Quantum Chemistry

Koichi OHNO

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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.

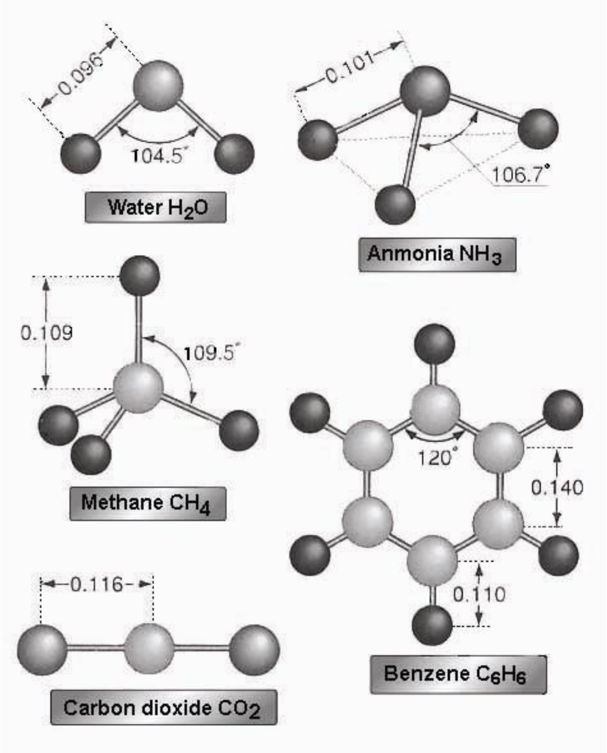


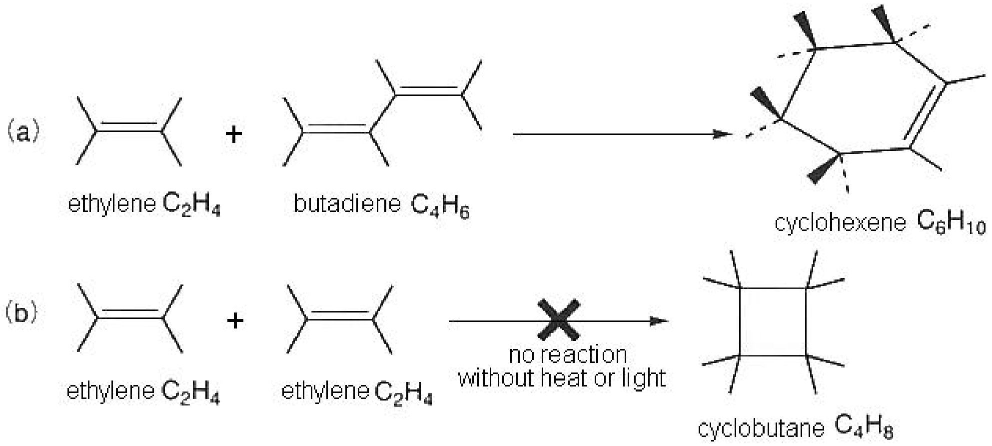
Figure 1.1: Skeletal structures of molecules. Numerical figures are bond lengths in nm and bond angles in degree.

(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

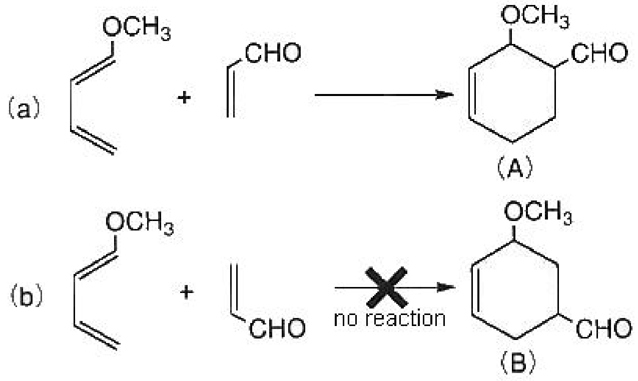
quantum chemical theory.



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

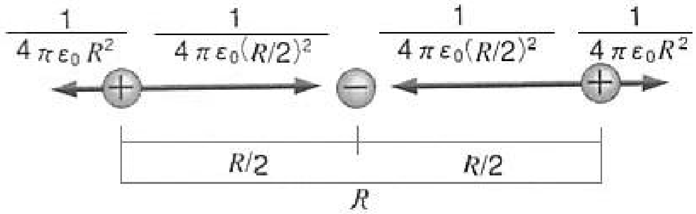
$$F = \frac{Q_1 \cdot Q_2}{4\pi\varepsilon_0 r^2} \tag{1.1}$$

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

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

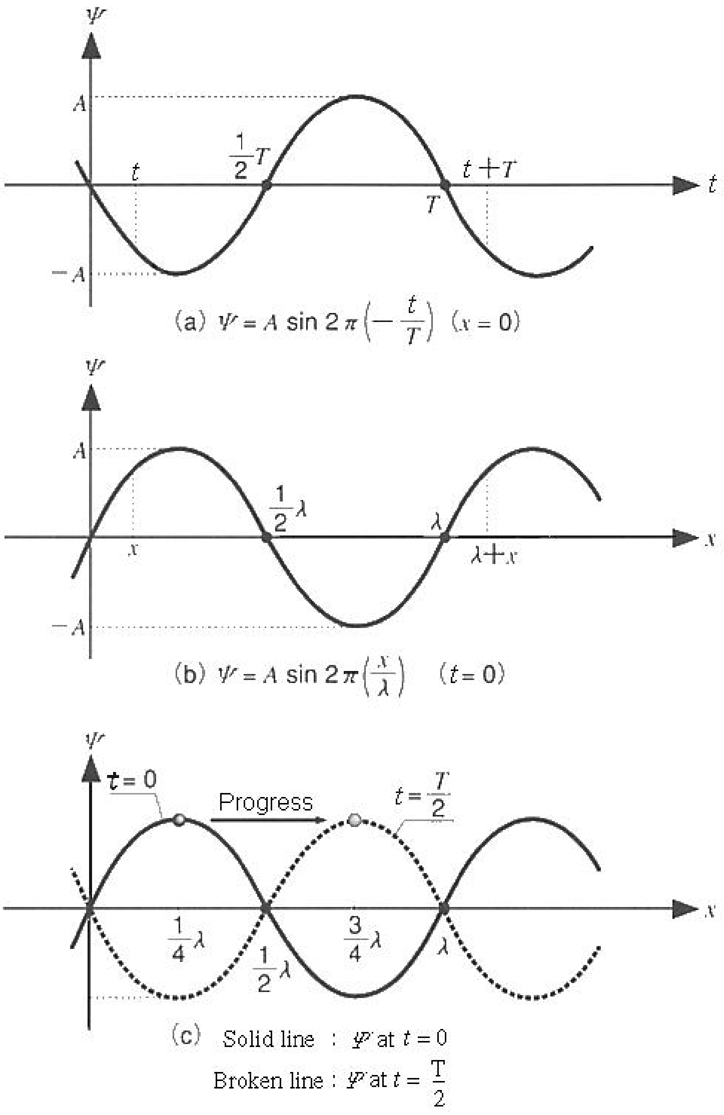


Figure 1.2: Sine waves

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

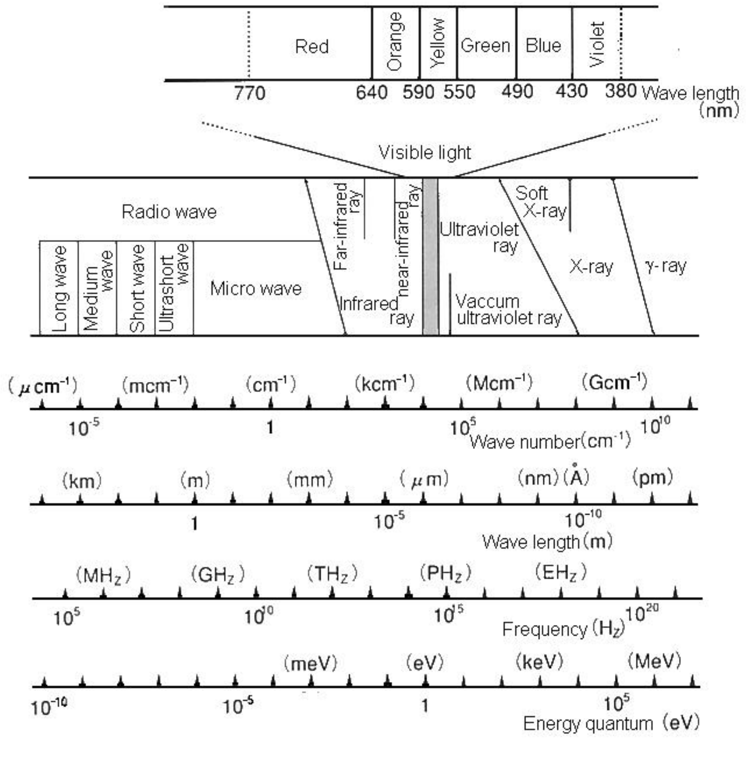


Figure 1.3: Classification of electromagnetic waves

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.

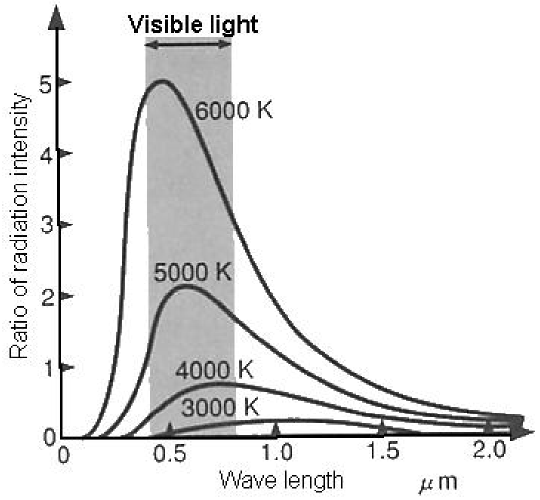


Figure 1.4: Spectra of black body radiation

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 $\lambda_{\max}$ and the absolute temperature T as

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

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

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

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.

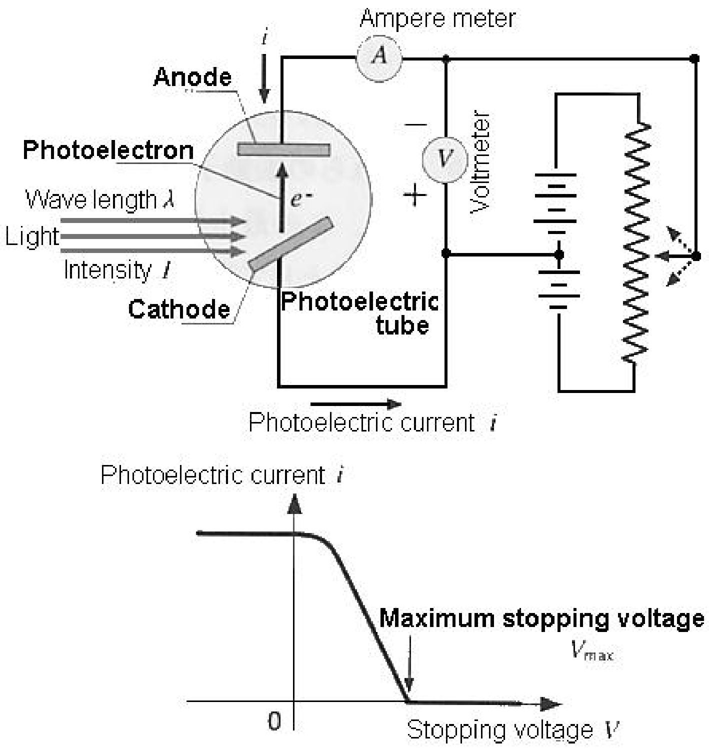


Figure 1.5: The relationship between the photocurrent and the retarding voltage in the photoelectric effect

(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).

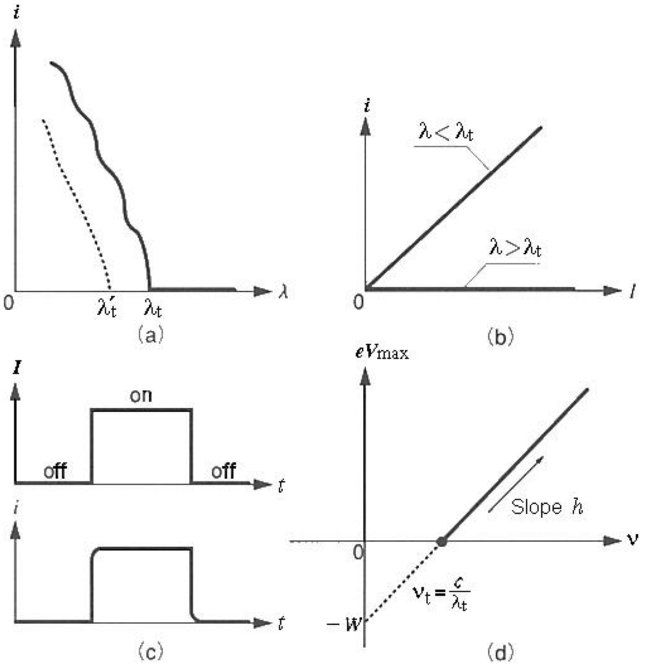


Figure 1.6: Observed features of the photoelectric effect

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($400 \sim 800$ 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.

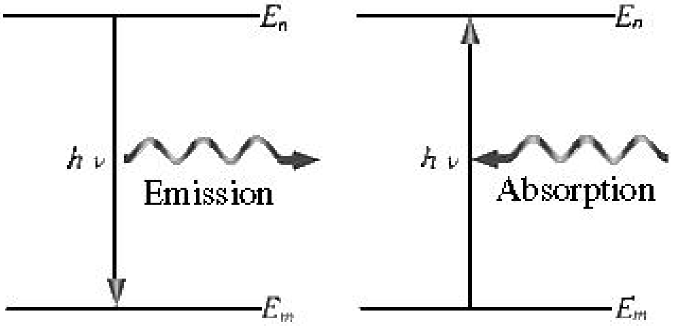


Figure 1.7: Light absorption and emission and Bohr's frequency condition

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.

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

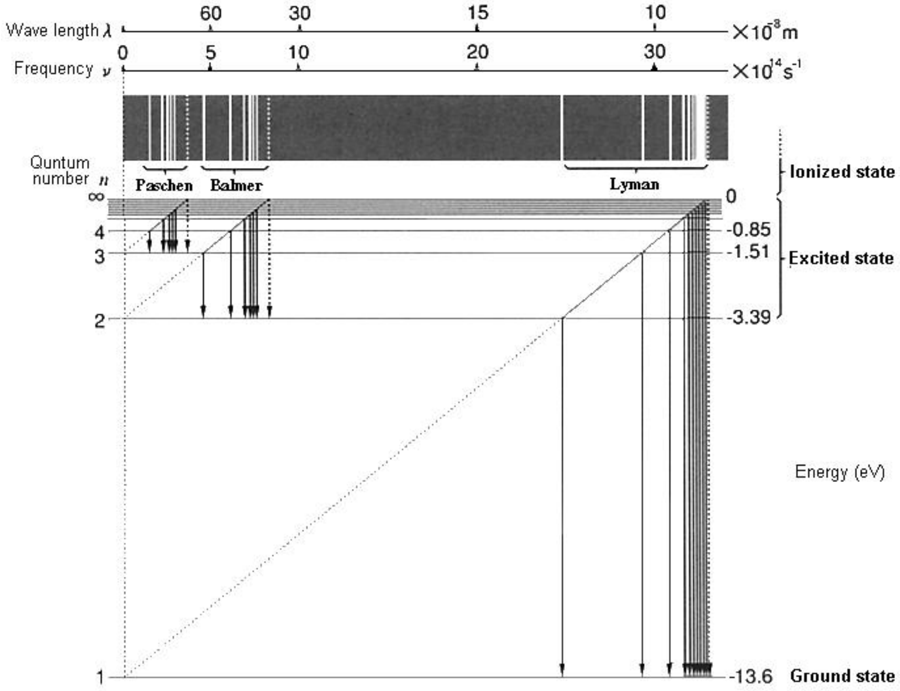


Figure 1.8: Energy levels and spectra of hydrogen atom

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

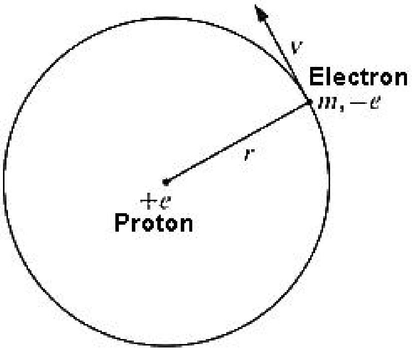


Figure 1.9: Bohr's model

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.

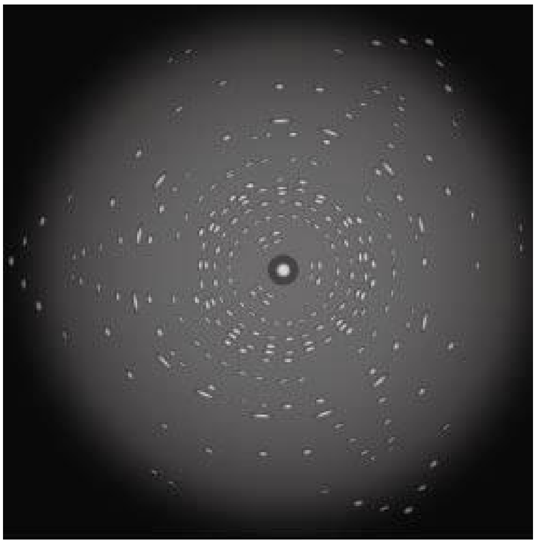


Figure 1.10: Laue spots of calcium carbonate (provided by Rigaku Denki)

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

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

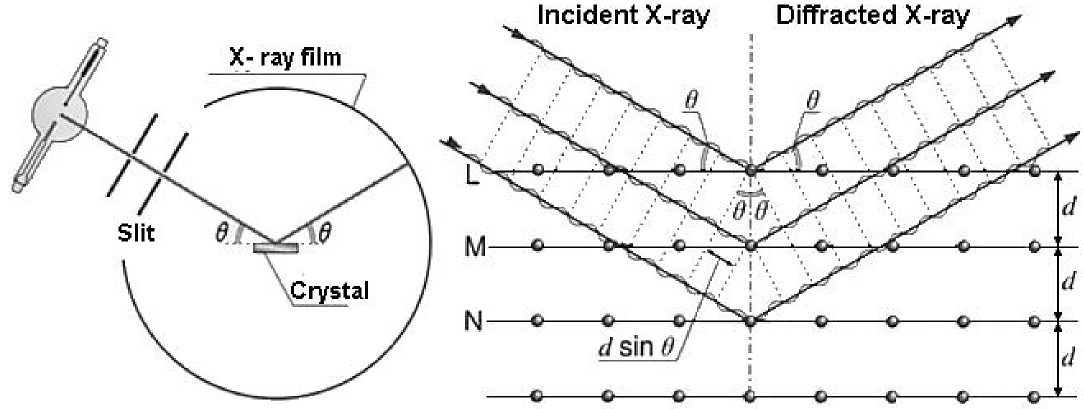


Figure 1.11: X-ray diffraction by crystal lattice

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.

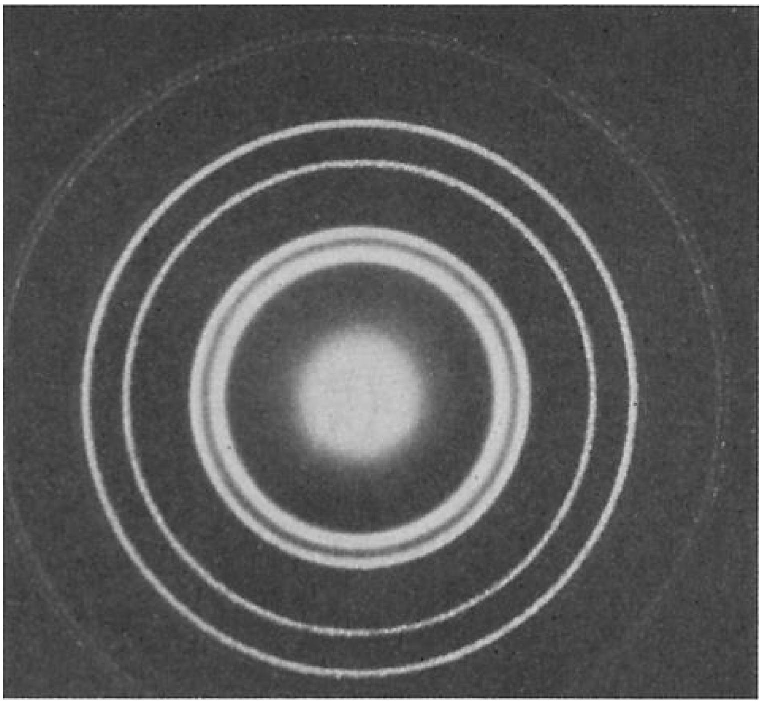


Figure 1.12: Electron diffraction pattern of gold polycrystals

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 $\mathrm{e}^{i\theta}$ 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.

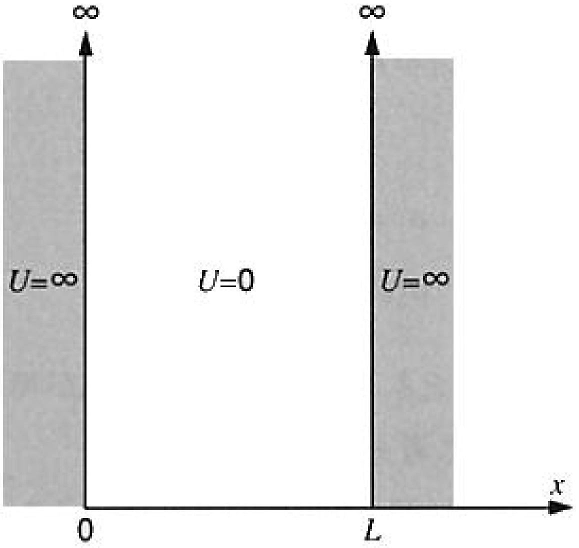


Figure 1.13: Potential energy U(x) for a particle in a one-dimensional box

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.

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

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

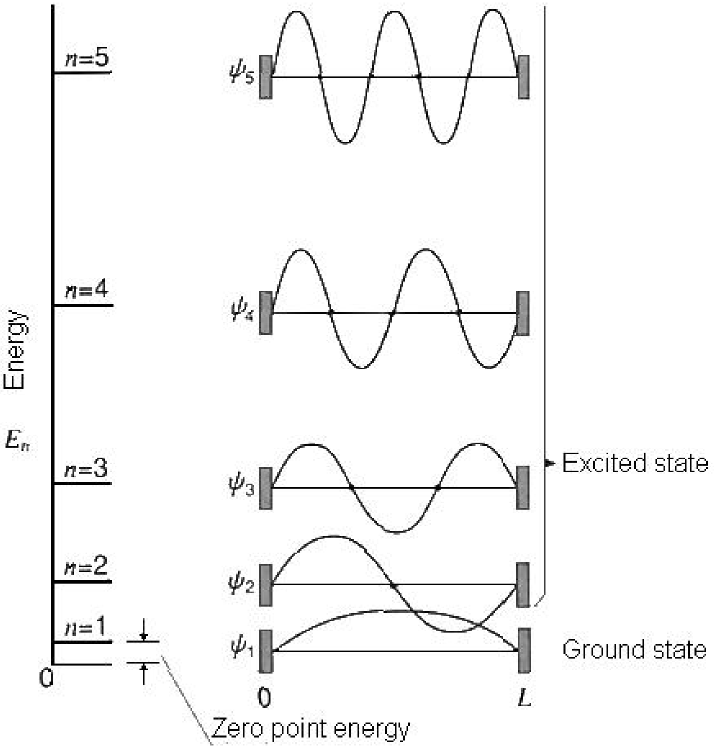


Figure 1.14: The energy levels $E_n = n^2h^2/8mL^2$ and the wavefunctions $\psi_n(x)$ for a particle in a one-dimensional box

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 $U_{\min} = 0$). The fact that $E_1 - U_{\min} > 0$ indicates that a particle can move with the energy of $E_1 - U_{\min}$, even at the absolute zero temperature where no energy can be removed from the system any more. Therefore, the energy of $E_1 - U_{\min}$ 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 $\mathrm{d}q$. 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

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

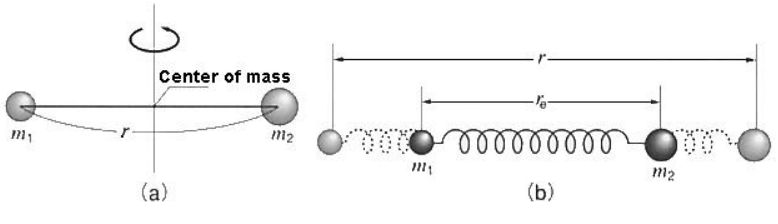


Figure 1.15: Relative motion of two-particle systems (a) Rotational motion with a fixed r (b) Vibrational motion

(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.

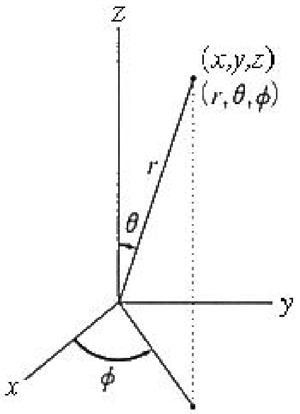


Figure 1.16: The polar coordinates

(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.

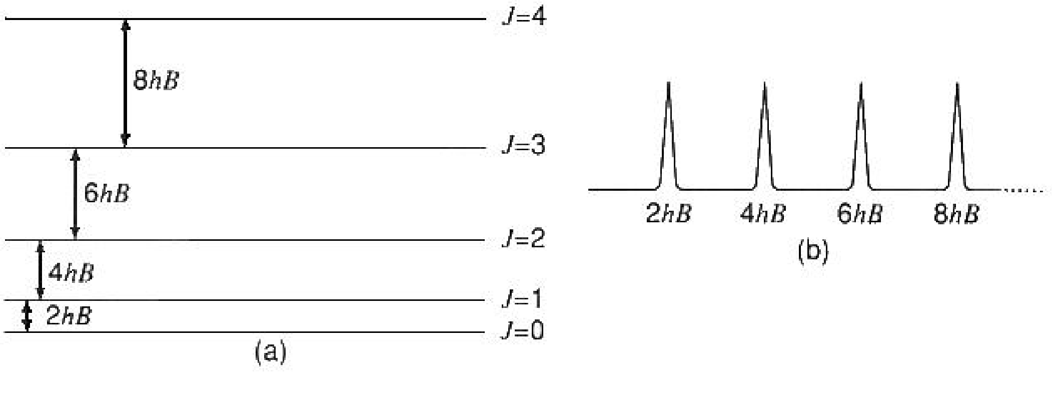


Figure 1.17: The rotational energy levels (a) and the rotational spectrum (b). The rotational constant, $B = \frac{h}{8\pi^2 \mu r^2}$. The selection rule for rotational transitions, $\Delta J = \pm 1$.

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).

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

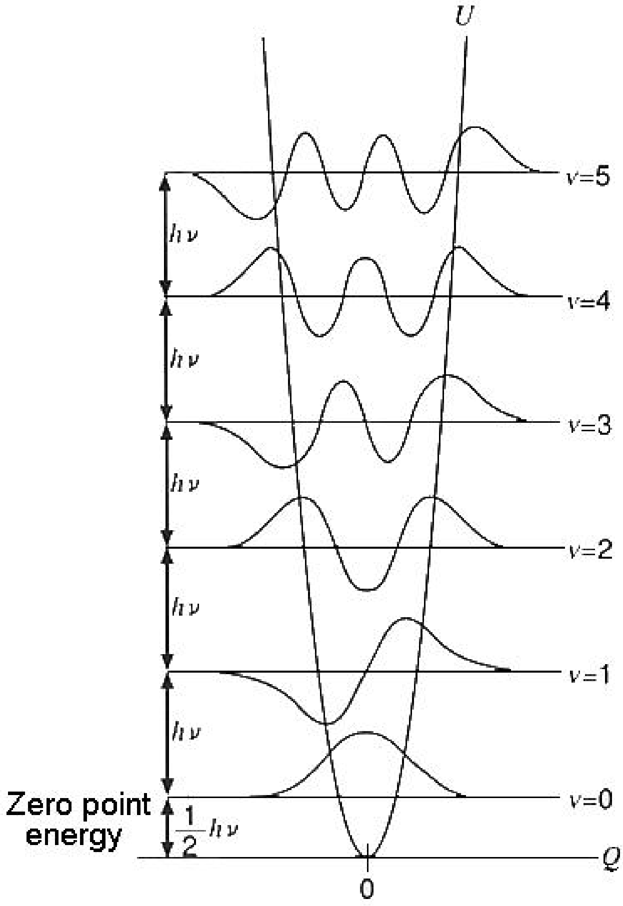


Figure 1.18: Potential energy $U = \frac{1}{2}kQ^2$ as well as energy levels and wavefunctions for a one-dimensional harmonic oscillator

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.

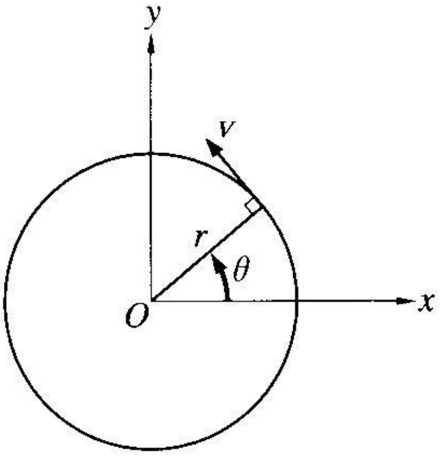
$$\begin{aligned} x &= r\cos\theta \\ y &= r\sin\theta \\ p_x &= mv_x = -mv\sin\theta \\ p_y &= mv_y = mv\cos\theta \end{aligned}$$

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, θ, ϕ), 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 $Y_{l,m}(\theta,\phi)$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

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

$$Y_{1,\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

$$Y_{2,\pm1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta \mathrm{e}^{\pm i\phi}$$

$$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta \mathrm{e}^{\pm i2\phi}$$

$$Y_{3,0} = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta)$$

$$Y_{3,\pm1} = \sqrt{\frac{21}{64\pi}}(5\cos^2\theta - 1)\sin\theta \mathrm{e}^{\pm i\phi}$$

$$Y_{3,\pm2} = \sqrt{\frac{105}{32\pi}}\cos\theta\sin^2\theta \mathrm{e}^{\pm i2\phi}$$

$$Y_{3,\pm3} = \sqrt{\frac{35}{64\pi}}\sin^3\theta \mathrm{e}^{\pm i3\phi}$$

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.