \geq 0)$ again, we obtain the following equation.

$$\frac{C_{\mathrm{B}}}{C_{\mathrm{A}}} = -\frac{|\beta|}{\beta}(t \pm \sqrt{t^2+1}) \tag{5.37}$$

The plus symbol of ± in this formula gives $({C_{\mathrm{B}}}^{\mathrm{b}}/{C_{\mathrm{A}}}^{\mathrm{b}})$ for the bonding orbital $(\phi_{\mathrm{b}}, \varepsilon_{\mathrm{b}})$, and the minus one gives $({C_{\mathrm{B}}}^{\mathrm{a}}/{C_{\mathrm{A}}}^{\mathrm{a}})$ for the antibonding orbital $(\phi_{\mathrm{a}}, \varepsilon_{\mathrm{a}})$.

Since for the bonding orbital $t + \sqrt{t^2+1} \geq 1$ at any value of $t \geq 0$, we obtain the following inequalities.

$$|{C_{\mathrm{B}}}^{\mathrm{b}}| \geq |{C_{\mathrm{A}}}^{\mathrm{b}}| \tag{5.38}$$

$${C_{\mathrm{A}}}^{\mathrm{b}}{C_{\mathrm{B}}}^{\mathrm{b}}\beta < 0 \tag{5.39}$$

Equation (5.38) shows that in the bonding orbital $\phi_{\mathrm{b}} = {C_{\mathrm{A}}}^{\mathrm{b}}\chi_{\mathrm{A}} + {C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{B}}$, a contribution of ${C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{B}}$ from the lower atomic orbital χ_{B} is dominant. Since the lower orbital is the more electronegative, electrons in the bonding orbital are displaced on the more electronegative atom. This explains the electric polarization associated with the formation of a chemical bond.

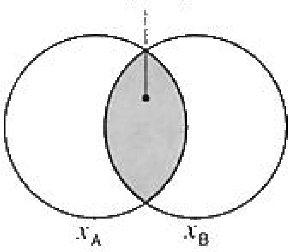
The equation (5.39) shows the constraint of the relative phases (signs) between the two orbital components. Using the relation of the opposite signs between the overlap integral S and the resonance integral β, we obtain

$${C_{\mathrm{A}}}^{\mathrm{b}}{C_{\mathrm{B}}}^{\mathrm{b}}S_{\mathrm{AB}} \Longleftrightarrow -{C_{\mathrm{A}}}^{\mathrm{b}}{C_{\mathrm{B}}}^{\mathrm{b}}\beta > 0 \qquad (\Longleftrightarrow \text{ indicates the opposite signs to each other})$$

Here, we should note that the sign of the overlap integral $S_{\mathrm{AB}} = \int \chi_{\mathrm{A}}\chi_{\mathrm{B}}\mathrm{d}\boldsymbol{r}$ is equal to the sign of $\chi_{\mathrm{A}}\chi_{\mathrm{B}}$ in the geometrical regions (the overlap regions) where absolute values for $\chi_{\mathrm{A}}\chi_{\mathrm{B}}$ become large. Thus, we obtain the following inequality.

$$({C_{\mathrm{A}}}^{\mathrm{b}}\chi_{\mathrm{A}})({C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{B}}) = {C_{\mathrm{A}}}^{\mathrm{b}}{C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{A}}\chi_{\mathrm{B}} \Longleftrightarrow {C_{\mathrm{A}}}^{\mathrm{b}}{C_{\mathrm{B}}}^{\mathrm{b}}S_{\mathrm{AB}} > 0 \tag{5.40}$$

This result shows that in the bonding orbital $\phi_{\mathrm{b}} = {C_{\mathrm{A}}}^{\mathrm{b}}\chi_{\mathrm{A}} + {C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{B}}$ the first component ${C_{\mathrm{A}}}^{\mathrm{b}}\chi_{\mathrm{A}}$ and the second component ${C_{\mathrm{B}}}^{\mathrm{b}}\chi_{\mathrm{B}}$ have the same sign (phase) in the overlap regions of χ_{A} and χ_{B}. Thus, electrons in the bonding orbital brings the positive interference strengthening the electron waves with the same sign, and hence electron densities in the overlap regions are increased. It follows that augmented electron densities between the nuclei result in binding forces acting on the two nuclei.



In the case of the antibonding orbital, always $1 \geq \sqrt{t^2+1} - t > 0$ for $t \geq 0$. Thus, we obtain.

$$|{C_{\mathrm{A}}}^{\mathrm{a}}| \geq |{C_{\mathrm{B}}}^{\mathrm{a}}| \tag{5.41}$$

$${C_{\mathrm{A}}}^{\mathrm{a}}{C_{\mathrm{B}}}^{\mathrm{a}}\beta > 0 \tag{5.42}$$

Equation (5.41) shows that in the antibonding orbital $\phi_\mathrm{a} = C_\mathrm{A}{}^\mathrm{a}\chi_\mathrm{A} + C_\mathrm{B}{}^\mathrm{a}\chi_\mathrm{B}$, the contribution from the higher atomic orbital χ_A is dominant. Using eq.(5.42), an analogous discussion with the case of the bonding orbital leads to the following inequality.

$$(C_\mathrm{A}{}^\mathrm{a}\chi_\mathrm{A})(C_\mathrm{B}{}^\mathrm{a}\chi_\mathrm{B}) \Longleftrightarrow C_\mathrm{A}{}^\mathrm{a}C_\mathrm{B}{}^\mathrm{a}S_\mathrm{AB} \Longleftrightarrow -C_\mathrm{A}{}^\mathrm{a}C_\mathrm{B}{}^\mathrm{a}\beta < 0 \tag{5.43}$$

This indicates that in the antibonding orbital $\phi_\mathrm{a} = C_\mathrm{A}{}^\mathrm{a}\chi_\mathrm{A} + C_\mathrm{B}{}^\mathrm{a}\chi_\mathrm{B}$ the first component $C_\mathrm{A}{}^\mathrm{a}\chi_\mathrm{A}$ and the second component $C_\mathrm{B}{}^\mathrm{a}\chi_\mathrm{B}$ have the opposite signs (phases) in the overlap regions of χ_A and χ_B. Thus, electrons in the antibonding orbital brings the negative interference canceling out the electron waves with the opposite signs, and hence electron densities in the overlap regions are decreased. It follows that the decreased electron densities between the nuclei result in antibinding forces repelling two nuclei each other.

Next, let us consider the extent of orbital mixing. When one of the coefficients is zero, the extent of mixing is minimum. Thus, we introduce the following quantity μ representing the extent of mixing.

$$\mu = \left|\frac{C_\mathrm{A}{}^\mathrm{b}}{C_\mathrm{B}{}^\mathrm{b}}\right| = \left|\frac{C_\mathrm{B}{}^\mathrm{a}}{C_\mathrm{A}{}^\mathrm{a}}\right| = \sqrt{t^2+1} - t \tag{5.44}$$

The right side equals to $F(t)$ introduced before, which satisfies $1 \geq F(t) > 0$ for $t = (\alpha_\mathrm{A} - \alpha_\mathrm{B})/2|\beta| \geq 0$. Thus, μ increases with the decrease of t. It follows that the extent of orbital mixing is governed by the principle of the energy difference and the principle of the overlap, as in the case of the extent of orbital energy changes.

The mechanisms producing new orbitals from mixing of two orbitals due to orbital interactions are summarized as rules of orbital mixing as follows.

> **Rules for orbital mixing** When a pair of orbitals χ_A and χ_B $(\alpha_\mathrm{A} \geq \alpha_\mathrm{B})$ having mutual overlap (the resonance integral is not vanishing) interact with each other, a pair of new orbitals ϕ_a and ϕ_b $(\varepsilon_\mathrm{a} > \alpha_\mathrm{A} \geq \alpha_\mathrm{B} > \varepsilon_\mathrm{b})$ are produced (cf. Fig.5.7). Among them, the bonding orbital ϕ_b is made mainly of the lower orbital χ_B together with a small contribution of the higher orbital χ_A in the same phase. On the other hand, the antibonding orbital ϕ_a is made mainly of the higher orbital χ_A together with a small contribution of the lower orbital χ_B in the opposite phase. The extent of variation from the form of the main component, namely the extent of mixing, is governed by the principle of the energy difference and the principle of the overlap. Especially for $\alpha_\mathrm{A} = \alpha_\mathrm{B}$ (a case with no energy difference), mixing of the two components are equally weighted.

Summarizing the above mentioned rules for orbital-energy changes, rules for orbital mixing, the principle of the energy difference, and the principle of the overlap, we denote these rules and principles as the principles of orbital interactions.

[The principles of orbital interactions]

(1) Without orbital interactions $(\beta = 0)$, the orbital energy and form remain unchanged.

(2) With nonvanishing orbital interactions $(\beta \neq 0)$ (cf. Fig.5.7), both the orbital energy and the form are changed. A bonding orbital is formed, which is stabilized than the lower (relatively the more negative) initial orbital χ_B among a pair of orbitals χ_A and $\chi_\mathrm{B}(\alpha_\mathrm{A} \geq \alpha_\mathrm{B})$. On the other hand, an antibonding orbital is formed, which is destabilized than the higher (relatively the more positive) initial orbital. The extent of mixing is such that the lower orbital is the main component for the bonding orbital, whereas for the antibonding orbital the main component is the higher one. If the energy difference between orbitals is vanishing $(\alpha_\mathrm{A} = \alpha_\mathrm{B})$, two components are equally weighted.

(3) The extent of orbital-energy changes and orbital mixing is governed by the energy difference and the overlap; they become larger for the smaller energy difference and the large overlap, and conversely they become smaller for the larger energy difference and the smaller overlap.

Example 5.1 (The two to one orbital interactions)

Two orbitals of χ_A and χ_B of one species having orbital energies of α_A and $\alpha_B(\alpha_A > \alpha_B)$ are mutually orthogonal and interact with another orbital χ_C of the other species (denoted as the partner) having an orbital energy of α_C. Respective resonance energies are β_{AC} and β_{BC} ($\beta_{\mathrm{AC}} \neq 0$, $\beta_{\mathrm{BC}} \neq 0$). Answer the following questions.

(1) Derive the following inequalities for three orbitals produced by interactions, which are denoted as $\varepsilon_{\mathrm{a}}, \varepsilon_{\mathrm{m}}, \varepsilon_{\mathrm{b}}$ in the order of the higher energies.

$$\varepsilon_{\mathrm{a}} > \alpha_{\mathrm{A}} > \varepsilon_{\mathrm{m}} > \alpha_{\mathrm{B}} > \varepsilon_{\mathrm{b}}$$

(2) Orbitals corresponding to the orbital energies of $\varepsilon_{\mathrm{a}}, \varepsilon_{\mathrm{m}}, \varepsilon_{\mathrm{b}}$ are denoted as $\phi_{\mathrm{a}}, \phi_{\mathrm{m}}, \phi_{\mathrm{b}}$. Explain relative phases of the atomic orbital components $\chi_{\mathrm{A}}, \chi_{\mathrm{B}}, \chi_{\mathrm{C}}$ in the new orbitals qualitatively, based on the principles of orbital interactions.

(Solution)

(1) Because of the mutual orthogonality between χ_A and χ_B, $S_{\mathrm{AB}} = 0$ and thus the resonance integral is vanishing ($\beta_{\mathrm{AB}} = 0$). Considering the given condition, we obtain the secular equation for the simple Hückel method.

$$\begin{vmatrix} \alpha_{\mathrm{A}} - \varepsilon & 0 & \beta_{\mathrm{AC}} \\ 0 & \alpha_{\mathrm{B}} - \varepsilon & \beta_{\mathrm{BC}} \\ \beta_{\mathrm{AC}} & \beta_{\mathrm{BC}} & \alpha_{\mathrm{C}} - \varepsilon \end{vmatrix} = 0$$

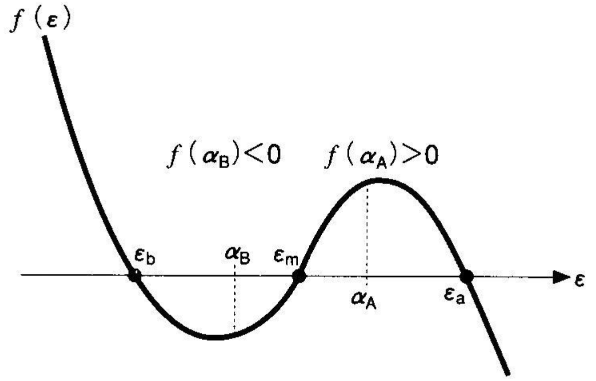
Expanding this equation and denoting it as $f(\varepsilon)$,

$$f(\varepsilon) = (\alpha_{\mathrm{A}} - \varepsilon)(\alpha_{\mathrm{B}} - \varepsilon)(\alpha_{\mathrm{C}} - \varepsilon) - {\beta_{\mathrm{AC}}}^2(\alpha_{\mathrm{B}} - \varepsilon) - {\beta_{\mathrm{BC}}}^2(\alpha_{\mathrm{A}} - \varepsilon)$$

This is a cubic function of ε including $-\varepsilon^3$. In order to know the regions giving solutions, we look up signs of $f(\alpha_{\mathrm{A}})$ and $f(\alpha_{\mathrm{B}})$.

$$f(\alpha_{\mathrm{A}}) = -{\beta_{\mathrm{AC}}}^2(\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}}) > 0, \quad f(\alpha_{\mathrm{B}}) = -{\beta_{\mathrm{BC}}}^2(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}) < 0$$

Thus, the equation $f(\varepsilon) = 0$ has different three real solutions $(\varepsilon_{\mathrm{a}}, \varepsilon_{\mathrm{m}}, \varepsilon_{\mathrm{b}})$, as can be seen from a figure below. Since $\alpha_{\mathrm{A}} > \alpha_{\mathrm{B}}$, ε_{a} is in the region of $\varepsilon > \alpha_{\mathrm{A}}$, $(\varepsilon_{\mathrm{m}})$ is in the region of $\alpha_{\mathrm{A}} > \varepsilon > \alpha_{\mathrm{B}}$, and $(\varepsilon_{\mathrm{b}})$ is in the regions of $\alpha_{\mathrm{B}} > \varepsilon$. It follows that $\varepsilon_{\mathrm{a}} > \alpha_{\mathrm{A}} > \varepsilon_{\mathrm{m}} > \alpha_{\mathrm{B}} > \varepsilon_{\mathrm{b}}$.

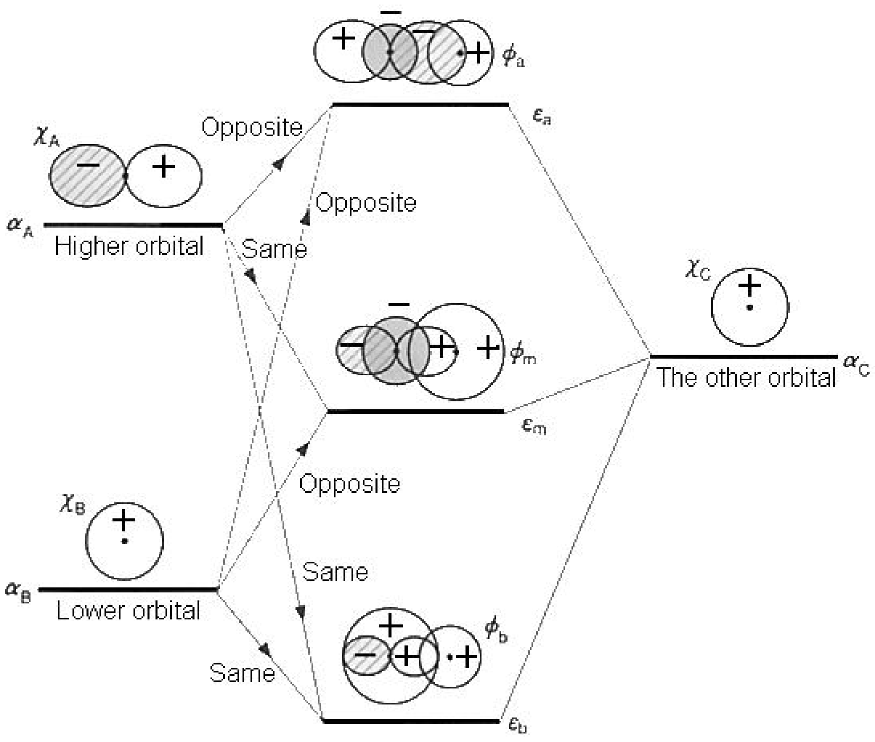


(2) According to the principle of orbital interactions (cf. Fig.5.7), the contribution of an orbital lower than the new orbital is in the opposite phase with respect to the other orbital along an upward arrow, and the contribution of an orbital higher than the new orbital is in the same phase with respect to the other orbital along a downward arrow. These characteristics can be applied to relative phases of the components in new three orbitals (from the highest, $\phi_{\mathrm{a}}, \phi_{\mathrm{m}}, \phi_{\mathrm{b}}$), which are produced by interactions of the higher χ_{A} and the lower χ_{B} orbitals with the orbital χ_{C} of the partner as follows.

$\phi_{\rm a}$: With respect to $\chi_{\rm C}$ of the partner, both $\chi_{\rm A}, \chi_{\rm B}$ interact upward in the opposite phase to yield a highly antibonding orbital.

$\phi_{\rm m}$: With respect to $\chi_{\rm C}$ of the partner, the higher $\chi_{\rm A}$ interacts downward in the same phase, and the lower $\chi_{\rm B}$ interacts upward in the opposite phase, to produce a weakly bonding or antibonding orbital depending on the magnitude of interactions with $\chi_{\rm C}$.

$\phi_{\rm b}$: With respect to $\chi_{\rm C}$ of the partner, both $\chi_{\rm A}, \chi_{\rm B}$ interact downward in the same phase to give a highly bonding orbital.



5.4 AH type and AH$_2$ type molecules

The principle of orbital interactions studied in the previous section can be used to deducing form and energy levels of molecular orbitals qualitatively. Let us first summarize procedures using the principle of orbital interactions. Then we will apply it to simple hydride molecules and study mechanisms for production of the electric polarization in chemical bonds and mechanisms for determination of the bond angles.

5.4.1 Procedures using the principle of orbital interactions

Let us summarize procedures using the principle of orbital interactions for various problems. For readers who want to study from concrete examples, the next section for AH type molecules may be studied without reading this section, and if necessary, he may come back to refer this section.

[1] Consider electronic configurations for each system before interactions. Show energy levels to be considered in both sides separately. Usually energy levels from inner-shell electrons to valence electrons should be considered. Energy levels much higher than valence electron levels need not be considered from the beginning, since interactions with valence electrons can be neglected due to the principle of the energy difference. Treatments of inner-shell electrons are rather simple, and thus inner-shell electrons can be disregarded except for considering the total number of electrons.

[2] Using rules for orbital-energy changes in the principle of orbital interactions, deduce new energy levels, and show them in the intermediate space between the initial levels in both sides. Consider strengths of the interactions based on the principle of the energy difference and the principle of the overlap. Levels with no appreciable interactions should be shown at the same heights as before, since no level shifts are expected for them. Bonding orbitals should be stabilized to the lower energy, and antibonding orbitals should be unstabilized to the higher energy.

[3] When orbital forms are needed to be considered, deduce forms of new orbitals using the rules for orbital mixing in the principle of orbital interactions. For graphical illustrations, show an s orbital as a circle and a p orbital as a pair of ellipses in the figure of 8. Contributions of the components can be expressed by the size of circles and ellipses. Phases can be indicated by plus and minus symbols, or the signs can be specified by two ways of drawings, such as solid and dashed lines, thick and thin lines, or white and black paintings. The phase for the first component may be arbitrarily chosen, though the relative phases of other components should be represented in accordance with the first choice.

[4] Build up the new electronic configuration by placing electrons from both sides into new orbitals according to the Pauli principle. In the case of degenerate levels, Hund's rule should also be considered. Electrons should be shown as $\uparrow$ or $\downarrow$ in the energy levels in order to represent their spins. The choice of the spin for the first unpaired electron may be arbitrary. If spins can be disregarded, $\circ$ or $\bullet$ may be placed in the level diagram in place of the arrows.

5.4.2 AH type molecules

Chemical bonds between different atoms have an electric polarization. In order to discuss the electric polarization of bonds in connection with the bond formation, let us consider a H_2 molecule followed by LiH and HF molecules as typical examples of polar molecules.

H_2 molecule

Show energy levels of two H atoms in the right and the left sides separately. In this case, the electronic configuration of a H atom includes only one electron in 1s orbital, and thus only 1s energy level should be shown in the left and the right sides as in Fig.5.8. The higher energy levels such as 2s orbital need not be shown, since interactions of the 1s orbital with other orbitals in the higher levels can be neglected on account of the principle of the energy difference.

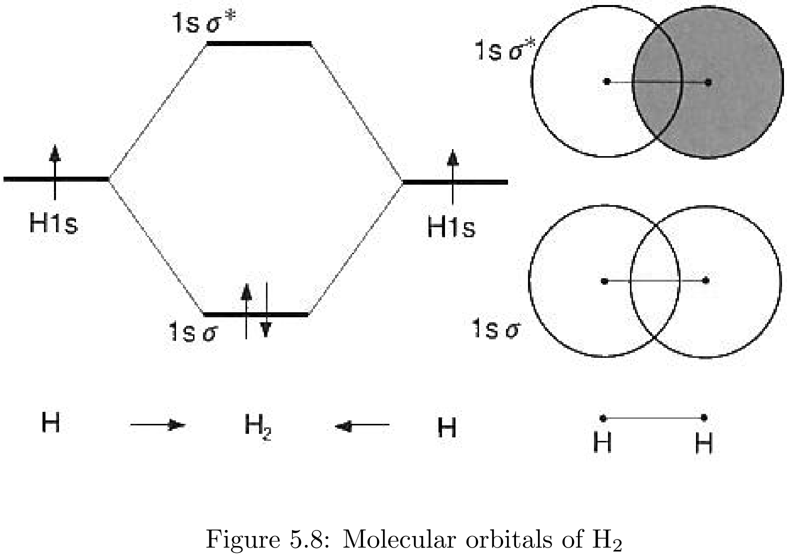


Figure 5.8: Molecular orbitals of H_2

Use rules for orbital-energy changes to deduce new energy levels. In this case, interactions between two 1s orbitals of H atoms due to a σ type overlap lead to a bonding orbital of $1s\sigma$ and an antibonding orbital of $1s\sigma*$. The bonding orbital is stabilized to the lower energy with respect to the 1s energy level of a H atom, and the antibonding orbital becomes more unstable to the higher energy.

Use rules for orbital mixing to deduce forms of new orbitals. Interactions between equivalent 1s orbitals lead to a couple of orbitals made of one to one mixing of two components. The bonding orbital has the same phase, while the antibonding orbital has the opposite phase.

In the final step, two electrons from the left and the right H atoms should be placed in the new energy levels from the lower one. In this case, the bonding 1sσ orbital accepts an electron pair, and they produce the stabilization of two bonding electrons. Since the 1sσ orbital is composed of even contributions of the left and the right H1s orbitals, no electric polarization appear in the bond formed between the H atoms.

The bond in a H_2 molecule is formed by augmented electron densities between two nuclei due to a pair of electrons in a molecular orbital, and it follows that this bond can be considered as a prototype of a covalent bond or an electron-pair bond.

LiH molecule

Show energy levels for both atoms in the right and the left sides separately. Only 1s orbital may be considered for a H atom as in the case of a H_2 molecule. For a Li atom with the electronic configuration $(1s^2)(2p)^1$, only 1s and 2s electrons need to be considered. The Li1s orbital is an inner-shell orbital, whose ionization energy is much larger than those for valence orbitals. On the other hand, the energy level for the Li2s orbital is higher than that for the H1s orbital. This situation can be understood from the fact that the ionization energy of a Li atom is much smaller than that of a H atom, because the electronegativity of a Li atom is much smaller than a H atom. Since the Li2p levels are not so much higher than the 2s levels, the Li2p levels had better be considered as well. However, we omit contributions from the Li2p orbitals, because the same conclusion will be obtained for the chemical bond of a LiH molecule. The higher levels such as Li3s and H2s levels need not be considered, since they are considerably higher than the valence electron levels.

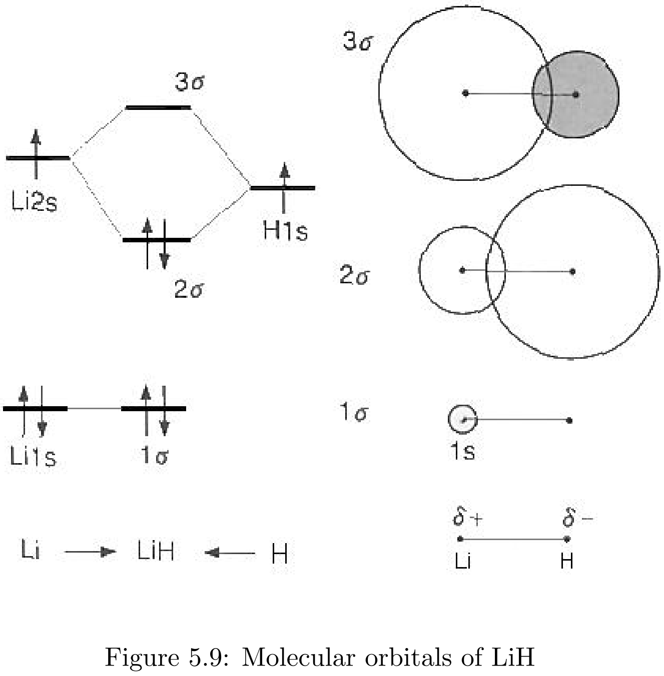


Figure 5.9: Molecular orbitals of LiH

Based on the principle of the energy difference, the Li1s level, which is much lower than the H1s level, becomes the most stable level with its orbital form unchanged from the shape of the Li1s orbital. This new orbital is the most stable orbital classified as a σ orbital, and thus it is called 1σ orbital. Next, one to one interactions between Li2s and H1s orbitals lead to the 2σ orbital, which is more stable than the lower H1s orbital, and the 3σ orbital, which is more unstable than the higher Li2s orbital. The 2σ orbital is a bonding orbital, which is made mainly of the lower H1s orbital together with a small contribution of the higher Li2s orbital in the same phase. Valence electrons, one from Li and another from H, become an electron pair in the 2σ orbital for LiH. The dominant component of this electron pair is H1s, and it follows that the electron distribution is concentrated on the H atom to yield a strong polarization. Thus a LiH molecule is highly ionic with the negative charge on the H atom (cf. Table 5.1). This is consistent with the larger electronegativity of a H atom in comparison with a Li atom. The 3σ orbital is an antibonding orbital, which is made mainly of the higher Li2s orbital.

Table 5.1: Electric polarization for diatomic molecules

$A^{\delta+}B^{\delta-}$	Electric dipole moment $\lvert\mu\rvert(10^{-30}\,\mathrm{C\,m})$	Dissociation energy D_0(eV)	Equilibrium internuclear distance R(pm)
H_2	0.0	4.4781	74.144
HF	6.1	5.84	91.71
HCl	3.6	4.43	127.46
HBr	2.7	3.75	141.4
HI	1.4	3.06	160.9
LiH	19.4	2.5	159.6
LiF	21.0	6.6	156.4
NaF	27.2	5.3	192.6
NaCl	30.0	3.58	236.1

HF molecule

Electron configurations of the atoms are $H(1s)^1$ and $F(1s)^2(2s)^2(2p)^5$, and only orbitals contained in these configurations may be considered (Fig. 5.10).

F1s is an innershell level, and its energy is very low. Since a F atom is more electronegative and has larger ionization energy than a H atom, F2p level is lower than H1s level. F2s level is further lower than F2p level. The innershell F1s orbital may be treated to have no interaction with H1s due to the principle of the energy difference, and thus it becomes the most stable molecular orbital 1σ in a HF molecule, whose shape is nearly the same as the shape of a F1s atomic orbital. Interactions among valence orbitals are one to four interactions between H1s and $\mathrm{F2s}, \mathrm{F2p}_x, \mathrm{F2p}_y, \mathrm{F2p}_z$. On account of the symmetry for overlaps, these interactions are decomposed into the simpler ones.

H1s orbital is symmetric with respect to an arbitrary plane including the bonding axis (the axis connecting H and F atoms is taken as z axis), and thus H1s orbital does not interact with $\mathrm{F2p}_x$ and $\mathrm{F2p}_y$ orbitals having directions perpendicular to z axis and pararell with x and y axes. It follows that $\mathrm{F2p}_x$ and $\mathrm{F2p}_y$ levels become degenerate 1π levels for molecular orbitals of a HF molecule without modification from the atomic orbitals. These orbitals retain the shapes of the F2p atomic obitals having perpencicular directions to the bonding axis. After all, the remaining F2s and $\mathrm{F2p}_z$ orbitals undergo two to one interactions with H1s to yield 2σ orbital, which is a bonding orbital having a dominant component of F2s orbital in the same phase with the H1s component and morestable than the lower F2s level. To this bonding orbital $\mathrm{F2p}_z$ orbital gives a samll contribution in the same phase with the H1s component to strengthen the bonding character.

Since the contribution of H1s to 2σ is small, 2σ orbital has a strong electric polarization with the negative side on the F atom. 3σ level appears between the lower F2s and the higher $\mathrm{F2p}_z$ levels. 3σ orbital contains an out-of-phase contribution of the lower F2s orbital from the downward to the upward and an in-phase contribution of the higher $\mathrm{F2p}_z$ orbital from the upward to the downward with respect to H1s, and the main contribution is $\mathrm{F2p}_z$ with the nearer energy level to result in a weakly bonding orbital having a negative electric polarization on the F atom. 4σ level is higher than the higher $\mathrm{F2p}_z$ and in this case much higher than H1s. 4σ orbital is composed of out-of-phase contributions of both the higher $\mathrm{F2p}_z$ and the lower F2s with respect to H1s, which results in a strongly antibonding orbital having H1s orbitals as the main component.

Ten electrons, one from H and nine from F, are accommodated in the energy levels form the lower ones as electron pairs to give an electron configuration of $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$, as can be seen from Fig.5.10. 1σ orbital is an inner shell orbital, and hence it does not contribute to the

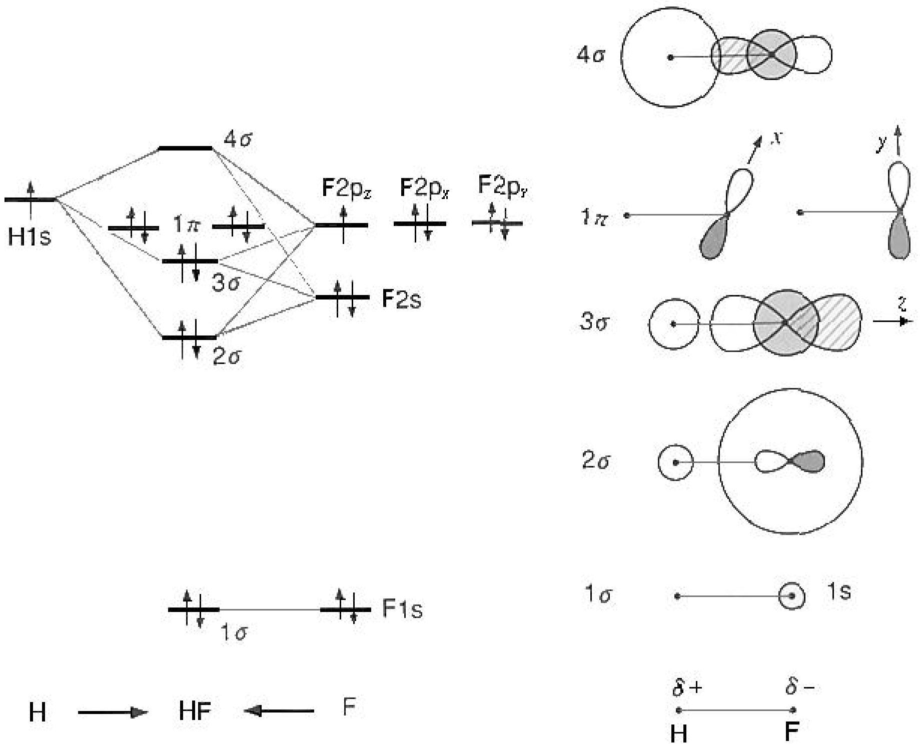


Figure 5.10: Molecular orbitals of HF

bonding force. The degenerate 1π orbitals almost purely composed of atomic F2p orbitals with a pair of electrons are nonbonding orbitals, and these may be considered as unshared electron pairs without bonding characters. 2σ and 3σ orbitals show bonding characters, and both orbitals have a negative electric polarization on the F atom. Thus, a HF molecule has an electric polarization with the negative side on the F atom (Fig.5.1).

Although both HF and LiH molecules have two electrons in a bonding orbital producing an enhancement of electron densities in the bonding regions between the two nuclei to result in a contribution of the electron-pair bond, the bond is highly polarized as an ionic bond in a NaCl molecule. In such a marginal case, the electron-pair bond and the ionic bond cannot clearly be distinguished from each other.

5.4.3 AH$_2$ type molecules

In an AH$_2$ type molecule such as H$_2$O, the bond angle is an important parameter for the molecular structure in addition to the bond length. Here, we will study composition of molecular orbitals for AH$_2$ type molecules from BeH$_2$ to H$_2$O and elucidate the mechanism for bond angles. Now, let us construct molecular orbitals of an AH$_2$ type molecule according to the following procedures.

[1] Step 1 in Fig.5.11

At first, advance a H atom toward another H atom up to a distance (ca.1.4 Å) approximately two times larger than the normal bond length of a H$_2$ molecule. This process produces formally a bonding 1sσ level and an antibonding 1sσ^* level, though the level shifts for stabilization and destabilization are small, because of a very small overlap due to the long distance. Forms of the produced orbitals are in-phase and out-of-phase combinations of H1s components, and these orbitals for a pseudo-hydrogen molecule are denoted as a bonding ϕ_b orbital and an antibonding ϕ_a orbital, respectively.

[2] Step 2 in Fig.5.11

Next, introduce the A atom (Be $\sim$ O atoms) along a line bisecting the bond of the pseudo-hydrogen molecule (denoted as the z-axis) from the infinity toward the center of the bond up to a

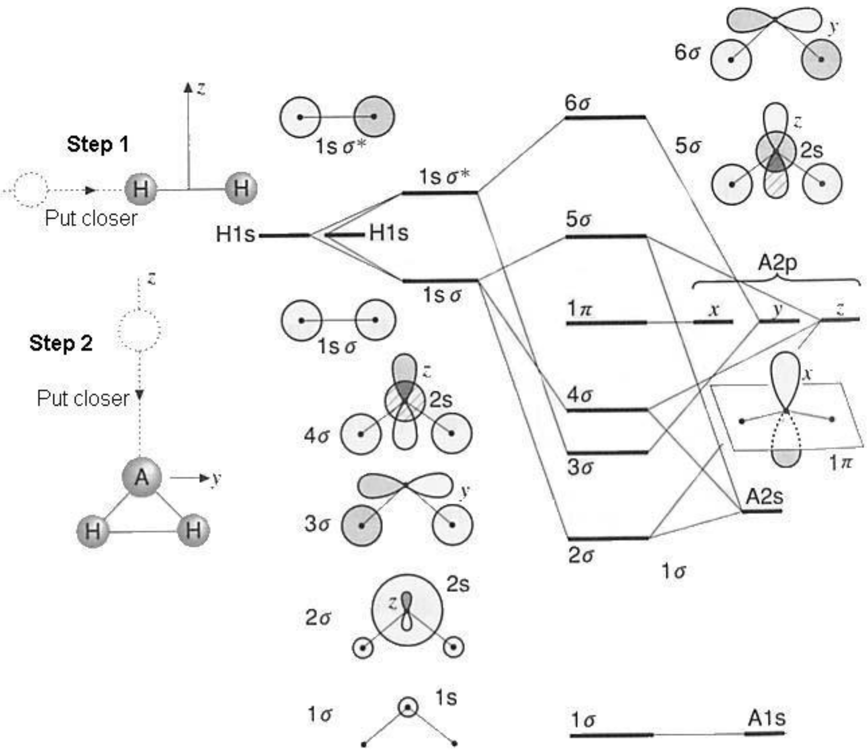


Figure 5.11: Molecular orbitals of an AH_2 type molecule (the right angle form)

distance just producing a right angle form. Via this procedure, we can easily construct molecular orbitals for the right angle form of an AH_2 molecule based on interactions between orbitals of a pseudo-hydrogen molecule and 1s, 2s, 2p orbitals of the A atom.

[3] Step 3 in Fig.5.12

Finally, vary the bond angle θ from the right angle form to the linear form with keeping the bond length constant, and study changes in the energy level diagram.

Composition of a right angle form AH_2 molecule

Composition of molecular orbitals of the right angle form begins with a set of 1s, 2s, and $2p_x$, $2p_y$, $2p_z$ orbitals for energy levels of the A atom (Be∼O atoms). Among interactions of these orbitals with orbitals of the pseudo-hydrogen molecule, some interactions can be considered to be negligible. First of all, the 1s orbital of the A atom can be considered as a molecular orbital 1σ with the energy and orbital form almost unchanged, based on the principle of the energy difference, because the energy level of the inner shell 1s orbital of the A atom is very low.

Next, a direction bisecting the H–H with a right angle is taken as the z axis as shown in Fig.5.11, a direction parallel to H–H passing through the A atom is taken to be the y axis, and the normal direction to the y–z plane is taken as the x axis. $A2p_x$ orbital is an antisymmetric orbital with its sign alternating depending on the position up or down with respect to the y–z plane, whereas both of $1s\sigma$ and $1s\sigma^*$ orbitals are symmetric with respect to this plane. On account of the difference of the orbital symmetries, $A2p_x$ orbital does not interact with $1s\sigma$ and $1s\sigma^*$ orbitals, and then $A2p_x$ orbital becomes a molecular orbital 1π of the AH_2 molecule with nearly the same energy as the atomic energy level.

The remaining interactions are classified into two types, (1) interactions among symmetric orbitals with respect to the x–z plane, and (2) interactions among antisymmetric orbitals with respect to the x–z plane. For orbitals symmetric to the x–z plane, $1s\sigma$, A2s, and $A2p_z$ orbitals interact with each other, according to the two to one orbital interactions. The most stable level arising from these interactions is located under the level of A2s orbital. The corresponding molecular orbital 2σ includes A2s orbital as a main component in addition to a component of $A2p_z$, which mix with the central part of $1s\sigma$ between two H atoms in the same phase. This molecular

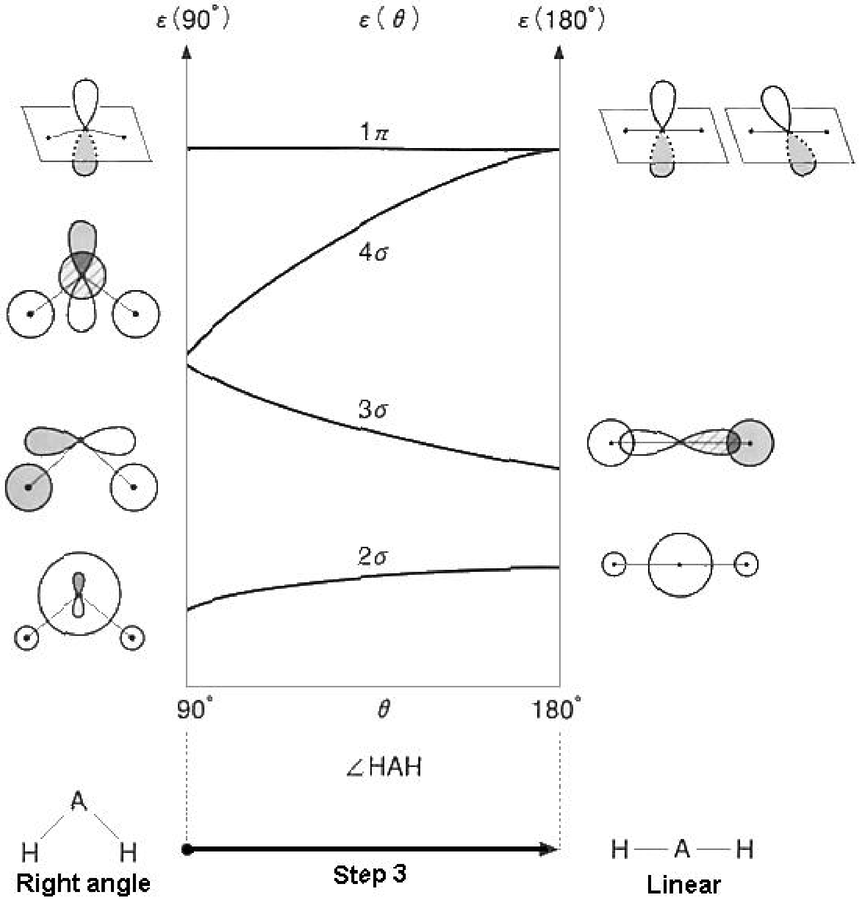


Figure 5.12: Molecular orbitals of an AH_2 type molecule as functions of the bond angle θ

orbital is a bonding orbital binding all three atoms mutually. The orbital energy level with an intermediate stability arising from the two to one orbital interactions appears between A2s and A2p$_z$ levels. This intermediate level corresponds to 4σ orbital. This orbital is composed of an inpahse component from upward to downward for the upper A2p$_z$ as well as an out-of-phase component from downward to upward for the lower A2s, and this orbital becomes antibonding between A and H and weakly bonding between H and H. As mentioned below, electrons in this orbital have an effect causing the angle ∠HAH smaller.

The most unstable level arising from the two to one orbital interactions becomes higher than 1sσ and A2p$_z$ levels. The corresponding orbital is composed of the upper A2p$_z$ and the lower A2s, which mix with 1sσ in out-of-phase at the central part of H and H, and thus this orbital becomes 5σ molecular orbital, which is antibonding between A and H and almost nonbonding between H and H.

Antisymmetric orbitals with respect to the x–z plane, 1sσ^* and A2p$_y$, interact with each other according to the one to one orbital interactions. The bonding orbital energy level arising from the interactions appears lower than both of 1sσ^* and A2p$_y$ orbital levels, and an in phase overlap of these two orbitals between A and H atoms gives a bonding type 3σ molecular orbital. The reason why this 3σ is lower than 4σ will be explained below.

The most important interactions are those between A2p and H1s orbitals. In the case of the right angle type, the direction of the p orbital component with respect to the AH bond is in the angle of 45° for both 3σ and 4σ orbitals. Therefore, overlaps between A2p and H1s orbitals are nearly the same for these cases. However, for 4σ orbital a contribution due to A2s, which overlaps with H1s in an opposite phase contrary to the case of A2p, gives a weaker bonding character in the AH region than 3σ. This results in the higher energy level of 4σ than that of 3σ.

The most unstable energy level is due to 6σ orbital, which is a strongly antibonding orbital composed of out-of-phase overlaps of 1sσ^* and A2p$_y$. This level is thus much higher than 1sσ^* and A2p$_y$ levels.

Changes from the right angle form to the linear form

Let us study changes of energy levels on going from the right angle form of the bond angle $\theta = 90°$ to the linear form of $\theta = 180°$. As for the lowest level, 1σ, which is almost entirely composed of A1s, is nearly independent of θ to give a horizontal line. Next, 2σ slightly goes up with the increase of θ, because the in-phase overlap between two H atoms decreases and also because the in-phase contribution of A2p$_z$ becomes vanishing at 180° by the symmetry. Since the overlap between H1s and A2p$_z$ increases on going to the linear form, 3σ becomes a strongly decreasing curve toward larger angles. On the other hand, 4σ goes upwards on going to the linear form, because the in-phase overlap between two H atoms as well as the in-phase contribution of A2p$_z$ decrease, and finally it becomes a moiety of the degenerate π orbitals in the linear form. Since 1π orbital of the right angle form does not interact with other orbitals by the symmetry even if the θ increases up to 180°, its energy level remains to be horizontal. Although the antibonding character of 5σ has a little change, 6σ becomes more strongly antibonding and increases its energy on going to the linear form.

A graphic representation of orbital energies as functions of bond angles such as Fig.5.12 is called the Walsh diagram. As discussed below, we may anticipate bond angles qualitatively based on the Walsh diagram.

5.4.4 The Walsh diagram and the bond angle

When an electron is inserted in a level descending with the angle in Fig.5.12, it has a function opening the bond angle, since the system tends to decrease its energy. Conversely, an electron in a level ascending with the angle has an opposite function closing the bond angle. A horizontal level has no effect on the bond angle, since no energy change with angles is expected irrespective of the occupation number of electrons. Based on these principles, we can discuss a relationship between the bond angle and the number of valence electrons for the AH_2 molecule, as can be seen in Table 5.2.

Table 5.2: Molecular structures of AH_2 type molecules and electron configurations. The bond angle and the bond lenglth for BeH_2 are theoretical values obtained from accurate calculations, since no experimental values are available. Other data are experimental values.

	Number of	Bond angle	Bond length	Electron configuration					
AH_2	valence electrons	$\theta°$	R_{AH}(pm)	1σ	2σ	3σ	4σ	1π	Spin state
BeH_2	4	180	133	↑↓	↑↓	↑↓			Singlet
BH_2	5	131	118	↑↓	↑↓	↑↓	↑		Doublet
CH_2	6	136	108	↑↓	↑↓	↑↓	↑	↑	Triplet
CH_2	6	102.4	111	↑↓	↑↓	↑↓	↑↓		Singlet
NH_2	7	103.4	102	↑↓	↑↓	↑↓	↑↓	↑	Doublet
H_2O	8	104.5	96	↑↓	↑↓	↑↓	↑↓	↑↓	Singlet

In BeH_2 there are four valence electrons, two from a Be atom and one from each H atom, and thus two levels up to 3σ are doubly occupied. Since 3σ level is steeply descending to the larger angles as can be seen from Fig.5.12, the linear form with a bond angle of 180° is most stable for BeH_2.

There are five valence electrons in BH_2, and one electron is added into 4σ level in comparison with BeH_2. Careful studies on the angular dependence of overlaps between p and s orbitals lead to a conclusion that the energy change between 90° and 180° for 4σ is twice as large as that for 3σ. It is thus expected that one electron in 4σ nearly cancels out effects of two electrons in 3σ. This indicates that the bond angle of BH_2 may be in the middle of 90° and 180°, which is in good agreement with the observed angle of 131°.

Methylene CH_2 has one more electron. Based on the right angle form, doubly occupied levels from 1σ to 4σ results in a singlet state of methylene, which is expected to have a much smaller bond angle than 131° in BH_2. The observed bond angle 102.4° for a singlet methylene is really much smaller than the bond angle of BH_2. On the other hand, in the linear structure, 4σ and 1π have the same energy to degenerate. Thus, Hund's rule suggests a triplet state in which one electron added as an unpaired electron into 1π has a parallel spin with that of an unpaired electron in 4σ. In a triplet methylene, levels from 1σ to 3σ are doubly occupied, whereas 4σ and 1π are singly occupied. An electron in the 1π level with a constant energy has no effect on the bond angle. It follows that the bond angle of a triplet methylene is expected to be nearly equal to the angle of BH_2 (131°), which agrees well with the really observed angle of 136° for a triplet methylene.

Further addition of an electron leads to an amino radical NH_2 with seven valence electrons. In this case, one electron addition to either methylene results in the same electron configuration, in which levels from 1σ to 4σ are doubly occupied, while an electron occupies 1π level. Since 1π electron is not related to bond angle changes, the bond angle of NH_2 is expected to be nearly the same as the bond angle for the singlet methylene (102.4°) with an electron configuration of fully occupied levels up to 4σ, which is in good agreement with the really observed bond angle of 103.4° for NH_2.

In the last H_2O of the series, all levels up to 1π are doubly occupied. As 1π electrons are not related to the bond angle, the bond angle of H_2O is expected to be similar to those for the singlet methylene (102.4°) and NH_2 (103.4°). This expectation agrees well with the observed angle of 104.5° for H_2O.

5.5 A_2 type molecules

There are many types of bonds with various strengths. It is interesting to study how such varieties of chemical bonds are formed. In this section, let us qualitatively construct molecular orbitals and their energy levels of A_2 type molecules and study electron configurations and bond orders.

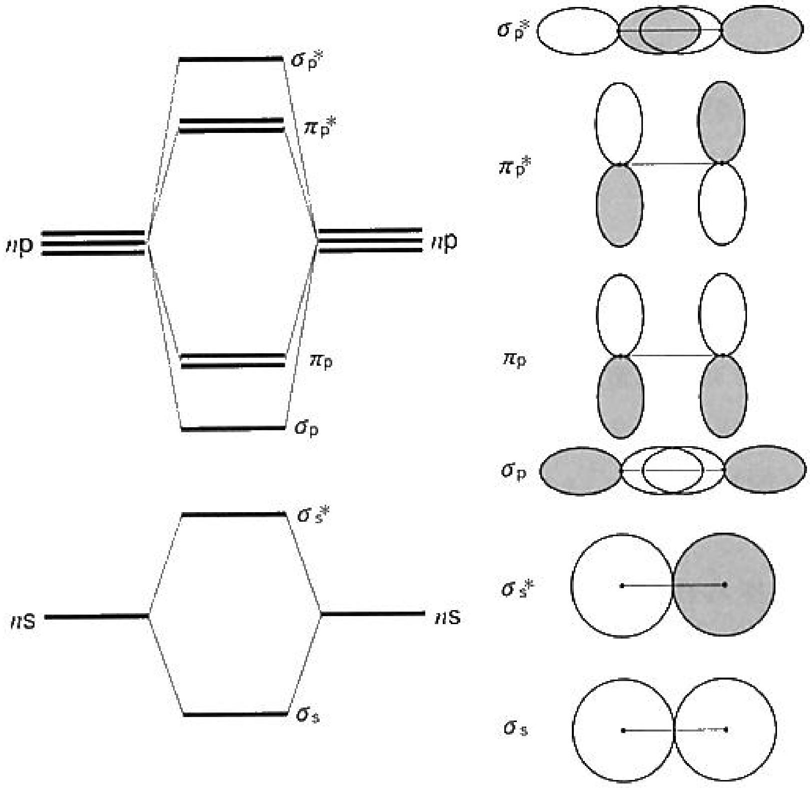


Figure 5.13: Orbital interactions in A_2 type molecules

A diatomic molecule A_2 composed of the same kind two A atoms is denoted as the homonuclear diatomic molecule. Since larger overlaps and smaller energy differences give stronger orbital interactions, construction of molecular orbitals of an A_2 molecule can be started with simple interactions between couples of the same type orbitals to obtain Fig.5.13. In-phase combinations yield bonding orbitals of σ_{s}, σ_{p}, π_{p}, and out-of-phase combinations give antibonding orbitals of $\sigma_{\mathrm{s}}*$, $\sigma_{\mathrm{p}}*$, $\pi_{\mathrm{p}}*$. π_{p} and $\pi_{\mathrm{p}}*$ orbitals are composed of π type overlaps of p orbitals with directions vertical to the bonding axis z. Thus, two types of p orbitals with directions of x and y axes lead to the two-fold degeneracy for π_{p} and $\pi_{\mathrm{p}}*$ orbitals.

In many electron atoms, orbital energy levels are in the order of $n\mathrm{s} < n\mathrm{p}$, and overlaps between orbitals are in the order of $\pi_{\mathrm{p}} < \sigma_{\mathrm{p}}$. It follows that when the energy difference between ns and np levels ($n\mathrm{s} - n\mathrm{p}$ energy gap) is very large, energy levels for an A_2 type molecule can be expressed by Fig.5.13 or Fig.5.14(a), σ_{p} becomes more stable and lower than π_{p}. On the other hand, $\sigma_{\mathrm{p}}*$ becomes higher than $\pi_{\mathrm{p}}*$. Fig.5.13 or Fig.5.14(a) expresses the standard pattern of energy levels in A_2 type molecules with large $n\mathrm{s} - n\mathrm{p}$ energy gaps. This pattern can be applied to right hand atoms in the periodic table.

In left hand atoms in the periodic table, interactions between s orbitals and p orbitals become significant, because $n\mathrm{s} - n\mathrm{p}$ energy gaps are small as shown in Fig.5.14(b). It follows that the same symmetry orbitals, (σ_{s}, σ_{p}) and ($\sigma_{\mathrm{s}}*$, $\sigma_{\mathrm{p}}*$), mix with each other to yield modified energy levels. Rules for mixing in orbitals can be summarized as follows.

(1) The lower orbital increases its bonding character (or decrease its antibonding character) to decreases its energy.

(2) The higher orbital increases its antibonding character (or decrease its bonding character) to increases its energy.

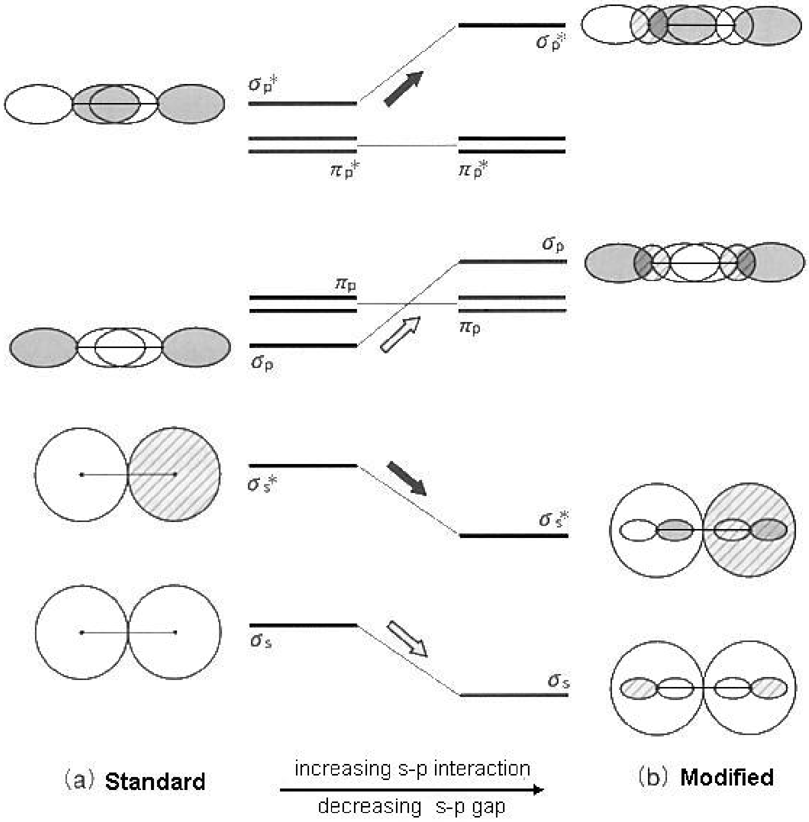


Figure 5.14: Energy levels for homonuclear diatomic molecules

For example, the more stable σ_s is formed by a little mixing of σ_p into σ_s in order to increase in-phase overlap in the middle regions between two nuclei. The more stable $\sigma_\mathrm{s}*$ is produced by a little mixing of $\sigma_\mathrm{p}*$ into $\sigma_\mathrm{s}*$ so that out-of-phase overlap may be decreased to strengthen the bonding character relatively. Modified energy levels for A_2 type molecules make the σ_p level higher than the $\pi_\mathrm{p}*$ level in comparison with the standard form.

Whether a chemical bond is formed or not depends on the electron configuration in the energy levels of Fig.5.14(a) or (b). As a qualitative index that indicates the strength of the bond in an A_2 type molecule, the bond order can be defined by the following equation.

$$P = \frac{\text{(number of electrons in bonding orbitals} - \text{(number of electrons in antibonding orbitals)}}{2} \tag{5.45}$$

According to this equation, a pair of bonding electrons give a bond order of unity. In this equation, a pair of electrons in an antibonding orbital decrease the bond order by one. This definition of the bond order is a useful index to understand the multiplicity of electron-pair bonds(covalent bonds).

Let us compose electron configurations based on Fig.5.14 and obtain bond orders by using Eq.(5.45). H_2 has an electron configuration of $(\sigma_\mathrm{1s})^2$, and its bond order is given as $P = (2-0)/2 = 1$. Thus the hydrogen molecule has a single bond with a pair of bonding electrons. He_2 has an electron configuration of $(\sigma_\mathrm{1s})^2(\sigma_\mathrm{1s}{}^*)^2$ leading to a bond order of $P = (2-2)/2 = 0$. $P = 0$ does not give a stable chemical bond. In the case of Li_2, σ_2s orbitals contain electrons (see Fig.5.15), the electron configuration becomes $(\sigma_\mathrm{1s})^2(\sigma_\mathrm{1s}{}^*)^2(\sigma_\mathrm{2s})^2$. In this expression, inner core 1s electrons of $(\sigma_\mathrm{1s})^2(\sigma_\mathrm{1s}{}^*)^2$ corresponds to the electron configuration for He_2. This part gives no contribution to the bond order. Thus, only valence electrons are significant in the bond order. The configuration of valence electrons in this case is $(\sigma_\mathrm{2s})^2$, and thus the bond order for Li_2 becomes $P = 1$ as in the case of $(\sigma_\mathrm{1s})^2$ in H_2. In general, a homonuclear diatomic molecule of the first Group element (H, Li, Na, K, etc.) in the periodic table has an electron configuration of $(\sigma_{ns})^2$ $(n = 1, 2, 3, \cdots)$, and atoms are connected by a single bond of $P = 1$.

In Be_2 $\sigma_{2s}{}^*$ also contains a pair of electrons, and the valence electron configuration becomes $(\sigma_\mathrm{2s})^2(\sigma_\mathrm{2s}{}^*)^2$ to give $P = 0$, which means no chemical bond as in the case of He_2. Similarly, a homonuclear diatomic molecule of the second Group element of the periodic table is expected not to form a stable molecule. However, diatomic molecules of Mg_2 and Ca_2 do exist though their bonds are thermally unstable to decompose very easily. The dissociation energy D_0 of Ca_2 is only 0.13 eV, which is 3% of D_0(4.478 eV) of H_2.

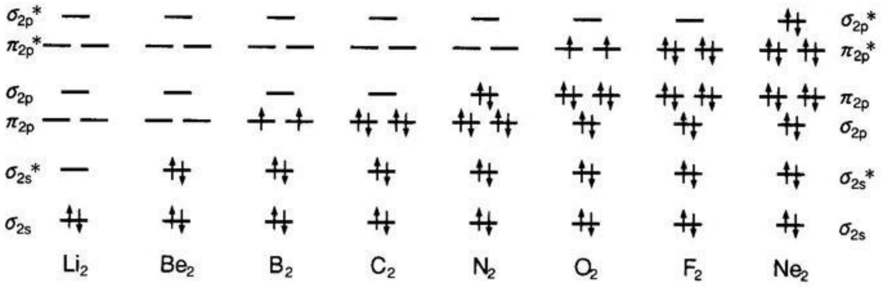


Figure 5.15: Valence electron configurations for $Li_2 - Ne_2$

B_2 has six valence electrons, and the last two electrons are contained in either π_2p or σ_2p. In the case of a B atom, the s-p gap is so small that the modified type of energy levels in Fig.5.14 should be used, and degenerate π_2p levels accept two electrons. It follows that the valence electron configuration of B_2 becomes to be a triplet with a pair of unpaired electrons with a parallel spin owing to Hund's rule as can be seen in Fig.5.15. Thus, a group of B_2 molecules show paramagnetic properties that an application of a magnetic field yields a magnetization along the direction of the field. In B_2, contributions to the bond order from $(\sigma_\mathrm{2s})^2$ and $(\sigma_{2s}{}^*)^2$ cancel out each other, and then only a contribution from $(\pi_{2p})^2$ remains to give $P = 1$. Therefore, a B_2 molecule has a π bond, which is considered as a single bond with a bond order of 1.

In C_2 π_{2p} accepts electrons prior to σ_{2p} as in the case of B_2, and the π_{2p} orbital becomes the HOMO. The chemical bond in C_2 is a double bond $P = 2$ composed of two π bonds. It is interesting to compare B_2 and C_2 molecules. The dissociation energy of a doubly bonded C_2 molecule (6.21 eV) is nearly twice as large as that of a B_2 molecule (3.02 eV). The equilibrium bond length of C_2 is much shorter than B_2.

N_2 is just at the border of the standard and the modified types in Fig.5.14. Either type gives the bond order of $P = 3$ for the bond of a N_2 molecule, which is a triple bond made up of two π bonds and one σ bond. Experiments such as photoelectron spectroscopy give a confirmation that the HOMO is σ_{2p} rather than π_{2p}, which indicates that the modified levels are more consistent with the observation. The dissociation energy of a N_2 molecule (9.759 eV), which is slightly larger than triple times of the dissociation energy of B_2 (3.02 eV), is the largest among homonuclear diatomic molecules.

In O_2 the standard type should be used because of the large 2s-2p gap, and hence the degenerate antibonding $\pi_{2p}{}^*$ orbitals become to be the HOMOs to yield a triplet type electron configuration. The bond order of O_2 should be decreased by one from that of N_2, because two additional electrons are accommodated in the antibonding orbitals, and thus an O_2 molecule has a double bond made up of one π bond and one σ bond. The electron configuration of O_2 is a triplet of two unpaired electrons with a parallel spin as in the case of B_2, and it follows that oxygen has paramagnetic properties. In F_2 further addition of two electrons in $\pi_{2p}{}^*$ orbitals decreases the bond order by one from that of O_2, which makes a single bond of a σ bond.

In the electron configuration of Ne_2, electrons fully occupy up to $\sigma_{2p}{}^*$, and bonding characters gained by bonding orbitals are completely canceled by antibonding electrons to result in a bond order of $P = 0$. It follows that a stable Ne_2 molecule is expected not to exist as in the case of He_2. However, Ne_2 really exists under a special condition in which thermal effects are not effective to decompose molecules. The dissociation energy of Ne_2 is very small as 0.0036 eV, which is about one tenth of the kinetic energy of a molecule in gaseous state at room temperature.

Table 5.3 lists valence electron configurations, bond orders, dissociation energies, equilibrium nuclear distances for homonuclear diatomic molecules and some of their ions. When properties are compared among A_2 type molecules of the same row elements, the larger the bond order becomes, the larger the dissociation energy becomes, and then the shorter the bond length (equilibrium internuclear distance) becomes. When a comparison is made among A_2 type molecules of the same Group elements, the bond strength for $P > 0$ is larger for the higher elements. This indicates that upper row atoms have compact electron orbitals to result in shorter distances between augmented electron densities in the bonding region (the covalent electron pair) and two nuclei, which causes strong binding forces between the nuclei. Very weak bonds of $P = 0$ such as Mg_2, Ca_2, Ne_2, and Ar_2 are quite different from the usual electron-pair bonds (covalent bonds), and their dissociation energies become larger on going to the lower rows in the periodic table.

Example 5.2 Obtain the bond order P of $O_2{}^+$. Compare the dissociation energy D_0 and the bond length R of $O_2{}^+$ with those of O_2 and N_2.

(Solution) The electron configuration of $O_2{}^+$ is given by $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}{}^*)^1$, in which the number of electrons in $\pi_{2p}{}^*$ is decreased to one from two in the case of O_2. Noting 8 electrons in bonding orbitals and 3 electrons in antibonding orbitals, we obtain the bond order of $O_2{}^+$ as $P(O_2^+) = (8 - 3)/2 = 2.5$.

Since O_2 has one more antibonding electron than $O_2{}^+$, the bond order of O_2 can easily be obtained as $P(O_2) = 2$. In N_2 an antibonding electron is removed from the electron configuration of $O_2{}^+$, and thus $P(N_2) = 3$. In general, the larger P becomes, D_0 becomes larger and R becomes smaller. It follows that we obtain the following conclusions (see Table 5.3).

Dissociation energy	$D_0(N_2) > D_0(O_2{}^+) > D_0(O_2)$
Bond length	$R(N_2) < R(O_2{}^+) < R(O_2)$

Table 5.3: Electron configurations and structures for homonuclear diatomic molecules and ions

Molecule	Valence electron configuration						Bond order	Dissociation energy	Bond length
	σ_{2s}	$\sigma_{2s}{}^*$	σ_{2p}	π_{2p}	$\pi_{2p}{}^*$	$\sigma_{2p}{}^*$		D_0(eV)	R(pm)
H_2	2						1	4.4781	74.144
He_2	2	2					0		
Li_2	2						1	1.046	267.29
Be_2	2	2					0		
B_2	2	2		2			1	3.02	159.0
C_2	2	2		4			2	6.21	124.25
N_2	2	2	2	4			3	9.759	109.77
O_2	2	2	2	4	2		2	5.116	120.75
F_2	2	2	2	4	4		1	1.602	141.19
Ne_2	2	2	2	4	4	2	0	0.0036	309
Na_2	2						1	0.73	307.9
Mg_2	2	2					0	0.0501	389.1
Si_2	2	2	2	2			2	3.21	224.6
P_2	2	2	2	4			3	5.033	189.34
S_2	2	2	2	4	2		2	4.3693	188.92
Cl_2	2	2	2	4	4		1	2.4794	198.8
Ar_2	2	2	2	4	4	2	0	0.0104	376
K_2	2						1	0.514	390.51
Ca_2	2	2					0	0.13	427.73
Br_2	2	2	2	4	4		1	1.9707	228.11
Kr_2	2	2	2	4	4	2	0	0.0160	400.7
I_2	2	2	2	4	4		1	1.5424	266.6
Xe_2	2	2	2	4	4	2	0	0.0230	436.2
$H_2{}^+$	1						0.5	2.648	106.0
$He_2{}^+$	2	1					0.5	2.365	108.1
$N_2{}^+$	2	2	1	4			2.5	8.71	111.64
$O_2{}^+$	2	2	2	4	1		2.5	6.663	111.64
$Ar_2{}^+$	2	2	2	4	4	1	0.5	1.33	248
$Kr_2{}^+$	2	2	2	4	4	1	0.5	1.15	279
$Xe_2{}^+$	2	2	2	4	4	1	0.5	1.03	317

5.6 Hybridization of orbitals

In the preceding sections, we studied some examples how orbitals are mixed to form new orbitals via orbital interactions. In some cases, both of two orbitals in one atom interact with an orbital in the other atom. In such cases, new orbitals can be considered to be produced from interactions of hybrid orbitals composed of two orbitals in one atom with orbitals of the other atom. In this section, we will study hybridization of orbitals and some applications of hybrid orbitals.

5.6.1 Mixtures of orbitals in the same atom

Let us study effects of mixtures of orbitals in the same atom. As shown in Fig.5.16(a), a mixture of p_x and p_y orbitals becomes equivalent with a p orbital with a direction rotated in the $x - y$ plane. The direction depends on coefficients of the linear combination, and any direction within the plane including the axes of the two p orbitals is possible. a mixture of three p orbitals, p_x, p_y, and p_z, may produce a p orbital with arbitrary direction in the full three dimensional space. It is thus possible to reorganize p orbitals to produce the most suitable linear combination to overlap efficiently with the orbital of the incoming atom or molecule, even if the other species comes from any direction. Basically, selection of directions of p orbitals or choice of coordinates can be made arbitrarily for computational convenience. However, essential characteristics of orbital interactions do not depend on the choice of the coordinate system, and this nature of orbital interactions can be denoted as the invariance in the coordinate system. Reorganization of p orbitals is an important property that guarantee the invariance in the coordinate system.

Next, we will study mixtures of an s orbital and p orbitals of the same atom. Since a mixture of p orbitals is equivalent to one p orbital with a suitable direction, we only need to consider a mixture of one s orbital and one p orbital. The result can be seen in Fig.5.16(b); a constructive effect occurs in the direction where phases coincide for s and p orbitals, whereas the mixing effect is destructive in the opposite direction. These effects result in a production of a big lobe at the in-phase direction together with a small lobe at the opposite direction. Such an augmentation of directional properties associated with mixture of the same atom orbitals to produce a highly directional orbital is denoted as hybridization, and produced orbitals are called hybridized orbitals or hybrid orbitals.

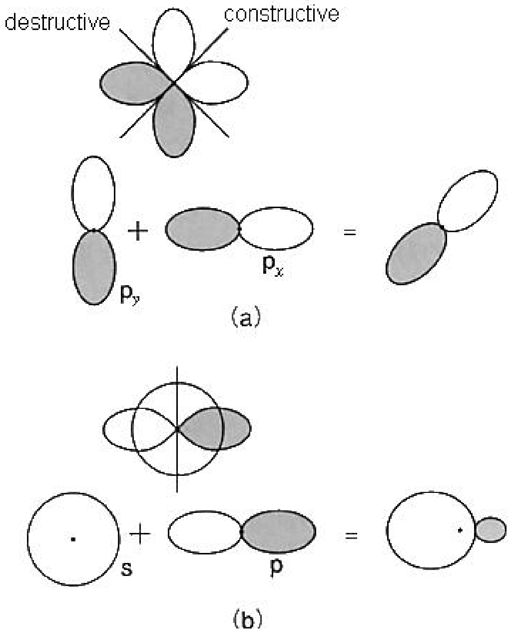


Figure 5.16: Mixing effects of the same atom orbitals. (a) Directional change on mixture of p orbitals with different directions. (b) Augmentation of direction on mixture of s orbital and p orbital (the hybridization effect).

Hybrid orbitals have the following important characteristics related to formation of chemical bonds.

[Characteristic features of hybrid orbitals]

(1) Directionality becomes higher, and the overlap with a coming species from the direction increases.

(2) The electron distribution of itself becomes asymmetric, and electron densities at the augmented direction become higher to produce a strong attractive force between its nucleus and the incoming nucleus.

Although many textbooks comment only on the feature (1), the feature (2) is also very important, as easily be understood from Feynman's electro static theorem in Section 4.2. In addition, a mixture of 2p orbitals into 1s orbital as well as a mixture of 3d orbitals into 2s and 2p orbitals also have some effects mentioned above.

Such mixing effects of higher orbitals other than valence orbitals on deformation of electron distributions around an atom are denoted as polarization effects. Additional functions with higher azimuthal quantum numbers other than valence orbitals to improve basis functions are called polarization functions. In comparison with hybridization effects of orbital mixing among orbitals of the same principal quantum number, polarization effects are rather moderate by the principle of the energy difference, since polarization effects involve orbitals with higher principal quantum numbers. Calculations with minimal basis sets which only contain valence orbitals include hybridization effects but neglect polarization effects.

5.6.2 sp hybridization

One to one hybridization of valence s and p orbitals gives sp hybrid orbitals, which are composed of mutually orthonormal two orbitals expressed as follows.

$$\begin{aligned}\phi_\mathrm{a} &= \tfrac{\mathbf{s}+\mathbf{z}}{\sqrt{2}}\\ \phi_\mathrm{b} &= \tfrac{\mathbf{s}-\mathbf{z}}{\sqrt{2}}\end{aligned} \tag{5.46}$$

Here, we used (p_z) orbital as the p orbital. p_z and s orbital functions are expressed simply as $\mathbf{z}$ and $\mathbf{s}$. Two hybrid orbitals in eq.(5.46) are equivalent for their energies and shapes, though the directions are different with a mutual angle of 180° as can be seen in FIg.5.17. The energy of sp hybrid orbitals ε_sp is just an average value of orbital energies of s and p orbitals, which are expressed as α_s and α_p, respectively.

$$\varepsilon_\mathrm{sp} = \frac{\alpha_\mathrm{s}+\alpha_\mathrm{p}}{2} \tag{5.47}$$

sp hybrid orbitals lead to linear molecules of A−B−C or A−B−C−D (such as $\mathrm{BeCl_2}, \mathrm{HgBr_2}$,HCN, $\mathrm{C_2H_2}$) linearly connected by σ bonds with bond angles of 180°. In HCN and $\mathrm{C_2H_2}$, in addition to CNσ and CCσ bonds formed by sp hybridization two sets of π bonds due to πtype overlaps by p orbitals with directions parallel to the σ bond, and it follows that triple bonds of C≡N and C≡C are formed.

5.6.3 sp^2 hybridization

From one s orbital and two p orbitals (p_x and p_y orbitals, whose functions are expressed simply by $\mathbf{x}$ and $\mathbf{y}$), we can construct a set of three hybrid orbitals, $\phi_\mathrm{a}, \phi_\mathrm{b}, \phi_c$, which are equivalent in energies and shapes with directions mutually 120° displaced within a plane (Fig.5.17) and denoted as sp^2 hybrid orbitals.

$$\begin{aligned}\phi_\mathrm{a} &= \tfrac{1}{\sqrt{3}}\mathbf{s} + \sqrt{\tfrac{2}{3}}\mathbf{x}\\ \phi_\mathrm{b} &= \tfrac{1}{\sqrt{3}}\mathbf{s} - \tfrac{1}{\sqrt{6}}\mathbf{x} + \tfrac{1}{\sqrt{2}}\mathbf{y}\\ \phi_c &= \tfrac{1}{\sqrt{3}}\mathbf{s} - \tfrac{1}{\sqrt{6}}\mathbf{x} - \tfrac{1}{\sqrt{2}}\mathbf{y}\end{aligned} \tag{5.48}$$

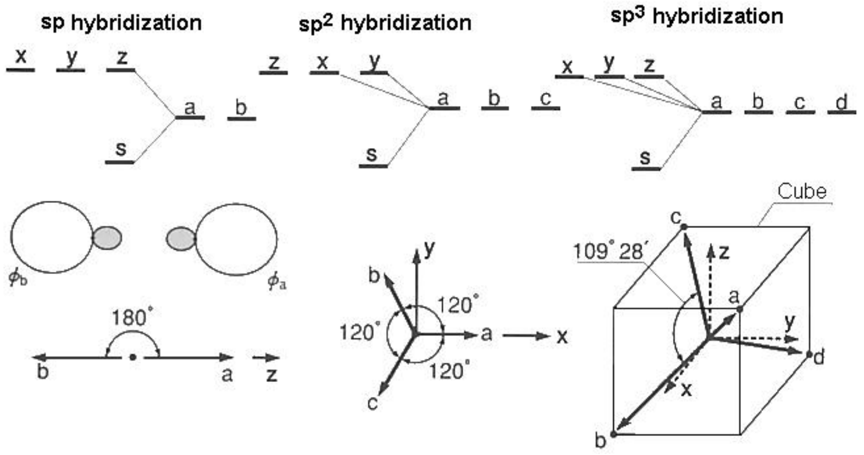


Figure 5.17: sp^n hybrid orbitals $(n = 1, 2, 3)$

These orbitals satisfy the orthonormality. Since electron density is proportional to $|\phi|^2$, squares of atomic orbital coefficients give relative magnitude of s and p components; the s orbital component is estimated as $(1/\sqrt{3})^2 = 1/3$, and the p orbital component is $(\sqrt{2/3})^2 = (1/\sqrt{6})^2 + (1/\sqrt{2})^2 = 2/3$. It follows that s : p = 1 : 2. The energy of sp^2 hybrid orbitals ε_{sp^2} is an average value of orbital energies of s and p orbitals with weights of s : p = 1 : 2.

When sp^2 hybrid orbitals make three σ bonds with other species in the directions of $0°, 120°, 240°$, they produce triangle form molecules such as $NH_3{}^+, BH_3, BF_3$ with all bond angles of 120° and ethylene C_2H_4 in which angles are slightly deformed form 120°, $\angle HCH = 117.5°$. Benzene C_6H_6 can also be produced by sp^2 hybridization. In ethylene and benzene, π type overlaps between out-of-plane p orbitals which are not involved in sp^2 hybridization yield π bonds. Thus, an ethylene molecule has a CC double bond. Six CCπbonds in benzene are equivalent, and they have an intermediate character between a single bond and a double bond, which can be confirmed from bond-orders by molecular orbital methods.

5.6.4 sp^3 hybridization

From one s orbital and three p orbitals (orbital functions are expressed simply by **x**, **y**, and **z**), we can construct a set of four hybrid orbitals, $\phi_a, \phi_b, \phi_c, \phi_d$, as shown in Fig.5.17. Energies and shapes of these orbitals are equivalent, and they are directed to four corners from the center of a tetrahedron.

$$\begin{aligned} \phi_a &= \frac{\mathbf{s}+\mathbf{x}+\mathbf{y}+\mathbf{z}}{2} \\ \phi_b &= \frac{\mathbf{s}+\mathbf{x}-\mathbf{y}-\mathbf{z}}{2} \\ \phi_c &= \frac{\mathbf{s}-\mathbf{x}-\mathbf{y}+\mathbf{z}}{2} \\ \phi_d &= \frac{\mathbf{s}-\mathbf{x}+\mathbf{y}-\mathbf{z}}{2} \end{aligned} \tag{5.49}$$

These orbitals satisfy the orthonormality. The electron density is proportional to $|\phi|^2$. Thus, squares of atomic orbital coefficients give relative magnitude of s and p components. The s orbital component is estimated as $(1/2)^2 = 1/4$, and the p orbital component is $(1/2)^2 \times 3 = 3/4$. It follows that s : p = 1 : 3. The energy of sp^3 hybrid orbitals ε_{sp^2} is an average value of orbital energies of s and p orbitals with weights of s : p = 1 : 3.

$$\varepsilon_{sp^3} = \frac{\alpha_s + 3\alpha_p}{4} \tag{5.50}$$

When sp^3 hybrid orbitals make four σ bonds with other species, they produce tetrahedral molecules such as $CH_4, SiH_4, NH_4{}^+$ with the tetrahedral bond angles of 109.47°.

5.6.5 other types of hybridization

In addition to the above hybrid orbitals, some other types of hybrid orbitals involving d orbitals are important. As shown in Table 5.4, they are related to formation of various molecular structures.

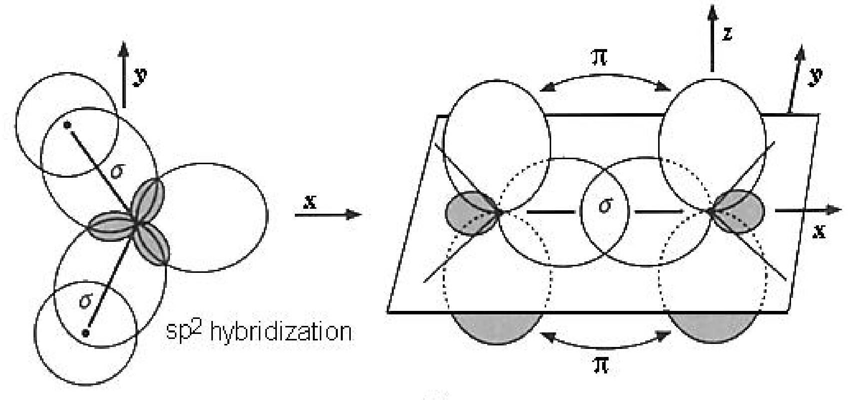
Table 5.4: Hybridization and moelcular structures

Hybrid orbital	Structure	Bond angle	Example
sp	Linear form	180°	$C_2H_2, HCN, BeH_2, HgCl_2$
sp^2	Equilateral traiangle	120°	$BF_3, NH_3{}^+, C_6H_6$
sp^3	Tetrahedron	109.47°	$CH_4, NH_4{}^+, SiH_4, SO_4{}^{2-}$
dsp^2	Square plane	90°	$Ni(CN)_4{}^{2-}, AuCl_4{}^-$
sp^3d	Trigonal-bipyramid	90° 120° 180°	$PCl_5, AsF_5, SbCl_5$ (Note)
d^2sp^3	Octahedron	90°	$Co(NH_3)_6{}^{3+}, PtCl_6{}^{2-}$
sp^3d^2	Octahedron	90°	SF_6

(Note) The trigonal-bipyramid structue of PCl_5 can be explained by three-center-two electron bonds as discussed below.

Example 5.3 Explain the molecular structure of ethylene C_2H_4 using hybrid orbitals.

(Solution) In each C atom, three sp^2 hybrid orbitals together with a perpendicular p orbital can be considered for valence orbitals, and four valence electron are inserted in either one of the four orbitals. A combination of sp^2 hybrid orbitals of two C atoms yields a CC bond due to σ type overlaps. Remaining two sp^2 hybrid orbitals with angles of 120° with respect to the CC bond axis can be used to form a pair of CHσ bonds of σ type overlaps, which results in a production of a CH_2 unit. In this step, two CH_2 units can rotate with each other along the CC bond axis, since the CC bond is a single bond, which can rotate freely to have an arbitrary angle of the rotation.



(1) CH_2 unit and CHσ bonding (2) CCπ bonding and CCσ bonding

However, an overlap between a pair of p orbitals remaining at each C atom produces a CC bond due to the π type overlap, which is most effectively formed, when the p orbitals have parallel directions, namely two CH_2 become coplanar. Thus, between two C atoms, one CCσbond between two sp^2 hybrid orbitals and additionally one CCπ bond from a pair of parallel p orbitals are formed to give a CC double bond. On account of the restriction of the rotation around the CC axis by the π bond, all six atoms are located in a plane, and it follows that an ethylene molecule has a planar structure.

Effects of electrostatic attractive forces due to bonding electrons on the carbon nuclei are much stronger in the CC double bond than in CH single bonds. Thus the pulling forces by the bonding electron densities are stronger along the double bond, and hence the HCH bond angle (the bond angle between two CH bonds) should become a little smaller than 120° so that resultant forces from electron densities in two CH bonds may be balanced with the opposite force cause by the electron densities in the CC double bond; really the observed HCH angle is 117.5°.

5.7 The three-center-two-electrton-bond and the hydrogen bond

As studied in the earlier parts of this chapter, a pairing of electrons is not necessary to bind two nuclei by attractive forces caused by electron densities located at middle regions between the nuclei. It is important for formation of bonds how electron densities distribute in the bonding regions between the nuclei. In this section, we will study bonds of three atoms formed by an action of two electrons.

5.7.1 Three center orbital interactions

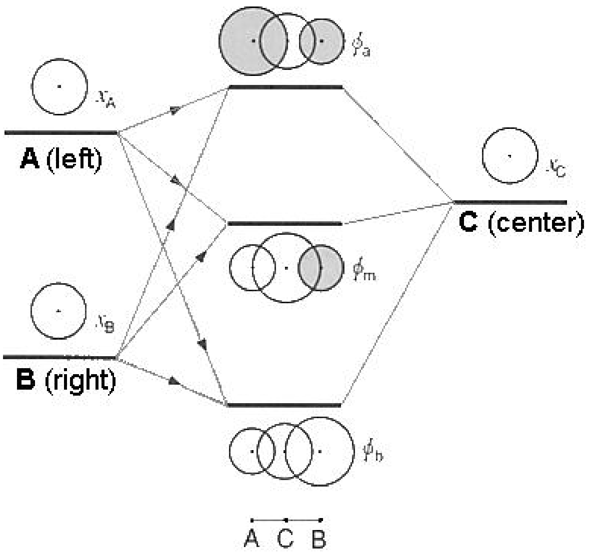
Let us study orbital interactions involved in a system of three atoms, A, B, and C, in which C is the middle, using the simple Hückel molecular orbital metohd. An orbital of C χ_{C} can interact with orbitals χ_{A}, χ_{B} of both ends of A and B, where resonance integrals are $\beta_{\mathrm{AC}} \neq 0$, $\beta_{\mathrm{BC}} \neq 0$. Since the resonace integral for the long distance can be neglected, $\beta_{\mathrm{AB}} = 0$. Coulom integrals for these atoms are denoted as $\alpha_{\mathrm{A}}, \alpha_{\mathrm{B}}, \alpha_{\mathrm{C}}$. The secular equation to obtain molecular orbitals is given as follows.

$$\begin{vmatrix} \alpha_{\mathrm{A}} - \varepsilon & 0 & \beta_{\mathrm{AC}} \\ 0 & \alpha_{\mathrm{B}} - \varepsilon & \beta_{\mathrm{BC}} \\ \beta_{\mathrm{AC}} & \beta_{\mathrm{BC}} & \alpha_{\mathrm{C}} - \varepsilon \end{vmatrix} = 0 \tag{5.51}$$

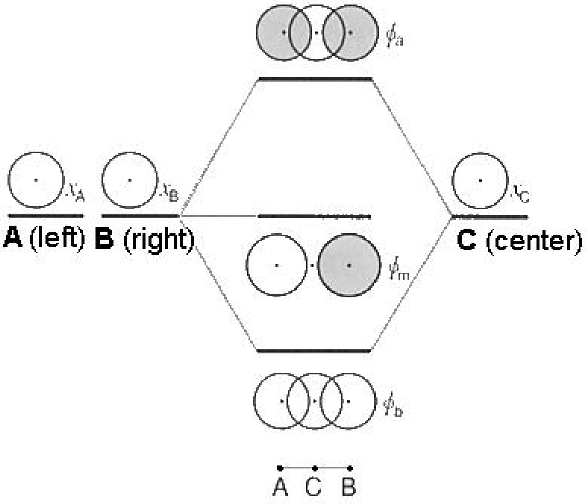
This is just the same as the secular equation in Example 5.1 (the two to one orbital interactions) in section 5.3. Thus, among the new orbitals produced by the interactions of three orbitals, the most stable orbital ϕ_{b} becomes lower than the lower one of χ_{A}, χ_{B}, and the most unstable orbital ϕ_{a} becomes higher than the higher one of χ_{A}, χ_{B}, as can be seen from Fig.5.18.

ϕ_{b} is a highly bonding orbital, which is composed of the same phase combinations of the central atomic orbital with those of both ends in order to increase electron densities in the middle regions between nuclei. ϕ_{a} is a highly antibonding orbital, which is made of the opposite phase combinations of the central atomic orbital with those of both ends in order to exclude electron densities out of the middle regions between the nuclei. On the other hand, the new orbital with intermediate stability ϕ_{m} is formed in an intermidiate level between the levels of orbitals for both ends. If orbitals of both ends degenerate, the level of the intermediate orbital is equal to the degenerate levels. In the shape of ϕ_{m}, the higher one mixes with the central orbital in the same phase, and the lower one mixes with the opposite phase. This leads to a weakly bonding character in ϕ_{m}, as shown in Fig.5.18(a). It should be noted that, if orbitals of both ends are degenerate, one of them might be in the same phase, but the other necessarily becomes in the opposite pahse. By symmetry in the degenerate case, the contiribution from the the central atom is completely vanishing in ϕ_{m} as shown in Fig.5.18(b), thus ϕ_{m} becomes almost nonbonding, because direct interactions between both ends are negligibel from the distance.

When an electron is included in the bonding orbital ϕ_{b} of the three-center interactions, three atoms can be connected with their neighbors. A pair of electrons in ϕ_{b} gives the more strong bonding. Such types of bonds produced by a pair of electrons in the bonding orbital of the three center are called the three-center-two-electron-bond. Now, let us stuy some examples.



(a) $\chi_A > \chi_B$



(b) $\chi_A = \chi_B$

Figure 5.18: Three center orbital interactions

5.7.2 Linear three-center-two-electron-bonds

Putting fluorine F atoms on both sides of a xeone Xe atom, we can obtain a XeF_2 molecule, in which a pair of electrons in a 5p orbital of a Xe atom interact with unpaired electrons in 2p orbitals of two F atoms aligned linearly with the central Xe atom.

$$:\underset{\cdot}{\overset{\cdot\cdot}{F}}: + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Xe}}: + :\underset{\cdot}{\overset{\cdot\cdot}{F}}: \longrightarrow F - Xe - F$$

Relevant energy levels can be summarized in Fig.19.

Ionization energies of a Xe atom and a F atom are 12.1 eV and 17.4 eV, respectively. Thus, Xe5p orbitals have higher energy levels than F2p orbitals. F2p orbitals do not interact each other because of the long distance and shown in the left-hand side of Fig.5.19. An electron-pair in the bonding molecular orbital ϕ_b is displaced nearer to the lower energy F2p, and a Xe atom and a F atom are bonded by electron densities of an electron. The molecular orbital of the intermediate

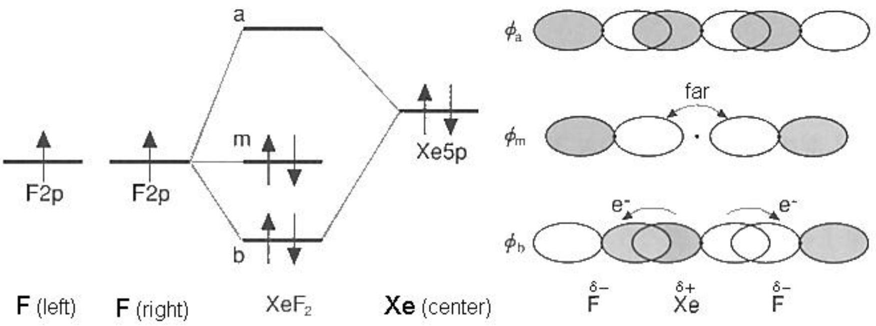


Figure 5.19: Three center two electron bonds in XeF_2

stability ϕ_{m} can be considered as a nonbonding orbital, and a pair of electrons in this orbital have no effects on the bonding and they are distributed on both F atoms, one by one in average. It follows that XeF_2 has linear three-center-two-electron-bonds with a bond-order of 1/2 for each XF bond. Although these bonds are also denoted as the three-center-four-electron-bonds, they are essentially the three-center-two-electron bonds.

Replacing a Xe atom by an iodide ion I^- with the same electron configuration and also replacing F atoms by other halogen atoms I or Cl, we can obtain linear molecular ions of I_3^- and ICl_2^- shown in Fig.5.20. In XeF_2, one electron-pair of a 5p orbital is used for a set of three-center-two-electron-bonds. Here, another electron-pair of other 5p orbitals can also be used to produce another set of three-center-two-electron-bonds with a different direction. These two sets of three-center-bonds yield a square planar form of XeF_4 (Fig.5.20). One more set of the electron-pair in Xe5p can also be used to obtain XeF_6. The observed form of XeF_6 is slightly distroted from the expected octahedral shape.

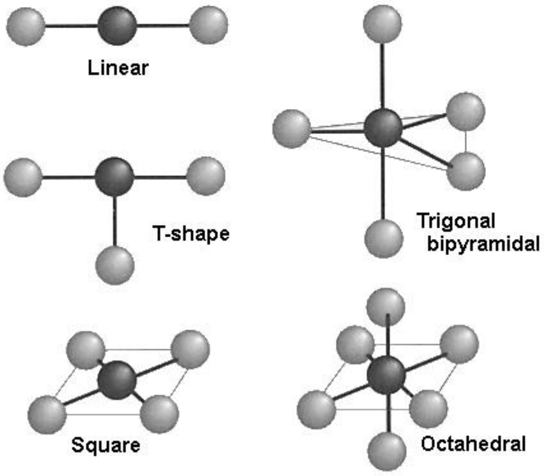


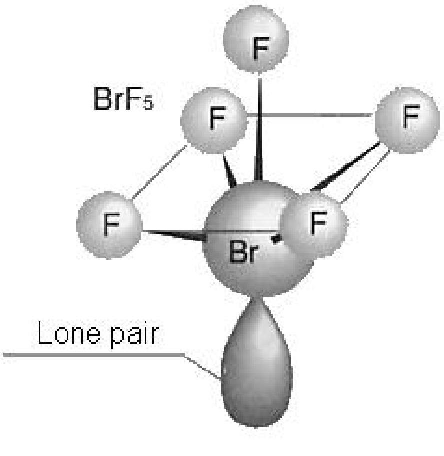
Figure 5.20: Various shapes of molecular structures

There are many other examples for the three-center-two-electron-bonds composed of an electron-pair in a p orbital and a couple of unpaired electrons in halogen atoms. In a PCl_5 molecule, each of three sp 2 hybrid orbitals around the P atom has an unpaired electron and makes an electron-pair bond with an unpaired electron in a Cl atom. It follows that an equilateral triangular form is produced. Remaining two electrons among five valence electrons of the P atom are in a vertically directed 3p orbitals as an electron-pair, which may be used to form a set of three-center -two-electron-bonds with unpaired electrons in two Cl atoms. Thus a trigonal bipyramidal molecule can be produced (Fig.5.20). Three covalent PCl bonds with a bond-order of unity in the triangle plane are denoted as equatorial bonds (experimental bond-length is 201.7 pm), which are stronger and much shorter than two vertical PCl bonds denoted as axial bonds (experimental bond-length is 212.4 pm), since these bonds are weak bonds with a bond-order of 1/2. Although the trigonal bipyramidal structure of PCl_5 can be explained by hybrid orbitals in Table 5.4, it becomes difficult to explain differences in the bond lengths.

As similar examples including sp^2 hybrid orbitals together with a vertical p orbital leading to a set of three-center-two-electron-bonds, AB_3 type molecules, such as ClF_3 and BrF_3 can be produced. In these cases, the hybrid orbitals of the central halogen atom are composed of one unpaired electrons and two electron-pairs, and the unpaired electron is able to form a covalent bond with an unpaired electron in a F atom. Two electron-pairs in the hybrid orbitals become unshared electron-pairs. A p orbital vertical to the plane of hybridization contains an electron-pair, which can be used to produce a set of three-center-two-electron-bonds with two F atoms. Thus a T shaped molecule shown in Fig.5.20 can be formed. The horizontal line of the T shape is made of three-center bonds, and therefore the distances from the central atom in the horizontal bonds are longer than the vertical bonds (covalent bonds). Unshared electron-pairs made of hybrid orbitals are more tightly attracted with the central atom than the electron-pair in the covalent bond, and it follows that the central atom is pulled upward to give a slightly deformed form like an upward arrow ↑.

Example 5.4 The molecular structure of BF_5 is a form of the following figure. Using a combination of covalent bonds and three-center-two-electron-bonds, explain the molecular structure of this molecule.

(Solution) The outer-most shell electron configuration of a Br atom is $(4s)^2(4p)^5$. In a Br atom,



$4p_x$ and $4p_y$ orbitals contain an electron-pair, and a pair of sp hybrid orbitals composed of 4s and $4p_z$ orbitals are formed. One of the sp hybrid orbitals (towards lower) contains an electron-pair, and another one (towards upper) contains an unpaired electron. On the other hand, each F atom has an unpaired electron in a p orbital. An unpaired electron of the sp hybrid orbital in the z direction can form a covalent bond coupled with a F atom. $4p_x$ and $4p_y$ orbitals of the Br atom can be used to produce three-center-two-electron-bonds with F atoms in both x and y directions, and a square structure where four F atoms are placed on the corners is formed. The BrF bond directed upward is a strong covalent bond with a shorter bond length (the observed bond length is 171.8 pm), and BrF bonds in the horizontal plane are weak bonds due to three-center-two-electron-bonds with a longer bond length (the observed bond length is 178.8 pm). The Br atom is slightly displaced to the downward from the plane of the square, since the downward directed electron-pair pulls the Br atom more strongly than the upward directed electron-pair in the covalent bond does (the observed angle is $\angle$F(horizontal)BrF(vertical) = 85.1°). Alternatively an octahedral structure by sp^3d^2 hybridization can be assumed, but the short axial bond of the square pyramid will become difficult to be explained.

5.7.3 Bent three-center-two-electron-bonds

An interesting example includes bent three-center bonds with a H atom in the middle. Such a bond can be seen in hydrated compounds of boron (generally called borane). Diborane B_2H_6 is a typical example. There are two BHB bonds in a diborane molecule, and the geometrical shape has a bridge structure as shown in Fig.5.12.

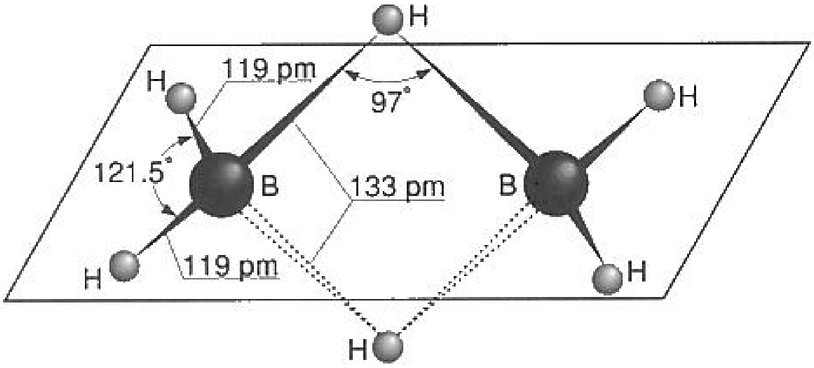


Figure 5.21: The bridge structure in diborane B_2H_6

For the B atoms sp^3 hybridization can be assumed. Two of the four sp^3 hybrid orbitals have unpaired electrons, one has an electron-pair, and the remaining one is a vacant orbital with no electron. Each of two unpaired electrons makes a covalent BH bond with a H atom, whose bond-order is unity. In the bridge structure, an unpaired electron in a H atom in the middle interact with an electron-pair in a B atom and also with a vacant orbital of another B atom to give energy levels shown in Fig.5.22, since the ionization energy of a H atom is much larger than a B atom. Orbital interactions yield bent orbitals as shown in the figure. Only the bonding orbital ϕ_b contains an electron-pair. The B atoms and a middle H atom are bonded by three-center-two-electron-bonds with a bond-order of 1/2. Depending on the difference in the bond-orders, bridge BH bonds have longer bond lengths than the terminal BH bonds.

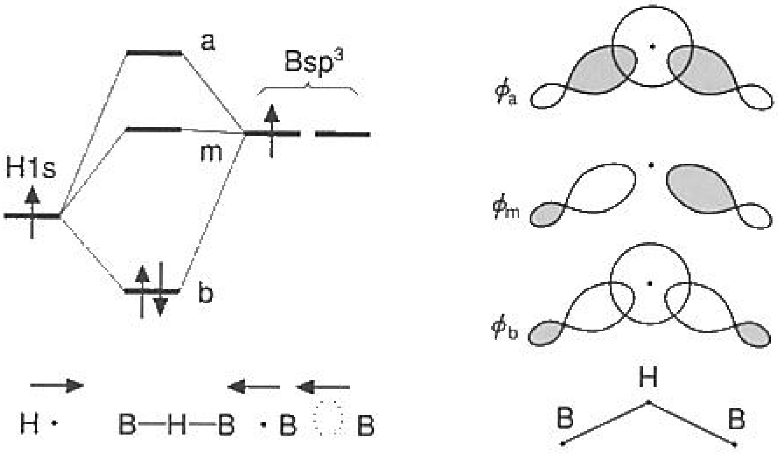


Figure 5.22: Molecular orbitals of diborane

5.7.4 The hydrogen bond

When a H atom bonded to a strongly electronegative atom X makes a new bond with another electronegative atom Y, such a bond is called the hydrogen bond. The hydrogen bond can also be considered as a sort of the three-center-two-electron-bonds. In this case, the unpaired electron energy level is rather high in comparison with valence orbitals of the electronegative atoms, and energy levels in Fig.5.23 are obtained. In this figure negative atoms X and Y are shown in the same side for convenience, though they are separated in a long distance and may be different in their energies. The electron-pair in the bonding orbital ϕ_b connect three atoms via the H atom. The XH bond becomes rather weaker than the case without the hydrogen bonding. When the negativity of the Y atom is not strong enough, the electron-pair of the bonding ϕ_b orbital concentrates its electron densities on the XH bond. The electron-pair of the ϕ_m orbital is almost nonbonding, and it has no effect on formation or dissociation of the hydrogen bond.

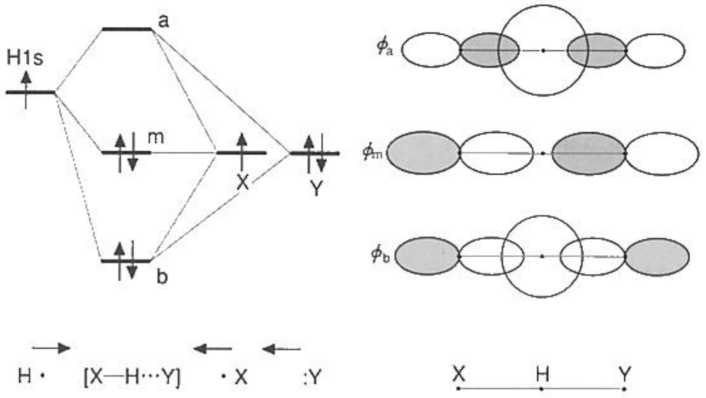


Figure 5.23: The hydrogen bond

5.8 Electron energy levels and photoelectron spectra

As studied in section 4.3, the orbital energy ε_i can be related with the observed ionization energy I_i via Koopmans formula.

$$I_i = -\varepsilon_i \tag{5.52}$$

This relationship is approximate, and the exact numerical agreement cannot be expected. As far as molecules with the singlet ground electronic states are concerned, observed ionization energies have been found to give a satisfactory one-to-one correspondence with energy levels of molecular orbitals. In this section, we will study relationships among photoelectron spectra, ionization energies, and energy levels of molecular orbitals. A photoelectron spectrum of the hydrogen molecule will also be studied in connection with the dissociation energies.

5.8.1 Photoelectron spectra and electron energy levels of molecular orbitals

The kinetic energy $\frac{1}{2}mv^2$ of a photoelectron ejected from a substance irradiated by a photon of $h\nu$ with a frequency ν in the photoelectric effect can be given by the following formula.

$$\frac{1}{2}mv^2 = h\nu - I_i \tag{5.53}$$

Here, I_i is the ionization energy of the substance. Using Koopmans' formula we obtain

$$\frac{1}{2}mv^2 = h\nu + \varepsilon_i \tag{5.54}$$

Thus, the kinetic energy of the photoelectron depends on the energy level of the molecular

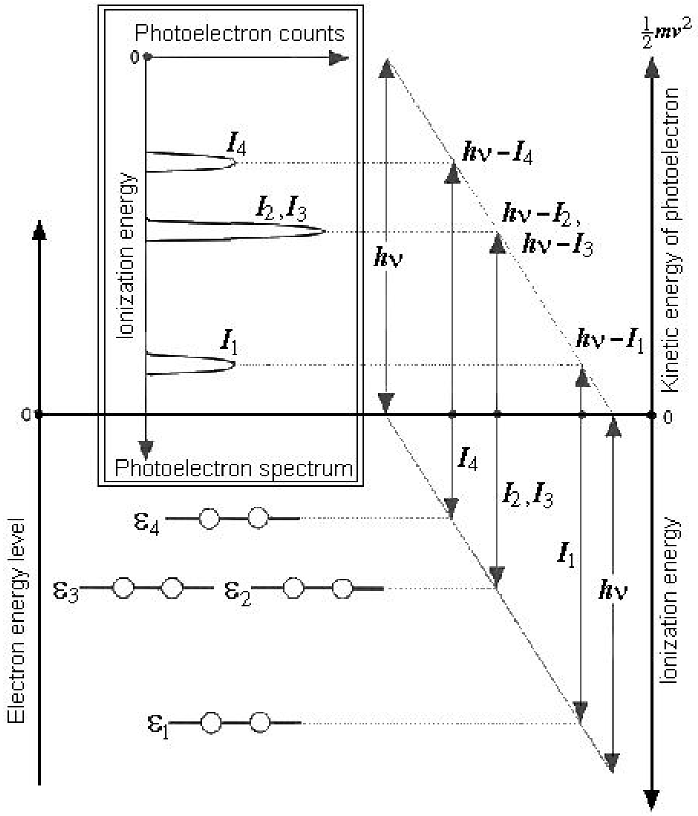


Figure 5.24: Relationships between photoelectron spectra and electron energy levels of molecular orbitals

orbital from which the photoelectron is ejected. It follows that measurements of kinetic energy distributions of photoelectrons caused by a given energy photons $h\nu$ give a photoelectron spectrum, which correspond to energy levels of molecular orbitals, as illustrated in Fig.5.24.

In general, a method measuring counts of electrons as functions of electron kinetic energies is called the electron spectroscopy. An application of the electron spectroscopy to photoelectrons ejected from sample substances by photoelectric effects is the photoelectron spectroscopy.

Fig.5.25 shows an example of an X-ray photoelectron spectrum (XPS) for a H_2O molecule measured with a photon source of the characteristic X-ray of Mg (Kα line: 1253.6 eV). In this spectrum, there are clearly resolved five peaks corresponding to molecular orbitals. One of them is a group of the slowest photoelectrons, which can be assigned to a molecular orbital mainly composed of oxygen 1s orbital. The formula of eq.(5.54) gives a transformation of the kinetic energy to the ionization energy, and thus we obtain $I(\mathrm{O1s}) = 539.9$ eV. Other photoelectrons have much larger energies with higher velocities, and they are slightly smaller than the photon energy 1253.6 eV of the X-ray source, since the ionization energies of the corresponding valence orbitals are much smaller than the ionization energy of the inner shell O1s level. Among the valence photoelectrons, the slowest ones give a peak of a molecular orbital mainly composed of O2s orbital, and the corresponding ionization energy is determined as $I(\mathrm{O2s}) = 32.2$ eV. Further, peaks with ionization energies of 18.5 eV, 14.7 eV, 12.6 eV can be assigned as the following molecular orbitals of the H_2O molecule.

18.5 eV	OH bonding molecular orbital containing O2p$_y$ atomic orbital.
14.7 eV	HH bonding molecular orbital containing O2p$_z$ atomic orbital.
12.6 eV	Nonbonding molecular orbital containing O2p$_x$ atomic orbital.

Based on the above correspondence, we can confirm that ten electrons in a water molecule are

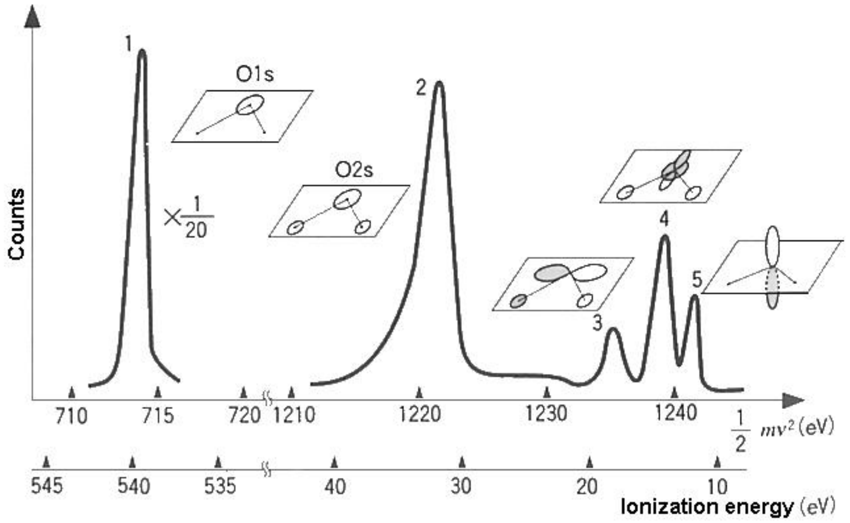


Figure 5.25: X-ray photoelectron spectrum (XPS) of the H_2O molecule measured with the Mg Kα line

accommodated in the five molecular orbitals; in each orbital two electrons are contained as an electron-pair.

Table 5.5 lists a comparison of ionization energies I from an X-ray photoelectron spectrum with calculated orbital energies ε by an *ab initio* molecular orbital method. Although exact agreement could not be obtained, absolute values of the orbital energies agree well with the observed ionization energies within the error of 10%.

Table 5.5: Ionization energies I by XPS and orbital energies ε by an *ab initio* molecular orbital method for H_2O

Peak number	I(eV)	ε(eV)	Molecular orbital character	Main atomic orbital component
1	539.9	−558.3	Inner shell	O1s
2	32.2	−36.8	Bonding	O2s
3	18.5	−19.3	OH Bonding	O2p$_y$
4	14.7	−15.2	HH bonding	O2p$_z$
5	12.6	−13.6	Nonbonding	O2p$_x$

5.8.2 Photoelectron spectrum of the hydrogen molecule and the binding energies

A photoelectron spectrum measured with the ultraviolet photons is called ultraviolet photoelectron spectrum (UPS). For measurements of UPS, photons of 21.22 eV irradiated from a helium discharge, which are due to $2^1P \rightarrow 1^1S$ transitions (from 2p orbital to 1s orbital), are used in many cases. Since ultraviolet (UV) photons have much smaller energies in comparison with X-ray photons, UV photons are not enough to ionize inner-shell electrons. However, electron kinetic energies are so small that more fine structures can be resolved in UPS. When a molecular vibration is excited upon ionization, the kinetic energy of the photoelectron becomes smaller by an amount of the energy required for the vibrational excitation, since this energy is further consumed from the photon energy. In highly resolved photoelectron spectra, vibrational fine structures often appear as many peaks. In Fig.5.26 a photoelectron spectrum of the hydrogen molecule is shown as an example.

Peaks labeled by 0, 1, 2, $\cdots$ in the figure indicate the vibrational quantum v of the vibrational states of produced ion $H_2{}^+$. $v = 0$ corresponds to the vibrational ground state of $H_2{}^+$, which is the state of zero-point vibration of the hydrogen molecule-ion. Fig.5.26 shows the most strong

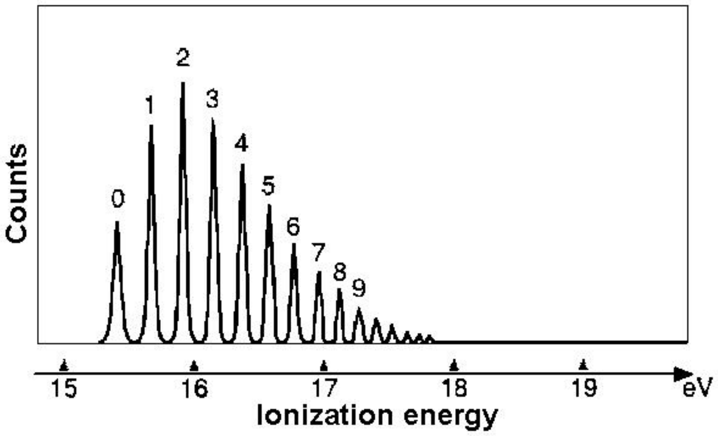


Figure 5.26: Ultraviolet photoelectron spectrum of the H_2 molecule

peak for $v = 2$. This is related to Franck-Condon principle, which is a well known rule for electronic transitions in molecules. According to Franck-Condon principle, electronic transitions can be considered to occur without nuclear motion. It follows that for potential energy curves as in Fig.5.27 only vertical transitions are acceptable. In real cases, vertical transitions are most likely to occur, and slightly displaced transitions can also appear though the probabilities are small. Transitions requiring large nuclear displacements hardly occur.

Since the bonding force becomes weaker in the hydrogen molecule-ion, the equilibrium nuclear distance is expected to become longer in the ion than the hydrogen molecule. The most outstanding peak of $v = 2$ in the photoelectron spectrum in Fig.5.26 indicates that just on the vertical line from the equilibrium position of H_2 the potential curve of the ion crosses with the vibrational level of $v = 2$. The ionization energy corresponding to the vertical transition is called the vertical ionization energy in general. In the case of ionization of the hydrogen molecule, the vertical ionization energy can be determined as 15.96 eV from Fig.5.26. The minimum ionization energy of the hydrogen molecule on the other hand correspond to an ionization transition to the level of $v = 0$ in the ion. Such a minimum ionization energy without vibrational excitation is called the adiabatic ionization energy, which is estimated to be 15.43 eV in the case of H_2.

What does the limit of $v \to \infty$ in the vibrational excitation means? This corresponds to a dissociated state where the bond is completely broken. In the photoelectron spectrum in Fig.5.26 this limit of $v \to \infty$ corresponds to a dissociation of ${H_2}^+$ into a H atom and a H^+ ion. Thus, if the position of $v \to \infty$ in the spectrum can be deduced, the dissociation energy of ${H_2}^+$, $D_0({H_2}^+)$ can be obtained from $I(\infty) - I(0)$. Noting that intervals between the peaks in the spectrum decrease with the increase of v, a graphical plot of the intervals as functions of v gives a position where the interval becomes vanishing. From this procedure we can obtain the right position of the dissociation limit. The result becomes $I(\infty) = 18.08\,\text{eV}$. From this value, we obtain $D_0({H_2}^+) = I(\infty) - I(0) = 18.08 - 15.43 = 2.65\,\text{eV}$ (see Table 5.3). Further, a correction of the zero point energy leads to determination of the binding energy D_e (in the case of H_2, it is the bond energy). A careful study of peak intervals shows that the intervals almost linearly decrease. From this line we can obtain the vibrational interval at $v = 0$, and one half of this can be a good estimate of the zero-point energy. Thus we obtain

$$D_\text{e}({H_2}^+) = D_0({H_2}^+) + 0.14 = 2.79\,\text{eV}$$

From the spectrum in the figure, the vibrational energy quantum of ${H_2}^+$ can be estimated as about 0.28 eV. This corresponds to a wave number of ca. 2260 cm^{-1}, which is considerably smaller than the wavenumber of 4401 cm^{-1} for the molecular vibration in H_2. This is because in the ion a loss of a bonding electron decreases the bonding force. In general, a loss of bonding electrons causing a reduction of the bonding force, which results in a reduction of the vibrational wavenumber. When a loss of antibonding electrons oppositely causes a relative increase of the bonding force to result in an increase of the vibrational wavenumber.

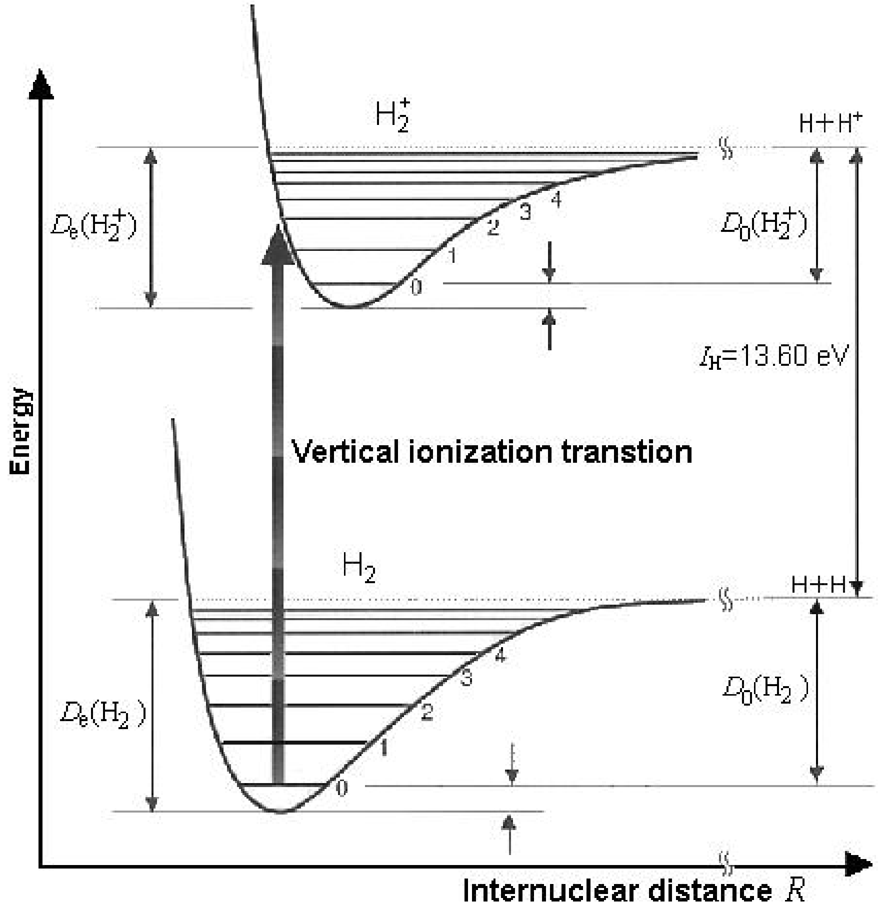


Figure 5.27: Potential energy curves for H_2 and $H_2{}^+$

Example 5.5 From the photoelectrons spectrum of Fig.5.26 and the ionization energy of the hydrogen atom (13.60 eV), obtain the dissociation energy of the hydrogen molecule.

(Solution) Let us denote the dissociation energy of the hydrogen molecue as $D_0(\mathrm{H}_2)$, the ionization energy of the hydrogen atom as I_H, an energy requied for ionization of the hydrogen molecule and dissociation of $H_2{}^+$ ion at the same time as $I(\infty)$. Then, we obtain the following relation.

$$D_0(\mathrm{H}_2) + I_\mathrm{H} = I(\infty)$$

Both sides of this equation correspond to the energy required to produce a disociated state of the hydrogen molecule ion (a state dissociated into H and H^+) starting from the vibrational ground state (the zero-point vibrational state) of the hydrogen molecule. The left side is a path of dissociation of a hydrogen molecule in the first step followed by ionization of one of two hydrogen atoms in the second. The right side is another path of a direct transition into the dissociated ionic state. The latter can be estimated from Fig.5.26 as

$$I(\infty) = 18.08\,\mathrm{eV}$$

Then, using $I_\mathrm{H} = 13.60\,\mathrm{eV}$, we obtain

$$D_0(\mathrm{H}_2) = I(\infty) - I_\mathrm{H} = 18.08 - 13.60 = 4.48\,\mathrm{eV} \qquad \text{(see Table 5.3)}$$

Exercises

5.1 The secular equation of π orbitals for allyl CH_2CHCH_2 in the simple Hückel method is given by

$$\begin{vmatrix} \alpha-\varepsilon & \beta & 0 \\ \beta & \alpha-\varepsilon & \beta \\ 0 & \beta & \alpha-\varepsilon \end{vmatrix} = 0$$

Solve this equation, and obtain π orbital functions and their energy levels for allyl.

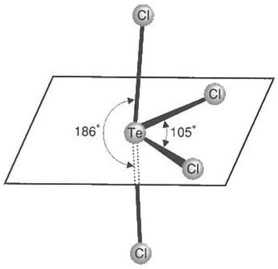
5.2 Obtain the bond-order P of ${N_2}^+$, and compare the dissociation energy D_0 and the bond-length R of ${N_2}^+$ with those of O_2 and N_2.

5.3 Explain qualitatively molecular orbitals and their energy levels of the HCl molecule using the principle of orbital interactions.

5.4 Explain qualitatively molecular orbitals and their energy levels of the N_2 molecule based on the principle of orbital interactions and the Example 5.1 for the two to one orbital interactions.

5.5 Explain the molecular structure of propene $CH_3CH = CH_2$ using hybrid orbitals.

5.6 Explain the molecular structure of the $TeCl_4$ molecule as shown in the following figure.



5.7 Using atomic orbitals (χ_j), 1s for the H atom, $1s, 2s, 2p_x, 2p_y, 2p_z$ for a F atom, molecular orbitals ($\phi_i = \sum_j C_{ji}\chi_j$) of the HF molecule were calculated and listed in Table 5.6. The uppermost row shows orbitals energies (ε_i eV) for molecular orbitals $\phi_i (i = 1, \cdots, 6)$. In the lower rows, coefficients C_{ji} for atomic orbitals χ_j are listed. Phases (signs) for χ_j were chosen as follows; phases of s orbitals were chosen to be positive at longer distances, and phases for p orbitals were chosen to be positive at the positive direction on the respective coordinate axis commonly defined for all atoms. Carefully study this table, and answer the following questions.

(1) Classify $\phi_1 - \phi_6$ into σ orbitals and π orbitals.

(2) Which one among $\chi_1 - \chi_6$ is F1s orbital?

(3) Which one among $\chi_1 - \chi_6$ is H1s orbital?

(4) Which is(are) vacant orbital(s) among $\phi_1 - \phi_6$?

(5) Which orbital(s) among $\phi_1 - \phi_6$ is(are) most responsible for the bonding force between the H and F atoms.

Table 5.6:

ϕ_i	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ε_i(eV)	-704.8	-40.03	-15.92	-12.63	-12.63	-17.12
χ_1 C_{1i}	0.995	-0.249	0.083	0	0	0.085
χ_2 C_{2i}	0.023	0.936	-0.435	0	0	-0.560
χ_3 C_{3i}	0	0	0	1	0	0
χ_4 C_{4i}	0	0	0	0	1	0
χ_5 C_{5i}	-0.003	-0.090	-0.702	0	0	0.825
χ_6 C_{6i}	-0.006	0.158	0.521	0	0	1.090

5.8 Molecular orbitals (MO) of C_2H_4 were calculated as linear combinations of atomic orbitals (AO), 1s for the H atom and $1s, 2s, 2p_x, 2p_y, 2p_z$ for the C atom, and Table 5.7 lists the results for nine MO from the lowest in energy. The uppermost row includes orbital energies of molecular orbitals in the unit of eV. The lower rows list coefficients for AO ($1 \sim 14$). As AO, Slater type orbitals (STO) called STO3G were used in the calculations. Phases for s orbitals were chosen to be positive in the longer distances, and phases for p orbitals were chosen to be positive at the positive direction on the respective coordinate axis. Table 5.8 lists employed Cartesian coordinates for six atoms in the unit of Å. Carefully study these results, answer the following questions. Note that only one answer is not assumed, and find all possible answers.

(1) Which are hydrogen atomic orbitals among $1 \sim 14$ in Table 5.7 ?

(2) Which is carbon 2s atomic orbital among $1 \sim 14$ in Table 5.7 ?

(3) Which is the lowest unoccupied molecular orbitals (LUMO) among MO (1) $\sim$ (9) in Table 5.7 ?

(4) Which MO contribute to formation of the CCπ bond among MO (1) $\sim$ (9) in Table 5.7 ?

(5) Which MO contribute to formation of the CHσ bond among MO (1) $\sim$ (9) in Table 5.7 ?

(6) Which AO is $2p_x$ orbital for (1) atom in Table 5.8 ?

(6) Which AO is 1s orbital for (5) atom in Table 5.8 ?

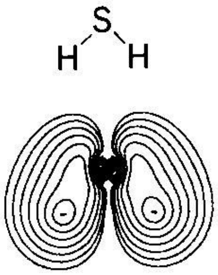
Table 5.7:

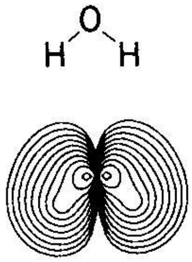
エネルギー	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
(eV)	−299.9	−299.8	−26.6	−20.2	−16.4	−14.4	−12.6	−8.8	8.6
1	0.702	0.701	−0.178	−0.137	0.000	0.015	0.000	0.000	0.000
2	0.702	−0.701	−0.178	0.137	0.000	0.015	0.000	0.000	0.000
3	0.020	0.031	0.471	0.416	0.000	−0.026	0.000	0.000	0.000
4	0.020	−0.031	0.471	−0.416	0.000	−0.026	0.000	0.000	0.000
5	0.002	−0.004	−0.112	0.198	0.000	0.502	0.000	0.000	0.000
6	−0.002	−0.004	0.112	0.198	0.000	−0.502	0.000	0.000	0.000
7	0.000	0.000	0.000	0.000	−0.394	0.000	0.392	0.000	0.000
8	0.000	0.000	0.000	0.000	−0.394	0.000	−0.392	0.000	0.000
9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.636	0.810
10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.636	−0.810
11	−0.005	0.005	0.115	−0.224	−0.260	0.217	−0.348	0.000	0.000
12	−0.005	0.005	0.115	−0.224	0.260	0.217	0.348	0.000	0.000
13	−0.005	−0.005	0.115	0.224	−0.260	0.217	0.348	0.000	0.000
14	−0.005	−0.005	0.115	0.224	0.260	0.217	−0.348	0.000	0.000

Table 5.8:

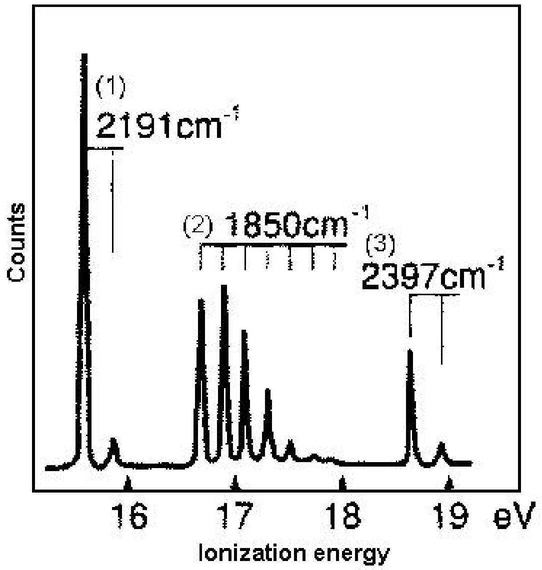
	X	*Y*	*Z*
(1)	1.338	0.0	0.0
(2)	0.0	0.0	0.0
(3)	−0.564	0.929	0.0
(4)	−0.564	−0.929	0.0
(5)	1.902	0.929	0.0
(6)	1.902	−0.929	0.0

5.9 Next figures show electron density contour maps for molecular orbitals in H_2O and H_2S molecules, which are most responsible for production of OH and SH bonds, respectively. Deduce relative magnitude of ionization energies of three atoms, S, O, and H based on these figures.





5.10 A figure below shows an observed photoelectron spectrum of the nitrogen molecule N_2 using ultraviolet photons of $h\nu = 21.218\,\mathrm{eV}$ emitted from a helium discharge. Peaks of (1)-(3) are associated with vibrational structures due to excitation of molecular vibrations of ${N_2}^+$ ion. A comparison of observed vibrational frequencies (wavenumbers) for ionic states with those for N_2 ($2345\ \mathrm{cm}^{-1}$) leads to the following conclusions; (1) is a weakly bonding orbital, (2) is a strongly bonding orbital, and (3) is a weakly antibonding orbital. Assign the observed bands of (1)-(3) to molecular orbitals $1\pi_\mathrm{u}, 3\sigma_\mathrm{g}, 2\sigma_\mathrm{u}$, whose electron density maps are shown in Fig.4.5. Deduce the order of bondlengths of ${N_2}^+$ in the ionic states corresponding to (1)-(3) by comparing with the bondlength for N_2.



Chapter 6

Molecular orbital and chemical reaction

Chemical reactions are phenomena in which systems of nuclei and electrons undergo changes of geometrical configurations and compositions. As we have studied, binding or antibinding forces are caused by electrons. In this chapter, we will study basic quantum chemical principles of chemical reactions based on functions of electrons.

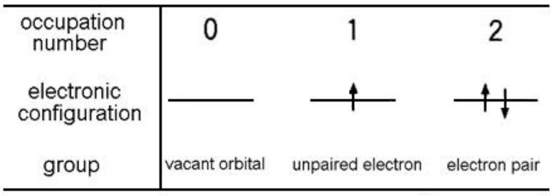
6.1 Orbital theory of reactivity

In Chapter 5 we studied composition of new molecular orbitals and energy levels based on orbital interactions. However, whether really new bonds are formed or not depends on electron configurations. In this section, let us first study relationships between electron configurations and reactivity as well as relationships between unpaired electrons and reactivity, and then we will study the HOMO-LUMO principle and the frontier orbital theory.

6.1.1 Electron occupation number and reactivity

Occupation numbers of electrons in one energy level are limited to be either of $2, 1, 0$ according to the Pauli exclusion principle, and they are classified into three cases listed in Table 6.1.

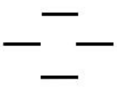
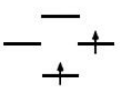
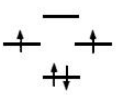
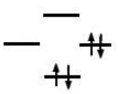
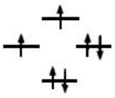
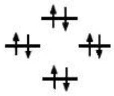
Table 6.1: Classification of electron energy levels



occupation number	0	1	2
electronic configuration	—	—↑—	—↑↓—
group	vacant orbital	unpaired electron	electron pair

Orbital interactions can also be classified into six patterns shown in Table 6.2. Pattern(1) is an interaction between vacant orbitals with no electrons leading to an occupation number of zero, which results in no bond formation. An example is interactions between 2s vacant orbitals of a pair of He atoms. Pattern(2) is an interaction between a vacant orbital and an unpaired electron, and in this case an electron in the bonding orbital yields one-electron bond with a bond-order of 1/2. A real example of this type is a production of ${H_2}^+$ ion from H and H^+ already studied in Chapter 5. The next Pattern(3) is an interaction between two unpaired electrons, which gives an electron-pair (covalent) bond with a bond-order of unity, as can be seen from a typical example of $H + H \rightarrow H_2$. An electron-pair bond can also be produced via Pattern(4), an interaction between a vacant orbital and an electron-pair, and an example is $H^+ + H^- \rightarrow H_2$; it is of note that H^- can exist, since the electron affinity of the H atom is positive.

Table 6.2: Fundermental patterns of orbital interactons and bond-order

pattern	(1)	(2)	(3)	(4)	(5)	(6)
electronic configuration						
bond order	0	1/2	1	1	1/2	0

Pattern(5) involving an interaction between an unpaired electron and an electron-pair gives an electron in the untibonding orbital in addition to two electrons in the bonding orbital, and thus the bond-order becomes $(2-1)/2 = 1/2$ equivalent to the one-electron bond. A typical example of this sort is $He^+ + He \rightarrow He_2{}^+$. As shown in Table 5.3, the dissociation energy and the bond length of $He_2{}^+$ are very similar to those of $H_2{}^+$, because the bond-orders are 1/2 in both cases. The last Pattern(6) includes interactions between electron-pairs, and in this case the bonding character of the bonding electron-pair cancells out with the antibonding character of the electron-pair in the antibonding orbital to result in no bond formation. Interactions between 1s electron-pairs in two He atoms belong to this type. The reason for no production of a He_2 molecule can be given by Patterns (1) and (6) in Table 6.2.

In the above arguments, we assumed that two orbitals effectively interact with each other. In real problems, we should consider whether the orbital interactions are effective or not, especially the conditions concerning with the principles of the energy difference and the overlaps between the interacting orbitals.

A careful analysis of electron occupation numbers and bond-orders for the six patterns in Table 6.2 leads to a conclusion that reactivity is governed by combinations of electron ocupation numbers, as summarized as follows.

(1) No reaction occurs between vacant orbitals or between electron-pairs. [Pattern (1) (6)]
(2) Unpaired electrons can react with any types. [Pattern (2) (3) (5)]
(3) A vacant orbital and an electron-pair can react. [Pattern (4)]

Atoms and moelcules with unpaired electrons are called redicals. When radicals meet with other species, they usually react promptly to yield other species. Therefore, radicals are chemically unstable. Radicals are often produced by dissociation of smoe cahmical bonds in stable chemical compounds. The chemial stability of compounds is thus not to react easily and to keep themselves unchanged longtime, even if they meet with other species. The stability of molecules by themselves is the physical stability, which is different from the chemcial stability. Under special conditions, where probabilities making contact with other species are supressed to be very low, as under high vacuum or at very low temperature, radicals can survive as they are. When the level of the unpaired electron has a very large energy separation or a negligibly small overlap with other orbitals, radicals do not interact with others to be able to exist with a good chemical stability.

Reactions by Pattern(3) and Pattern(4) will stop in most cases because of no unpaired electrons in the products. On the other hand, products of Pattern(2) or Pattern(5) also have unparied electrons, and further reactions wiil occur in many cases. Through such mecanisms, radicals produced by thermal decomposition, photolyses, or radiolyses of molecules often arouse chain reactions or even explosion.

One-electron bonds by Pattern(2) or Pattern(5) have the lower physical stability because of the lower bondo-order than electron-pair bonds by Pattern(3) or Pattern(4). One-electron bonds are chemically unstable because of the unpaired electron. In usual textbooks for the introductory chemistry, chemically stable bonds are considered to be formed by a bond of an electron-pair. In this sense, the important stability is the chemical stability. Even if the system is physically very stable, it is not necessarily chemicaly stable. No unparied electron can be considered as a necessity condition for the chemical stability except for some special cases. However, no unpaired electron does not necessarily mean the chemical stability, since Pattern(4) give reaction possibilites without unpaired electrons. Systematic considerations of conditions governing the chemical stability will be made afterward.

Here, we should note the physical stability in more detail. The physical stability becomes larger, when the dissociation energy((bond energy) - (zero-point energy)) becomes larger. Qualitatively, the higher the bond-order, the higher the physical stability. If the bond energy is too small, the system becomes getting out of the potential well by the zero-point vibration. This means that even if the bond energy is positive, the bond may be physically unstable unless the bond energy is larger than the zero-point energy. Furthermore, the bond may become unstable, when the thermal energy is larger than the bond energy. The thermal energy depends on the absolute temperature T, and it is approximately an order of kT, where k is the Boltzmann constant. Themal decompositiom may occur, when a thermal energy getting into the system is large enough to dissociate a bond. It follows that a bond with a high bond energy is thermally stable. In addition, the higher the bond energy brcomes, the lower the probability that undergoes exchange of chemical bonds becomes. In a thermal equilibrium, the lower energy has the higher possibility; the probability for a state of an energy E is proportional to $\mathrm{e}^{-E/kT}$. Thus, the larger bond energy means that the state is more stable and that the probability changing into other higher energy state is less probable.

In Pattern(4) for interactions between a vacant orbital and an electron-pair, a vacant orbital is coordinated with an elctron-pair, and the electron-pair is donated to the vacant orbital. This mecahnism corresponds to interactions of vacant orbitals of $\mathrm{H}^+, \mathrm{Zn}^{2+}, \mathrm{BF}_3$ with unshared-electron-pairs of $\mathrm{NH}_3, \mathrm{H}_2\mathrm{O}, \mathrm{CN}^-$ leading to comlex formation by coordinate bonds or dative bonds. This pattern of bond formation is associated with an electron distribution transfer from an electron-pair to a vacant orbital. A phnomenon accomanied with an electron distribution transfer due to orbital interactions is called the cahrge transfer, and compounds or complexes formed by the charge transfer are called the charge-transfer compounds or the charge-transfer complexes. In charge transfer, a substance giving an electron is called the electron donor, and a substance receiving an electron is called the electron acceptor. The bond formation via interactions between a vacant orbital and an electron-pair, an electron reception of a vacant orbital as well as an electron donation of an electron-pair are associated. Key factors governing the formation of new chemcial bonds via this Pattern(4) are very important and will be studied in more detail in the last part of this section.

6.1.2 Number of unpaired electrons and the valency

The number of unpaired electrons and the number of stable bonds to be produced are closely related, because unparied electrons can be paired to produce an electron-pair bond via Pattern(3) in Table 6.2. This is also related with the number of valnce electrons and the valence. Table 6.3 lists the number of the outermost electron shell, the number of valence elecrons, the number of unpaired electrons, and the ususal valency for atoms with atomic numbers smaller than 11. The number of unpaired electrons may change depending on electron configurations of the atoms. When we only

Table 6.3: The number of unpaired electrons and valency

Atom	Number of electrons		Number of unpaired electrons		Usual Valency
	Outermost electron shell	Valence electron	Ground electron configuration	Valence state	
H	1	1	1	1	1
He	2	0	0	0	0
Li	1	1	1	1	1
Be	2	2	0	2	2
B	3	3	1	3	3
C	4	4	2	4	4
N	5	5	3	3	3
O	6	6	2	2	2
F	7	7	1	1	1
Ne	8	0	0	0	0

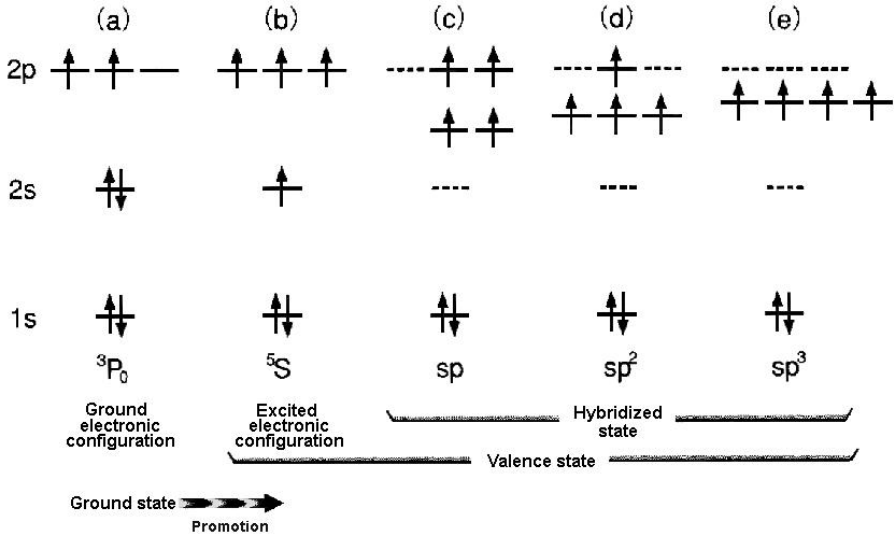


Figure 6.1: Valence states of the C atom and promotion

consider the ground electronic configuration, some discrepancies from the conventionally used will be found for C and Be atoms. This problem will be solved by considering valence states introduced below.

In the case of the C atom, the electron configuration is $(1s)^2(2s)^2(2p)^2$, and the C atom has only two unpaired electrons as shown in Fig.6.1(a). If an electron is excited to an electron configuration (b) in Fig.6.1, then we have four unpaired electrons, which agree well with the usual valency of four. Similarly electron configurations using hybridization as shown in Fig.6.1(c)-(e) give four unpaired electrons in agreement with the usual valency. These electron configurations giving the usual valency are called the valence states. Therefore, in order to obtain the usual valency, valence states with a higher energy need to be made. Such a process is called the promotion, and energies required are called the promotion energies. Promotion energies for the above (b)-(e) are the same, since they are just to promote a 2s electron up to a 2p level. If the stabilization energy gained by the bond formation is larger than the promotion energy, the reaction via the valence state with promotion becomes possible energetically. Be, B, and C atoms really show usual valency via valence states, because of sufficiently large bond energies much greater than the promotion energies.

6.1.3 The HOMO–LUMO principle and the frontier orbital theory

Let us study reactions without unpaired electrons of Pattern(4) in Table 6.2. This type of interactions between a vacant orbital and an electron-pair need conditions with a sufficiently small energy separation as well as an enough overlap between the orbitals. In the ground electron configuration without electron pairs, electron-pairs occupy lower levels up to the HOMO, and upper levels from the LUMO are vacant as can be seen in Fig.6.2. Thus, the required condition with a sufficiently small energy separation leads to the following important conclusions.

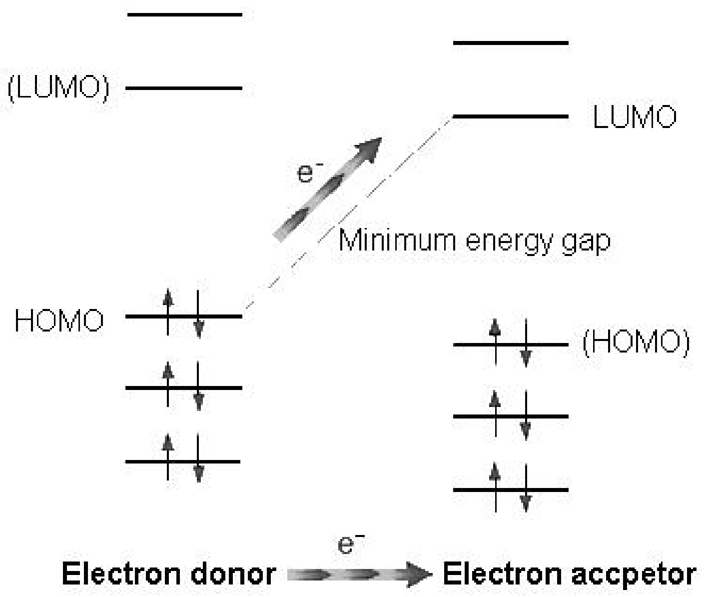


Figure 6.2: HOMO-LUMO interactions and the charge transfer

[The HOMO–LUMO principle]

> Interactions between a vacant orbital and an electron-pair occur most effectively between a HOMO of one species and a LUMO of the other.

This is denoted as the HOMO–LUMO principle, and an interaction between a HOMO and a LUMO is called a HOMO-LUMO interaction.

A comparison of HOMO–LUMO interactions among various compounds indicates that the higher MOMO and the lower LUMO give the smaller energy separation to become the better combination of an electron acceptor and an electron donor for the charge transfer or the electron transfer. This propensity can be summarized as follows.

[The principle of charge transfer interactions]

(1) The electron donation to the other species most easily occurs at the HOMO.

(2) The electron reception from the other species most easily occurs at the LUMO.

(3) The higher HOMO (the smaller ionization energy) gives the stronger ability of the electron donation to the other species.

(4) The lower LUMO (the larger electron affinity) gives the stronger ability of the electron reception from the other species.

(5) The higher LUMO and the lower HOMO result in the lower ability of electron donation and reception.

The occupation number of electrons in an unpaired electron orbital is unity, which is one half of the maximum occupation of electrons, and thus this type of orbitals is denoted as the singly-occupied molecular orbital (SOMO). The special reactivity of the unpaired electron orbital (SOMO) with arbitrary types of electron configurations in addition to the HOMO–LUMO principle and the principle of charge transfer interactions indicate that key roles in chemical reactions are played by HOMO, LUMO, and SOMO. These three types of orbitals are called the frontier orbitals, and the theory noting the roles of these orbitals is the frontier orbital theory proposed by Kenichi Fukui in 1951, who have developed quantum chemical theories of chemical reactions together with R. Hoffmann.

6.2 The chemical stability and the reactivity of rare gases

In this section, conditions for the chemical reactivity are summarized, and the reactivity of rare gases are discussed.

6.2.1 Conditions for the chemical stability

The chemical stability is not to change into other substances easily. This requires the physical stability, since the system should keep itself when it exits alone. In addition, the following four conditions for the chemical stability are important in order to keep itself even if it encounters with other species.

[**Conditions for the chemical stability**]

(1) No unpaired electrons

(2) HOMO is very low. (Almost no ability for the electron donation, because of the too large ionization energy)

(3) LUMO is very high. (No ability for the electron reception, because of the negative electron affinity)

(4) Spatial regions where HOMO and LUMO extend are not accessible by orbitals of other species.

If the above three conditions (1)–(3) hold, no reactions occur with other species having no unpaired electrons. The condition (4) can be satisfied when the system is placed under vacuum or in a solid matrix at low temperature (this technique is called the matrix isolation). This condition (4) can be fulfilled approximately, if the regions where HOMO and LUMO extend are protected physically from other species by a large functional group (such a technique is called the steric protection). Under the condition (4), reactions are suppressed even if the other species are radicals with unpaired electrons. When the condition (4) is not satisfied, an encounter with a radical having a large extension of SOMO may lead to reactions, even if the conditions (1)–(3) are satisfied.

In order to be chemically stable, the system needs also to be physically stable. Thus the system should be in the lowest electronic energy state (the ground electronic state). Further, except for monoatomic systems the bonding energy should be larger than the thermal energy. It is rather easy to maintain these physical conditions; we should only be careful not to introduce energetic actions by heat and light. When light is absorbed to give an electronic excitation to an excited state, the physical condition becomes unsatisfied, and simultaneously chemical conditions (1)–(3) also become unsatisfied.

In order to keep substances unchanged long time, those unstable thermally or photochemically should be saved under cold and dark places. Those reactive with water or oxygen should be kept in a nitrogen atmosphere or under a vacuum state. Special cares appropriate for each substance should be made considering the above conditions.

6.2.2 The reactivity of rare gases

Rare gas atoms in the ground state satisfy conditions (1)–(3) for the chemcal stability ((1) No unpaired electrons, (2) the ionization energy is too large, and (3) the electron affinity is negative), and thus their reactivity is very low. However, some reactions can occur if the conditions become partly unsatisfied. Although ionization energies of rare gas atom are large, their values decrease as He(24.6 eV), Ne(21.6 eV), Ar(15.8 eV), Kr(14.0 eV) in this order, and the ionization energy of Xe becomes 12.1 eV, which is smaller than the ionization energy of the hydrogen atom (13.6 eV). This indicates that the condtion (2) does not hold for Xe. Noting this propensity, N. Bartlet synthesized $XePtF_6$ from Xe and PtF_6 in 1962, and also N. H. Classen et al. obtained XeF_4 via thermal reactions of Xe and F_2 in 1962. Further, XeF_2, XeF_6, XeO_3, XeO_4 and some other rare gas compounds have been synthesized, and it follows that a hypothesis of (rare gases)=(nonreactive gases) has been rejected.

Ions and excited atoms (He*, Ne*, Ar*, Kr*, Xe:) of rare gases do not satisfy the conditions (1)–(3) for the chemcial stability, and it follows that the following reactons can occur.

(a) $He^+ + He \longrightarrow He_2{}^+$, $He^+ + H \longrightarrow (HeH)^+$, $He^+ + N_2 \longrightarrow He + N_2{}^+$

(b) $Ar^* + F \longrightarrow (ArF)^*$, $Kr^* + F \longrightarrow (KrF)^*$, $Xe^* + Cl \longrightarrow (XeCl)^*$

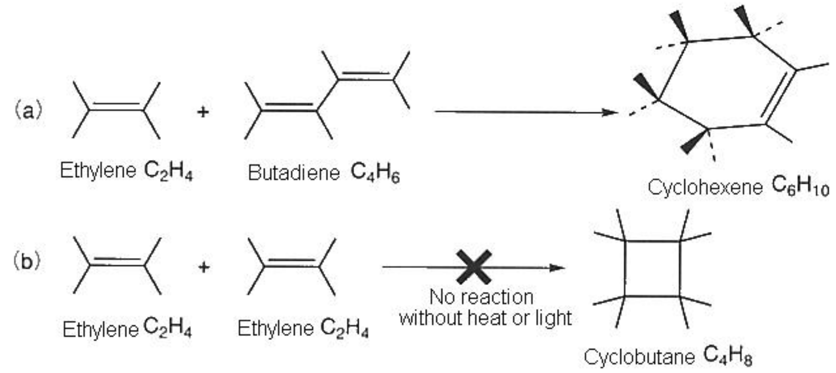
(c) $He^* + Ar \longrightarrow He + Ar^+ + e^-$, $Ar^* + H_2O \longrightarrow Ar + H_2O^+ + e^-$ In the reactions of (a), He^+ behaves as a very strong electron acceptor. Reaction products in (b) are called the excimers (the excited dimers), which are used for the laser oscilation. Reactions in (c) are ionization reactions associated with a collision between an excited atom and a molecule and called the Penning ionization.

6.3 Cyclic addition reactions and the exchange of chemical bonds

In this section, cyclic addition reactions will be studied as an example of chemical bond exchange mechanisms for reactions between species having no unparied electrons.

6.3.1 The Diels-Alder reaction

Addition of a compound having a CC unsaturated bond such as ethylene and acrolein to a diene such as butadiene yields a cyclic skeleton composed of six carbon atoms. This type of reaction is called the Diels-Alder reaction. A typical example is a reaction of butadiene and ethylene producing cyclohesene as shown in the next chart (a), which is easily occur.



On the other hand, another addition reaction (b) involving two ethylene molecules does not proceed without heating or irradiation of light. In order to elucidate the mechanism of the addition reaction (a), let us first study molecular orbitals and energy levels for ethylene and butadiene.

Molecular orbitals and energy levels for ethylene C_2H_4

As studied in section 5.6 and in Example 5.3, the moelcular skeleton of ethylen is on a plane, and the bond angles are about 120°. HOMO and LUMO of ethylene are a bonding π orbital π_b and an antibonding orbital π_a composed of the π type overlap of p orbitals vertical to the molecular plane as can be seen from Fig.6.3 and Example 6.1. In order to consider the mechanism of the Diels-Alder reaction, properties of these HOMO and LUMO are important.

Example 6.1 Compose molecular orbitals and their energy levels from two units of CH_2 (an application of the AH_2 molecule in Section 5.4).

(Solution) Place two units of bent CH_2 with a common central axis bisecting both units, and then get closer to each other (Fig. 6.4).

The lowest energy orbitals of each C_2H_2 unit is 1σ orbital almost purely composed of a C1s orbital, and an interaction of a couple of 1σ orbitals yields a σ orbital (1) due to their same phase mixture and another σ orbital (2) due to the opposite phase mixture. The energy levels become

(1)<(2). This difference is small, because the overlap between C1s orbitals is very small due to very tight electron distributions around the nuclei in the inner shell orbitals, though the energy difference is zero.

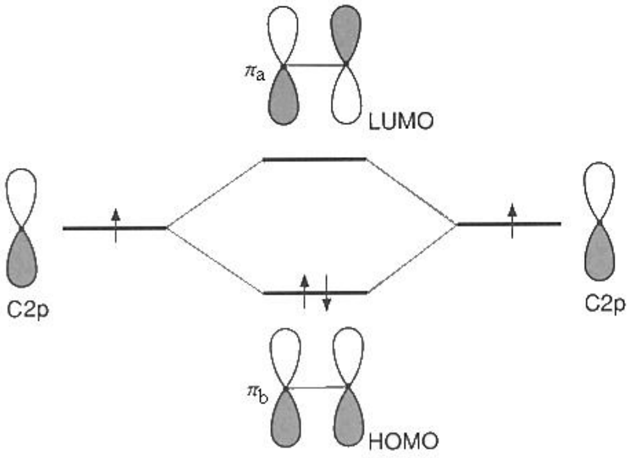


Figure 6.3: HOMO and LUMO of ethylene C_2H_4

Next, let us consider an interaction between 2s orbitals mainly composed of C2s. This interaction yields a C2sCC bonding σ orbital (3) due to the same phase mixture and a C2sCC antibonding σ orbital (4) due to the opposite phase mixture, and the levels become (3)<(4). In this case, the energy difference between (3) and (4) is significantly large because of a large overlap.

A paralell coupling of 3σ orbitals with strong CH bonding characters leads to an orbital (5) with a π bonding character together with an orbital (7) with an atibonding type, and the level ordering becomes (5)<(7).

Here, it should be noted that a same phase interaction at the CC bond region between 4σ orbitals with HH bonding characters yields a level of (6), which intervenes between the levels of (5) and (7). The interaction between 4σ is very strong because of the hybridization of 2s and 2p orbitals on the C atoms. It follows that an antibonding orbital produced by this interaction becomes the higher energy level than the forthcoming two π orbitals (8) and (9).

Since 1π orbital is composed of a p orbital vertical to the CH_2 plane, a bonding π orbital (8) and an antibonding π (9) are produced simply by π type interactions between the p orbitals.

A C_2H_4 molecule has 16 electtrons, and two electrons are accomodated in each orbital from (1)$\sim$(8). Thus, the bonding π orbital (8) is HOMO, and the antibonding π orbital is LUMO.

Molecular orbitals and energy levels for butadiene C_4H_6

A butadiene molecule can be constructed by an electron-pair bond between two radicals having an unpaired electron in each unit, which is produced from ethylen by taking away one H atom from a CH bond. The new CC bond thus produced has a double bond character a little by a reason mentioned below, and it follows that a butadiene molecule has a planar structure in which 10 atoms are placed on the molecular plane. Therfore, butadiene has two isomers, *cis* and *trans* forms (Fig. 6.5). Among them, the *trans* form is more stable. The Diels-Alder reaction of butadiene proceeds in the *cis* form, since this form is suitable to the reaction mechanism discussed below.

Example 6.2 Construct π orbitals and their energy levels of butadiene from p orbitals of four C atoms, starting from two sets of π orbitals of the ethylene type (Fig. 6.6).

(Solution) Let us suppose that π orbitals of butadiene are produced by an π type interaction of a pair of p orbitals at one end of each ethylene unit.

Based on the discussion for constructing A_2 type molecules in Section 5.5, let us consider interactions between bonding π_b orbitals and those between antibonding π_a orbitals. In-phase

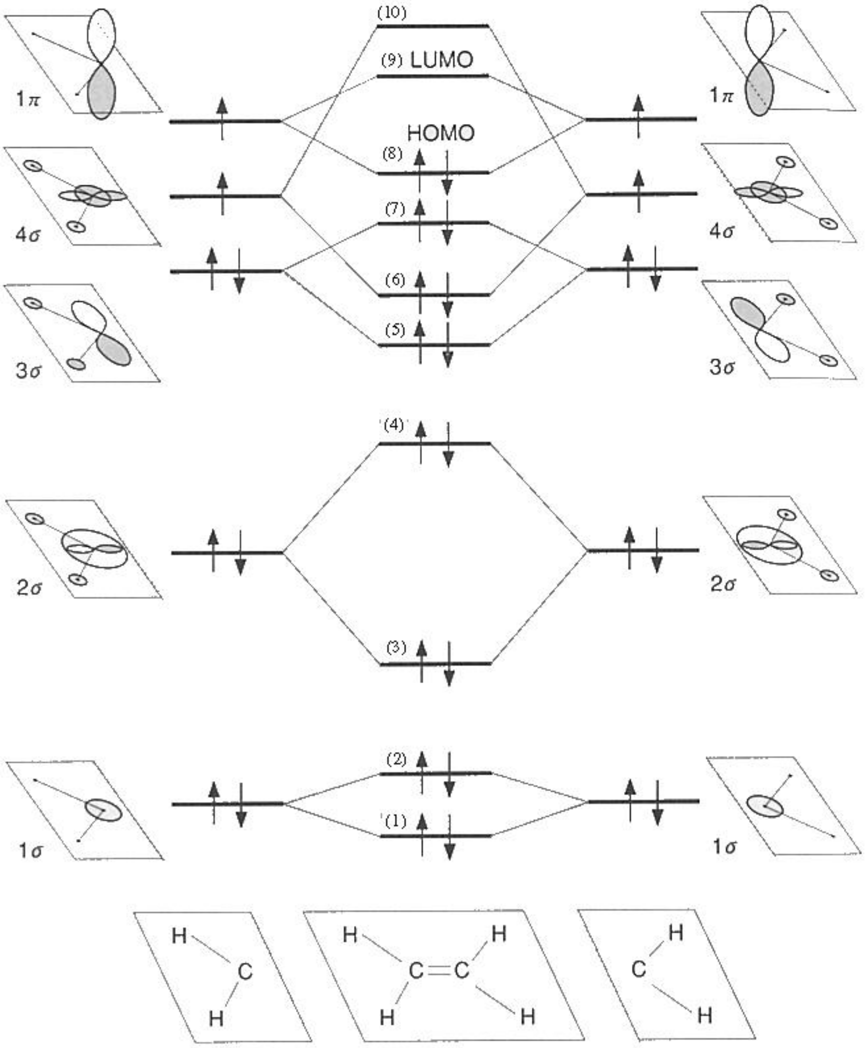


Figure 6.4: Moelcular orbitals of ethylene

interactions between π_b orbitals yield an orbital (1) which is entirely bonding for three CC bonds and expressed as bbb and another orbital (2) having antibonding character in the middle which is expressed as bab. The energy ordering of these orbitals becomes (1)<(2) as can be seen in Fig. 6.6(a). Similarly the same type interactions between π_a orbitals yield an aba type orbital (3) and an aaa type orbital (4). Thus, the energy level ordering becomes (1)<(2)<(3)<(4).

In the next step, let us consider interactions of a pair of orbitals, (1)(3) having a node and (2)(4) having no nodes at the central CC bond. Then, we obtain new orbitals modified by mixing effects shown in (b) of the figure. From the upward to the downward the bonding character is relatively strengthened, and from the downward to the upward the bonding character is relatively weakened.

The energy levels are numbered from the lowest as π_1, π_2, π_3, π_4, in which numbers of nodes are smaller than the numbering by one. This propensity is the same as the number of nodes in wave functions for a particle in a box. This similarity is due to the structure of the C-C-C-C skeleton which is one dimesional space where an electron is accomodated. Noting this similarity, characteristics of π orbitals in butadiene can also be deduced.

Since one electron is provided from a p orbital of each C atom, there are four π electrons in butadienem, which occupy π_1 and π_2 orbitals as electron-pairs. Thus, π_2 is HOMO, and π_3 is

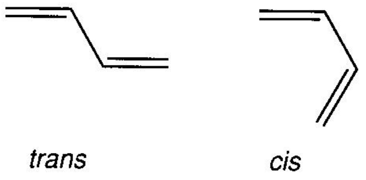


Figure 6.5: *trans* and *cis* forms of butadiene

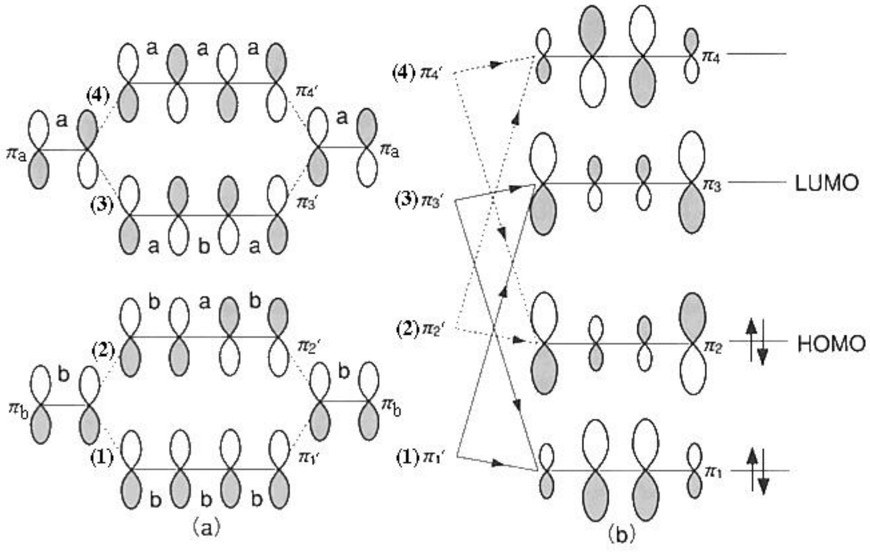


Figure 6.6: Molecular orbitals of butadiene

LUMO. At the central CC bond, the bonding contribution from π_1 is larger than the antibonding contribution from π_2, and hence this bond has slightly a double bond character (the bond length of the central CC bond in butadiene is 1.483 Å, which is a bit shorter than a pure single CC bond of ethane (1.536 Å) and longer than the pure double bond of ethylene (1.338 Å)).

6.3.2 HOMO–LUMO interactions and the symmetry of orbitals

Based on the above orbitals of ethylene and butadiene, let us consider HOMO–LUMO interactions of those orbitals. If ethylene and butadiene molecules are placed on the same plane, H atoms avoid mutual overlaps of π orbitals to result in insufficient interactions. Thus, two molecules should be placed on a pair of parallel planes, the upper and the lower, and we consider interactions of two orbitals, one extending from the upper plane to downward and the other from the lower plane to upward. In Fig. 6.7, ethylene is placed on the lower plane, and butadiene is placed on the upper plane. In this situation, C atoms 1 and 4 can interact with C atoms 6 and 5, respectively. When we place HOMO of ethylene and LUMO of butadiene to have in-phase couplings at the positions 1 and 6 as in Fig.6.7(a), the opposite ends at 4 and 5 can also have overlaps in the same phase. It follows that new bonds are simultaneously formed at 1∼6 and 5∼4.

Now, let us study effects of the above interactions in terms of changes in bonding characters associated with the electron transfer. Electrons in the electron-pair of ethylene flow into butadiene, and then bonding electrons around 5 and 6 go away to some extent to result in the decrease of the bonding between 5 and 6. This effect reducing the bonding can be denoted as (−) as shown in Fig. 6.8. As already mentioned, the electrons flow into the bonding regions of 1-6 and 4-5, where bonds are missing before the reaction. Thus, such an increase of the bonding in these regions can be denoted as (+). Also, the electrons flow into antibonding regions of 1-2 and 3-4 in

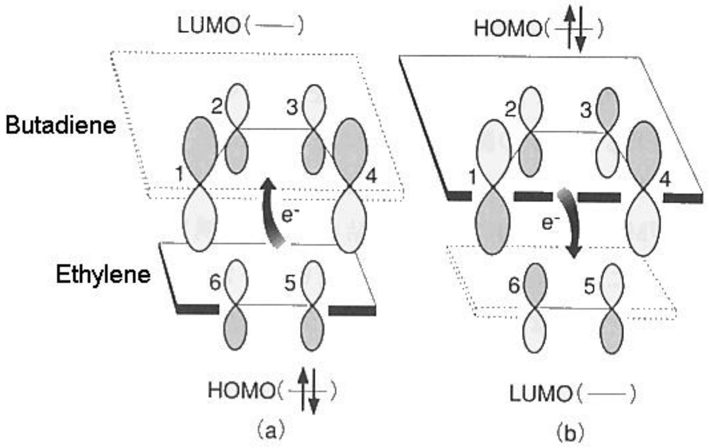


Figure 6.7: HOMO–LUMO interactions of ethylene and butadiene

LUMO, and these regions have (–) effects on bonding. The electron flow into the bonding region of 2-3 in LUMO gives a (+) effect. As summarized in the middle of Fig. 6.8, the above effects are alternating on the perimeter of the hexagon as +–+–+– to lead to bond-order changes of ±1 producing a skeleton of cyclohexene as shown in the right part of Fig. 6.8.

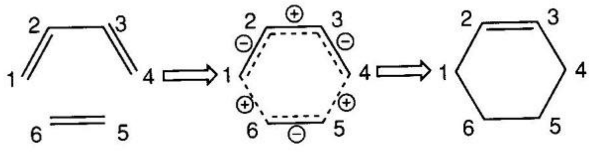


Figure 6.8: Bond-order changes in the Diels-Alder reaction

By the way, we should consider interactions between LUMO of ethylene and HOMO of butadiene as shown in Fig.6.7(b). Although this combination of orbital interactions has an opposite direction of the electron flow, associated changes in bonding characters are the same as those in Fig. 6.8. It follows that these effects of HOMO–LUMO interactions between ethylene and butadiene occur in a concerted way of bond-order changes to complete bond formation and destruction. It should be noted in two types of HOMO–LUMO interactions that one includes interactions between symmetric orbitals, and the other includes interactions between antisymmetric orbitals. Such a reaction with good symmetry combinations is called the symmetry allowed reaction.

In the case of two ethylene molecules, the cyclic addition reaction cannot proceed in a concerted way, because the symmetry matching at one end is not compatible with another symmetry matching at the other end, as can be seen in Fig. 6.9. Such a reaction without good symmetry combinations is called the symmetry forbidden reaction.

Example 6.3 Predict the stereo chemical structure of dichlorocyclohexene produced by cyclic addition reaction of *cis*-dichloroethylene and butadiene.

(Solution) Since Cl atoms of *cis*-dichloroethylene are on the same side of the plane of two C atoms in ethylene during the reaction process, two Cl atoms are also on the same side in the product cyclohexene ring with respect to C atoms 5 and 6 in Fig. 6.7, as can be seen in Fig. 6.10.

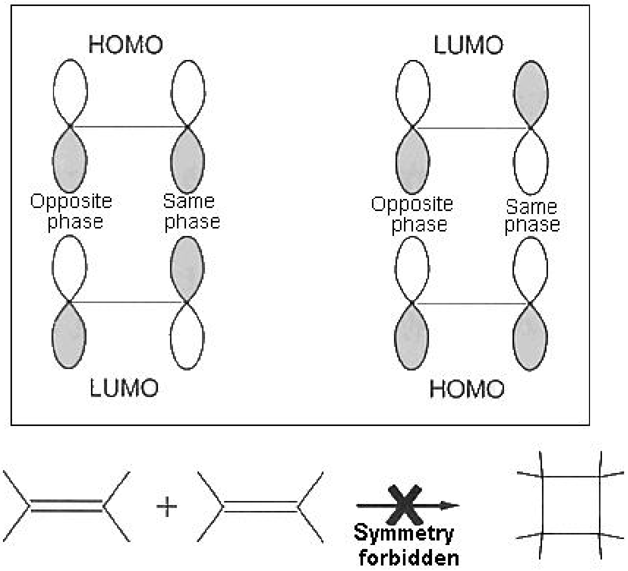


Figure 6.9: HOMO–LUMO interactions between two ethylene molecules

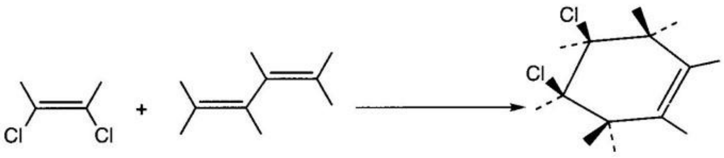


Figure 6.10: The structure of dichlorocyclohexene

6.4 Selectivity and substitution effects in chemical reactions

In view of obtaining chemical products utilizing chemical reactions, it is preferable to minimize the useless loss of the strating materials. For this purpose, by-products should not be produced. Production of by-products necessarily increases not only the useless loss of the starting materials but also additional efforts to separate and purify them from the aimed products. From actual needs for application, development of selective reactions as well as elucidation of their reaction mechanisms have been aroused interests of many chemists. In this section, we will study some selective reactions owing to introduction of functional groups.

6.4.1 Deformation effects of HOMO and LUMO by introduction of functional groups

When an electron accepting functional group X such as the formyl group CHO is introduced in ethylene, the vacant orbital of X interacts with π_{b} and π_{a} orbitals, and the shape of LUMO will have a substantially increased distribution at an end distant from X. This mechanism can be explained by interactions of π_{b} and π_{a} with X on the basis of the two to one orbital interactions as shown in Fig. 6.11. In the new LUMO, the higher π_{a} mixes with X in the same phase from the upward, and in addition the lower π_{b} slightly mixes with X in the opposite phase from the downward. It follows that the electron wave at the nearest part from X is weakened in the opposite phase, and that the electron wave at the distant part is strengthened in the same phase. Since the LUMO level becomes lower, the substituted ethylene becomes a stronger electron acceptor.

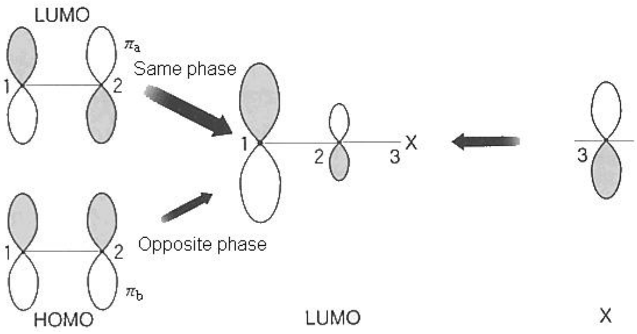


Figure 6.11: Deformation of LUMO by introduction of an electron accepting functional group X

When an electron donating functional group Y such as the methoxy group –OCH$_3$ is introduced in butadiene, the electron-pair of Y interacts with HOMO(π_2) and LUMO(π_3) of butadiene, and the shape of HOMO will have a substantially increased distribution at an end distant from Y. This mechanism can be explained by interactions of π_2 and π_3 with Y on the basis of the two to one orbital interactions as shown in Fig. 6.12. In the new HOMO, the lower π_2 mixes with Y in the opposite phase, and in addition the higher π_3 slightly mixes with Y in the same phase from the upward. It follows that the electron wave at the nearest part from X is weakened in the opposite phase from the downward, and that the electron wave at the distant part is strengthened in the same phase. Since the HOMO level becomes higher, the substituted butadiene becomes a stronger electron donor.

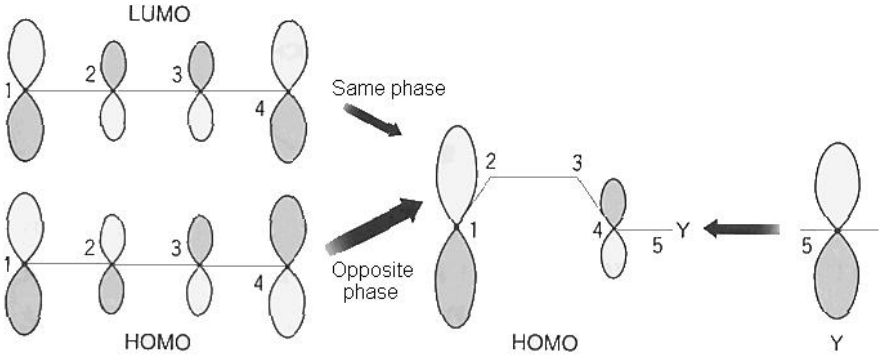
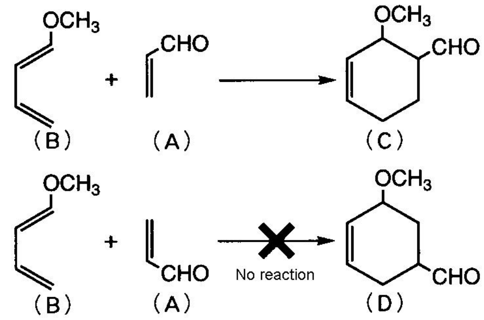


Figure 6.12: Deformation of HOMO by introduction of an electron donating functional group Y

As can be seen in the above examples, spatial extension of HOMO and LUMO can be modified upon introduction of functional groups, which changes the extent of overlaps in orbital interactions to result in variation of the reactivity. Whether accepting or donating power is aimed to be emphasized can be chosen by selection of the functional group. These techniques can be applied to selective control of reaction routes as can be seen in the following example.

6.4.2 Regioselectivity of reactions

Acrolein (A) is a compound produced by substitution of H in ethylene by the CHO group, and 1–methoxybutadiene (B) is a compound generated by substitution of H in one end of butadiene by the OCH$_3$ group. When (A) and (B) undergo addition reactions, a simple deduction neglecting effects of the functional groups leads to tow possible products, an *ortho*-adduct (C) and a *meta*-adduct (D) with the same probability. The substitution effects, however, emphasize the electron accepting ability of (A) as well as the electron donating power of (B). This means that LUMO in (A) and HOMO in (B) play dominant roles. It follows that only (C) is selectively synthesized without formation of (D).



Let us study the mechanism of the selective production of (C). As can be seen in Figs. 6.11 and 6.12, LUMO in (A) and HOMO in (B) have the substantial enlargement of orbital lobes at the distant end from the functional groups. On the other hand, at the nearest part from the functional groups the orbital lobes become smaller.

When orbital lobes for the most important parts of the orbital interactions are inequivalent to have different spatial extension, let us denotes the inequalities $a > b$ for one and $a' > b'$ for the other. Since the extent of an overlap depends on the overlap integral, we can estimate the magnitude of the interaction from the summation of respective products of the overlapping parts. Now let us compare pairs of the larger ones and smaller ones of $(aa' + bb')$ with combinations of different types, the larger with the smaller and the smaller with the larger, of $(ab' + a'b)$. The magnitude of the overlaps for the former case is always larger than the latter. This can be seen from the difference by the following equation.

$$(aa' + bb') - (ab' + a'b) = (a - b)(a' - b') > 0$$

Since the larger the overlap becomes the stronger the orbital interaction becomes, combinations of big ones together with those of small ones are selected in real chemical reactions. On account of this mechanism, new chemical bonds are formed at both of the nearest parts from the functional groups as well as at both of the distant ends. It follows that the *ortho*-adduct (C) in which the functional groups are placed in the adjacent positions is selectively produced.

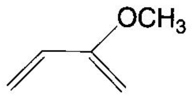
Exercises

6.1 A ground-state oxygen atom in the triplet state has two unpaired electrons, whereas an oxygen atom in the singlet state has a vacant p orbital among the valence p orbitals. Such a vacant orbital of an O atom can accept coordination of one of electron-pairs in a chloride ion Cl^- to yield a hypochlorous ion ClO^-. Noting this reaction as well as the similarity of electron configurations of S^{2-}, P^{3-}, Si^{4-} with the Cl^- ion, which have the same number of electrons (isoelectronic configuration), explain structures of the following compounds.

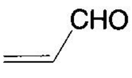
$$(ClO_4{}^-, SO_4{}^{2-}, PO_4{}^{3-}, SiO_4{}^{4-}, XeO_4)$$

6.2 Explain the reasons why rare gases are chemically inactive.

6.3 In 2-methoxybutadiene the electron donating ability of HOMO increases with the electron donating effect of the methoxy($-OCH_3$) group, and in addition LUMO of the butadiene skeleton slightly mixes with HOMO at the position 2. Considering these properties, predict the structure of the main product of the addition reaction of 2-methoxybutadiene with acrolein.



2-Methoxybutadiene



Acrolein