– 7 –

Elements of Quantum Mechanics

7.1 PARTICLE-WAVE DUALITY

7.1.1 De Broglie hypothesis

After the experiments and theoretical explanations that led to the revival of the corpuscular theory of light outlined in Section 6.6, it was logical to take the following step: restoring symmetry and assigning wave characteristics to those micro-objects that are known to us as particles. This step was taken in 1924 by the French theoretical physicist L. de Broglie (Nobel Prize, 1929). His idea consisted of the following. If quanta of electromagnetic radiation—photons—possess corpuscular characteristics, i.e., possess a mass ($m = E/c^2$), momentum ($p = hk$) and energy ($E = h\nu$), the converse must also be true, i.e., a wave process must be related to a moving particle. De Broglie suggested a formula for the wavelength of such a process:

$$\lambda = \frac{h}{m\upsilon}, \tag{7.1.1}$$

where h is the Planck's constant, m is the particle mass and v is its velocity. These waves are called "de Broglie waves."

It must be said that no one can imagine what lies behind this statement. We will see here a case that is quite typical in quantum mechanics: our normal imagination is not adequate to conceive of the main principles of this science. There is certainly an explanation for this effect. Indeed, let us imagine a 10 g bullet moving at a speed of 1000 m/sec. According the formula (7.1.1), the corresponding wave process (de Broglie wave) has the wavelength $\lambda \sim (10^{-34}/(10^{-2} \times 10^3)) \sim 10^{-35}$ m. In order to reveal the character of such a wave, we must find a grating with a comparable period. Certainly, there are no such gratings. Generalizing, it can be said that in the everyday world there is no way to prove that de Broglie waves corresponding to a moving body can be visualized. Therefore, it is purely academic. This is why the referee of de Broglie's thesis, the well-known French physicist P. Langevin, was not able to evaluate de Broglie's formula and stated "de Broglie's idea is either the fruit of his morbid imagination or, conversely, a brilliant idea, though in both cases it deserves high recognition." The Nobel Prize was the relevant award.

Quite a different situation occurs in the micro-world. Here, because of small particle masses, the de Broglie wavelength is commensurate with the interatomic distances in crystals; therefore, the corresponding experiment can be realized: a crystal can serve as a diffraction grating (refer to Section 6.3.5). In fact, according to formula (7.1.1) and the conservation law we can obtain

$$\lambda = \frac{h}{m\upsilon} = \frac{h}{(2meU)^{1/2}} = \frac{\sqrt{150}}{\sqrt{E}} \sim 10^{-10}\ \text{m}, \tag{7.1.2}$$

i.e., a voltage of 150 V is needed to produce an electron beam with a wavelength of 10^{-10} m and to observe diffraction.

It is quite natural to ask the question: what do the microparticles (electrons, neutrons, etc.), on one side, and the phonons on the other represent? The modern development of science enables it to be stated that all micro-objects simultaneously possess a set of properties, among which both wave and corpuscular properties are equally present, and they reveal them depending on the conditions to which an experimenter subjects them. This statement is the essence of corpuscular-wave dualism, which in turn is the basis of quantum mechanics.

7.1.2 Electron and neutron diffraction

Only 2 years were needed to prove electron diffraction experimentally. In 1927, simultaneously in several laboratories in different countries, attempts were made to observe electron diffraction. Davisson and Germer in America, Thomson in England and, several years later, Tartakovsky in Russia observed electron diffraction after the interaction of electrons with single crystals (C.J. Davisson and G.P. Thomson, Nobel Prize 1937) and polycrystalline films.

In a simplified representation, the principles of an electron diffraction device are depicted in Figure 7.1. The main part of the instrument is the vacuum column, in which all the elements of the device are contained. The heating filament 1 (cathode) emits electrons by thermoemission, which then speed in an electrostatic field with the potential difference *U*. Passing through the diaphragm, monochromatic electrons (i.e., electrons with constant wavelength, refer to formula (7.1.2)) fall onto the polycrystalline film sample 3. The polycrystalline sample contains an enormous number of small microcrystals, absolutely chaotically oriented in space. From the whole set of microcrystals, some are oriented with their crystallographic planes $p_{1,}$ with interplanar distance d_1 with respect to the incident beam of electrons at an angle θ_1, for which the Bragg condition is met (refer to 6.3.5). Planes p_1 of this crystal will give a reflected beam with an angle $2\theta_1$ with respect to the direction of the primary electron beam. In a polycrystalline sample, an ensemble of other microcrystals can always be found which have the planes p_1 identically oriented with the same reflecting angle θ; all the p_1 planes look like they are rotated around the primary beam direction. Therefore, all the reflected beams are situated on a cone around the direction of the primary beam with a cone opening angle $4\theta_1$. Each electron colliding with the fluorescence screen 5 produces a flash; all the flashes create a diffraction ring.

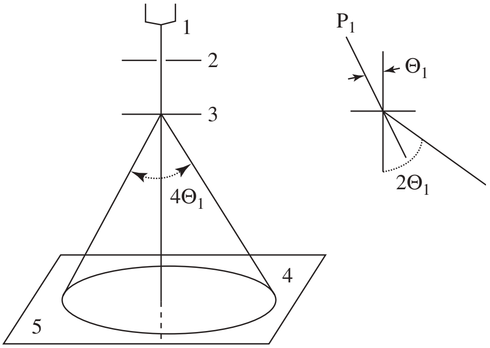


Figure 7.1 An electron diffraction investigation scheme.

Under known instrument parameters (distance from the sample to the screen L, applied voltage U, etc.), the diffraction circle diameter D is connected with the interplanar distance d (refer to Sections 6.3.5 and 9.1) by the formula

$$\lambda = \frac{nh}{\sqrt{2meU}} = 2d\sin\theta \cong 2d\theta = \frac{dD}{2L},$$

and, accordingly,

$$d = \frac{2Lh}{D\sqrt{2meU}}, \tag{7.1.3}$$

where m and e are the mass and charge of the electron.

There are other crystallographic planes p_2, p_3 and p_4 in the polycrystalline sample too, with other diffraction cone opening angles $4\theta_2$, $4\theta_3$ and $4\theta_4$, respectively. As a result, the typical electron diffraction pattern looks like a set of concentric circles, all circles having a different intensity.

The set of interplanar distances d_i and the corresponding intensity I_i of each circle characterize the material analyzed. The diffraction pictures of MgO films obtained by means of the diffraction of X-rays (usually accepted as waves) and electrons (usually considered as particles) are compared in Figure 7.2; since they were taken using different wavelengths, for the best comparison both pictures were brought to the same scale. (Spots on the electron diffraction rings are caused by the presence of partial crystalline order in the MgO film.) The similarity of the diffraction images made with electrons and X-rays can clearly be seen in this picture.

In 1932, the English scientist J. Chadwick discovered a neutral elementary particle—the neutron with a mass practically equal to the proton mass (Nobel Prize, 1935). Experiments to prove neutron diffraction immediately followed. In 1936, such experiments gave a positive result. However, in the modern view as it is currently used, neutron diffraction as a method of structure investigation became possible only after nuclear reactors were set up. Neutron diffraction became one of the most powerful methods for the analysis of

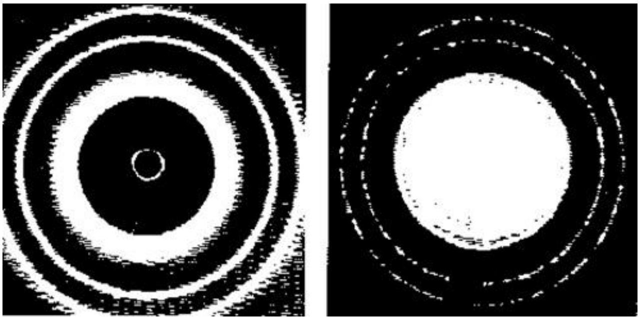


Figure 7.2 A MgO powder diffraction patterns obtained by X-ray (left) and electrons (right).

solids. In 1995, the American physicist C. Shull, who contributed most to the development of the method of neutron diffraction in physics and chemistry, was awarded a Nobel Prize.

Along with neutron diffraction, experiments of inelastic neutron scattering (where the neutron behaves as a material particle interacting with phonons (refer to Chapter 7.3), according to collision theory (refer to Section 1.5.5)), were also realized. For the discovery of inelastic neutron scattering and establishing a new method of solid state investigations, the Canadian physicist B. Brockhause was awarded the Nobel Prize (1995).

Thereby, the de Broglie hypothesis has been widely accepted as a scientific law. To reiterate, particle-wave dualism is one of the cornerstones of quantum mechanics.

EXAMPLE E7.1

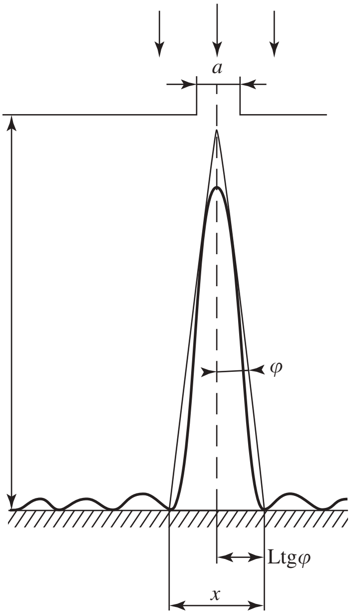
An electron acquires a kinetic energy K under an accelerating voltage U. Determine its de Broglie wavelength for two cases $U_1 = 51$ V and $U_2 = 510$ kV.

Solution: The electron wavelength λ depends on its momentum p: $\lambda = (2\pi\hbar/\mathrm{p})^*$. In the case of classic mechanics the momentum depends on energy $p = \sqrt{2m_0K}$; however, for a relativistic case this relationship is $p = (1/\mathrm{c})(\sqrt{(2E_0 + K)K})$. The relation * for two cases mentioned can accept the forms $\lambda = 2\pi\hbar/(\sqrt{2m_0K})$, and correspondingly $\lambda = 2\pi\hbar/\left((1/\mathrm{c})\sqrt{2E_0 + K)K}\right)$.

Compare the electron's kinetic energy for two cases and compare them with the electron's rest mass; the kinetic energy is 51 eV and 0.51 MeV; the electron's rest mass is just 0.51 MeV. Therefore, the second case corresponds to a relativistic one. The wavelengths for these cases are: $\lambda_1 = 2\pi\hbar/|\mathrm{e}|U_1 = 172$ and $\lambda_2 = 2\pi\hbar/\sqrt{3}m_0c =$ 1.4 pm.

EXAMPLE E7.2

Assume that on a narrow slit of a width $a = 1$ µm, a plane-parallel electron beam of very low intensity, having speed $\upsilon = 36.5 \times 10^6$ m/sec, is directed (Figure E7.2, refer also to Figure 6.15). Taking into account the electron wave properties, define the distance between two first minima of intensity of the first order (that is width of a zero maximum) in a diffraction spectrum. Assume the distance from the slit to the screen to be $L = 10$ cm.



Solution: Assume that according to de Broglie hypothesis, a wave of wavelength $\lambda = 2\pi\hbar/m\upsilon$* is attributed to a particle of mass m moving with a speed υ. Therefore, diffraction should be observed. The diffraction minimum in the spectrum can be found according to the relation $a \sin \varphi = (2k+1)(\lambda/2)$ (refer to Section 6.3.2), where k indicates the diffraction order (in our case $k = 0$; Figure E7.2). Besides diffraction angle is small, $\sin \varphi \approx \tan\varphi \approx \varphi$ and therefore, $a\varphi = (3/2)\lambda$. The sought distance x on the screen is .

$$x = 2L \tan \varphi \approx 2L(3/2)(\lambda/a) = 3L\lambda/a.$$

Using the equation * we obtain

$$x = \frac{6\pi\hbar L}{m\upsilon} \times a^{-1}.$$

Executing calculations, we obtain $x = 6 \times 10^{-5}$ µm. This means that a spectator can find a particular electron in this range, i.e., the uncertainty to locate the electron's position is x.

EXAMPLE E7.3

A plane-parallel incident electron beam falls on a crystallographic plane of a nickel single crystal at an angle of 64°. Diffraction takes place. Accepting the interplanar distance of the given crystallographic planes as $d = 200$ pm, define the de Broglie electron wavelength λ and their speed υ.

Solution: Diffraction of X-rays is described in Section 6.6.4; electrons exhibit the same property. The Bragg's equation is applicable to this case $2d \sin\theta = n\lambda$, n being the diffraction order, $n = 1$ in our case. From this equation we can find the wavelength $\lambda = 2d \sin\theta = 360$ pm. From the de Broglie relation the electron's speed can be found:

$$\upsilon = 2\pi \frac{\hbar}{m\lambda} = 2 \text{ Mm/s}.$$

7.2 HEISENBERG'S UNCERTAINTY PRINCIPLE

Particle-wave duality entails important consequences. The question is, can a micro-object simultaneously possess precise values of its coordinate and momentum? Indeed, a certain internal self-contradiction exists between the characteristics of a material particle that can be localized in space with arbitrary accuracy and the monochromatic de Broglie wave, which according to its nature is extended from $-\infty$ to $+\infty$ and is completely delocalized in space. However, it is exactly the latter that possesses a certain, exact wavelength and, accordingly, fixed momentum. Quantitative analysis allowed W. Heisenberg in 1927 to suggest the principle (Nobel Prize, 1932), which nowadays is given as follows: *there exists no state in which the coordinates of a microparticle and its momentum have precise values*.

If a micro-object is traveling along the x-axis, one can characterize the uncertainty of the coordinate and component of momentum by values Δx and Δp_x; then the Heisenberg principle (for coordinate and momentum) has the form

$$\Delta x \Delta p_x \geq h, \tag{7.2.1}$$

i.e., the product of the uncertainties in the coordinate and corresponding component of momentum cannot be less than h.

It is possible to apply another interpretation to the Heisenberg uncertainty principle. It is well-known that a wave can be characterized by the precise value of the wavelength, when it spreads from $-\infty$ to $+\infty$. It is also known that such a wave is a mathematical abstraction; any wave has an origin and an end. Accordingly, this model corresponds to the precise values of the wavelength (and wave vector $\boldsymbol{k}$) and, consequently, momentum p. It means that in this case, uncertainty in the momentum Δp_x is zero (Figure 7.3, on the left). As a result, we are unable to assign any position to the particle; its uncertainty is equal to infinity. Certainly, the product of Δx and Δp_x can be less than h. Such values of uncertainties save an equitable correlation of Heisenberg uncertainties.

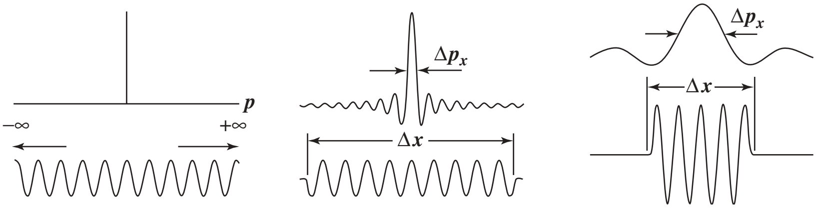


Figure 7.3. An uncertainty principle for x and p_x: the higher the particle localization, the lower the determination of its momentum.

However, if we try to reduce the uncertainty in the particle's position and put it in a state when Δx becomes any finite quantity, say a value L (Figure 7.3, middle), the product $L \times 0$ cannot be larger than h. In other words, this will bring about the appearance of an uncertainty in the momentum, which is displayed in Figure 7.3 (on the right) in the form of a curve, the maximum width of which is Δx (which can be evaluated as h/L).

The Heisenberg uncertainty principle imposes essential restrictions on some laws of classical mechanics. In particular, these affect a very important notion such as trajectory. As an example, let us consider a hydrogen atom within the framework of the Bohr model: an electron revolves around a proton along a circular orbit. From the known electron mass and charge, as well as the electrical constant, within the framework of classical electrodynamics one can define (at the order of magnitude) the linear electron velocity, which turns out to be approximately 10^6 m/sec. Then the uncertainty in the coordinate Δx is

$$\Delta x \geq \frac{h}{\Delta p} = \frac{h}{m\Delta \upsilon} = \frac{10^{-34}}{10^{-30} \times 10^{6}} \approx 10^{-10}\,\text{m},$$

i.e., it coincides with the atomic size. One can conclude, therefore, that the notion "trajectory" in this case (and in quantum mechanics, in general) loses it's meaning: the uncertainty in the electron coordinate is comparable with the object size. It is clear that a new approach to describing micro-objects is necessary.

The principle of uncertainty itself allows one, in some cases, to arrive at the decision not to solve the problem exactly. As an example, one can consider the state of a particle limited in its motion in space (i.e., existing in a potential well, refer to Section 1.5.4) by the width L. Let us pose a question: can the particle energy accept any values or an undetermined one in this case? Can a particle "settle down to the bottom" (i.e., possess exact (zero) energy and, accordingly, exactly determined momentum)? In order to decide, let us choose an uncertainty in the momentum: let this uncertainty be equal to 100%, i.e., it will accept $\Delta p \approx p$. Bearing in mind the relationship of energy E with the momentum, we can write: $p \approx \Delta p = \sqrt{2mE}$. The uncertainty in the coordinate Δx in this case is the width of well L: we know that the particle is in the potential well, but do not know precisely at what point. As a result, the uncertainty principle looks like $\Delta x \times \Delta px \geqslant (\sqrt{2mE}) \times L \geqslant h$, whence

$$E \geq \frac{h^2}{2mL^2}. \tag{7.2.2}$$

This shows that the answer to the question above is as follows: a particle cannot occupy a position on the bottom of a potential well of finite width, and the expression derived presents the lowest permitted value of energy. This solution has been reached only by the uncertainty principle, without using the main attributes of quantum mechanics. As we will see below, this conclusion complies well with the result of the exact solution of this problem.

The uncertainty principle also offers the energy E of a micro-object and the lifetime of a system in this state: the product of uncertainty in energy ΔE and in the time τ the system exists in this state cannot be less than h

$$\Delta E \times \tau \geq h. \tag{7.2.3}$$

For the ground state of a micro-object that can exist in this state infinitely long ($\tau \rightarrow \infty$), the uncertainty in energy ΔE is zero, i.e., the energy of the ground state can have an absolutely precise value. Though for excited states with a limited lifetime of, say 10^{-8} sec, the uncertainty in energy is: $\Delta E \approx 10^{-34}/10^{-8} = 10^{-26}\,\mathrm{J} \approx 10^{-7}\mathrm{eV}$. This is a very small value: however, in some cases it plays an important role in the physical phenomenon. In Figure 7.4, the illustration of broadening of a spectral line on account of uncertainty principle (for energy and time) is depicted.

The linewidth caused solely by the energy level broadening because of the Heisenberg uncertainty principle (i.e., not subjected to the influence of an instrumental imperfection), is called a natural spectral linewidth.

It is necessary to note that the uncertainty principle does not impose any restrictions on the possibility of the simultaneous existence of precise values of coordinates and momentums along different coordinate axis. In other words, products $\Delta y \times \Delta p_x$ and $\Delta x \times \Delta p_y$ can be equal to zero, i.e., the corresponding values of coordinates and component of momentums can be determined precisely.

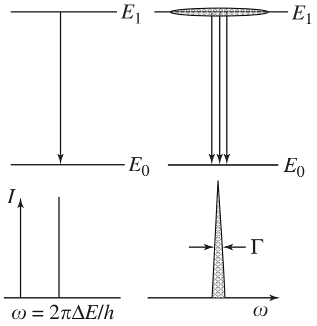


Figure 7.4 An uncertainty principle for energy and time of life. Two energy levels are presented (left) without uncertainty principle accounting (the both are infinitely narrow and a spectral line is infinitely narrow too); taking the principle mentioned into account leads to the broadening of the width of both an excited energy level E_1 and spectral line (Γ is the natural width of a spectral line).

EXAMPLE E7.4

An electron's kinetic energy in a hydrogen atom is of the order 10 eV. Using the Heisenberg uncertainty principle, determine the linear size of the hydrogen atom.

Solution: The momentum and coordinate uncertainties are related by eq. (7.2.1). Let the atom have a linear size l, then the electron will be somewhere in the limits $\Delta x = l/2$. The uncertainty principle can then be written as:

$$\ell \geq \frac{2\hbar}{\Delta p}.$$

Suppose that the physical reasonableness Δp should be less than p: $\Delta p \geqslant p$. Therefore, we can assume

$$\Delta p \approx \sqrt{2mK} \quad \text{and} \quad \ell_{\min} = \frac{2\hbar}{\sqrt{2mK}}.$$

Substituting the known and given values, we arrive at $l_{\min} = 124$ pm, i.e., commensurable to the atom's size.

EXAMPLE E7.5

Using the uncertainty principle of energy and time, define the natural width Γ of a spectral line in the excited state and at its transition from the excited state to the ground state. Define also the corresponding $\Delta\lambda$. Assume τ equal to 10^{-8} sec and wavelength $\lambda = 600$ nm.

Solution: The natural width of the energy level $\Delta E = \Gamma$ and the time of its life are related by the Heisenberg ratio $\Gamma\tau \sim \hbar$. Therefore the natural width is $\Gamma \sim \hbar/\tau$, i.e.,

$$\Gamma \approx \frac{10^{-34}}{10^{-8}} = 10^{-26}\ \text{J}.$$

Since the photon energy and the wavelength are related as

$$\varepsilon = \frac{2\pi\hbar c}{\lambda},$$

the uncertainty relation can be found by

$$\Delta\varepsilon = \frac{2\pi\hbar c}{\lambda^2}\Delta\lambda$$

(the minus sign is ignored). Hereafter,

$$\Delta\lambda = \frac{\lambda^2}{2\pi c\tau}.$$

Substituting the given value, we arrive at $\Delta\lambda = 2 \times 10^{-14}$ m

7.3 WAVEFUNCTION AND THE SCHRÖDINGER EQUATION

7.3.1 A wavefunction

What we have discussed above makes it necessary to develop another approach to the description of micro-objects, different from that in classical mechanics. This was done by the Austrian physicist E. Schrödinger (Nobel Prize, 1933), who (together with P. Dirac and W.K. Heisenberg) suggested the idea of the wavefunction $\psi(x, y, z, t)$ as well as, an equation that this wavefunction should obey. Accordingly, a microparticle state in quantum mechanics is defined by the wavefunction $\psi(x, y, z, t)$. Knowing the wavefunction, for instance for electrons in an atom, one can define their behavior when changing the chemical bonding between atoms, the probability of forming one or other molecular structures, judging the strength of interatomic bonding in molecules, etc. Thereby, the wavefunction of electrons is a key to deciding many principle problems of chemistry.

However, function ψ itself has no physical sense; it cannot be measured itself. The wavefunction presents a certain mathematical expression by means of which it is possible to find the probability of one or other real physical features of electrons in atoms and molecules.

In order to calculate these probabilities, we need to use a value $\psi\psi^*$, where ψ^* is a complex conjugate with ψ, since ψ in general can be a complex function. In a particular case, when a wavefunction is real, $\psi\psi^* = \psi^2$.

We will restrict ourselves to some limitations: we will only deal with those problems that do not depend on time; an electron spin will be incorporated further, see Section 7.5.5; besides, we have considered so far only nonrelativistic problems.

The physical meaning of $|\psi|^2$ consists in the following: $|\psi(x, y, z)|^2$ is proportional to the probability $dw(x, y, z)$ of finding a particle in the elementary volume dV in the vicinity of a point with coordinates x, y, z:

$$dw(x,y,z) = \left|\psi(x,y,z)\right|^2, \quad dV = \left|\psi(x,y,z)\right|^2 dxdydz. \tag{7.3.1}$$

The square of the wavefunction $|\psi(x, y, z)|^2$ is hence the probability density (i.e., the probability related to the unit volume) of finding a particle in a point x, y, z:

$$\frac{dw(xyz)}{dV} = |\,\psi(x,y,z)\,|^2 \tag{7.3.2}$$

Certainly, wavefunction can be dependent on time, because physics knows many problems that are time dependent. However, according to our task, we will consider only stationary processes, not depending on time: the force fields in which particles move are stationary (refer to (1.4.4), i.e., they do not depend on time). It is possible to show that in this case the wavefunction $\psi(x, y, z, t)$ disintegrates into two factors, one of which depends on coordinates only and the other cyclically depends on time:

$$\psi(x,y,z,t) = \mathrm{e}^{-\mathrm{i}\omega t}\psi(x,y,z) = \mathrm{e}^{-(\mathrm{i}/\hbar)Et}\psi(x,y,z), \tag{7.3.3}$$

where ω is frequency, and E is the total particle energy. In this case

$$\left|\psi(x,y,z,t)\right|^2 = \psi\psi^* = \mathrm{e}^{-\mathrm{i}\omega t}\psi\mathrm{e}^{\mathrm{i}\omega t}\psi^* = \left|\psi(x,y,z)\right|^2, \tag{7.3.4}$$

i.e., the wavefunction square is also time independent.

7.3.2 The Schrödinger equation

The wavefunction is the solution of a certain equation that was introduced by E. Schrödinger—the Schrödinger equation. This is the main equation in quantum mechanics. In general, it cannot be derived theoretically; however, its validity is proved in practice: the results obtained in solving this equation are confirmed in numerous experiments. Here it plays the same role as the second Newtonian law in classical physics (refer to Section 1.3.3).

For stationary nonrelativistic problems, the Schrödinger equation can be written as follows:

$$\Delta\psi(x,y,z) + \frac{2m}{\hbar^2}[E - U(x,y,z)]\psi(x,y,z) = 0. \tag{7.3.5}$$

Besides the well-known notions, a new one is presented in the equation: the Laplacian operator that is the sum of the second partial coordinate derivatives acting on the function that follows it (in our case on wavefunction $\psi(x, y, z)$):

$$\Delta = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right). \tag{7.3.6}$$

If a one-dimensional problem is being solved, only the first term of eq. (7.3.6) is used. The term $U(x, y, z)$ is the particular particle potential energy in the force field; the information on the particular type of problem is concentrated exactly in this term.

In order to solve a quantum mechanical problem, we should substitute an analytical expression for the particle potential energy in the given force field, $U(x, y, z)$, in eq. (7.3.5); find the values of parameter E at which the Schrödinger equation allows solutions and calculate the wavefunction $\psi(x, y, z)$ as a solution of this equation. The parameter E stands out as the particle energy.

7.3.3 Standard requirements that the wavefunction should obey

In all cases, the wavefunction $\psi(x, y, z)$ as the solution of the Schrödinger equation should possess some properties that themselves play an important role in quantum mechanics. Before describing the methods for solving Schrödinger equation, we have to analyze the standard requirements (conditions) that a wavefunction should obey; these requirements result from the type of equation and the physical sense of the functions. This especially concerns cases when the problem should be divided into pieces because of the complexity of the potential distribution.

So, the wavefunction $\psi(x, y, z)$, in any case, must be a single-defined (univocal) function of coordinates, finite and continuous in the whole range of variable coordinates x, y, z, including infinity. In the case of the potential energy partition, the most important is that $\psi(x, y, z)$ must join smoothly at the boundaries. The wavefunction must be finite, i.e., we require that $\psi(x) \to 0$ at $x \to \pm\infty$. As far as the Schrödinger equation contains the coordinate second derivatives, the first coordinate derivative $\psi(x, y, z)$ should be continuous also. All of these are obvious from physical and mathematical considerations. Certainly, $|\psi(x, y, z)|^2$, and, consequently, $\psi(x, y, z)$, must have no more than a single value under fixed coordinates x, y and z or under such operations which return a particle into the former point of space (requirement of univocacy). Otherwise the solution would be ambiguous, which would make no sense.

Furthermore, as we know that the micro-object really exists in the whole region, the wavefunction $\psi(x, y, z)$ should obey the normalization condition. The total probability of finding a particle in the whole range of variable must be unity, i.e.,

$$\int_{-\infty}^{+\infty} dw = \iiint_{\pm\infty} dw = \iiint_{\pm\infty} |\psi(x, y, z)|^2 \, dxdydz = 1. \qquad (7.3.7)$$

The properties mentioned are called the standard requirements (conditions) that the wavefunction should obey. They result from the type of equation and physical sense of these functions.

The requirements imposed on the wavefunction have the result that the Schrödinger equation, as a second-order differential equation in partial derivatives under the given $U(x, y, z)$, can have solutions satisfying them only at definite values of E, values which play the role of parameters in the equation. Values of E, under which the Schrödinger equation has solutions satisfying the standard conditions, are called *eigenvalues* of energy. The set of eigenvalues E forms an energy spectrum. If eigenvalues form a set of definite values E_1, E_2, E_3, etc., the energy spectrum is called a discontinuous one. If energy E can accept any values, the energy spectrum is called a continuous one. Below we will see that a discrete energy spectrum appears when a particle motion is restricted in space (motion is finite). In the case of infinite motion, the energy spectrum is continuous (energy can change continuously). The wavefunctions ψ_N that correspond to parameters E_N are called the *eigenfunctions*.

7.4 MOST GENERAL PROBLEMS OF A SINGLE-PARTICLE QUANTUM MECHANICS

7.4.1 A free particle

Let us consider first the simplest case: free particle motion. Free motion means the case with $U \equiv 0$, i.e., the motion of a particle on which no irrelevant forces are exerted. Such a particle is moving uniformly and in a straight line. Let the x-axis be directed along the particle motion. The Schrödinger equation in this case has the form

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}E\psi(x) = 0. \tag{7.4.1}$$

As ψ here depends on only one variable, the partial derivatives are replaced onto the full derivative. The energy in this case is kinetic energy, because potential energy for free particles is zero. Therefore,

$$E = \frac{p^2}{2m}, \tag{7.4.2}$$

where p is particle momentum. Let us introduce the definition

$$\frac{2mE}{\hbar^2} = k^2. \tag{7.4.3}$$

Then the equation accepts the form

$$\psi''(x) + k^2\psi(x) = 0. \tag{7.4.4}$$

The solution of such an equation is well-known:

$$\psi(x) = A\exp(-\mathrm{i}kx), \tag{7.4.5}$$

where $k = p/\hbar$ (refer to Section 1.6) and, correspondingly, $k = 2\pi/\lambda$ (eq. (2.8.4)).

Because of the fact that we are dealing with the uniform Schrödinger equation and the derivation from the wavefunction is taken on the coordinate x, this solution can be multiplied by any coefficient not depending on the coordinate. Let this coefficient be $e^{\mathrm{i}\omega t}$. Then the solution accepts the form $\Psi(x,t) = A\exp(-\mathrm{i}kx)\exp(\mathrm{i}\omega t) = A\exp(\mathrm{i}\omega t - \mathrm{i}kx)$. The real part of it is therefore the wave running in x direction

$$\Psi(x,t) = A\cos(i\omega t - ikx), \tag{7.4.6}$$

(refer to 2.8.2). It is of use to express this expression via the energy and momentum

$$\Psi(x,t) = A\cos\frac{1}{\hbar}(p_x x - Et). \tag{7.4.7}$$

The calculation of the probability density to find a particle on any point of the x-axis gives

$$\frac{dw(x)}{dx} = \Psi\Psi^{*} = A\exp(\mathrm{i}\omega t - \mathrm{i}kx)A\exp(\mathrm{i}\omega t + \mathrm{i}kx) = A^2, \tag{7.4.8}$$

i.e., the probability density is uniform along the whole x-axis.

Thereby, if a particle momentum is strictly defined (as in our case), its position in space is indefinite: there is no priority to find it on any point of the x-axis, the particle is as if it is smashed along the x-axis. It is worth noting that this result completely corresponds to the uncertainty principle (refer to Section 7.2).

Correlation (7.4.6) allows us to express carefully the statement (not attempting any of the serious generalization), that the wavefunction $\psi(x, t)$ in the form of waves can be called the wave of probability, although this statement certainly does not make the physical picture clearer. The real physical sense has only $\psi\psi^{*} = |\psi|^2$.

The solution obtained satisfies a standard condition: the energy E and particle momentum can accept any magnitude (the spectrum of energy is continuous). Motion is infinite and energy, as in classical physics, can accept any value.

We must pay attention to one more important property of the Schrödinger equation (7.4.1), apparent from its uniformity: *any superposition of solutions is also a solution of this equation*. Such a superposition property often leads to what in chemistry is called *hybridization*.

7.4.2 A particle in a potential box

Let us consider now the state of a particle placed in a one-dimensional square potential box. This problem is not a far-fetched abstraction, but presents a model of a bound molecule particle.

In Section 1.5.4, the Lennard-Jones potential was considered (and below the Morse potential will be used). It was shown that under the total energy E lower than the depths of the potential well, a particle makes an oscillatory motion (whether it is harmonic or anharmonic plays no essential role at present) near its equilibrium position. Exactly such a potential function has to be substituted in the Schrödinger equation to decide this problem.

To solve such an equation in analytical form, however, is impossible at the moment. Therefore, the potential of a complicated profile is approximated by a model, the consideration of which, certainly, does not solve the problem precisely, but nevertheless allows

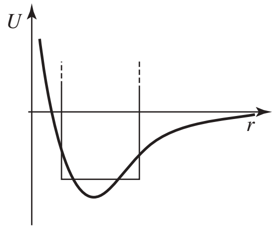


Figure 7.5 A Lennard-Jones' and a model's potentials.

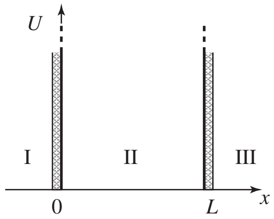


Figure 7.6 A one-dimensional infinitely deep potential box.

us to make a number of important conclusions. In Figure 7.5, the Lennard-Jones potential is approximated by a rectangular, one-dimensional potential box. In Figure 7.6, this box is provided in the form in which it will be used below.

First consider an infinitely deep potential box of the width L. Beyond the borders of the box, potential energy U is infinitely large, hence the particle cannot exist there. Inside, the potential U can be taken as zero. As a result a particle in the potential box is considered, the latter being assigned as follows (Figure 7.6): $U(x) = \infty$ at $x < 0$ and at $x > L$, $U(x) = 0$ at $0 \leqslant x \leqslant L$. Accordingly, three areas are presented in the scheme: I, II and III. In areas I and III, the particle cannot exist, the wavefunctions there are zero: $\psi_{\mathrm{I}}(x) = \psi_{\mathrm{III}}(x) = 0$. In area II the potential energy is zero ($U = 0$) and the Schrödinger equation gains the type

$$\psi_{\mathrm{II}}(x) + k_{\mathrm{II}}^2 \psi_{\mathrm{II}}(x) = 0,$$

similar to eq.(7.4.4). Solution of the equation in this area gains the form

$$\psi_{\mathrm{II}}(x) = A \sin kx + B \cos kx. \tag{7.4.9}$$

From standard conditions for wavefunction continuity, it follows that at the point $x = 0$, the wavefunctions on the left and on the right sides are zero: $\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$. It follows that $0 = A \times 0 + B \times 1$, hence $B = 0$.

At the point $x = L$ the same condition requires $A \sin kL$ to be zero. This signifies that $k_{\mathrm{II}}L = n\pi$, where n is an integer. Taking the expression (7.4.3) into account this equality can be rewritten as

$$E_{\mathrm{n}} = \frac{\pi^2 \hbar^2}{2mL^2} n^2. \tag{7.4.10}$$

The fundamental result has been obtained: the particle energy in an infinitely deep potential well can accept only discrete values! In other words the bound particle energy is quantized. The integer n, incorporated earlier as an arbitrary integer, now stands out as a certain parameter that determines the value of energy. This integer is called the quantum number. The position of the energy levels of a particle in the infinitely deep potential well is given in Figure 7.7.

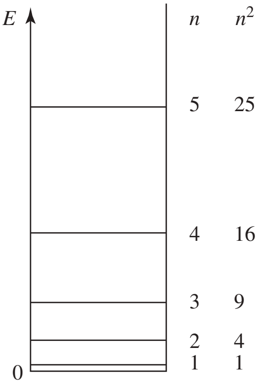


Figure 7.7 The derived energy levels of a particle in a one-dimensional infinitely deep potential box.

It is worth noting that the quantization of energy in this instance has resulted not from mathematical deduction but by using one of the standard conditions of wavefunction continuity. A result of the same significance (7.2.2) was obtained earlier in the analysis of the problem by means of the uncertainty principle; the particular expression differs from eq. (7.4.10) by only a constant multiplier nearer to unity. We want to emphasize this logical unity and intercoupling of different approaches in quantum mechanics, including the standard conditions the wavefunction must obey. Each of these aspects can be used in different cases when deciding a particular problem.

In order to obtain the total final expression for the particle wavefunction in the infinitely deep potential box, one has to define the normalizing multiplier. The normalizing condition (7.3.7) can be used here. In this instance it looks like

$$\int_0^L |\psi(x)|^2 dx = A^2 \int_0^L \sin^2 kx \, dx = 1. \tag{7.4.11}$$

Replacing the integrand according to the trigonometry formula $\sin^2 kx = (1/2) - (1/2)$ $\cos^2 kx$, we can arrive at $A^2 = 2/L$. Finally, the expression for the wavefunction of a particle inside the rectangular infinitely deep potential box is given as

$$\psi_{\mathrm{II}}(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x. \tag{7.4.12}$$

The graphs of the wavefunctions (a) and their squares (b) of the particle in the infinitely deep potential well in different quantum states are depicted in Figure 7.8. As a matter of convenience, they are distributed along the ordinate axis corresponding to the quantum numbers.

The specific question is, can n be equal to zero? This is equivalent to the question already discussed in Section 7.2: whether a particle can "lie" on the bottom of a well; to which we have already obtained a negative answer from the uncertainty principle.

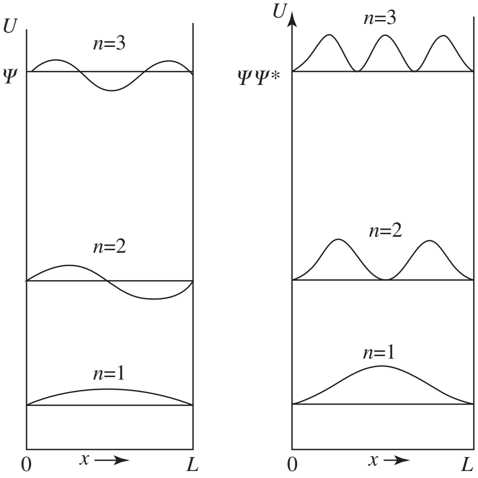


Figure 7.8 Wavefunctions of a particle in a one-dimensional infinitely deep potential box (a) and their squares (b).

Graphs of $\psi_\text{n}(x)$ are extremely reminiscent of graphs of standing waves and, particularly, the string oscillations (refer to 2.9.3). There is nothing amazing in this fact: moving in the potential box, particles are reflected from potential barriers on the right and on the left so that their wavefunctions interfere, forming standing waves. Half of the standing wavelength λ is equal to L/n (refer to formula (2.9.8)). Only in such a case is a state stable!

This example is suitable to illustrate the Bohr correspondence principle. It states that all regularities of quantum mechanics turn into the regularities of classical mechanics under the increasing quantum numbers. It is well known that the different levels of physical approximations are characteristic to certain areas of this science. Transformation from one area to another occurs not abruptly, but gradually. So, Newtonian mechanics becomes less and less exact when the velocity of particle motion increases, transforming into the relativistic one. We are interested here in the transition from quantum mechanics (in which quantization plays a fundamental role) to classical (in which the energy levels discontinuity is not observed).

Let us start from the formula for energy (7.4.10). From this formula and Figure 7.7, one can see that the distance between adjacent levels increases with increasing the quantum number n. However, if one analyzes not the absolute but the relative value of energy, this fraction with increasing n decreases. In fact, $(E_{n+1}-E_n)/E_n = \Delta E/E$ and

$$\frac{\Delta E}{E} = \frac{(n+1)^2 - n^2}{n^2} = \frac{2n+1}{n^2} \approx \frac{1}{n} \to 0, \tag{7.4.13}$$

manifestation of quantization decreases rapidly.

Consider now (on the qualitative level) what will occur if the depth of a potential box becomes finite; let it be denoted U_0 (Figure 7.9). Suppose herewith, that the total particle

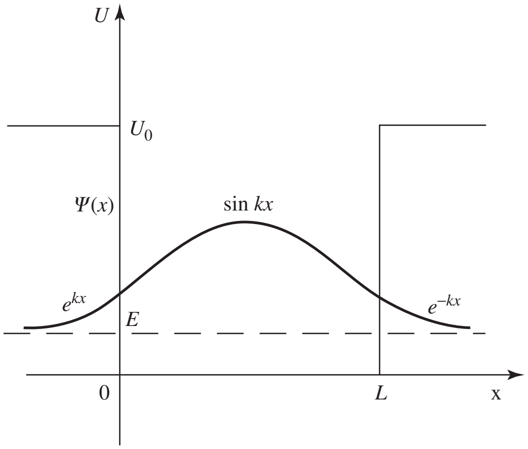


Figure 7.9 A wavefunction of a particle in a one-dimensional potential box of a definite depth.

energy E is less than U_0, i.e., the particle remains bounded. In this case the potential U in the Schrödinger equation (7.3.5) will not be equal to infinity and the wavefunction in areas I and II will not be zero. Moreover, the expression in brackets (E – U) is negative. In order to avoid the operation with complex qualities let E and U change their places in the brackets

$$\psi''(x) - [\mathrm{U}_0 - \mathrm{E}]\psi(x) = \psi''(x) - \mathrm{k}^2\,\psi(x) = 0. \tag{7.4.14}$$

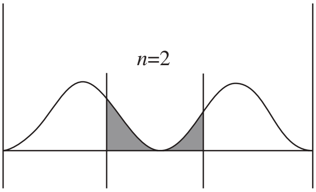
This problem can be solved exactly, but we will restrict ourselves to qualitative consideration. From the given equation, one can see that the second derivative from the wavefunctions on the coordinate in areas I and III must have the same sign as the function itself. An exponent $A_\mathrm{I}\exp(\pm k_\mathrm{I}x)$ satisfies this condition. In the area I ($-\infty < x < 0$), the requirement for the wavefunction to be finite corresponds to a sign "+" in the exponent. Therefore, the solution for $\psi_\mathrm{I}(x)$ must be of the form $A_\mathrm{I}\exp(+k_\mathrm{I}x)$. In area III ($L < x < +\infty$), for the preservation of the wavefunction to be finite, the sign in the exponent must be negative: $\psi_\mathrm{III}(x) = A_\mathrm{III}\exp(-k_\mathrm{III}x)$. Constants A_I and A_III are to be determined from boundary conditions $\psi_\mathrm{I}(0) = \psi_\mathrm{II}(0)$ and $\psi_\mathrm{II}(L) = \psi_\mathrm{III}(L)$.

The solution for wavefunction expression and conditions of quantization are, certainly, changed, though not in principle. The graph of relationship $\psi^2(x)$ for $n = 1$ is schematically depicted in Figure 7.9.

The most important point is that the particle wavefunction is not zero even in those areas of space where $E < U_0$, i.e., where the total energy is less than the potential or where the kinetic energy is formally negative. In classical physics, this cannot be the case: total energy must always be higher than potential since kinetic energy cannot be negative; the particle cannot exist where this condition is not fulfilled. The explanation of this apparent confusion is contained in the uncertainty principle! The fact is, potential energy depends on the particle positions, but kinetic energy is a function of momentum. Therefore, a particle in quantum mechanics cannot simultaneously possess precise values of potential and kinetic energy. Quantum mechanics operates mainly with total and potential energy, and only in some cases considers kinetic energy when a system does not possess potential energy at all.

EXAMPLE E7.6

An electron is in a one-dimensional potential box of infinite depth and width of *l*. Calculate the probability to find the electron in the excited state ($n = 2$) in the middle third of the box (see Section 7.4.2) and Figure E7.6).



Solution: The probability to find a particle in an interval $x_1 < x < x_2$ is defined by an integral

$$w = \int_{x_1}^{x_2} |\psi_n(x)|^2 dx,$$

where $\psi(x)$ is normalized wavefunction corresponding to a given state. In our case this function is

$$\psi_n(x) = \sqrt{\frac{2}{\ell}} \sin \frac{\pi n}{\ell} x$$

($n = 2$) (eq. (7.4.12)). Substitute all given values into this equation, we obtain

$$w = \frac{2}{\ell} \int_{x_1}^{x_2} \sin^2 \frac{2\pi}{\ell} x dx.$$

In our case $x_1 = (l/3)$ and $x_2 = (2l/3)$. Using a trigonometric equation,

$$\sin x^2 \frac{2\pi}{\ell} x = \frac{1}{2}\left(1 - \cos \frac{4\pi}{\ell} x\right)$$

we arrive at $w = 0.195$.

7.4.3 A potential step

The results we obtained in preceding sections can help us to analyze quantitatively some other quantum mechanical problems, not having analogues in classical physics. We will consider further a potential step and a potential barrier.

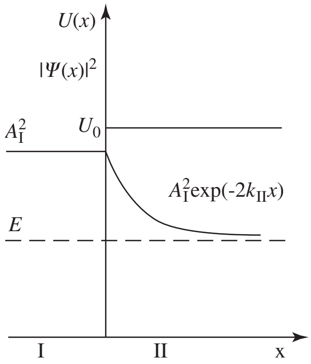


Figure 7.10 A rectilinear potential step.

The graph of potential energy as a function on the distance (along the axis of particle motion x) in quantum mechanics is referred to as a potential step: $U(x) = 0$ at $x < 0$ and $U(x) = U_0$ at $x > 0$ (Figure 7.10). This problem can be solved at two total energy E: higher and lower the heights of the potential step U_0. The latter case $E > U_0$ corresponds to an infinite particle motion; consequently, the energy E can accept a continuous spectrum of values. We will move our attention to another case with $E < U_0$.

The problem can be solved analytically in the framework of Schrödinger's equation and the standard conditions for $\psi(x)$, in particular using the requirement to be continuous at the step boundaries (at $x = 0$). As in preceding cases, divide the problem into two parts: $x < 0$ (area I) and $x > 0$ (area II). In area I the particle motion is infinite; it can be described by the periodic wavefunction $\psi_I(x)$ (7.4.2) with constant probability of finding a particle in any point of this area.

Let us denote the amplitude of the de Broglie wave $A_{I,}$ then $|\psi_I(x)|^2 = A_I^2$. In area II the energy $E < U_0$, therefore all that has been said in Section 7.4.2 about the wavefunction behavior outside a potential box of finite depth (see above) is applicable to the particle falling onto the potential step (Section 7.4.2). The Schrödinger equation is the same as above (eq. 7.4.14). The solution of this equation is analogous to the case of exponential decrease of the probability of finding the particle while moving away from the boundary, i.e., $A_{II}\exp(-k_{II}x)$. This wavefunction corresponds to the probability reduction of finding a particle under the step at $x > 0$. From the condition of the wavefunctions continuity, it follows that $A_I = A_{II}$.

In Figure 7.10 a graph of the wavefunction $|\psi_{II}(x)|^2 = A_I^2\exp(-2k_{II}x)$ is presented. It can be seen that the probability of finding a particle under the potential step is exponentially decreased when moving away from the border.

Considering this problem, we ignore the possibility of a wave reflection from the potential step boundary: this does not change the essence of the solution and is not important for us at the moment.

7.4.4 A potential barrier: a tunnel effect

Let us apply the results obtained to the consideration of the problem of a potential barrier depicted in Figure 7.11. Consider the case when the total particle energy E is lower than

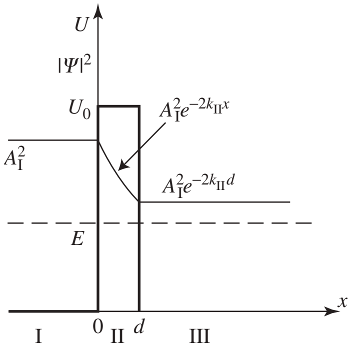


Figure 7.11 A rectilinear potential barrier.

the height of the barrier U_0. As previously, we subdivide the problem into three areas: area I ($-\infty < x$), area II ($0 \leq x \leq d$) and area III ($d < x$). The Schrödinger equation may be written as follows:

$$\psi''(x) + k^2\psi(x) = 0, \tag{7.4.15}$$

for areas I and III with $k^2_{\mathrm{I,III}} = (2mE/\hbar^2)$, and

$$\psi''(x) - k^2\psi(x) = 0 \tag{7.4.16}$$

for area II with

$$k^2_{\mathrm{II}} = \frac{2m(U_0 - E)}{\hbar^2}$$

Solutions should be sought in the following form:
In area I: $\psi_{\mathrm{I}}(x) = A_{\mathrm{I}}\exp(-\mathrm{i}k_{\mathrm{I}}x) + B_{\mathrm{I}}\exp(\mathrm{i}k_{\mathrm{I}}\,x)$;
In area II: $\psi_{\mathrm{II}}(x) = A_{\mathrm{II}}\exp\,(-k_{\mathrm{II}}x) + B_{\mathrm{II}}\exp(k_{\mathrm{II}}x)$; (7.4.17)
In area III: $\psi_{\mathrm{III}}(x) = A_{\mathrm{III}}\exp(\mathrm{i}k_{\mathrm{III}}x)$.
In these expressions, the amplitudes marked by the letter A correspond to the wavefunction propagation from left to right and amplitudes B describe a reflection from external and internal edges of the potential barrier. We shall not take reflected waves into account and, accordingly, shall not consider the waves containing the amplitudes marked by B (the exact solution using the boundary conditions and the wavefunction's properties does not present a particular difficulty though they have no special interest). We denote the incident wave amplitude as A_{I} and will express all other qualities using this value.

A graph of the wavefunction's amplitudes is given in Figure 7.11. In area I, the value of the square of the wavefunction amplitude A_{I}^2 is depicted. As was shown earlier for free particles, this value does not depend on coordinates and, within the given area, is constant. In area II the solution is not periodic but exponential (as was obtained when solving a potential step problem). The boundary conditions consideration gives: $A_\mathrm{I}(0) = A_\mathrm{II}(0)$. So the solution for the second area is given by the expression:

$$\psi_\mathrm{II}(x) = A_\mathrm{II}\exp(-k_\mathrm{II}x),$$

which is also depicted in Figure 7.11.

In the third area a motion once again is infinite and, accordingly, wavefunction is presented by periodic function and constant probability density. Its absolute magnitude is defined by one of the boundary conditions (condition of continuity). It links A_III with A_I by the correlation

$$|\psi_\mathrm{III}(x)|^2 = A_\mathrm{III}^2 = A_\mathrm{I}^2\exp(-2k_\mathrm{II}d). \tag{7.4.18}$$

Since $k_\mathrm{I} = k_\mathrm{III}$, the de Broglie wavelengths in areas I and III are the same, whereas the amplitudes are different. The result also shows that, regardless of the energy of the falling particles, they can penetrate the barrier from area I to area III.

Let us estimate what part of the particles falling onto the barrier penetrates the barrier or, what amounts to the same thing, how probable is it that a single particle shall penetrate it. We can call this value the barrier transparency and denote it by the letter *D*. Because of the fact that squares of amplitudes describe the “intensity” of de Broglie waves in a particular area, the barrier transparency can be defined as the ratio of their “intensities,” or

$$D = \frac{|\psi_\mathrm{III}(d)|^2}{|\psi_\mathrm{I}(0)|^2} = \frac{A_\mathrm{I}^2\exp(-2k_\mathrm{II}d)}{A_\mathrm{I}^2} = \exp(-2k_\mathrm{II}d) = \exp\left(-\frac{2d}{\hbar}\sqrt{2m(U_0 - E)}\right). \tag{7.4.19}$$

One can see that the transparency of the rectangular potential barrier depends exponentially upon several factors: on the particle mass, on the barrier width and on the difference $(U_0 - E)$. The table below illustrates the barrier transparency for electrons upon the barrier width.

d (10^{-10} m)	1.0	1.5	2.0	2.5
D	0.1	0.03	0.008	10^{-7}

If the barrier is not rectangular and its form is described by the function $U(x)$ (Figure 7.12), the barrier transparency can be given by the expression

$$D = \exp\left(-\frac{2}{\hbar}\int_a^b \sqrt{2m[U(x) - E]}\,dx\right). \tag{7.4.20}$$

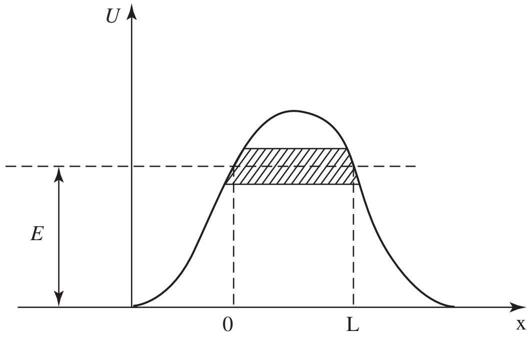


Figure 7.12 A potential barrier of an arbitrary form.

EXAMPLE E7.7

An electron with an energy $E = 4.9$ eV moves in the positive direction of the x-axis (see Figure 7.11). The height of the potential barrier is U_0 is 5 eV. At what width of the barrier will the probability to penetrate it be $w = 0.2$?

Solution: The penetration probability (the barrier transparency) is given by the eq. (7.4.19)

$$w = \left(\frac{2d}{\hbar}\sqrt{2m(U_0 - E)}\right)$$

and hereafter,

$$\ell n w = -\frac{2d}{\hbar}\sqrt{2m(U_0 - E)}.$$

It is possible now to find the main equation:

$$d = \frac{\hbar \ell n(1/w)}{2\sqrt{2m(U_0 - E)}}.$$

Calculation gives $d = 4.95 \times 10^{-10}$ m $= 0.495$ nm.

7.4.5 Tunnel effect in chemistry

An approximate formula for the temperature dependence of the reaction rate coefficient K is given by the Arrhenius equation:

$$K = \exp\left(-\frac{Q}{\kappa T}\right), \tag{7.4.21}$$

where Q is an activation energy and κ is the Boltzmann constant. If the activation energy is constant, a plot of ln K versus $1/T$ gives a straight line. This equation is often given in so-called Arrhenius coordinate (Figure 7.13):

$$\ln K = -\frac{Q}{\kappa T}. \tag{7.4.22}$$

In order to give a demonstrative presentation of the activation energy, let us imagine some group of atoms having two equilibrium states in two potential wells. Let them be characterized by two potential curves as depicted in Figure 7.14 (refer to Section 1.5.4). Such a state can be characteristic, for instance, for two atoms creating a molecule after their collision, or for two independent molecules forming a more complex molecule, or monomer molecules joining in polymer chains, and others. Certainly, different states are characterized by potential wells of a different form and depth: the more stable states have a deeper potential well. Suppose that the energy of an initially stable (ground) state in one potential well is characterized by the energy level noted in Figure 7.14 by a horizontal line. In order for the reaction to occur, the system should overcome the potential barrier Q, noted in the same scheme. This can occur either if the system has enough energy and can overcome the potential barrier Q (concentration of such active particles was calculated in eq. (3.3.7), Figure 3.6) or by means of penetration of the potential barrier.

The overwhelming majority of chemical reactions really complies with the Arrhenius law and, in the logarithmic scale, is schematically expressed by a straight line (Figure 7.13). However, not long ago, the effect of the limitation of chemical reactions' ratio at low temperatures was observed, the ratio became constant (Figure.7.13), in contradiction to Arrhenius theory. An explanation of this behavior can be given within the framework of the tunnel mechanism.

In Figure 7.14, it can be seen that a system can overcome the potential barrier, not by climbing over the barrier, but having penetrated the barrier from one potential well into another one (in the manner of using an underpass in a mountainous area). From eq. (7.4.19)

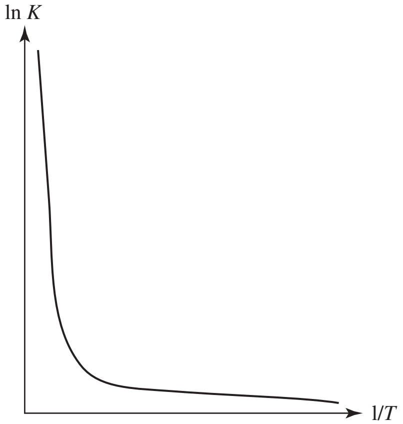


Figure. 7.13 A chemical reaction ratio K versus reciprocal temperature $1/T$.

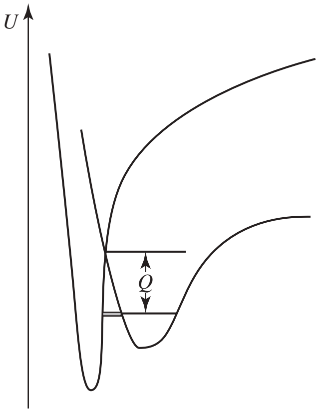


Figure 7.14 A Scheme of activation (over a potential barrier with activation energy Q) and tunnel (penetration of a barrier) mechanisms of chemical reactions.

it can be seen that the barrier transparency indeed does not depend on temperatures. The penetration of the barrier is purely a quantum mechanical effect.

As an example, we will describe the polymerization reaction of formaldehyde. In Figure 7.15, the potential curves of formaldehyde both in monomer and polymer states are shown. From a comparison of the curves it can be seen that the polymeric state is more stable than the mixture of monomers. The scheme above shows chain linkage in monomers and in polymer. In order for a monomer molecule to join the polymer chain, an electron from the double C=O bond should abandon it and "penetrate" into the space between the atoms of carbon and oxygen of the adjacent molecule with the formation of a single bond C–O (this is shown in the middle of the scheme above). Certainly, herewith a redistribution of electron density occurs, developing and changing the interatomic distances: the density of polymer is higher than of the monomer mixture (the corresponding distances d_f, d_i and Δd are shown in the scheme). Since the polymerization process brings about greater energy of bonding (the potential well is deeper for the polymer) and the allocation of heat.

The time of joining of the next monomer molecule to the already created polymeric chain, measured by very sensitive equipment, proves to be 10^{-2} sec, whereas computed from the Arrhenius equation gives a value near 10^{30} years.

The effect of tunneling enables us to take quite a new look at some physical, chemical and, particularly, biological processes in respect of the organization and behavior of biologically active systems, accompanying all natural processes—from the formation of planets to the most complex particularities of biosyntheses. The scales of these phenomena are inconceivable though it is presently possible to assert that "tunneling effects" play a very important role in many processes of vital activity.

7.5 THE HYDROGEN ATOM

Consider now a more complex problem, which is very important for chemistry: the motion of a charged particle in a spherically symmetric electric field. In this case a particle's

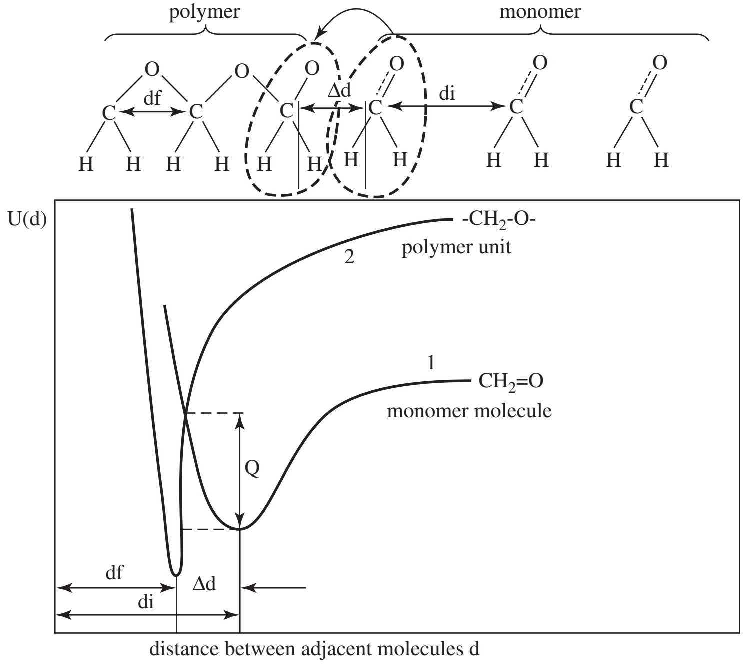


Figure 7.15 The tunnel effect of formaldehyde polymerization (after V.I. Goldanski et al.).

energy depends only on the distance from the center but not on direction (refer to expression (1.4.22)). The simplest problem of this kind is the motion of an electron in the field of a positively charged, dimensionless, heavy (in comparison with the electron) nucleus (proton), i.e., the problem of a hydrogen atom (and a singly ionized helium atom).

The solution to this problem has an exceptionally important role in quantum mechanics and especially in quantum chemistry. Firstly, this is a problem that can be solved analytically (though some special mathematical functions must be used). Secondly, the solution is of great importance for chemistry where the electronic orbits arise from the solution; moreover the theory of the chemical bond has been worked out using the results. Thirdly, an empirically modified hydrogen atom's orbits are widely used generally for heavier atoms because there are no other ways of achieving results.

7.5.1 The Schrödinger equation for the hydrogen atom

Let us choose the nucleus (proton) as the origin. Assume the nucleus is point-like. Because the proton's electric field is spherically symmetric, we have to change from a Cartesian (x, y, z) to a spherical (r, θ, φ) coordinate system. Figure 7.16 illustrates this transform:

$$\begin{aligned} x &= r \sin\theta \sin\varphi, \\ y &= r \sin\theta \cos\varphi, \\ z &= r \cos\theta. \end{aligned} \tag{7.5.1}$$

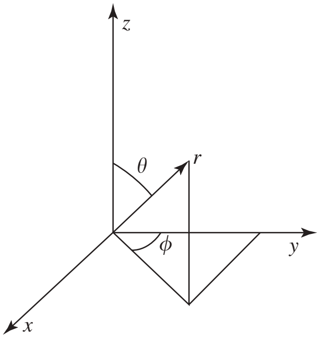


Figure 7.16 Spherical coordinate system.

Note, that the z-axis is formally distinguished from the other axes. It can be said that this axis is selected: it is specially distinguished only geometrically, though it is always specially distinguished if there is an outer influence (electric, magnetic, etc.). It is said that z is the distinguished axis.

The Schrödinger equation for hydrogen atom has the form (refer to (7.3.5))

$$\Delta\psi(x,y,z)+\frac{2m}{\hbar^2}[E-U(x,y,z)]\psi(x,y,z)=0, \tag{7.5.2}$$

in which $U(x, y, z)$ is the electron's potential energy in the proton's Coulomb field

$$U(x,y,z)=U(r)=\frac{1}{4\pi\varepsilon_0}\frac{\mathrm{e}^2}{r}, \tag{7.5.3}$$

(refer to Section 4.1.4), where $\mathrm{r}=\sqrt{x^2+y^2+z^2}$. This expression has to be substituted into the Schrödinger equation and solved.

As was noted earlier, this problem can be solved analytically; however, it takes much effort and a long time. Therefore, we will use a reasonable mathematical simplification paying more attention to the physical meaning.

The Laplace operator (7.3.6) in spherical coordinates has the form:

$$\Delta(r,\theta,\varphi)=\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}. \tag{7.5.4}$$

The Schrödinger equation in this case can be expressed as

$$\begin{aligned}&\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right]+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\psi(r,\theta,\varphi)\right]\right.\\&\left.+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi(r,\theta,\varphi)\right\}+\frac{2m}{\hbar^2}[E-U(r)]\psi(r,\theta,\varphi)=0.\end{aligned} \tag{7.5.5}$$

Let us represent the wavefunction $\psi(r, \theta, \varphi)$ as the product of three independent functions where each function depends only on one argument: either on a radial coordinate or on the angles θ and φ:

$$\psi(r,q,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) = R(r)Y(\theta,\varphi), \tag{7.5.6}$$

where,

$$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) \tag{7.5.7}$$

is the so-called angular part of the wavefunction, and the function $R(r)$ is the radial part.

Consider first the electron's motion along a spherical surface at fixed radial coordinate. This corresponds to the expressions $r =$ const. and $\partial Y/\partial r = 0$. This permits us to find the electron's probability distribution on a sphere of fixed radius. The first term in eq. (7.5.5) becomes zero and therefore, the equation for the angular part of the wavefunction will be of the form

$$\begin{aligned} &\frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}Y(\theta,\varphi)\right]+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}Y(\theta,\varphi)\right\} \\ &+\frac{2\mu r^2}{\hbar^2}[E-U(r)]Y(\theta,\varphi)=0. \end{aligned} \tag{7.5.8}$$

The problem has been reduced to the investigation of the motion of a body along a sphere with fixed radius. Such a problem is called the rigid rotator; the classic version of which was considered in Section 1.3.9 (Figure 1.17). Recall that the electron's angular momentum L in the framework of the Bohr model is

$$\mathbf{L} = [\mathbf{rp}] = m[\mathbf{r}\boldsymbol{v}]. \tag{7.5.9}$$

It is perpendicular to the two vectors $\mathbf{r}$ and $\mathbf{p} = m\boldsymbol{v}$. If the angle between the two vectors $\mathbf{r}$ and $\mathbf{p}$ is 90°, the magnitude of $\mathbf{L}$ is

$$\mathbf{L} = m\mathbf{r}\boldsymbol{v} \tag{7.5.10}$$

It was shown in Section 1.3.9 that the rotation of two masses with distance d between them around a motionless center of mass O can be represented by the planar rotation of one mass $\mu = (m_1m_2)/(m_1m_2)$(the reduced mass) around the axis that passes through the center of mass. The result relates both to rotation of a diatomic molecule relative to its center of mass and to the rotation of the electron relative to the nucleus.

The moment of inertia is called the reduced moment of inertia I_e

$$I = \mu d^2, \tag{7.5.11}$$

where d being the interparticle distance. It is worth to notice that the reduced mass for hydrogen atom is half of electron mass whereas for hydrogen molecule is half of hydrogen atom mass.

The kinetic energy of rotation is

$$K = \frac{L^2}{2I} = \frac{L^2}{2\mu d^2}. \tag{7.5.12}$$

One can see that the same approach applies both to diatomic molecular rotation and to the hydrogen atom.

7.5.2. The eigenvalues of the electron angular moment projection L_z

The kinetic energy of a free particle forms a continuous spectrum, i.e., can possess any value. Within the framework of quantum mechanics we can ask: is the spectrum of values of the kinetic energy of a molecule's free rotation (within the framework of the rigid rotator model) as well as an electron in the hydrogen atom either discrete or continuous? The answer is not a priori obvious. To answer this question we need first to solve the Schrödinger equation (7.5.8) with boundary conditions imposed on the wavefunction.

For the rotation of the electron in the hydrogen atom, it is necessary to find a solution for the function $\Phi(\varphi)$. With reference to Figure 7.16, it will be noticed that this function describes the electron's rotation in a xy plane, which is perpendicular to the z-axis. Consequently, it describes the behavior of the projection of the angular moment L onto the z-axis, i.e., L_z.

It was shown above that free particle translational motion is described by the wavefunction $\Psi(x) = a \exp(\mathrm{i}p_x x/\hbar)$ (time dependence is not important here). If we remember that the formulas of translational and rotational motion have the same structure (Section 1.3.9, Table 1.1), it is easy to write down the wavefunction for rotation by replacing p_x on L_z and x by φ. Therefore, we can write

$$\Phi(\varphi) = a \exp\left(\frac{i}{\hbar} L_z \varphi\right). \tag{7.5.13}$$

The condition of a single-valued solution has the form

$$\Phi(\varphi) = \Phi(\varphi + 2\pi). \tag{7.5.14}$$

Certainly, one revolution brings a system back to the initial state. Combining eqs. (7.5.13) and (7.5.14), and using the Euler formula we obtain:

$$a \exp\left(\frac{\mathrm{i}}{\hbar} L_z \varphi\right) = a \exp\left(\frac{\mathrm{i}}{\hbar} L_z \varphi\right) \exp\left(\frac{\mathrm{i}}{\hbar} L_z 2\pi\right),$$

and further,

$$\cos\left(\frac{L_z 2\pi}{\hbar}\right) + \mathrm{i} \sin\left(\frac{L_z 2\pi}{\hbar}\right) = 1.$$

It follows from this equation that $(L_Z/\hbar)2\pi = m(2\pi)$, where m is integer. And finally,

$$L_z = m\hbar. \tag{7.5.15}$$

Thus, without solving the Schrödinger equation, starting only from the boundary condition of uniqueness of the wavefunction, an important conclusion has been obtained: the projection of the angular momentum onto the distinguished z-axis can take only integer values of $\hbar$. The integer m, equal to 0, ±1, ±2, ±3, etc., is a quantum number that defines the value of L_z projection.

The wavefunction $\Phi(\varphi)$ is, consequently, expressed as

$$\Phi_m(\varphi) = a\exp(\mathrm{i}m\varphi). \tag{7.5.16}$$

The magnitude a can be found from the normalization condition:

$$\int_0^{2\pi} \left|\Phi(\varphi)\right|^2 d\varphi = a^2 \int_0^{2\pi} \mathrm{e}^{\mathrm{i}m\varphi} e^{-\mathrm{i}m\varphi}\, \mathrm{d}\,\varphi = a^2\, 2\pi = 1, \tag{7.5.17}$$

$$\text{i.e., } a^2 = (1/2\pi) \text{ and finally } \Phi(\varphi) = \sqrt{\frac{1}{2\pi}}\mathrm{e}^{\mathrm{i}m\varphi}. \tag{7.5.18}$$

Thus the angular part $\Phi(\varphi)$ of the wavefunction has been specified.

7.5.3. Angular momentum and magnetic moment of a one-electron atom

Eq.(7.5.8) is modified by taking into account that $E - U$ is the kinetic energy K because of the fact that in this particular case the potential energy of free rotation is zero ($K = E$), and $m = \mu$ is the reduced mass of the rigid rotator. Since the angular part of the wavefunction is the product of two functions $Y(\theta, \varphi) = \Phi(\varphi)\Theta(\theta)$, we can obtain

$$\frac{\Phi(\varphi)}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right] + \frac{\Theta(\theta)}{\sin^2\theta}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} + \frac{2\mu r^2}{\hbar^2}(E-U)\Phi(\varphi)\Theta(\theta) = 0. \tag{7.5.19}$$

Multiplying the equation by $\sin^2\theta/\Phi(\varphi)\Theta(\theta)$ we can obtain

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right] + \frac{1}{\Phi(\varphi)}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} + \sin^2\theta\frac{2\mu r^2}{\hbar^2}E = 0. \tag{7.5.20}$$

Note that in the last equation each term depends either on φ or on θ. They can be grouped in the following manner:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right] + \sin^2\theta\frac{2\mu r^2}{\hbar^2}E = -\frac{1}{\Phi(\varphi)}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2}. \tag{7.5.21}$$

A function $\Theta(\theta)$ is on the left-hand side and a function $\Phi(\varphi)$ is on the right-hand side. Therefore, this equality can be satisfied only if both sides are equal to a constant value. Since the function $\Phi(\varphi)$ (7.5.18) is already known, we can find that constant. In fact, this function is equal to:

$$-\frac{1}{\Phi(\varphi)}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} = m^2. \tag{7.5.22}$$

It means that

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right]+\sin^2\theta\frac{2\mu r^2}{\hbar^2}E=m^2. \tag{7.5.23}$$

This illustrates the previous statement that the wavefunction of the hydrogen atom can be presented as a product (7.5.6).

The eq. (7.5.23) is a Legendre equation. It follows from the theory of Legendre equations that they have solution only if the coefficient of expression at $\sin^2\theta$ is equal to

$$\frac{2\mu r^2}{\hbar^2}E=\ell(\ell+1), \tag{7.5.24}$$

where l is an integer with

$$\ell\geq|m|. \tag{7.5.25}$$

Taking into account eq. (7.5.12) one can write $E=\dfrac{\hbar^2}{2I}\ell(\ell+1).$ (7.5.26)

Therefore, we have found the energy eigenvalues of hydrogen atom and rigid rotator energy. The angular eigenvalues will be given later in Section 7.5.7.

Thus the answer to the question that we posed earlier is: the rotational energy can take only definite discrete values (i.e., it is quantized).

Using eq. (7.5.12), we can obtain also $L^2=\hbar^2 l(l+1)$ or

$$L=\hbar\sqrt{\ell(\ell+1)}, \tag{7.5.27}$$

i.e., the quantization of the kinetic energy of the rigid rotator originates from the quantization of the absolute value of angular momentum.

The expression (7.5.27) and a gyromagnetic ratio (see Section 5.2.1) allow us to determine an orbital magnetic moment of the one-electron atom. Because the gyromagnetic ratio is $\mu/L=g|e|/2m$ (where $g=1$), the magnetic moment is as:

$$\mu=\frac{|e|\hbar}{2m}\sqrt{\ell(\ell+1)}=\mu_B\sqrt{\ell(\ell+1)}. \tag{7.5.28}$$

The value $\mu_B=(|e|\hbar)/(2m)$ is known as the Bohr magneton.

The general solution of eq. (7.5.23) for the function $\Theta(\theta)$ can be written with Legendre polynomials. The expressions for $Y(\theta,\varphi)$ for the quantum number $l=0,1,2$ are given below in Table 7.1.

Two important conclusions can be drawn from the solution obtained. One concerns the quantization of the rigid rotator energy; the other describes the properties of angular momentum in quantum mechanics. We will use the first one later in Section 7.8.2 in the description of rotational spectroscopy; here, we consider the properties of the angular momentums in quantum mechanics.

As has already been noted, if one has to select a particular axis it is usually identified with the z-axis. It follows from the results described by eqs. (7.5.15), (7.5.25) and (7.5.27), that the

Table 7.1

Wavefunctions for *s*-, *p*- and *d*-electrons

n	l	m$_l$	
1	0	0	$\psi_{1\mathrm{s}} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-\sigma}$
2	0	0	$\psi_{2\mathrm{s}} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)\mathrm{e}^{-(\sigma/2)}$
2	1	0	$\psi_{2\mathrm{p}_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma \mathrm{e}^{-(\sigma/2)}\cos\theta$
2	1	±1	$\psi_{2\mathrm{p}_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-(\sigma/2)}\sin\theta\,\cos\varphi$
			$\psi_{2\mathrm{p}_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma \mathrm{e}^{-(\sigma/2)}\sin\theta\,\sin\varphi$
3	0	0	$\psi_{3\mathrm{s}} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\sigma+2\sigma^2)e^{-(\sigma/3)}$
3	1	0	$\psi_{3\mathrm{p}_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma \mathrm{e}^{-(\sigma/3)}\cos\theta$
3	1	±1	$\psi_{3\mathrm{p}_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma \mathrm{e}^{-(\sigma/3)}\sin\theta\,\cos\varphi$
			$\psi_{3\mathrm{p}_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\sigma \mathrm{e}^{-(\sigma/3)}\sin\theta\,\sin\varphi$
3	2	0	$\psi_{3\mathrm{d}_z 2} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 \mathrm{e}^{-(\sigma/3)}(3\cos^2\theta-1)$
			$\psi_{3\mathrm{d}_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 \mathrm{e}^{-(\sigma/3)}\sin\theta\,\cos\theta\,\cos\varphi$

(*Continued*)

Table 7.1 (*Continued*)

n	*l*	m*l*	
3	2	±1	$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{+_0}\right)^{3/2}\sigma^2 e^{-(\sigma/3)}\sin\theta\cos\theta\sin\varphi$
3	2	±2	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-(\sigma/3)}\sin^2\theta\cos 2\varphi$
			$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-(\sigma/3)}\sin^2\theta\sin 2\varphi$

Note: The following units are accepted in the table:$\sigma = (Z/a_0)\sqrt{2r}$; $a_0 = (h^2/4\pi\mu e^2)$

absolute value of angular momentum and its projection on the *z*-axis satisfy certain conditions; in particular they signify that the absolute value of the angular momentum vector is always longer than the length of any (even the longest) of its projections (Figure 7.17). Indeed, $m_{\max} = l$ and $l < \sqrt{l(l+1)} = \sqrt{l^2+l}$ and , therefore L_z is always smaller than |**L**| (with one exception when $l = 0$). Therefore, the vector **L** is fixed in the space within angle θ. It follows also from the results presented that the vector **L** can never lie on the *z*-axis. This law concerning angular momentum vectors is called spatial quantization. Figure 7.18 shows the spatial quantization for several *l* values.

Moreover, the theory gives no way of finding the other projections (L_x and L_y); they are completely nondeterminated. This fact can conditionally be added to uncertainty principles. Note that this is not a lack of theory but is the law of nature. Generally speaking, there is no need to give visual evidence of a given fact: this is the nature of things. However, attempts to present a situation as a precession of the vector **L** around the axis *z* are sometimes met. According to our understanding, this interpretation is unlikely to be correct: with precession a certain frequency and, further, energy must be bound though no one has observed such an additional energy. More acceptable is a model of "uniform smearing" of the **L** vector upon a conical surface at a fixed angle, however this model also does not give any reliable ideas for further development.

At a given quantum number the quantum number m_l can accept $2l+1$ values. Therefore, the angular momentum vector can be situated on one of $2l+1$ cones (Figure 7.18). The opening angle η can be found as:

$$\cos\eta = \frac{L_Z}{L} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} \tag{7.5.29}$$

where η is an angle between the vector **L** and *z*-axis and *m* is one of the quantum numbers connected to *l*.

Complications appear also when we have to sum up the angular momentums vectors of several rotators (electron orbits). All restrictions described above are valid in this case too.

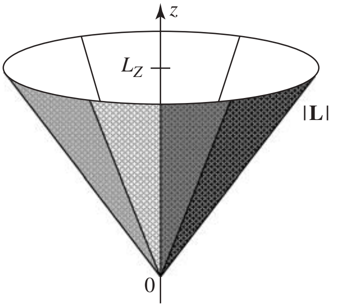


Figure 7.17 A space quantization of the angular momentum.

Suppose, for example, that it is necessary to sum up two vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ in order to obtain the third (resulting) vector $\mathbf{L}$.

One has to remember that the vectors being added cannot be exactly parallel or antiparallel to each other. Really, since $\sqrt{(\ell_1+\ell_2)(\ell_1+\ell_2+1)} < \sqrt{(\ell_1+1)\ell_1} + \sqrt{\ell_2(\ell_2+1)}$, the length of the resulting vector L is always less than the sum of the absolute values of composite vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ ($|\mathbf{L}|<|\mathbf{L}_1|+|\mathbf{L}_2|$).

Formally, one can write $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$, where $L_1 = \hbar\sqrt{\ell_1(\ell_1+1)}$ and $L_2 = \hbar\sqrt{\ell_2(\ell_2+1)}$, the resulting vector having magnitude $|\mathbf{L}| = \hbar\sqrt{\ell(\ell+1)}$. All the vectors have z-projections which are quantized: $L_{1z} = m_1\hbar$, $L_{2z} = m_2\hbar$, $L_z = m\hbar$, where $m_{\max} = \ell$ for all three vectors. Since projections are scalar values, projection of the resulting vector will be found as an algebraic sum of the projections of the individual vectors. The maximum value of the projection of the vector $\mathbf{L}$ is $L_z = \hbar\ell$, where $\ell = \ell_1+\ell_2$, whereas the shortest length of vector $\mathbf{L}$ will be if projections have opposite signs, $L = \hbar|\ell_1-\ell_2|$. Thereby, when adding the angular momentum vectors, the resulting vector L can take all values from maximum to minimum with quantum numbers ℓ, running over all values from $\ell = \ell_1 + \ell_2$ to $\ell = |\ell_1 - \ell_2|$ in integer steps. Figure 7.19, illustrate this summation. One should remember that the resulting vector $\mathbf{L}$ in quantized as well relative the new axis z.

Since the magnetic moment vector is tightly connected with the angular momentum, everything that has been said applies to them both.

The main conclusion from the whole consideration is that the summation of angular momentum vectors in quantum mechanics is accomplished according to a certain scheme. The procedure $\mathbf{L}_1 + \mathbf{L}_2 = \mathbf{L}$ must be understood as a summation of two quantum mechanical angular momentum vectors giving the third vector, complying to the same rules. An attempt to give a primitive image is presented in Figure 7.19.

However, it appears that there is no need to carry out such a huge drawing especially in the case of several vectors, reducing the geometric summation to the combination of quantum numbers. Sometimes, the prescription given above for vector summation is reduced to the symbolic sum $\boldsymbol{\ell} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2$, suggesting combining quantum numbers ℓ_1 and ℓ_2 according to the general rule presented above.

After introducing electron spin, we have to deal with the set of quantum numbers related to orbit and spin.

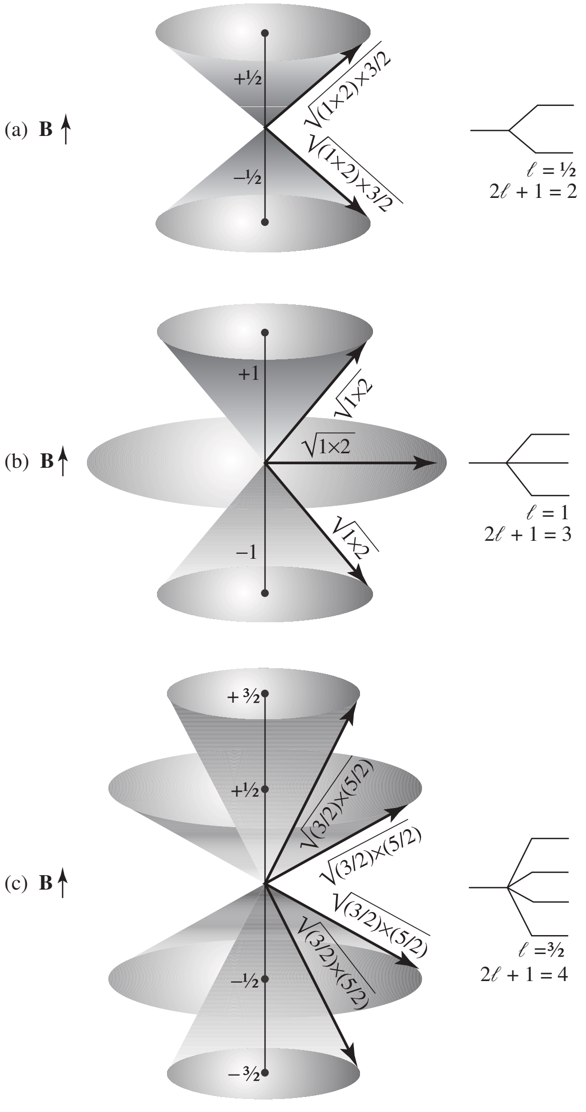


Figure 7.18 Permitted projections of the angular momentum vector. (a) $\ell = 1/2$, (b) $\ell = 1$, (c) $\ell = 3/2$.

7.5.4 A Schrödinger equation for the radial part of the wavefunction; electron energy quantization

Assume that the values of angles θ and φ are constant. Thus we set all partial derivatives of these arguments to zero and look at the behavior of the radial part of the wavefunction. The Schrödinger equation (7.5.5) in these circumstances will take the form

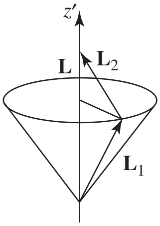


Figure 7.19 Summation of two angular momentum vectors.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial R(r)}{\partial r}\right]+\frac{2m}{\hbar^2}[E-U(r)]R(r)=0, \tag{7.5.30}$$

where instead of the reduced mass μ the electron mass m is again substituted. This equation has solutions at the definite values of the eigenvalues E, and the wavefunctions $R(r)$ are expressed via special functions, the adjoined Laguerre functions. The eigenvalues of energy can be expressed in terms of the fundamental physical constants:

$$E_n=-\frac{e^4m}{32\pi^2\varepsilon_0\hbar^2}\frac{1}{n^2}=-\frac{13.56}{n^2}\mathrm{eV}. \tag{7.5.31}$$

In this expression the energy E is given in eV in order to avoid a source of errors caused by the fact that in different systems of units, the constants are written differently. The integer n in this expression is the principal quantum number; it determines the electron energy E in the hydrogen atom. It can take any positive nonzero value. Eq. (7.5.31) describes the discrete spectrum of electron energies (Figure 7.20).

From this drawing, one can see that value –13.56 eV is the energy of the ground state of the hydrogen atom. Figure 7.20 also depicts the values of some excited states with $n = 1$–7. Excitation of an electron up to the energy $E = 0$ transfers it to a state with a continuous energy spectrum and infinite motion. This corresponds to the removal of the electron from the atom or, in other words, to the ionization of the atom. The first ionization potential is the lowest energy that should be given to an atom from outside to tear the ground state electron away. Consequently, the first ionization potential of a hydrogen atom is 13.56 eV. If the atom is already excited, the ionization energy is less. Accordingly, one can distinguish the second (3.4 eV), third (1.5 eV), etc., ionization potentials of the hydrogen atom.

The transitions between electron energy levels, associated with absorption or emission of a quantum of electromagnetic radiation, are not limited by selection rules, all transitions are permitted. The main equation is:

$$\hbar\omega=E_{\mathrm{n}}-E_{\mathrm{n}'}, \tag{7.5.32}$$

where n and n' are principal quantum numbers corresponding to the initial and final energy levels. Equation (7.5.32) corresponds to serial formula (6.7.13) (see Section 6.7).

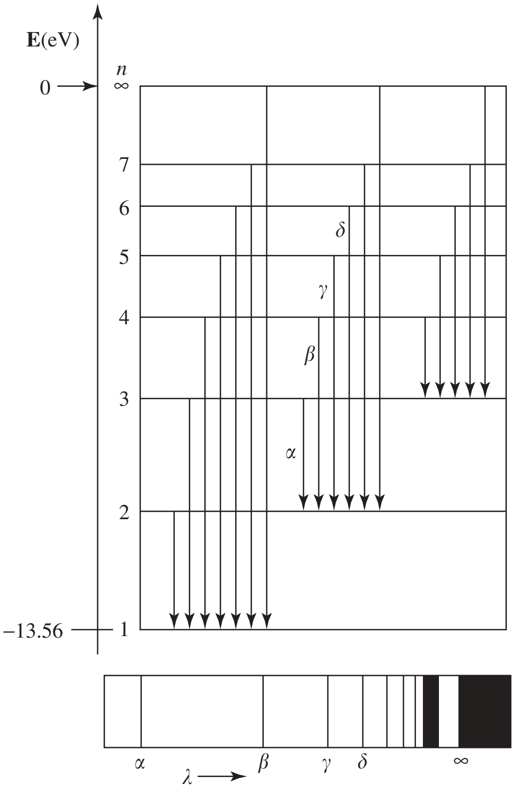


Figure 7.20 The hydrogen atom energy levels; the visible part of hydrogen atom radiation (Balmer series) is presented below: wavelengths α—656, β—486, γ—434 and δ—410 μm. A spectrum border is 365 μm.

Different series of spectral lines are associated with the quantum number n'. According to the quantum number n', the so-called series is distinguished: Lyman series ($n' = 1$), Balmer series ($n' = 2$), Pashen series ($n' = 3$), etc. The Balmer series lies in the visible region of the spectrum. The eigenfunctions $R(r)$ are presented in Section 7.5.7 and in Figure 7.22.

As has already been mentioned above, the Schrödinger equation can be solved exactly for several particular problems only, including the hydrogen atom and the helium ion He$^+$. Even for the neutral helium atom with its two s-electrons, the equation is rather complicated because the potential energy U must take into account not only the interaction of each electron with the nucleus, but the electrons' interaction with each other as well. The expression for the total potential energy takes the form

$$U(r_1, r_2) \sim \frac{1}{4\pi\varepsilon_0}\left[\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_{12}}\right], \tag{7.5.33}$$

r_1 and r_2 being the radial coordinates of each electron, and the last term takes into account the mutual interaction of the electrons. One can imagine to what extent the Schrödinger equation becomes complicated. This equation can be solved only approximately, though modern methods of quantum chemistry enable a solution with good enough accuracy to be obtained.

However, cases exist when the solution for the hydrogen atom can be successfully used for more complicated atoms. These are the so-called hydrogen-like atoms, in which a particular electron is rather more distant from the nucleus than the other electrons. The latter form a closed shell of inner electrons, and the residual electron is situated in the complex electric field. In this case the changes in the energy are taken into account by atomic number Z:

$$E = -\frac{13.56}{n^2} Z^2 \text{ eV}. \tag{7.5.34}$$

It must be emphasized however, that the value Z in this case is not an exact atomic number because an external, valence electron is presented in the effective field, created both by the nucleus and by inner electrons. This effect is termed "screening" because the inner electrons make a negative shield around the positive nucleus. Therefore, the effective Z value differs from the ideal atomic number and is often called the effective atomic number.

7.5.5 Spin of an electron

Besides an orbital angular momentum, the electron has an inherent angular momentum that has been called spin. This is often explained as the rotation of the electron around its own axis. However, neither orbital nor spin "motions" have been considered as motion, but as a state, characterized by definite quantum numbers. It was found by Einstein and de-Haas (1915) and Stern and Gerlach (1922) in classic experiments that the number of possible projections of the electron angular momentum vector on the selected axis is two. So in accordance with eq. (7.5.3) one can obtain $s = ½$ (because $2 = 2s+1$), s being the spin quantum number. This signifies that the length of electron intrinsic angular momentum vector L_S according to the general rule for the magnitude of the spin angular momentum vector is $\hbar\sqrt{s(s+1)}$, therefore,

$$|\mathbf{L}_S| = \hbar\sqrt{\frac{3}{4}} = \hbar\frac{\sqrt{3}}{2}. \tag{7.5.35}$$

According to the quantization rule this means that the spin projections onto the selected z-axis can have two values, namely,

$$L_z = \mathrm{m}_s\hbar = \pm\frac{1}{2}\hbar \tag{7.5.36}$$

where m_S is a quantum number of spin projection.

The quantum number m_S does not influence the electron wavefunction significantly; however, it influences the electron distribution among the energy levels and quantum cells to a great extent. The Pauli principle is a consequence of these quantum mechanical rules.

Because of the fact that not the absolute value of the angular momentums but their projections are measurable quantities, it can often be said that the electron spin is $\pm(1/2)\hbar$ or simply $\pm(1/2)$. The spin spatial quantization is depicted in Figure 7.21.

In full analogy with the orbital state, the spin magnetic moment can be determined through the gyromagnetic ratio g (Section 5.2.1). For spin $g = 2$ (in e/2 m units), the absolute value of spin magnetic moment is therefore equal to

$$\mathcal{M} = 2\frac{e}{2m}\hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1)} = 2\mu_B\sqrt{\frac{3}{4}}, \tag{7.5.37}$$

The projection of the magnetic moment on the z-axis is

$$\mathcal{M}_z = \pm\mu_B. \tag{7.5.38}$$

When chemists look at atomic and/or ionic electron states, and distribute electrons over the energy levels and/or fill in corresponding quantum cells by arrows in accordance with the Pauli exclusion principle (not more that two electrons into one quantum cell) and the Hund's rule, they bear in mind exactly these two projections of spin magnetic moment. Note that arrows are represented by schematically signs + and −, since projections themselves are not vector but algebraic values.

7.5.6 Atomic orbits: hydrogen atom quantum numbers

Now it is desirable to generalize the information that we have obtained following the analyses of the Schrödinger equation for the hydrogen atom and introducing the electron spin. We mean the systematization of the values characterizing an atom's state. Herewith

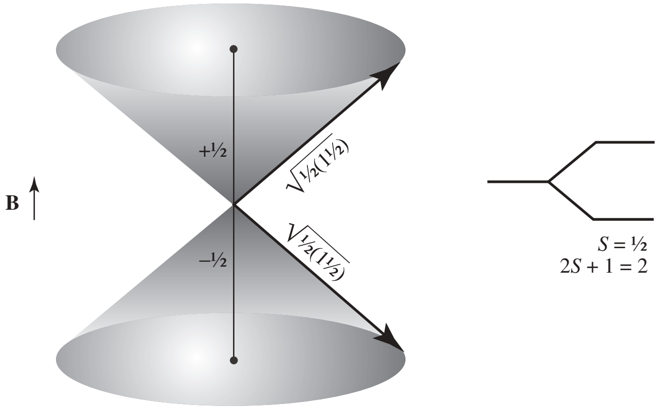


Figure 7.21 Spin space quantization.

we will try to analyze the approaches of physicists and chemists, which in some respect look different.

A typical quantum mechanical object such as an atom possesses some classic characteristics that are unexplainable within the framework of generally accepted presentations (refer to Section 6.7) (no orbital motion, yet the existence of angular momentum; no rotation of an electron around its own axis, yet intrinsic angular and magnetic moments, i.e., spin, etc.). As a result, these terms are used irrespective of their classical sense.

Moreover, the Bohr model is a transition from the purely classical presentations to the quantum mechanical ones: the motion of electrons along the orbits is accepted, but not all orbits are permitted; the angular momentum is accepted though its values, and orientations are the subject of strict limitation. It is possible to consider the Bohr model as a transition from the classical mechanics to quantum, with the preservation of many of its attributes. As a result, many of Bohr model notions will often be met in order to simplify the students' understanding.

Quantum mechanical angular momentums and its projections, as well as the electron energy, are defined now by quantum numbers: the electron energy is defined by the principal quantum number n, the angular momentum vector length is defined by quantum number l, its projection on the selected z-axis is given by a quantum number m_l. Each of the quantum numbers enumerated is included into a particular wavefunction, and their product gives total wavefunction describing an electron distribution in the language of probabilities. Such an image of wavefunctions and their squares brings about the atomic orbits. For chemists, it is precisely the most valuable result.

The quantum number m_S is characterized by the z projection of the electron spin angular momentum. In first approximation, it does not influence the energy and wavefunction shape, but influences significantly the electron distribution among the energy levels. Consequently, the total wavefunction is the product of all three parts (refer to eq. 7.5.6):

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) = R(r)Y(\theta,\varphi), \tag{7.5.39}$$

the $R(r)$ function depends on n and $Y(\theta, \varphi)$ on l and m_l.

7.5.7 Atomic orbits

The general expressions for $R(r)$, $\Theta(\theta)$ and $\Phi(\varphi)$ can be written using the special mathematical functions. They are presented in special literature on mathematics, quantum mechanics and quantum chemistry. We restrict ourselves to giving here the description of the main physical concepts of electron orbits as the basis for the theory of chemical bonding.

The state of an electron in an atom is much more sophisticated than can be expected from the Bohr theory. Quantum mechanics shows that an electron can be found in any point of space, but the probability of its presence changes from point to point. The notion of an electron orbit appears more productive than electron clouds. Under the electron orbit, the physicist often understands the mathematical expression of the wavefunction itself corresponding to definite quantum numbers. In chemistry, the orbit is understood as a set of electron positions around a nucleus taking the probabilities into account. This probability is defined by wavefunctions R, Θ, Φ.

Expressions for s-, p- and d-electrons in the analytical form in the spherical coordinate system (Figure 7.16) are given in Table 7.1. In the radial part of the wavefunction $R(r)$ argument r is given in atomic units, i.e., in the unit of the first Bohr atomic radius $a_0 = 0.5292 \times 10^{-10}$m. Graphs of the $R(r)$ functions (a) and the probability density curves, i.e., the probability density of finding an electron in the spherical layer with a thickness $dr(dw/dr = 4\pi r^2 R^2(r))$(b) as dependent on r are depicted in Figure 7.22. It should be noted that $R(r)$ at the point $r = 0$ (i.e., on the nucleus) has the maximum value. However, this does not contradict common sense because the probability of finding an electron at point $r = 0$ (Figure 7.22b) is equal to zero.

A scheme for drawing graphs of the angular part of the wavefunction $Y(\theta, \varphi)$ and its square $Y^2(\theta, \varphi)$ (particularly for p_z orbit) is given in Figure 7.23a and b, respectively.

The value of Y for the given θ is proportional to a line OM. It is worth noting that the function $Y(\theta)$ is presented as spheres, whereas the $Y^2(\theta)$ is presented as the elongated dumbbells more popular in chemistry.

The wavefunctions in Table 7.1 (above) are presented for n = 1, 2 and 3. In the first line the data for the 1s-state is given, in this case $R(r)$ has a maximum at $r = 0$ and falls down with increasing r. The $Y(\theta, \varphi)$ function depends neither on θ, nor on φ, therefore the $|\psi|^2$ graph is spherically symmetric. The same is true for the 2s- and 3s-states.

The analytical expression for $n = 2$, and 1, $m_l = 0$ and ± 1 are given in the next three lines. It can be seen that the p_z-orbit solution has the simplest look than the two others (p_x and p_y); such inequality is the result of the spherical coordinate system; moreover, the last ones have imaginary form. In order to obtain the expression in a real form, one should compose a linear combination of particular solutions, i.e., carry out the hybridization of orbits (since any combination of the solutions of the Schrödinger equation is also the equitable solution). We must use here the Euler formula and compose the linear combination of $Y_{1,1}$ and $Y_{1,-1}$ orbits:

$$\begin{aligned} Y_{p_x} &= \frac{1}{2}(Y_{1,1} + Y_{1,-1}) = \frac{1}{2}\sqrt{\frac{3}{8\pi}}\sin\theta\,[\cos\varphi - \mathrm{i}\sin\varphi + \cos\varphi + \mathrm{i}\sin\varphi] \\ &= \sqrt{\frac{3}{8\pi}}\sin\theta\cos\varphi \end{aligned} \tag{7.5.40}$$

and,

$$\begin{aligned} Y_{p_y} &= \frac{1}{2\mathrm{i}}(Y_{1,1} - Y_{1,-1}) = \left(\frac{1}{2\mathrm{i}}\right)\sqrt{\frac{3}{8\pi}}\sin\theta\,[\cos\varphi + \mathrm{i}\sin\varphi - \cos\varphi + \mathrm{i}\sin\varphi] \\ &= \sqrt{\frac{3}{8\pi}}\sin\theta\sin\varphi. \end{aligned} \tag{7.5.41}$$

The angular parts in the real form for electron d-states were also obtained in this way. In this form, they are widely used in chemistry. Having determined all parts of the wavefunction in any point, the $\mathbf{r}(r, \theta, \varphi)$, the total wavefunction can be derived by multiplication of all its parts.

In the abstract case of the absence of any external influence when there are no arguments for the choice of quantization of axis z, all solutions of the Schrödinger equation and

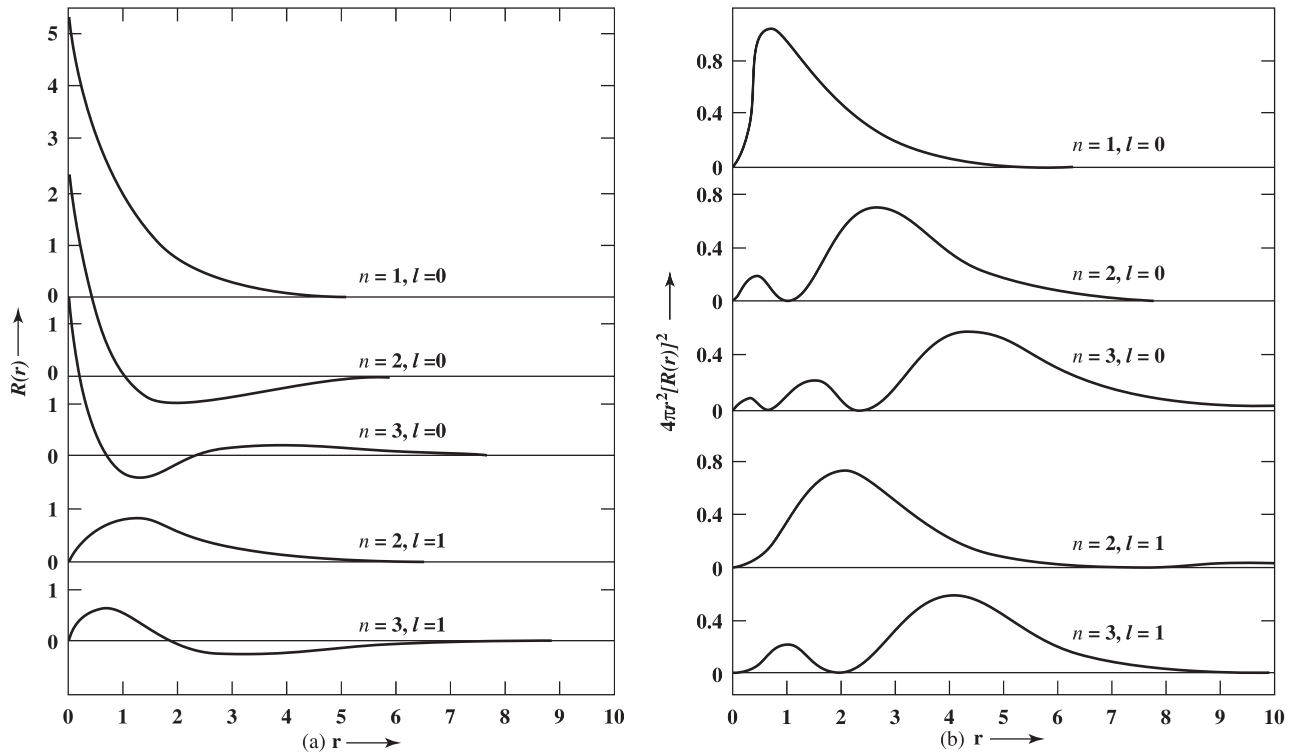


Figure 7.22 A wavefunction's radial parts R (a) and corresponding values $4\pi r^2 R^2$ (b) for some electron states.

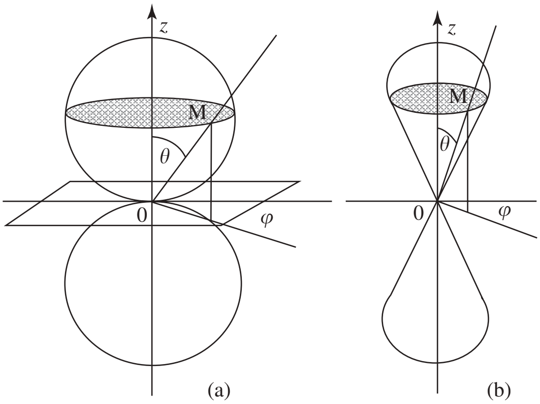


Figure 7.23 How to draw the wavefunction's angular parts $Y(\theta, \varphi)$ (a) and $Y^2(\theta, \varphi)$ (b).

all their linear combinations can virtually exist. However, there is no physical possibility of finding either all or some of them, because any attempt to select a quantization axis destroys the atom itself. This fact reveals a property of quantum mechanics: an instrument of investigation destroys the state of an object.

If the atom considered falls into the orbit of other atoms, the mutual chemical influence makes essential changes to their state. In different circumstances, it can appear that other linear combinations can be more advantageous, for example, the well-known s-p and s-p-d hybrid orbits are created (see Tables 7.1).

Note that the probability density of finding an electron in different points of an orbit graph is different. To depict the total electron distribution in three-dimensional form and to make them understandable to the reader is a very difficult task. Nevertheless, some efforts have been made to create a suitable image. The most recent is the presentation of electron density as a graph of the charge distribution $dq(r, \theta, \varphi) = |e||\psi|^2(r, \theta, \varphi)dV$ as a spatial pattern in the form of isolines and three-dimensional pictures. The results of X-ray diffraction investigation are at present given in such a form.

Graphs in the form of closed surfaces are often used in chemistry; inside a closed volume, a definite amount of atomic electrons are contained (more often 90%). Such a picture is presented in Figure 7.24 showing the orbits of different electron states in the hydrogen atom. Note that the orbits do not touch the origin (the nucleus). This is because of the fact that in this area the probability density of finding an electron is very small due to the radial part of the wavefunction (the argument r is too small). Therefore the total density is also small.

It turns out that, even for hydrogen-like atoms, atomic orbitals appear vastly more complex. Regrettably, it is impossible to obtain the exact solution even for these atoms. So in quantum chemistry different kinds of approximation are used, more or less successfully, to describe one system or another, and one atomic area or another. For instance, the factor ξ is introduced as a multiplier in the exponent order of the radial wavefunctions to describe an orbit's compression-expansion (Slater multiplier). Sometimes, not one but two, or even several, multipliers are used, each of which is better for describing the electron density near the nucleus or far from it. These empirical modifications for different atoms are given in quantum chemistry.

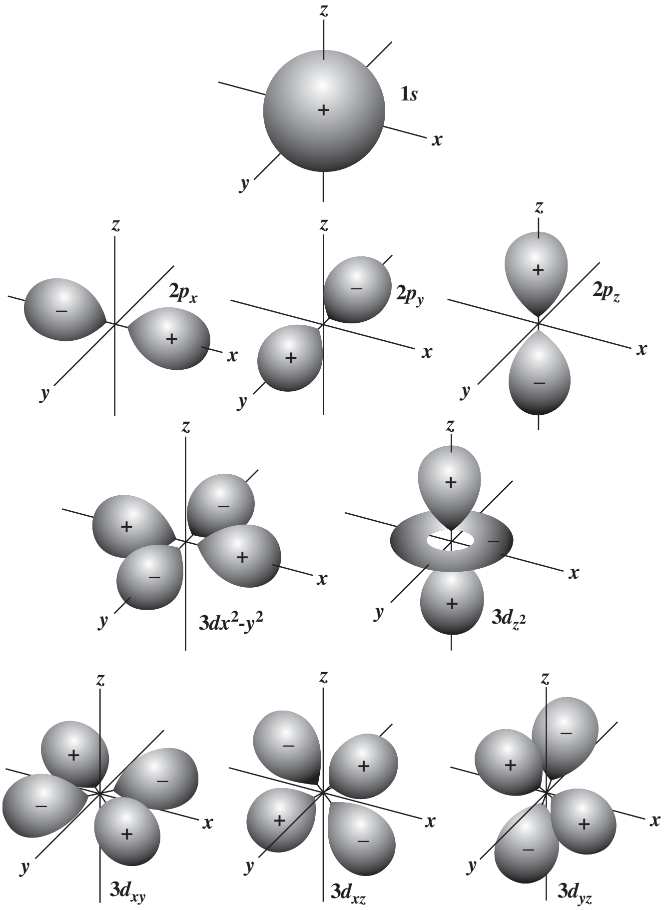


Figure 7.24 Representation of a wavefunction's angular parts in different electron states.

EXAMPLE 7.8

A hydrogen atom is in a ground 1s state. Determine the probability of finding an electron w in a sphere of radius $r = 0.1a$.

Solution: The probability of finding an electron in a spherically symmetric 1s state is given by the normalized wavefunction $\psi_{100}(r)(1/\sqrt{\pi a^3})\exp(-(r/a))$ the volume element being $dV = 4\pi r^2 dr$. Therefore

$$dw = \left|\frac{1}{\sqrt{\pi a^3}}\exp\left(\frac{r}{a}\right)\right|^2 4\pi r^2 dr = \frac{4}{a^3}\exp\left(\frac{2r}{a}\right) r^2 dr.$$

It is convenient to move to the atomic units further $\rho = r/a$; therefore $r^2 = \rho^2 a^2$, $dr = ad\rho$ and $dw = 4\exp(-2\rho)\rho^2 d\rho$. The probability can be found by integrating dw in limits $r_1 = 0$ to $r_2 = 0.1a$ (or from $\rho_1 = 0$ to $\rho_2 = 0.1$)

$$w = 4\int_0^{0.1} \rho^2 \exp(-2\rho) d\rho.$$

Decompose the exponential into a MacLoren series $\exp(-2\rho) \approx 1 - 2\sigma + ..$ and limit by two terms; we can present the integral as

$$\begin{aligned} w &= 4\int_0^{0.1} (1-2\rho)\rho^2 d\rho = 4\int_0^{0.1} \rho^2 d\rho - 8\int_0^{0.1} \rho^3 d\rho \\ &= \frac{4}{3}\rho^3 \Big|_0^{0.1} + 8\frac{\rho^4}{4}\Big|_0^{0.1} = \frac{4}{3}10^{-3} + 0.2\times 10^{-3}. \end{aligned}$$

Therefore the final result is $w = 1.53 \times \cdot 10^{-3}$. It is useful to compare this result with Figure 7.22.

7.5.8 A spin–orbit interaction (fine interaction)

The above scheme of the Schrödinger equation solution did not take two circumstances into account: firstly, relativistic effects and, secondly, electron spin. The relativistic effects appear when a particle possesses high energy and consequently moves at a speed close to the light velocity. In an atomic planetary model, the inner electrons are nearest to a nucleus (E is negative and great in the absolute value, refer to eq. (7.5.34) at $Z > 30$), are precisely the relativistic particle. In this case, one should take relativism into account; we will not, however, discuss this further.

Consideration of electron spin raises the question of the so-called spin–orbital interaction influencing the electron energy values. The mechanism of this interaction consists of the fact that the electron orbital "movement" produces the magnetic field acting on its own spin. In order to make the picture more understandable, let us place the origin in an electron, the nucleus in this case appears moving along the circular orbit around the electron under consideration, creating a magnetic field at its position. Interaction of the magnetic moment of the electron spin with the magnetic field produced by a nucleus is called the spin–orbit interaction. The energy of this interaction must be taken into account when estimating the atomic total electron energy. Fortunately, such a complex procedure can be considerably simplified using the procedure of substitution of the vectorial summation by the combination of quantum numbers (see Section 7.5.3). To account for the spin–orbit interaction, the additional quantum number j is introduced, j being the sum of quantum numbers l and s

$$j = \ell + s = \ell \pm \tfrac{1}{2} \tag{7.5.42}$$

Instead of the single energy level, characterized by quantum number n, two levels appear with quantum number l equal to $l \pm (1/2)$. (At $l=0$ quantum number j accepts only one value $j+(1/2)$.). Accounting for the spin–orbit interaction, the electron energy becomes dependent not only on the principal quantum number n but on the quantum number j as well. Exact calculations give

$$E_{n,j} = -\frac{13.56}{n^2} Z^2 + \frac{13.56 \times Z^4 \times \alpha^2}{n^3} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \tag{7.5.43}$$

(as in expression (7.5.30), the energy is given here in eV units). Estimation of $E_{n,j}$ shows that it is in the order 10^{-4} eV. The dimensionless value $\alpha = (e^2/\hbar c)$ with good accuracy is equal to 1/137; it is called the constant of the fine structure. Its rational value has been the reason for a great deal of speculation about the rational correlations between atomic characteristics and, accordingly, the creation of the united theory of elementary particles. However, all of these came to nothing and were personal tragedies for a number of scientists.

In spite of the fact that the energy of fine interactions is small, analysis of the last two formulas shows that because of fine interaction all energy levels with $l \neq 0$ split into two. This is developed, for instance, in the splitting of some spectral lines of atomic electron spectrums. So the well-known transition p→s in alkaline metal atoms instead of one spectral line contains two reliably measurable lines.

EXAMPLE E7.9

An excited electron is in a 3p-state. Find the change in the orbital magnetic moment of the atom's transformation to a ground state.

Solution: We have to find the difference $\Delta\mathscr{M}_l = \mathscr{M}_{l2} - \mathscr{M}_{l1}$. The orbital magnetic moment depends only on orbital quantum number: $\mathscr{M}_l = \mu_B \sqrt{\ell(\ell+1)}$. Therefore, in the ground state $l = 0$ and $\mu_{l2} = 0$. In the excited state, $l = 1$ and $\mathscr{M}_{l1} = \mu_B\sqrt{2}$. Hence the difference is $\Delta\mathscr{M}_l = - \mu_B\sqrt{2}$. Execute the calculation remember that $\mu_B = 0.927 \times 10^{-23}$ J/T, we arrive at the numerical value $\Delta\mathscr{M}_l = -1.31 \times 10^{-23}$ J/T.

7.6 A MANY-ELECTRON ATOM

As we already know, it is impossible to solve analytically the Schrödinger equation for atoms with two and more electrons. This prompted the development of new quantum mechanical methods of approximate solutions or modified solutions, equitable for the hydrogen atom, by introducing empirical adjustments. In this chapter we will consider intra-atomic interactions between electrons and the complication that this interaction causes. (Here we must emphasize that any complication in the theory forces the development of more sophisticated experimental methods of investigation, opening new possibilities of studying more precise questions relating to the chemical structure.)

The wavefunctions of many-electron atoms will not be studied in this book; these are the subject of quantum chemistry.

7.6.1 Types of electron's coupling in many-electron atoms

If there are several electrons in an atom, the total angular momentum (sometimes it is called a *mechanical* moment unlike magnetic) is obtained as a sum of mechanical moments of atomic electrons. Depending on the electron interaction energies there exists two ways to combine all mechanical moments (spin and orbital) into the total one: either to take into account the fine spin-electron coupling first (refer to Section 7.5.8), obtain the quantum numbers j's and corresponding L_J or primarily unite all mechanical moments of all electrons, orbital and spin separately, obtain total L_ℓ and L_s and finally obtain L_J. Such coupling is referred as Russell-Saunders binding. Consequently, to obtain the total angular momentum of a many-electron atom one should first to add to each other the orbital moments of all electrons L_L, then sum all spin moments into L_s and only afterwards to sum them both into the total one (ℓ and s being orbital and spin quantum numbers of a single electron and L and S the quantum numbers of the total angular momentum of the whole atom).

Herewith there is no need to combine vectors with provision for rules of the angular momentum summation in the quantum mechanics, it is easier do this by combination of the quantum numbers. Let us do the summation of the two electrons with quantum numbers l_1 and l_2, s_1 and s_2. Summation of orbital moments gives

$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, |\ell_1 - \ell_2|. \tag{7.6.1}$$

Consequently, the total angular momentum L_L, can accept as much values as many terms contain the series (7.6.1). Their values can be determined according the general rule (refer to 7.5.3)

$$|\mathbf{L}_L| = \hbar\sqrt{L(L+1)}. \tag{7.6.2}$$

We can operate quite analogously with spin angular momentums. As $s = 1/2$ and N is the number of electrons, the total spin angular momentums S can accept the values

$$S = N\tfrac{1}{2}, N\tfrac{1}{2} - 1, ..., 0, \tag{7.6.3}$$

when N is even and

$$S = N\tfrac{1}{2}, N\tfrac{1}{2} - 1, ..., \tfrac{1}{2}, \tag{7.6.4}$$

when N is odd. The total spin angular momentum is expressed by analogy with the previous expression

$$|\mathbf{L}_S| = \hbar\sqrt{S(S+1)}. \tag{7.6.5}$$

In order to obtain the total (atomic) angular momentum (mechanical moment), we must put the quantum numbers together

$$J = L + S,\ L + S - 1, \dots, |L - S|, \tag{7.6.6}$$

where J is the total atomic quantum number; it determines the atomic mechanical moments

$$|\mathbf{L}_J| = \hbar\sqrt{J(J+1)}. \tag{7.6.7}$$

Its z-projections are $L_{J,z} = \hbar m_J$ (7.6.8)
where

$$m_J = J, J-1, J-2, \dots, -J, \tag{7.6.9}$$

overall $2J + 1$ values.

The graphic summation will be given below.

When the individual electron spin–orbit interaction energy prevails over the spin–orbit interactions of different electrons, we first have to sum the orbital and spin moments of every electron (to obtain all *j*'), then sum these *j*' and further obtain the total atomic angular momentum quantum numbers and finally the overall quantum number *J*, characterizing the total angular momentum of the atom. This type of binding is called a j–j bond. Since the spin–orbit interaction is proportional to Z^4, this type of binding occurs mainly in heavy atoms. We will not consider further this type of coupling.

Sometimes all states with the same quantum number *J* have the same energy, because different m_l' does not often influence it. In these cases, states are called degenerated ones. However, there are often cases when the energy with definite *J* and different m_l' have different energy. These are cases without degeneration. Sometimes, this only partly concerns a state. For instance, in a state with $J = 2$ corresponding to $2J + 1$ values of m_J (2, 1, 0, –1, –2), all of them can possess the same energy. Such states are called fivefold degenerate ones. An external influence (for instance, a crystal field) can split one degenerated fivefold electron level into twofold and triple fold split levels (this situation is often encountered in the d-state of d-element complexes).

Such a process is called lifting (or removing, or waiving,) the degeneration. In this case the degeneration is removed only partly. Which quantum number the degeneration lifting relates to is usually indicated.

7.6.2 Magnetic moments and a vector model of a many-electron atom. The Lande factor

In Section 5.2.1 the gyromagnetic ratio *g*, the ratio of the magnetic moment to the angular momentum, was introduced. This ratio is given in the unit ($e/2m$) and allows the determination of the magnetic moment knowing the angular (mechanical) moment. The g value for the orbit ($g = 1$) can be calculated theoretically, whereas for spin ($g = 2$) it is determined experimentally. In this section, we shall consider the problem of what to do if, in the many-electron atom with a Russell-Saunders coupling scheme, both orbit and spin participate in producing the magnetic moment. The vector model of an atom will help us.

Formally, one can write the expression for the magnetic moment

$$\left|\mathcal{M}_J\right| = g\mu_{\mathrm{B}}\sqrt{J(J+1)}, \tag{7.6.10}$$

where μ_{B} is the Bohr magneton and J is the total quantum number of atomic mechanical moments. Our task is to determine the g-value when both orbit (quantum number L) and spin (quantum number S) participate in magnetic moment creation.

The mutual disposition of all total atomic mechanical and magnetic moments is presented in Figure 7.25. The vectors $\mathbf{L}_L$ and $\mathbf{L}_S$, obtained according to the rule described above for Russell–Saunders coupling can be seen in the picture. Their sum gives the general mechanical moment $\mathbf{L}_J$ (all of them in the scale of $\hbar$). The magnetic moments (in the scale μ_{B}) correspond to each mechanical moment; all of them are directed oppositely to their counterparts because of the negative electron charge. The length of magnetic moments takes into account the corresponding g-factor: $g = 1$ for orbit and $g = 2$ for spin. Therefore, their sum $\boldsymbol{\mu}_J$* is directed not strictly antiparallel to its counterpart μ_J , but at some angle (denoted as η) to the line of $\mathbf{L}_J$. (In an atom, as in any other rotating system, the main vector is the angular (mechanical) momentum vector; it specifies the main system axis). Therefore, the total atomic magnetic moment is not $\boldsymbol{\mu}_J^*$, but μ_J that is a projection of the first on an axis specified by the $\mathbf{L}_J$ vector. It is seen in Figure 7.25 that

$$\mathcal{M}_J = \mathcal{M}_J^{*}\cos\eta \tag{7.6.11}$$

The total vector $\boldsymbol{\mu}_J$ length is a sum

$$\mathcal{M}_J = \mathcal{M}_L\cos\alpha + \mathcal{M}_S\cos\beta. \tag{7.6.12}$$

As $\mathcal{M}_L = 1\times(e\hbar/2\mathrm{m})\sqrt{L(L+1)} = 1\times\mu_{\mathrm{B}}\sqrt{L(L+1)}$ and $\mathcal{M}_S = 2\times(e\hbar/2m)\sqrt{S(S+1)} = 2\times\mu_{\mathrm{B}}\times\sqrt{S(S+1)}$ we have to determine cos α and cos β.

Let us consider a triangle with sides $\mathbf{L}_L$, $\mathbf{L}_S$ and $\mathbf{L}_J$. According the cosine theorem:

$$\mathrm{L}_S^2 = \mathrm{L}_L^2 + \mathrm{L}_J^2 - 2\mathrm{L}_L\mathrm{L}_J\cos\alpha \text{ and } \mathrm{L}_L^2 = \mathrm{L}_S^2 + \mathrm{L}_J^2 - 2\mathrm{L}_S\mathrm{L}_J\cos\beta.$$

Then,

$$\cos\alpha = \frac{\mathrm{L}_L^2 + \mathrm{L}_J^2 - \mathrm{L}_S^2}{2\mathrm{L}_L\mathrm{L}_J} = \frac{L(L+1)+J(J+1)-S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}}$$

and

$$\cos\beta = \frac{\mathrm{L}_S^2 + \mathrm{L}_J^2 - \mathrm{L}_L^2}{2\mathrm{L}_S\mathrm{L}_J} = \frac{S(S+1)+J(J+1)-L(L+1)}{2\sqrt{S(S+1)}\sqrt{J(J+1)}}.$$

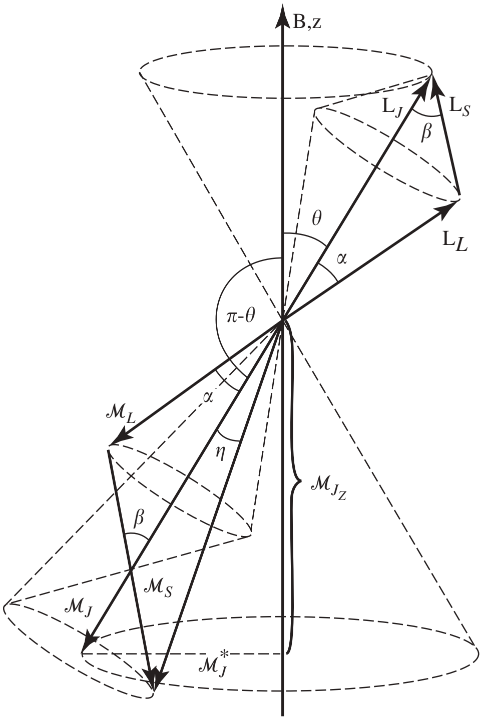


Figure 7.25 The vector diagram of a multielectron atom.

Substituting these values into eq. (7.6.12), we arrive at

$$\mathcal{M}_J = \mu_B \times \left(L(L+1)\frac{L(L+1)+J(J+1)-S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}} \right.$$
$$\left. +2S(S+1)\frac{S(S+1)+J(J+1)-L(L+1)}{2\sqrt{S(S+1)}\sqrt{J(J+1)}} \right).$$

This expression can be re-written as:

$$\mathcal{M}_J = \mu_B \times \left(1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \right)\sqrt{J(J+1)}. \tag{7.6.13}$$

Comparing expressions (7.8.10) and (7.8.13), we obtain

$$g = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \tag{7.6.14}$$

Expression (7.6.16) determines the so-called Lande factor (multiplier). It permits us to write the expression of the magnetic moment of the multi-electron Russell–Saunders atom in a compact form:

$$\mathcal{M}_J = \mu_B g\sqrt{J(J+1)} \tag{7.6.15}$$

In the particular cases at $S = 0$, $J = L$ and the Lande factor is, certainly, equal to 1; at $L = 0$, $J = S$ $g = 2$, which correspond to purely spin magnetic moment.

Expressions that determine the magnetic moments of multielectron atom are obtained in full.

7.6.3 The atomic terms

It is obvious now that an atomic state has to be characterized not only by the electron distribution between energy levels (with Pauli exclusion principle validity), but also by moments: total $\mathbf{L}_J$, orbital $\mathbf{L}_L$ and spin $\mathbf{L}_S$, their mutual positions being taken into account. The range of quantum numbers *J*, *L* and *S* comprise the so-called atomic term. The symbolic presentation of the atomic term is given as: $^{\beta}A_J$: A is characterized by the quantum number *L* according to the following scheme:

L	0	1	2	3
A	S	P	D	F

The number β is called the term multiplicity; it characterizes the number of acceptable states at fixed quantum number *L*. The multiplicity β is equal to $2S + 1$ at $S < L$ and $2L + 1$ at $S > L$. For example, for states with $L = 1$ and $S = \frac{1}{2}$ multiplicity β is equal $2\times\frac{1}{2}+1=2$ (term $^2P_{1/2}$, $^2P_{3/2}$); for states with $L = 1$ and $S = 2$, $\beta = 2 \times 1 + 1 = 3$ (terms $^3P_3$, $^3P_2$ and $^3P_1$), etc.

The definite energy corresponds to each term. However, systems can often be degenerated. The external action can remove the degeneration, i.e., make each term have its own energy.

7.6.4 Characteristic X-rays: Moseley's law

As we saw in Section 6.6.4, an electro-magnetic radiation with a wavelength of 10^{-10}–10^{-11} m is regarded as an X-ray. Two types of X-rays are known; both of them are produced in an X-ray tube as the result of the interaction of primary radiation (X-rays or electrons) with an anode material. X-rays of the first type are produced as a result of intra-atomic energy transitions and are called characteristic X-rays; their line spectrum is specified by the anode material's atoms. The second are bremsstrahlung X-rays emitted while an electron moves with high deceleration in the surface layers of the anode material. This spectrum is white, i.e., it contains a continuous range of wavelengths (see Section 6.6.4). In both cases a great amount of heat is emitted and then removed by a special water flow inside the anode.

White radiation is used in material X-ray radiography (translucence, human body). Its properties were mentioned in Section 6.6.4. We will restrict ourselves in this section to a consideration of characteristic X-rays.

The primary electrons in the X-ray tube (see Figure 6.39) are emitted by a heated cathode by thermo-emission and accelerated by an electrostatic field between anode and cathode with the potential difference 10^3–10^5 V. In the nonexcited atoms of the anode, all lower levels are occupied in accordance with the Pauli exclusion principle. Rapidly moving electrons strike a metal target (refer to Section 6.6.4). Colliding with the atom, the accelerated electron kicks the inner, lower-level electron out producing free places (holes) in the low-lying (ground) levels. An upper-level electron drops down to fill the hole. The transition is accompanied by photon emission, its wavelength λ being determined by the energy difference: $\lambda = 2\pi c/(E'' - E')$, where $(E'' - E')$ is the energy difference.

In Section 7.5.4, the spectrum of the hydrogen atom was discussed. Equation (7.5.34) shows that the energy levels, at least for the hydrogen-like atoms, go down (in a negative region) proportional to Z^2: the potential well deepens though the relative positions of the levels do not change significantly. At the above-mentioned voltage difference and Z~10–40, the emitted photons enter the X-ray range. In other types of atoms, the mutual positions of levels are changed: now the energy level depends not on the principal quantum number n only but on the orbit L, spin S and total J numbers as well. A spectral fine structure appears (Figure 7.26).

It can be seen that the X-ray spectrum has a line feature with a relatively small (in comparison with optic molecular spectra) number of spectral lines. The X-ray tube radiation usually contains low intensity white radiation background and strong lines of characteristic spectral lines rise above it (Figure 7.27). The most important fact is that the appearance

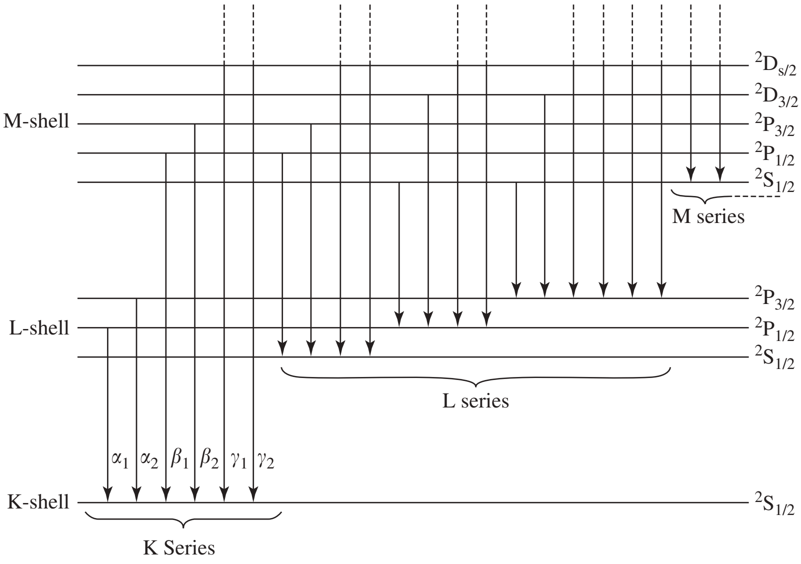


Figure 7.26 Electron levels of a multielectron atom.

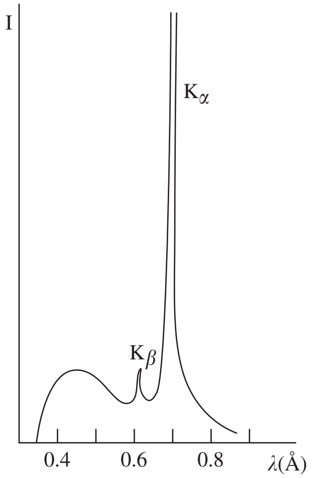


Figure 7.27 The tube's X-ray spectrum; high-intensity characteristic spectral lines over the background of a white bremsstrahlung can be seen.

of the spectrum is very specific: each element has its own spectrum and it can be used to reveal the material that has emitted from the spectrum.

The X-rays resulting from electron transition from any higher level to a lower level with the principal quantum number $n = 1$ are known as K-series; transition to a level with n = 2 are known as L-series; and series M, N... describe with n = 3, 4..., etc. Because of the fact that every level after K is split, the transition L → K in particular produces three closely set lines, the most intense being denoted as $K_{\alpha 1}$.

A Z-dependence of an emitted X-ray radiation frequency ν is given by Moseley's law (1913). The British scientist H.G.J. Moseley found that the most intense short-wavelength line in the characteristic K-series X-ray spectrum from a particular target (anode) element varied evenly with the element atomic number Z (Figure 7.26). He also found that this relationship could be expressed in terms of X-ray frequency by a simple formula

$$\nu = 2.48(Z-1)^2 10^{15}\ \text{Hz} \tag{7.6.17}$$

The $Z-1$ value is the so-called effective atomic number. The point is that one electron kicked out of the K level left a second one untouched. The latter takes part in the screening of the positive nuclear charge by the negative electron charge.

The above formula only applies to an L→K transition. An analogous expression describes the other series. An illustration of Moseley's law for K-series lines of different elements is given in Figure 7.28. The X-ray spectra of all elements are tabulated.

Moseley's discovery is closely connected with the Bohr atomic model, both being announced in the same year (1913).

The spectra discussed are produced by inner transitions and are not affected by the valence state and chemically bonded atoms. Therefore the characteristic spectra are the probe of the chemical composition of the material investigated. Analysis of the specimen

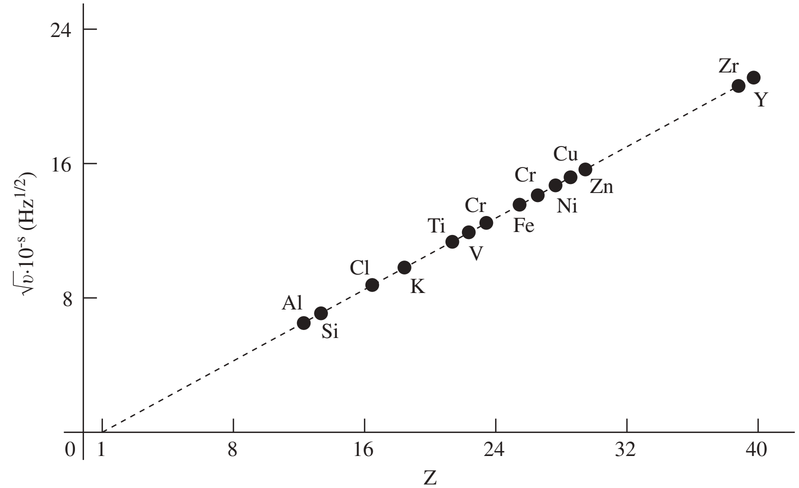


Figure 7.28 A graph of versus periodic number of a chemical element *Z* (Moseley law).

chemical composition on the basis of Moseley's law is the essence of the chemical X-ray fluorescent method.

For excitation, a corresponding device can use either the primary X-ray beam or primary electron beam described above (refer to Section 7.2). In the latter case, special magnetic coils (lenses) can squeeze the electron beam down to microns and carry the experiment out to the chemical element distribution point by point. Such devices are called quantometers.

In order to see the composition of secondary X-ray radiation, X-ray diffraction analyzers are used (refer to Section 6.3.5): an analyzing crystal with a known structure and, hence, with known crystal interplanar distance enables the measuring of the reflecting angle and then the wavelength of the secondary radiation. By consulting tables of the characteristic X-rays, one can find the sample chemical composition in every point, in crystallites and intercrystallite junctions, and in amorphous samples, etc.

As an example, the characteristic spectrum of a $BaTiO_3$ ceramic is presented in Figure 7.29. The wavelength is plotted along the abscissa and the relative intensity along the ordinate. The numbers below are the tabulated data of corresponding elements and series of Ti, Ba and O. The line intensity is proportional to the relative amount of a particular element in the sample (at the point irradiated). The spectral lines of Ti-K_α and Ba-L_α are located near each other, whereas the O-K_α line is at a great distance from the first ones. Moreover, such a wavelength is the subject of intense absorption by the air molecules. Therefore, a high vacuum device is needed for such experiments.

The method is successfully used with relatively heavy substances (from Be up to U). The analysis of light element (C, S, O, etc.) is rather troublesome because their fluorescent radiation is of a long wavelength and is strongly absorbed by air. Therefore, the precision and sensitivity increases with the increase in the atomic mass of the analyzing materials; however, the possibility does exist to analyze elements with $Z > 2$. Its application ranges from on-line industrial analysis and in-field inspection of geological samples to ultra-trace analysis of semiconductor surfaces.

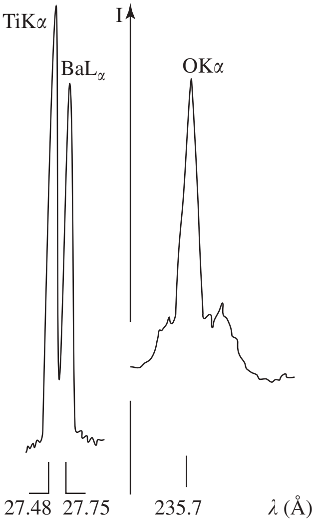


Figure 7.29 Results of X-ray investigation of a chemical composition of the ferroelectric ceramic $BaTiO_3$: in an arbitrary scale as a graph of the X-ray intensities versus the wavelength is presented (after Yu. Ya. Tomashpolsky et al.).

7.7 AN ATOM IN THE MAGNETIC FIELD: THE ZEEMAN EFFECT

The Zeeman effect consists of atomic energy level splitting and, accordingly, the splitting of the spectral lines of a sample when an external magnetic field is imposed on a sample. If a multi-electron atom is placed in an external magnetic field, depending on the magnitude of the magnetic field induction **B,** two cases can occur. In the first case, the weak magnetic field is unable to tear out the Russell–Saunders coupling; this is the case of a weak magnetic field or anomalous Zeeman effect. In this particular case, Larmor precession definitely takes place, indeed all cones in Figure 7.25 are precession cones: the whole "construction" takes part in the precession around the direction of this field (z-axis) and mechanic vectors. In the second case, corresponding to a strong magnetic field, the Russell–Saunders coupling is thrown out, and the orbital and spin angular momentums participate in precession independently (normal Zeeman effect).

Consider first the case of a weak magnetic field when the bonding of the orbit and spin angular momentums remains unbroken. It was shown in Section 5.1.5 (eq. (5.1.35)) that magnetic moment $\boldsymbol{\mu}$ in the magnetic field with induction **B** depending on the angle α between vectors $\mathcal{M}$ and **B** acquires additional energy $(\mathcal{M}\mathbf{B}) = -\mathcal{M}B\cos\alpha$. This energy can be expressed in the form

$$\Delta E = -(\mathcal{M}_J \mathbf{B}) = -\mathcal{M}_J B\cos(\pi-\theta) = \mathcal{M}_J B\cos\theta, \tag{7.7.1}$$

(refer to Figure 7.25). $(\pi - \theta)$ is an angle between vectors $\mathcal{M}$ and **B**. The product $\mathcal{M}_J\cos\theta$ is the projection of the magnetic moment onto the z-axis, eq. (7.6.15), i.e., $\mathcal{M}_J^*$. Then,

$$\Delta E = \mathcal{M}_j^* \mathrm{B} = g\mu_\mathrm{B}\mathrm{m}_J B. \tag{7.7.2}$$

The value ΔE is, accordingly, that energy which an atom admits by the interaction of its magnetic moment with the external magnetic field (with induction **B**) and which is added to the main electronic energy levels. As a consequence of ΔE depending on the quantum number m_J, and taking $2J + 1$ values, the subsidiary energy also takes such values. This signifies that the main electron energy level splits into $2J + 1$ sublevels. If, before the imposition of the magnetic field, the states with different m_J had the same energy, the magnetic field has brought about the levels splitting, i.e., lifting the degeneration on this quantum number m_J. The number of sublevels depends on the quantum numbers, i.e., splitting depends on the atomic term.

In Figure 7.30 an example of the splitting of the atomic S- and P-levels in an external magnetic field is presented. Before the field was imposed, each term was degenerated, the S-level was double, and the P-level was sixfold degenerated; both levels can be regarded as singular (Figure 7.30b), i.e., the energy of all sublevels is the same. The energy transition between them is defined by the energy difference E_P - E_S = ΔE, which corresponds to the quantum emission with the frequency

$$\omega_0 = \frac{\Delta E}{\hbar}. \tag{7.7.3}$$

At the same time, the spin–orbit interaction, even in the absence of an external field (**B** = 0), brings about the splitting of the P-level into two (one of them with $J = 3/2$ and the other with $J = 1/2$, Figure 7.30c). This corresponds to the lifting of the degeneration on the quantum number J. The S-level remains singular. The value of splitting of the P-level is defined by the expression (7.7.2). In the experimentally measured spectrum, provided the resolution is sufficient, instead of one line with the frequency ω_0, two lines (a doublet) appear, whereas the central line disappears (as shown in the scheme below). The shift of the lines from the position of the central (absent) line ω_0 is defined by the value of energy $g\mu_6\mathbf{B}$ divided by $\hbar$.

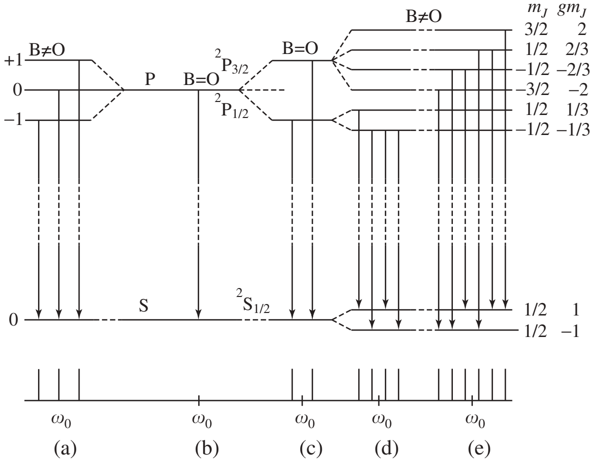


Figure 7.30 Zeeman effect: (a) normal Zeeman effect, (b) energy levels before imposing a magnetic field, (c) transition P→S (without the magnetic field), splitting because of spin–orbit interaction, (d) and (e) an anomalous Zeeman effect.

Further splitting occurs when the external field is imposed ($\mathbf{B} \neq 0$, Figures 7.30d and e). The degeneration on the quantum number m_J is lifted according to eq. (7.7.2): at $J = 3/4$ four levels appear, at $J = 1/2$ there are two. In Figures 7.30d and e, the splitting scheme is presented specified by values m_J and gm_J for all sublevels.

Transitions can occur between levels (and sublevels). Selection rules limit their number. Strictly speaking, selection rules follow from the analysis of quantum mechanical transition probabilities, however, a qualitative explanation of these rules can be suggested; the law of spin conservation can be attracted. The point is that an electromagnetic radiation quantum (photon) carries away from a system (from an atom) the spin equal to its own spin. The latter equals 1 $\hbar$. The spin angular momentum can be oriented in a triple way regarding the photon wave vector: perpendicular to it (upward ($+\hbar$) and downward ($-\hbar$)) and along it (0). Accordingly, Δm_J can accept three values

$$\Delta m_J = 0, \pm 1 \tag{7.7.4}$$

Transitions with $\Delta m_J = 0$ are referred to as π and with $\Delta m_J = \pm 1$ as σ transition; photons are differently polarized, correspondingly.

Thus, at transitions $P_{1/2} \rightarrow S_{1/2,}$ four spectral lines occur whereas at transition $P_{3/2} \rightarrow S_{1/2}$ there are six of them (Figures 7.30d and e). The line's shift relative ω_0 is defined as:

$$\Delta\omega = \frac{\mu_B B}{\hbar}(m_J'' g'' - m_J'' g'), \tag{7.7.5}$$

where two strokes characterize the top and one stroke characterizes the bottom levels.

This description of splitting of the spectral lines, corresponding to an abnormal Zeeman effect, is given only by quantum physics and cannot be explained within the framework of classical physics.

Quite a different picture appears when a high magnetic field is imposed; the Russell–Saunders coupling is torn out, and the orbital and spin moments participate separately in

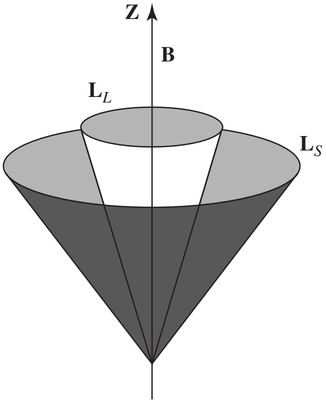


Figure 7.31 A Russell–Saunders coupling breakdown in a high magnetic field.

precession around the direction of an external field (Figure 7.31). The additional energy ΔE consists of the contribution of both the orbit and spin accounting for the gyromagnetic ratio anomaly:

$$\Delta E = \mu_{\mathrm{B}} B m_L + 2\mu_{\mathrm{B}} B m_S = \mu_B B(m_L + 2m_S). \tag{7.7.6}$$

Because transitions with a change of spin quantum number are forbidden (as a quantum emission is connected only with the orbital atomic state change), the spin term in the sum (7.7.6) is excluded and only the degeneration lifting on m_L is considered. The S-level remains single- and doublefold degenerated, whereas the P-level (with $L = 1$) splits into three doublefold degenerated levels (Figure 7.30*a*) (i.e., the degeneration on m_L is lifted). The spectral triplet turns out to be exhibited. The shift of each spectral line from the central one is defined as

$$\Delta\omega = \pm\frac{\mu_{\mathrm{B}} B}{\hbar}, \tag{7.7.7}$$

In spite of the fact that D-, F- and the other subsequent levels split into a greater number of sublevels because the g-factor is equal to unity in all level splitting, and the selection rule is still valid here as well, *the normal Zeeman effect is exhibited as a spectral triplet regardless of the transitions*. The exhibiting of a triplet is referred to as a *normal Zeeman effect.*

A normal Zeeman effect can be explained within the framework of classical physics. Displacement of both the energy levels and the spectral line (7.7.7) corresponds to the Larmor precession frequency (refer to eq. (5.2.19))

$$\omega = \frac{eB}{2m}, \tag{7.7.8}$$

This coincides with the previous statement that it is possible to treat the additional energy obtained by the magnetic moment in the external magnetic field either as a shift of the energy level on the value $(\boldsymbol{\mathcal{M}}\boldsymbol{B})$, or as the energy of the Larmor precession (7.7.8).

In conclusion, we have established that the precession gives a gain of additional energy. Therefore, to treat spatial quantization of the angular momentum (7.5.3) as precession is incorrect from our point of view, because this effect does not produce any specific energy.

7.8 A QUANTUM OSCILLATOR AND A QUANTUM ROTATOR

7.8.1 Definitions

Like translational motion, all molecular motions accomplish rotational and oscillatory motions, too. In Section 2.4.5, an example was given of a diatomic molecule with an interatomic distance d rotating around a stationary axis z passing through the molecular center of inertia. It was shown that rotation of these two masses can be substituted by the rotation of one reduced mass μ accomplishing rotation around the same axis at the same distance d. Remember that any molecule rotated around a stationary axis is called a rotator; if the molecular intra-atomic distance remains constant the rotator is referred to as a rigid one.

The expression for the reduced moment of inertia $I_e = \mu d^2$ and kinetic energy $K = I_e\omega^2/2$ was also given there. No requirement on the value of rotational kinetic energy is imposed in Newtonian physics. Since, in this case, the potential energy is accepted as zero, the kinetic energy is the total one.

In Section 1.5.4, a potential curve for classic harmonic oscillations in parabolic form (refer to Figure 1.33), as well as a potential curve describing anharmonic oscillations (Lennard-Jones potential "6–12", Figure 1.31) were presented. In both cases, the total particle energy in a potential well can have a continuous range of values. Also remember that any oscillating system is called an oscillator.

The quantum mechanical consideration of molecular rotation and intramolecular oscillation is of significant interest since it is the basis of optical methods of investigation, both scientific and technological.

7.8.2 Quantum oscillators: harmonic and anharmonic

The potential energy of a system accomplishing small oscillations around an equilibrium position was considered in Section 2.4. The condition "small" signifies that the restoring force is linearly dependent on displacements; oscillations then behave according to the harmonic law (sine or cosine). For classical harmonic oscillation, alongside the continuous spectrum of energy, is the distinctive fact that the probability of finding a system beyond the amplitude displacements is zero. Because we consider here a conservative process, the total mechanical energy is preserved (remember that in a conservative system the energy does not dissipate).

In accordance with Section 7.3.2, in order to solve the quantum harmonic oscillator problem, we have to write the potential energy expression in the form $\beta x^2/2$, to substitute it into the Schrödinger equation (7.3.5), find the wavefunction satisfying the standard condition and then find the spectrum of the energy whether it is continuous or discrete. This particular problem can be solved in analytical form. However, while not solving the Schrödinger equations, we will give here the essence of the results.

Firstly, the equation for the quantum harmonic oscillator shows that the energy can accept only definite values of energy equal to

$$\Delta E = \hbar\omega\left(\mathrm{v} + \tfrac{1}{2}\right), \tag{7.8.1}$$

where v is the oscillation quantum number. The corresponding spectrum of allowed energies is depicted in Figure 7.32 on the background of the classical potential curve. It consists of the equidistant levels with the interlevel distance

$$\Delta E = \hbar\omega\left[\left(\mathrm{v} + 1 + \tfrac{1}{2}\right) - \left(\mathrm{v} + \tfrac{1}{2}\right)\right] = h\omega. \tag{7.8.2}$$

Secondly, the number of levels is not limited; the quantum number v can accept any value.

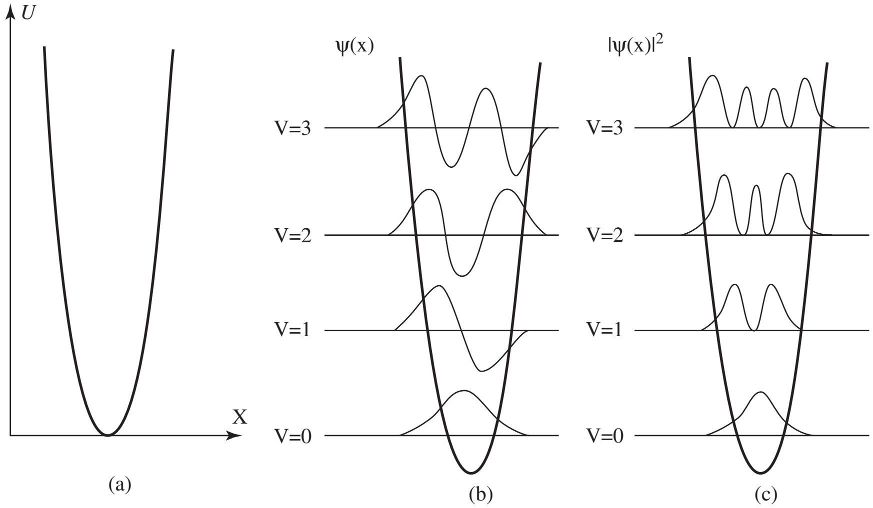
Thirdly, calculations of the quantum mechanical probability of the energy transitions showed that the quantum number can be changed in increments of 1 only ($\Delta v = \pm 1$); the transitions are allowed only between the adjacent levels. In other words, since the levels are equidistant, only one spectral line can be emitted (or absorbed) regardless of which levels the transition takes place between. The emitted/absorbed quantum energy is in any case, always $\hbar\omega$.

Fourthly, at $T = 0$ K ($v = 0$), the oscillations do not come to an end. The so-called zero oscillations are preserved even at absolute zero temperature. The zero point oscillation energy is equal to $\hbar\omega/2$.

Finally, the eigenvalues of the wavefunctions can be expressed by Hermite special polynomials. Some of these, together with heir squares, are depicted in Figure 7.32. The principle difference from the classic case is that the probability of finding the oscillator beyond the amplitude values is not zero; it vanishes as the deviation is increased. Of course, we are interested mostly in the oscillation of atoms in molecules. For the sake of simplicity we will deal with the diatomic molecule. As a rule they are the anharmonic ones, i.e., described by a nonsymmetrical potential curve. One with the prevailing potential of such a type in physical chemistry is the Morse potential presented in Figure 7.33:

$$U(r) = U_0\ [1 - e^{-\alpha(r-r_0)}]^2. \tag{7.8.3}$$

The potential curve $U(r)$ is equal to zero at $r = r_0$; this is an equilibrium interatomic distance [$U(r) = U(r_0) = 0$]. In the case of small oscillations near $r = r_{0,}$ the exponent can be decomposed into a series $1-\alpha(r-r_0)\pm\ldots$ and we arrive at the quadratic harmonic law



(a)

(b)

(c)

Figure 7.32 A linear harmonic quantum oscillator: (a) classic potential energy curve, (b) wavefunctions and (c) their squares.

$U(r) \approx \alpha^2(r - r_0)^2$. At large values of r the exponent approaches zero and $U(\infty) \to U_0$. Therefore U_0 is the depth of the potential well. Notice that the Lennard-Jones and Morse potentials resemble each other; they differ in the choice of origin of the ordinate axis (one is lifted relative to another by a value of U_0; this is insignificant because the potential energy is determined accurate to the constant, U_0 in this case; refer to Section 1.5.4).

To solve the quantum mechanical problem of anharmonic atomic oscillations in a diatomic molecule it is necessary to accomplish the standard procedure: substitute the Morse potential expression into the Schrödinger equation and solve it, the eigenvalues of energy and eigenwave functions can be found. The given problem cannot be solved in analytical form. We will use only eigenvalues of energy $E(\mathrm{v})$. This is given by the approximate expression

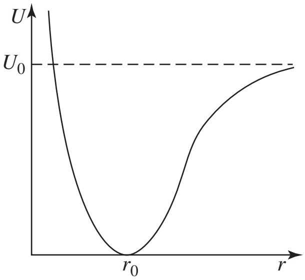
$$E(\mathrm{v}) = \hbar\omega\ [(\mathrm{v}+\tfrac{1}{2}) - \gamma(\mathrm{v}+\tfrac{1}{2})^2]. \tag{7.8.4}$$

In this expression γ is the anharmonicity coefficient that characterizes the peculiarities of the interatomic interactions. For some simple diatomic molecules γ lies in the limit 0.01–0.07; it can be found in the reference books for many molecules.

The Morse potential curve is depicted in Figure 7.34 with energy levels of anharmonic oscillations. At small v the second term in eq. (7.8.4) is small and the energy levels are approximately the same as for the harmonic oscillator. While increasing the quantum number v, the negative contribution of the second term increases. As a result, the curve $E(\mathrm{v})$ has a maximum and further increase of the v value brings about a decrease of energy (Figure 7.35): this reduction has no physical sense. So the number of levels of the inharmonic oscillator is limited, i.e., there exists a maximum value of v ($\mathrm{v} = \mathrm{v}_{\max}$).

There are two ways to find the value of this limiting quantum number: either find the extreme value of the functions $E(\mathrm{v})$ from an equation $dE/dx=0$, or equate ΔE to zero at $\mathrm{v} = \mathrm{v}_{\max}$. In the latter case one obtains

$$0 = \Delta E(\mathrm{v}_{\max}) = \hbar\omega\Big[\big(\mathrm{v}_{\max}+1+\tfrac{1}{2}\big) - \mathrm{v}\big(\mathrm{v}_{\max}+1+\tfrac{1}{2}\big)^2 - \big(\mathrm{v}_{\max}+\tfrac{1}{2}\big) + \mathrm{v}\big(\mathrm{v}_{\max}+\tfrac{1}{2}\big)^2\Big], \tag{7.8.5}$$



Figures 7.33 Potential Morse for unharmonic oscillator.

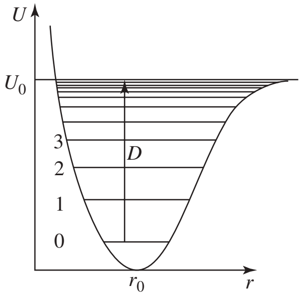


Figure 7.34 Potential Morse, the energy levels and the dissociation energy *D*.

therefore,

$$\hbar\omega[1-\gamma(\mathrm{v}_{\max}+1)]=0, \tag{7.8.6}$$

and further,

$$\mathrm{v}_{\max}=\frac{1}{2\gamma}-1. \tag{7.8.7}$$

As far as $\gamma \ll 1$, one can obtain

$$\mathrm{v}_{\max}\approx\frac{1}{2\gamma}. \tag{7.8.8}$$

Substituting this value into the general expression for energy (7.8.4), we obtain the maximum energy and, consequently, the depth of the potential well

$$E_{\max}=U_0=\frac{\hbar\omega}{4\gamma}. \tag{7.8.9}$$

In order to tear out the interatomic bond, one has to excite a molecule into the state with $E \geq U_0$, i.e., into the state when an infinite motion of one atom relative to another is realized. If the molecule is in the lower energy quantum state, this energy is

$$\Delta E=U_0-E_0=\frac{\hbar\omega}{4\gamma}-\frac{\hbar\omega}{2}.$$

The energy *D* required for tearing out the chemical bond of the molecule being in the lower state with v = 0 is called the dissociation energy. Accordingly, it is equal to ΔE, i.e.,

$$D=\frac{\hbar\omega}{4\gamma}-\frac{\hbar\omega}{2}=\frac{\hbar\omega}{4\gamma}(1-2\gamma). \tag{7.8.10}$$

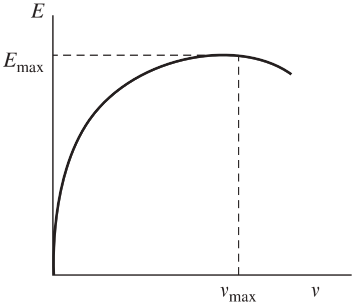


Figure 7.35 Energy of unharmonic oscillator versus the oscillation quantum number v.

The coefficient γ can be derived from the last expression:

$$\gamma = \frac{\hbar\omega}{4D - 2\hbar\omega}. \tag{7.8.11}$$

As can be seen, the dissociation process is tightly connected with the molecule's anharmonic oscillation. Within the framework of the harmonic model, it is impossible to explain the dissociation process.

The frequency ω, appearing in all the last equations, is the frequency of natural vibrations, i.e., a frequency corresponding to the lower molecule energy level $E = \hbar\omega/2$; the anharmonic term brings a negligible contribution to this energy.

When a molecule turns from one energy level into another, emission or absorption of energy in the form of quantum of the electromagnetic radiation occurs. The energy of such quanta is equal to the energy difference. The quantum mechanical calculations show that all transitions are allowed, i.e., there are no selection rules in this case.

The frequency of a photon emitted at transitions between adjacent levels is equal: $\omega_{\mathrm{ph}} = \pm\hbar^{-1}(E_{\mathrm{v}+1} - E_{\mathrm{v}})$. The corresponding wavelength λ is

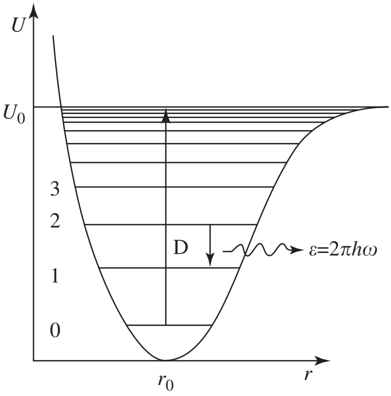
$$\lambda = \frac{2\pi\hbar c}{E_{v+1} - E_{v}}. \tag{7.8.12}$$

An arbitrary quantum transition has been shown in Figure 7.34.

EXAMPLE E7.10

The natural frequency of HCl molecule vibration is 5.63×10^{14} sec^{-1}, its anharmonicity coefficient is $\gamma = 0.0201$. Find (1) the energy $\Delta E_{2,1}$ molecule transition from the second to the first energy levels (in eV) of the oscillatory spectra; (2) the highest quantum number $\mathrm{v}_{\max}$; (3) the maximum oscillatory energy $E_{\max}$; (4) the dissociating energy D.

Solution: (The theory of molecular anharmonic oscillations is presented in Section 7.8.2 (eq. (7.8.4))).



(1) The energy difference at transition is $\Delta E_{v+1,v}=\hbar\omega[1-2\gamma(v+1)]$ the quantum number v being the lowest level. Executing calculations, we obtain $\Delta E_{2,1} = 1.09 \times 10^{-19}$ $J = 0{,}682$ eV.

(2) The $v_{\max}$ can be found according to eq. (7.8.8) $V_{\max} = 1/(2\gamma) \approx 23$.

(3) The $E_{\max}$ can be obtained if we substitute $v_{\max}$ into the expression for oscillation energy (7.8.4). We can obtain ($E_{\max}=\hbar\omega/4\gamma$). Substituting all values already obtained we arrive at $E_{\max} = U_0 = 7.38 \times 10^{-19}$ $J = 4.61$ eV.

(4) The dissociation energy is given by eq. (7.8.10) $D = U_0(1\text{-}2\gamma)$. Calculation shows that $D = 4.43$ eV.

The corresponding drawings is presented in Figure E7.10.

7.8.3 A rigid quantum rotator

The rotation of micro-objects around a motionless axis was analyzed in Section 7.5.3. The orbital motion of an electron was used as an example. It was found that in this case the rotational energy can accept only discrete values defined by eq. (7.5.26). Since potential energy in free rotation is accepted to be equal to zero, the total energy is kinetic. One of the important characteristics of such movement is the rotational constant B:

$$B = \frac{\hbar^2}{2I_e}. \tag{7.8.13}$$

The I_e value is called the reduced moment of inertia μd^2. The quantum number in the optical rotational spectroscopy is defined by another letter (letter j instead of l). Therefore the rotational energy can be written as

$$E = Bj(j+1), \tag{7.8.14}$$

(compare with eq. (7.5.26)). No restrictions in quantum number are present here. Besides, j can accept the value $j = 0$, corresponding to zero rotational energy. The rotational energy levels $E(j)$ are depicted in Figure 7.36. The selection rule in the case of rotational spectra

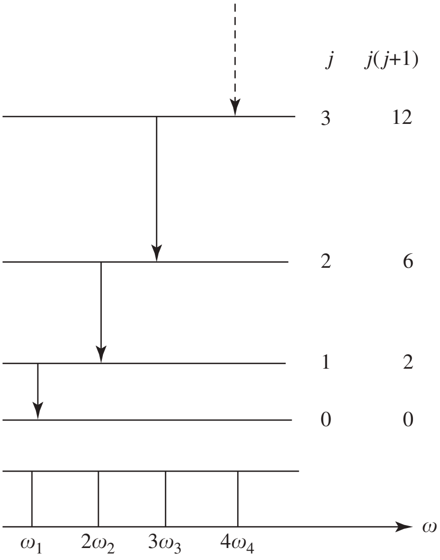


Figure 7.36 The rigid quantum rotator energy levels.

is the same as in harmonic oscillations, the quantum number difference can accept values $\Delta j = \pm 1$, i.e., transitions between adjacent levels only are allowed.

It is easy to calculate the energy distance between rotational levels. Naturally,

$$\Delta E = E_{j+1} - E_j = B[(j+1)(j+2) - j(j+1)] = 2B(j+1). \qquad (7.8.15)$$

The absolute distance between levels increases at increasing *j;* however, the relative values, $\Delta E/E$ vice versa, decrease. This corresponds to the Bohr correspondence principle.

EXAMPLE E7.11

For an HCl molecule determine: (1) the moment of inertia; interatomic distance is $d = 91.7$ pm, relative atomic masses are correspondingly 1 and 19 a.m.u.; (2) the rotational constant; (3) the energy necessary to excite the molecule from the ground state to the first rotational level ($j = 1$) (see Section 1.3.9, Figure 1.17 and Section 7.8.2, Figure 7.36.)

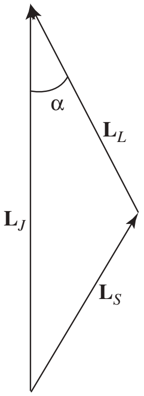
Solution: (1). The moment of inertia can be found according to eq. (1.3.50) $I = 1.33 \times 10^{-47}$ kg m^2.

(2) The rotational constant is given by eq. (7.8.13). Calculation gives $B = 4.37 \times 10^{-23} J = 2.73$ meV.

(3) The energy in question can be calculated according to eq. (7.8.15) $\Delta E_{1,0} = 2B = 5.46$ meV.

EXAMPLE E7.12

A multielectron atom is in a state ^3P. For this term draw a vector diagram for the maximal atomic orbital angular momentum **L** (Figure E7.12) and determine the angle α between this vector and the orbital angular momentum L_L (refer to Figure 7.19)



Solution: The atomic term ^{3}P is characterized by a set of quantum numbers (refer to Sections 7.5 and 7.6.3): $L = 1$ and $S = 1$. One can draw three vector diagrams like that depicted in Figure 7.19 for different J (which can take on values from $L + S$ to $|L - S|$, i.e., 2, 1, 0. It was mentioned in the problem situation that the maximum value of **L** is supposed ($J = 2$). Hence the vector diagram is presented in Figure E7.12 according to $L_S = \hbar\sqrt{2}$, $L_L = \hbar\sqrt{2}$ and $L_J = \hbar\sqrt{6}$ (see eqs. (7.6.5), (7.6.2) and (7.6.7)). The angle sought can be found according to cosine law (Figure 7.25), angle α

$$\cos\alpha = \frac{L(L+1) + J(J+1) - S(S+1)}{2\sqrt{L(L+1)}\sqrt{J(J+1)}} = \frac{\sqrt{3}}{2}.$$

Hence $\varphi = \arccos \sqrt{3}/2 = (\pi/6) = 30°$.

EXAMPLE E7.13

A beam of neutrons is thermolyzed by a room temperature moderator ($T = 300$ K) in a nuclear reactor. It then passes a special collimator in a hole in the reactor wall and falls on a graphite single crystal. A diffracted plane of the first order $n = 1$ from the graphite base with interplanar spacing $d = 33.5$ pm was measured at an angle $2\theta = 25.5°$. Find neutron wavelength λ, its velocity υ and mass m.

Solution: Produced in chain nuclear reactions, fast neutrons should be slowed down in order to participate in further reaction (refer to Section 1.5.5 and Example E1.25). Besides, slow neutrons are widely used in crystal structure investigation and solid state physics (refer Section 7.1.2). Therefore, this example has a practical interest.

According to Bragg's law (eq. (6.3.11) and Figure 6.20) at $n = 1$ we can write $2d\sin\theta = \lambda$. Knowing d and angle 2θ we can find the neutron wavelength λ.

$$\lambda = 2 \times 3.35 \times 10^{-10} \sin 12.75° = 1.46 \times 10^{-10} \text{ m}.$$

The neutron mass can be found from de Broglie formula (7.7.1) and rms thermolyzed neutron velocity (eq. (3.3.7″′))

$$m = \frac{h^2}{\lambda^2 \times 3\kappa T} = \frac{43.96}{2.13 \times 9 \times 1.38} 10^{-27} = 1.66 \times 10^{-27} \text{ m.}$$

Dimension checking gives

$$\frac{\text{J}^2\text{s}^2}{\text{m}^2(\text{J/K})\text{K}} = \text{m.}$$

EXAMPLE E7.14

Define into how many sublevels will energy levels ^{2}S, ^{3}P, ^{4}D, ^{9}F split in atoms with Russell-Saunders bonds mode owing to spin–orbit interaction and write down the terms describing each sublevel.

Solution. In light atoms, a Russell-Saunders type of electron interaction usually take place. In Section 7.6 the method is described in detail. The atomic energy state, in this case, is characterized by a set of quantum numbers: the total orbital quantum number *L*, total spin quantum number *S* and total internal quantum number *J*. Thus quantum number *J* can accept values from $J_{\max} = L + S$ up to $L_{\min} = |L - S|$, changing on unit. A certain energy state of atom (spin–orbital interaction) corresponds to each value *J,* i.e., an energy sublevel appears. The number of sublevels or number of possible mutual orientations of vectors $\mathbf{L}_L$ and $\mathbf{L}_S$ at is defined by the ratio $2S + 1$ referred as multiplicity. At $L < S$ the number of sublevels is defined by another ratio $2L + 1$ (see Section 7.6.3).

Accordingly, for a term ^{2}S we have: multiplicity $2S + 1 = 2$, since $S = ½$; $L = 0$ corresponds to symbol *S* (to not be confused with S-state). Hence, condition $L < S$ and the number of sublevels determined by expression $2L + 1 = 1$ is valid. This means that the given energy level is not split and is characterized by quantum number $J = L + S = ½$ and accordingly term $^2\text{S}_{1/2}$ is created.

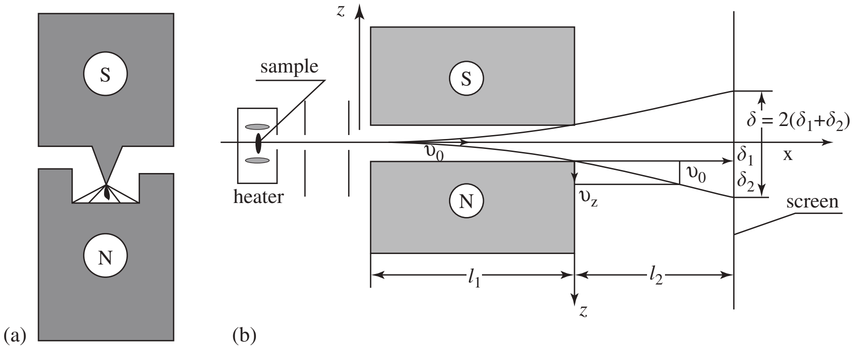
For term ^3P multiplicity is $2S + 1 = 3$, therefore $S = 1$; to symbol P corresponds $L = 1$ and $L = S$; the number of sublevels determined by expression $2S + 1 = 3$ coincides with term multiplicity, i.e., it is equal 3. Thus, to each sublevel there corresponds the term with various *J* values. As $J_{\max} = L + S = 2$ and $J_{\min} = |L - S| = 0$. *J* accepts values 0, 1, 2 and then corresponding terms will be as $^3\text{P}_0$, $^3\text{P}_1$, $^3\text{P}_2$.

The term ^{4}D corresponds to $S = 3/2$, since multiplicity is $2S + 1 = 4$, $L = 2$ (D state). As condition $L > S$ is valid *J* accepts values from $L + S = 2 + 3/2 = 7/2$ up to $(L - S) = (2 - 3/2) = 1/2$, i.e.,1/2, 3/2, 5/2, 7/2. For this set of sublevels the quantum numbers is equal to multiplicity (i.e., 4); the corresponding terms are $^4D_{1/2}$, $^4D_{3/2}$, $^4D_{5/2}$, $^4D_{7/2}$.

The term ^{9}F has $S = 4$ (i.e. $2S + 1 = 9$); therefore, the F-state meets $L = 3$. Thus, inequality $L <$ S and the number of possible mutual orientations of vectors $\mathbf{L}_L$ and $\mathbf{L}_S$ and consequently the number of sublevels is defined by a ratio $2L + 1 = 2\times3 + 1 = 7$ is fulfilled. Thus quantum number *J* will accept the following values; 1, 2, 3, 4, 5, 6, 7 and each sublevel will be characterized by a term: $^9\text{F}_1$, $^9\text{F}_2$, $^9\text{F}_3$, $^9\text{F}_4$, $^9\text{F}_5$, $^9\text{F}_6$, $^9\text{F}_7$.

EXAMPLE E7.15

In the Stern–Gerlach experiment a narrow beam of sodium atoms in the ground state was passed through a highly nonuniform magnetic field (Figure E7.15). What nonuniformity of the magnetic field $\partial B/\partial z$ should be provided so that the distance between the components of the sodium atoms split beam fixed on the screen will be equal to $\delta = 6$ mm? The installation dimensions are $l_1 = 10$ cm, $l_2 = 15$ cm, speed of atoms is equal to $\upsilon_0 = 400$ m/sec. The whole installation is placed in a hermetic vacuum shield.



Solution. Figure E7.15a shows the main way of producing a highly nonuniform magnetic field due to tailor-made poles and Figure E7.15b describes the path the atom travels. We have to consider some details.

The basis for the decision of this problem is formula (5.1.32): a force working on a magnetic dipole depends on both the nonuniformity of the magnetic field and the orientation of the atomic magnetic moments relative to the quantization axis z. If the atomic magnetic moments submit to laws of classical physics, there could be any values of angles and the experiment would result in a fuzzy maximum. However, in quantum mechanics this is not a case!

The force working on an atom depends on atomic state, degree of nonuniformity of the magnetic field in the device and a set of magnetic quantum numbers. Eq. (5.1.32) is still valid in quantum physics though the angle α depends here on the set of quantum numbers mentioned: $\mathcal{M}_z/\mathcal{M} = \cos\alpha = m_J/\sqrt{J(J+1)}$. The quantum number m_J can accept an amount of the discrete values dependent on quantum number J, that is in all $2J + 1$ values. Since to each value m_J corresponds the force as in eq. (5.1.32), the atomic beam is split on some component; there will be a system of strips on the screen. To each strip there corresponds a certain number of m_J.

The sodium atom in the ground state has one 3s electron in M shell. Therefore, the set of quantum numbers are: $L = 0$, $S=1/2$ and $J=1/2$, this corresponds to $m_J=\pm 1/2$. So we know that there should be two strips on the screen. In order to calculate the distance between them and find the magnetic field nonuniformity, we have to solve the problem qualitatively. There is no need to calculate g-factor Lande since we know that only spin contributes to the sodium atomic magnetic moment, i.e., $g = 2$ (see Section 7.6.2).

In Figure E7.15, a beam of atoms from a heater pass some of the slits shown. Entering the nonuniform magnetic field, a beam splits into two parts, which move along curvilinear (parabolic) trajectories. The acceleration inside the magnet can be calculated according to the second Newtonian law $a_z=F_z/m$. Then the shift is $\delta_1=\frac{a_z t_1^2}{2}$ where $t_1=\frac{\ell_1}{\upsilon_0}$ and $\delta_1=\frac{a_z \ell_1^2}{2\upsilon_0^2}$. The movement along l_2 is assumes uniform. In time t_2 the atom acquires the velocity $\upsilon_z = a_z t_2$. The shift gained is $\delta_2=\upsilon_z t_2=a_z t_1 t_2=a_z\frac{\ell_1\ell_2}{\upsilon_0^2}$. The total relative shift is then $\delta = 2(\delta_1+\delta_2)$ and $\delta = \frac{a_z\ell_1}{\upsilon_0^2}(\ell_1+2\ell_2)$. Taking into consideration all calculations we obtain

$$\delta=\frac{g\mu_B\left(\frac{\partial B}{\partial z}\right)|m_J|}{m\upsilon_0^2}\ell_1(\ell_1+2\ell_2).$$

Therefore, we arrive at

$$\frac{\partial B}{\partial z}=\frac{\delta A\upsilon_0^2}{\mu_B\ell_1(\ell_1+2\ell_2)N_A}$$

(keeping in mind that $g|m_J| = 1$). Executing calculations we obtain

$$\frac{\partial B}{\partial z}=\frac{6\times10^{-3}\times23\times10^{-3}\times400^2}{9.27\times10^{-24}\times0.1\times(0.1+2\times0.15)\times6.02\times10^{23}}\ \text{J/T}$$
$$= 98.9\ \text{J/T} \approx 1\ \text{T/cm}.$$

7.8.4 Principles of molecular spectroscopy

The electromagnetic radiation emitted or absorbed by the substances under investigation is the subject of the oscillation–rotation (molecular) spectroscopy. In this section, the main attention is concentrated on molecular spectroscopy near and within the optical range of frequencies.

Emission of the radiation quanta or their absorption is defined by energy transitions. Therefore, the basis of all spectroscopy methods is the discontinuity of energy spectrum and the mutual position of energy levels. Of course, this is only a general treatment: many factors playing an important role in spectroscopy remain outside our discussion.

Naturally, the best effect in the interaction of radiation with matter can be reached in the case when the energy of radiation quanta used coincides in order of values with energy transitions. Therefore, we will consider that range of quanta energy complies with that of energy transition on the basis of the data given in Table 5.3.

The total molecule energy can be written as a sum:

$$E=E_n+E_\text{v}+E_j, \tag{7.8.16}$$

where quantum numbers n, v and j denote electronic, oscillatory and rotational contributions. Let us evaluate each part separately.

The electronic energy levels are assigned by eqs. (7.5.31) and (7.5.34). Depending on the nuclear charge Z the ground state energy varies from -10 eV up to -100 keV. Therefore, only transitions among the high lying atomic levels enter the optical frequency range (for example, the Balmer series with v = 2).

In order to evaluate the oscillatory energy levels, it is necessary to know their intrinsic frequencies. Experiments show that they are $10^{12}-10^{14}$ Hz. Correspondingly, the emission frequency belongs to the IR radiation region and the wavelengths are 10^{-4}–10^{-6} m.

The purely rotational frequencies lie in the frequency range dependent on the molecule's rotational constant (7.8.13). Estimations show that $B \approx (10^{-68}/10^{-47}) \approx 10^{-21}$ J or $10^{-2}-10^{-3}$ eV. This corresponds to the wavelength $\lambda \approx 10^{-3}$ m, which corresponds to a microwave frequency far from the optical range.

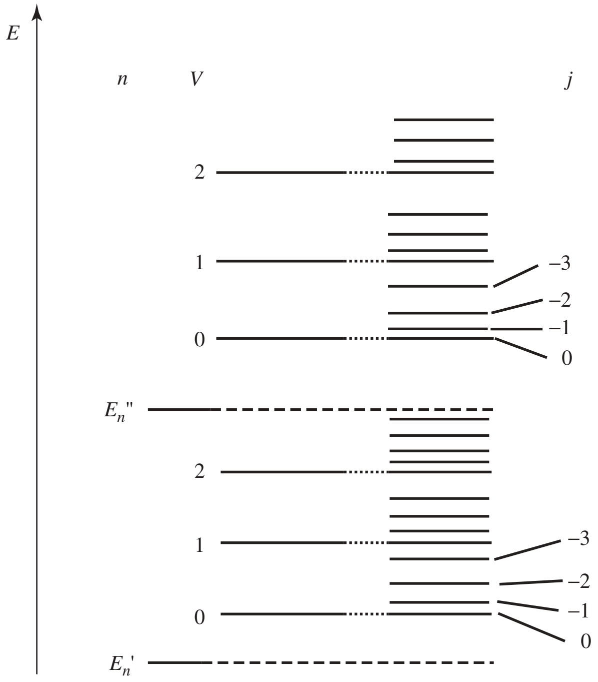
Important conclusions follow from these consideration. First, emission and/or absorption due to electron transition, lying far from the optical range in the short wavelength side, are not considered in molecular spectroscopy. Second, the same applies to purely rotationary spectra, though the shift is in the long wavelength region. The main interest in optical molecular spectroscopy concerns oscillatory-rotationary transitions, presented by the last two terms of the sum (7.8.16). The energy transitions in this case correspond precisely to the visible and adjoining wavelength regions (IR and UV).

An arrangement of the electronic, oscilationary and rotationary levels of energy of a hypothetical molecule is submitted in Figure 7.37. The distances between oscillatory levels only, determined by (eq. (7.8.2)), are larger than distances in the rotationary levels (eq. (7.8.14)). Therefore, rotary levels settle down between oscillatory levels (according to the sum (7.8.16)), however, the number of rotary levels between the next oscillatory levels is limited to the distance between the last. If $\Delta E(\mathrm{v})$ accepts a certain value, the number of rotationary levels is defined by their highest value (in an accepted interval $\Delta E(\mathrm{v})$). In other words, the difference $\Delta E = Bj_{\max}(j_{\max} + 1)$ should be less than or equal to ΔE. Transitions are carried out between levels with two sets of quantum numbers (v, j).

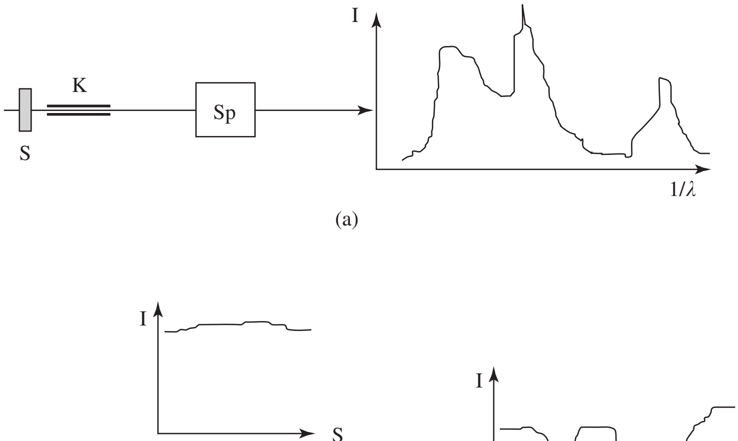
Let us consider in general the scheme of a spectroscopic experiment. We usually distinguish emission spectroscopy (Figure 7.38a) and adsorption spectroscopy (Figure 7.38b). In the first case, the sample under investigation is excited in order to force it to emit quanta of radiation (e.g., by heating the sample). Radiation is directed onto the spectral device with a prism or diffraction grating (see 6.3.4), decomposing the radiation in a spectrum along wavelengths. The investigator writes down the results on a paper (screen) as the dependence of intensity on wavelength (wavenumber). In adsorption spectroscopy the light source emits a "white" spectrum (containing the entire wavelength in a certain interval), which then goes through the sample. The falling radiation is absorbed by the substance that cuts out a definite characteristic wavelength from the incident beam. The corresponding spectral device gives the results as strips with the "cut out" frequencies. As an example, the absorption spectrum of chloroform is presented in Figure 7.39.

Traditionally in molecular spectroscopy energy is measured in wavenumbers $\tilde{\nu} = 1/\lambda$, i.e., it is expressed in cm^{-1}. It is simple to derive the relation between wavenumbers and energy:

$$\hbar\omega = \frac{2\pi\hbar c}{\lambda} = hc\tilde{\nu}. \tag{7.8.17}$$



Figures 7.37 The overall electronic, oscillator and rotator electron levels (not to scale).



(b)

Figure 7.38 Molecular spectroscopy schemes: (a) emission, (b) absorption; are samples, K collimation slits, Sp spectral recorder, E source of radiation, $I(1/\lambda)$ type of specter's measured. Incertion: corresponding source spectra.

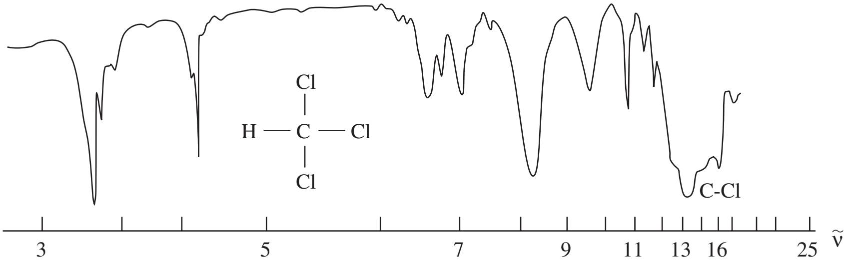


Figure 7.39 Chloroform absorption optical spectrum.

In conclusion, we should note that when translating from the SI system to reciprocal centimeters (cm^{-1}), it is necessary to divide the result by 100.

PROBLEMS/TASKS

7.1. A narrow beam of sodium atoms in the ground state passes through a Stern-Gerlach device with a nonuniformly magnetic field ($\partial B/\partial z = 1$ T/cm) and $l = 10$ cm in length. Determine the distance δ between the components of a split beam at the outlet of the magnet. The sodium atom's speed is $\upsilon = 300$ m/sec (refer to Figure E7.15).

7.2 An atomic state is characterized by the two spectral terms ^1D and ^1P. Find all possible quantum numbers J for these terms and draw a scheme of level splitting in a weak magnetic field.

7.3. Determine the minimum energy of $|\Delta E|_{\min}$ (in meV) of an atom in the state ^2F in a uniform magnetic field $B = 0.8$ T.

7.4. An atom is in a state characterized by the term ^4D. Calculate the minimum value of the total angular momentum L_J and draw the corresponding vector model (refer to Figure 7.19). Determine the angle φ between the spin L_S and total L_J angular momentums.

7.5. An electron of energy $E = 0.5\ U_0$ moves in the positive direction of an axis x. Estimate the probability that the electron will penetrate through the potential barrier of height $U_0 = 10$ eV and width $d = 0.1$ nm. It is useful to make a corresponding drawing.

7.6. An electron of energy $E = 9$ eV moves in the positive direction of an axis x. At what width of potential barrier d will the transparency factor be equal to $D = 0.1$ if the height of the barrier U_0 is 10 eV? It is useful to make a corresponding drawing.

7.7. A monochromatic electron beam meets in its motion a potential barrier $d = 1.5$ nm in width. At what energy difference ($U_0 - E$) (in eV) will the barrier penetrate 0.001 of incident electrons. It is useful to make a corresponding drawing.

7.8. An electron meets in its motion a potential barrier of the height $U_0 = 10$ eV and in width $d = 0.2$ nm. At what electron energy E (in eV) will the barrier transmission probability w be $w = 0.01$. It is useful to make a corresponding drawing.

7.9. A particle is in an infinitely deep potential box of width L. The particle state corresponds to wavenumber $k = (\pi/L)$. What is the probability of finding the particle in an area $(L/2) \leq x \leq (L/4)$?

It is useful to make a corresponding drawing.

7.10. A particle is in an infinitely deep potential box of width L. The particle state corresponds to the quantum number $n = 2$. What is the probability of finding the particle in an area $(L/3) \leq x \leq (2L/3)$? It is useful to make a corresponding drawing.

7.11. A vanadium atom in the state $^4F_{3/2}$ passes through a Stern-Gerlach device (refer to Figure E7.15b). The atom's velocity is $\upsilon = 400$ m/sec. Determine the distance between the upper and lower component of the split beams spots if $l_1 = l_2 = 10$ cm and $\partial B/\partial z = 3$ T/cm.

7.12. A silver atom's beam is passed through a Stern-Gerlach device (refer to Figure E7.15b). The atom's velocity is $\gamma = 300$ m/sec. Determine the magnetic field gradient $\partial B/\partial z$ if the distance between the ends component of the split beam is $\delta = 2$ mm, $l_1 = 10$ cm and $l_2 = 0$. Silver atoms are in the ground state ($L = 0$, $J = 1/2$, $g = 2$).

7.13. Find the number N of vibration energy levels for HBr molecule if the anharmonicity coefficient is $\gamma = 0.0201$.

7.14. Knowing the natural angular frequency of a CO molecule ($\omega = 4.08 \times 10^{14}$ sec^{-1}), find its rigidity (quasi-elastic) coefficient β.

7.15. Determine the dissociation energy D (in eV) of a CO molecule if the natural frequency is $\omega = 4.08 \times 10^{14}$ sec^{-1} and the anharmonicity coefficient is $\gamma = 5.83 \times 10^{-3}$.

7.16. For an O_2 molecule, find (1) the reduced mass μ, (2) the internuclear distance d, if the rotational constant $B = 0.178$ meV, (3) the angular velocity ω if the molecule is on the first rotational energy level.

7.17. Find the angular momentum of an O_2 molecule if its rotational energy E_J is 2.16 meV.

7.18. Can monochromatic electromagnetic radiation with wavelength $\lambda = 3$ µm excite vibrational and rotational energies of the HF molecules if it is in a ground state?

7.19. Determine the multiplicity of the energy levels of a diatomic molecule with quantum number J.

7.20. Calculate the internuclear distance d in CH molecules, if the $\Delta\tilde{V}$ interval in the purely rotational emission spectrum is 29 cm^{-1}.

ANSWERS

7.1. $$\delta = \frac{\mu_B g J l^2 (\partial B/\partial z)}{m\upsilon^2} = 2.70 \text{ mm}.$$

7.2. For the term ^1P $J = 1$ and $m_J = 0, \pm 1$; for the term ^1D $J = 2$ and $m_J = 0, \pm 1, \pm 2$.

7.3. $|\Delta E|_{\min} = \mu_B g\, |m_J|_{\min}, B = 0.0199$ meV ($g = (6/7)$ at $J = (5/2)$; $|m_J|_{\min} = (1/2)$.

7.4. $$L_{J,\min} = \frac{\hbar\sqrt{3}}{2}; \cos\varphi = -0.447; \varphi = 166.5°$$

7.5. $w = \exp\left[-\frac{2d}{\hbar}\sqrt{2m(U_0 - E)}\right] = 0.1$

7.6. $d = \frac{\hbar\,\ell n(1/D)}{2\sqrt{2m(U_0 - E)}} = 0.22\,\text{nm}.$

7.7. $(U_0 - E) = \frac{\left[\hbar\ell\text{n}(1/w)\right]^2}{8md^2} = 0.20\,\text{eV}.$

7.8. $E = U_0 - \frac{[\hbar\ell\text{n}(1/w)]^2}{8md^2} = 5.0\text{ eV}.$

7.9. $w = \frac{1}{4} - \frac{1}{2\pi} = 0.409.$

7.10. $w = \frac{1}{3} - \frac{\sqrt{3}}{4\pi} = 0.196.$

7.11. $\delta = \frac{3\mu_B Jgl^2 \frac{\partial B}{\partial z}}{mv^2} = 3.7\text{ mm}.$

7.12. $\frac{\partial B}{\partial z} = \frac{mv^2\delta}{3\mu_\text{B} gJ\ell^2} = 116\,\text{T/m}.$

7.13. $N = V_{\max} = (1/2\gamma) \approx 24.$

7.14. $\beta = \omega^2 = 1.91\text{ k}N\text{/m}.$

7.15. $D = \hbar\omega\frac{1-2\gamma}{4\gamma} = 11.4\,\text{eV}.$

7.16. (1) $\mu = 1.33 \times 10^{-26}$ kg , (2) $d = 121$ pm, (3) $\omega = 7.61 \times 10^{11}\text{ sec}^{-1}$.

7.17. $L = 3.66 \times 10^{-34}$ J sec.

7.18. Only rotational motion occurs.

7.19. $2J + 1$.

7.20. $d = 112$ pm.