

## Chapter 2

# SCHRÖDINGER EQUATION

The first quantum mechanical theory, that gave the explanation of the discrete spectra of atomic emission, was based on the equation proposed by Schrödinger [2] in 1927. In this chapter we discuss briefly the basic principles and main concepts of quantum mechanics. We start with the Schrödinger and Heisenberg equations, then we introduce the main quantum mechanical operators, and consider the properties of the wave functions and operators. The problem on the electron motion in Coulomb field for Schrödinger equation is analyzed in details. The analysis of the problem on the two oppositely charged particles interaction enables us to introduce the reduced mass. The concept of reduced mass plays the crucial role in the theory of atomic spectra. Finally we consider the problem on the energy spectra of atom placed in atomic trap and analyze the specific features of interaction of the trapped atom with electromagnetic wave.

### 2.1 Schrödinger equation

To remind the basic principles of the quantum mechanics we start here with the Schrödinger and Heisenberg equations and discuss briefly the boundary conditions for the states of discrete and continuous energy spectra for particle moving in attractive potential.

#### 2.1.1 Schrödinger and Heisenberg equations

The first quantum-mechanical equation was proposed by Schrödinger [2] in 1927. The Schrödinger equation is

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = H_0 \psi(\mathbf{r}, t), \quad (2.1)$$

where  $H_0$  is the Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m_0} + U(\mathbf{r}). \quad (2.2)$$

The first term in the Hamilton  $H_0$  is the kinetic energy, which depends on the momentum operator  $\mathbf{p} = -i\hbar\nabla$ , and the second term is the potential energy depending on the coordinate operator  $\mathbf{r}$ . The particle coordinate  $\mathbf{r}$  and momentum  $\mathbf{p}$  operators obey the following commutation relations

$$[p_i, x_j] = -i\hbar\delta_{ij},$$

where  $i = 1, 2, 3$ .

The solution of equation (2.1) for the case of free particle, i.e.  $U(\mathbf{r}) = 0$ , is

$$\psi(\mathbf{r}, t) = \sum_{\mathbf{k}} [C_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}) + C_{-\mathbf{k}} \exp(-i\mathbf{k}\mathbf{r})] \exp\left(-i\frac{E_{\mathbf{k}}t}{\hbar}\right),$$

where the energy of particle  $E_{\mathbf{k}}$  in the state with the momentum  $\hbar\mathbf{k}$  is

$$E_{\mathbf{k}} = \frac{\hbar^2\mathbf{k}^2}{2m_0},$$

the constants  $C_{\pm\mathbf{k}}$  determine the initial state of the particle and can be determined from the initial condition

$$\psi(\mathbf{r}, 0) = \sum_{\mathbf{k}} [C_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}) + C_{-\mathbf{k}} \exp(-i\mathbf{k}\mathbf{r})].$$

Thus the state of the free particle is described by the superposition of plain waves, and the particle energy depends quadratically on its momentum.

The general algorithm of obtaining equation for particle interacting with the electromagnetic field from free particle equation consists in the use of the following replacements

$$i\hbar\frac{\partial}{\partial t} \rightarrow i\hbar\frac{\partial}{\partial t} - q\varphi, \quad -i\hbar\nabla \rightarrow -i\hbar\nabla - \frac{q}{c}\mathbf{A}, \quad (2.3)$$

where  $q$  is the particle charge,  $\varphi(\mathbf{r}, t)$  and  $\mathbf{A}(\mathbf{r}, t)$  are the scalar and vector potentials of the electromagnetic field, respectively. By applying the replacements (2.3) to the Hamiltonian of free particle, we get the following wave equation for the particle interacting with the electromagnetic field

$$i\hbar\frac{\partial\psi(\mathbf{r}, t)}{\partial t} = \left[ \frac{1}{2m_0} \left( \mathbf{p} - \frac{q}{c}\mathbf{A} \right)^2 + q\varphi \right] \psi(\mathbf{r}, t). \quad (2.4)$$

The eigenfunctions of the equation (2.1) enable us to determine the quantum mechanical average of the arbitrary functions  $f(\mathbf{r}, \mathbf{p})$  of operators  $\mathbf{r}$  and  $\mathbf{p}$ . The quantum mechanical average are determined by

$$\bar{f} = \int \psi^*(\mathbf{r}, t) f(\mathbf{r}, \mathbf{p}) \psi(\mathbf{r}, t) dV.$$

The quantum mechanical representation in which the operators are the function of canonically conjugated operators  $\mathbf{r}$  and  $\mathbf{p}$ , while the wave functions are time-dependent, is called by Schrödinger representation.

Along with the Schrödinger representation the Heisenberg representation is widely used in quantum mechanics. In Heisenberg representation the operators are time-dependent. The temporal evolution of the operators is described by the Heisenberg equation

$$\frac{df}{dt} = \frac{1}{i\hbar} [f, H] + \frac{\partial f}{\partial t}. \quad (2.5)$$

If the equation (2.5) and Hamiltonian (2.2) are applied to the coordinate operator  $\mathbf{r}$  then we get the following equation for the particle velocity

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \frac{1}{i\hbar} [\mathbf{r}, H_0] = \frac{\mathbf{p}}{m_0}.$$

It is seen that the relationship between the particle velocity  $\mathbf{v}$  and momentum  $\mathbf{p}$  coincides with that in classical mechanics.

In the similar way, we obtain the expression for the velocity of a particle interacting with the electromagnetic field

$$\mathbf{v} = \frac{1}{i\hbar} [\mathbf{r}, H] = \frac{1}{m_0} \left( \mathbf{p} - \frac{q}{c} \mathbf{A} \right), \quad (2.6)$$

where we have used the Hamiltonian of the equation (2.4):

$$H = \frac{1}{2m_0} \left( \mathbf{p} - \frac{q}{c} \mathbf{A} \right)^2 + q\varphi. \quad (2.7)$$

The equation (2.6) shows that the operator  $\mathbf{p}$  corresponds to the generalized momentum in classical electrodynamics

$$\mathbf{p} = m_0 \mathbf{v} + \frac{q}{c} \mathbf{A}.$$

The generalized momentum plays an auxiliary role in classical and quantum mechanics, but in both cases the observable value is the particle velocity.

This book is devoted to the study of energy spectra of the hydrogenlike atoms, therefore we shall use mainly the Schrödinger representation. The Heisenberg representation is convenient when we study the evolution of atom driving by some external electromagnetic wave. Nevertheless the Heisenberg representation will also widely used here, because it enables us to study the symmetry properties of different Hamiltonians and to define the integrals of motion. Indeed according to the equation (2.5) the operator  $f(\mathbf{r}, \mathbf{p})$  is integral of motion if it commutes with the Hamiltonian

$$[f, H] = 0.$$

It is well known that the integrals of motion play an exceptional role in the classical and quantum mechanics.

### 2.1.2 Continuity equation, boundary conditions, and normalization condition

The equation for the bilinear combination of the wave function enable us to introduce the concept of the charge density and current density of the matter field. Multiplying both sides of equation (2.4) by complex conjugated wave function  $\psi^*$  and subtracting from the obtained equation its complex conjugated we get

$$\frac{\partial |\psi|^2}{\partial t} = -\frac{1}{2m_0} \nabla \left\{ \psi^* \left( -i\hbar \nabla - \frac{q}{c} \mathbf{A} \right) \psi + \left[ \left( -i\hbar \nabla - \frac{q}{c} \mathbf{A} \right) \psi \right]^* \psi \right\}.$$

This equation can be written in the form

$$\frac{\partial \rho}{\partial t} + \text{div } \mathbf{j} = 0, \quad (2.8)$$

where

$$\rho(\mathbf{r}, t) = q |\psi(\mathbf{r}, t)|^2, \\ \mathbf{j}(\mathbf{r}, t) = \frac{q}{2m_0} \left\{ \psi^* \left( -i\hbar \nabla - \frac{q}{c} \mathbf{A} \right) \psi + \left[ \left( -i\hbar \nabla - \frac{q}{c} \mathbf{A} \right) \psi \right]^* \psi \right\}.$$

The equation (2.8) has the form of the classical continuity equation. Hence, the function  $\rho(\mathbf{r}, t)$  can be associated with the charge density of a particle, and the function  $\mathbf{j}(\mathbf{r}, t)$  plays the role of the electric current density.

Integrating the equation (2.8) over the whole space we get

$$\frac{d}{dt} \left( q \int |\psi(\mathbf{r}, t)|^2 dV \right) = - \int_{S(r \rightarrow \infty)} \mathbf{j}(\mathbf{r}, t) \cdot d\mathbf{S}. \quad (2.9)$$

If the particle is in the bound state of some potential well then the current density should be equal to zero at infinity. As a result we obtain the following boundary condition at infinity

$$\psi(\mathbf{r})|_{r \rightarrow \infty} \rightarrow 0. \quad (2.10)$$

The equation (2.9) together with the boundary condition (2.10) generates the following normalization condition for the wave function

$$\int |\psi(\mathbf{r}, t)|^2 dV = 1. \quad (2.11)$$

It is seen that the condition (2.11) means that the charge associated with the particle is always equal to the elementary charge  $q = \pm |e|$ .

The equations (2.1) and (2.4) are the second order differential equation with respect of the space variables. Therefore to define unambiguously the radial wave function we need additionally in the second boundary condition. It is assumed usually that the wave function should be finite everywhere. For example, if we consider the particle motion in the Coulomb field it is assumed that the wave function should be finite at  $r = 0$ .

For the particle interacting with the attracting static electric and magnetic fields, the equation (2.4) together with the boundary conditions at  $r \rightarrow \infty$  and  $r = 0$  generates the eigenvalue problem

$$E_n u_n(\mathbf{r}) = \left[ \frac{1}{2m_0} \left( \mathbf{p} - \frac{q}{c} \mathbf{A}(\mathbf{r}) \right)^2 + U(\mathbf{r}) \right] u_n(\mathbf{r}). \quad (2.12)$$

The eigenfunctions  $u_n(\mathbf{r})$  corresponding to the different eigenvalues  $E_n$  are orthogonal

$$\int u_n^*(\mathbf{r}) u_m(\mathbf{r}) dV = \delta_{nm}.$$

Usually, the particles, producing the external (with respect to considered particle) fields, are located in the finite spatial volume, therefore the potentials of electromagnetic field, produced by them, tend to zero with the increase of distance:  $\mathbf{A}(\mathbf{r})|_{r \rightarrow \infty} \rightarrow 0$ ,  $\varphi(\mathbf{r})|_{r \rightarrow \infty} \rightarrow 0$ . As a result, the potential energy of a particle, interacting with the external fields, is equal to zero at  $r \rightarrow \infty$ . Hence, the energy of the bound states of particle is negative,  $E_n < 0$ .

If  $E_n > 0$  it means that the kinetic energy of a particle at  $r \rightarrow \infty$  is non-zero, hence the particle can make an infinite motion. The spectrum of the positive energy eigenvalues is continuous. As far as  $\mathbf{A}(\mathbf{r})|_{r \rightarrow \infty} \rightarrow 0$ ,  $\varphi(\mathbf{r})|_{r \rightarrow \infty} \rightarrow 0$  the solutions of the equation (2.12) have

the following asymptotic form at  $r \rightarrow \infty$

$$\psi(\mathbf{r}) = C \frac{\sin(kr + \delta)}{r} Y_{lm}(\theta, \varphi),$$

where  $k = \sqrt{2m_0 E}/\hbar$ , and  $Y_{lm}$  are the spherical harmonics.

The normalization condition for the wave functions of the continuous spectrum is also determined by the equation (2.9). The general form of solution is

$$\psi(\mathbf{r}) = R_{kl}(r) Y_{lm}(\theta, \varphi).$$

The spherical harmonics are normalized by the condition

$$\frac{1}{4\pi} \int Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) d\Omega = \delta_{ll'} \delta_{mm'}.$$

In accordance with the definition (2.8), the charge of the spherical layer  $(r, r + dr)$  is

$$dq = q \left( \int |\psi(\mathbf{r})|^2 r^2 d\Omega \right) dr.$$

It is assumed that the unite charge should pass through the spherical surface of the infinite radius in the unit time. Hence

$$\frac{dq}{dt} = q \left( \int |\psi(\mathbf{r})|^2 r^2 d\Omega \right) \frac{dr}{dt} = qv$$

or

$$\int_{S(r \rightarrow \infty)} \mathbf{j}(\mathbf{r}, t) d\mathbf{S} = qv = q \frac{\hbar k}{m_0}.$$

As a result the normalization condition is

$$\int R_{kl}^{(\infty)*}(r) R_{k'l}^{(\infty)}(r) r^2 dr = 2\pi \delta(k - k'),$$

where  $R_{kl}^{(\infty)}(r)$  is the asymptotic form of the positive energy solutions of equation (2.12).

### 2.1.3 Gauge transformation

The equation (2.4) is gauge invariant. Indeed, if simultaneously with the gauge transformation of vector and scalar potentials

$$\begin{aligned} \mathbf{A}'(\mathbf{r}, t) &= \mathbf{A}(\mathbf{r}, t) + \nabla \chi(\mathbf{r}, t), \\ \varphi'(\mathbf{r}, t) &= \varphi(\mathbf{r}, t) - \frac{1}{c} \frac{\partial \chi(\mathbf{r}, t)}{\partial t}, \end{aligned}$$

we make the following transformation of the wave function

$$\psi'(\mathbf{r}, t) = \psi(\mathbf{r}, t) \exp \left[ \frac{iq}{\hbar c} \chi(\mathbf{r}, t) \right]. \quad (2.13)$$

then the Schrödinger equation (2.4)

$$i\hbar \frac{\partial \psi}{\partial t} = H(\mathbf{A}, \varphi) \psi$$

becomes

$$i\hbar \frac{\partial \psi'}{\partial t} = H(\mathbf{A}', \varphi') \psi'.$$

It is seen that the Schrödinger equation does not change its form.

The gauge transformation of the wave function (2.13) does not change the quantum mechanical average of the operators  $f(\mathbf{r})$  which depend on the coordinate operator only. At the same time, the quantum mechanical average of the generalized momentum operator  $\mathbf{p}$  is changed

$$\int \psi'^* \mathbf{p} \psi' dV = \int \psi^* \left( \mathbf{p} + \frac{q}{c} \nabla \chi \right) \psi dV \neq \int \psi^* \mathbf{p} \psi dV.$$

This is not unexpected, because the generalized momentum operator does not correspond to the observable value. As we have mentioned above the observable value is particle velocity. For the quantum mechanical average of the particle velocity operator,  $\mathbf{v} = \mathbf{p} - \frac{q}{c} \mathbf{A}$ , we have

$$\begin{aligned} \int \psi'^* \mathbf{v} \psi' dV &= \frac{1}{m_0} \int \psi'^* \left( \mathbf{p} - \frac{q}{c} \mathbf{A}' \right) \psi' dV = \\ &= \frac{1}{m_0} \int \psi^* \left( \mathbf{p} + \frac{q}{c} \nabla \chi - \frac{q}{c} \mathbf{A} - \frac{q}{c} \nabla \chi \right) \psi dV = \int \psi^* \mathbf{v} \psi dV. \end{aligned}$$

It can be easily shown also that any degrees of the velocity operator are gauge invariant too.

Hence, the quantum mechanical averages of the arbitrary functions of the coordinate and velocity operators,  $f\left(\mathbf{r}, \mathbf{p} - \frac{q}{c} \mathbf{A}\right)$ , are the gauge invariant values.

## 2.2 Quantum mechanical operators

In previous section we have introduced the coordinate, momentum, and Hamiltonian operators. The exceptional role in atomic spectroscopy plays the parity operator and angular momentum operator. Here we discuss shortly the properties of these two additional quantum mechanical operators. As we have already mentioned above the Hamiltonian is the

basic operator in quantum mechanical theory. Its quantum mechanical average is the energy of a system. The energy of an isolated system of particles should not vary when we make the transformations of the reference frame. The quantum mechanical operators are closely related with the operators of the orthogonal transformations of the reference frame.

### 2.2.1 Momentum operator

The energy of an isolated system of particles is invariant with respect to the spatial translation, i.e. when the coordinates of all particles in the system are changed in the following way:  $\mathbf{r}_a \rightarrow \mathbf{r}_a + \delta\mathbf{r}$ . We can consider the infinitesimally small translation  $\delta\mathbf{r}$ , because any finite translation is a sum of the infinitesimally small translations. If we apply this transformation to the wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$  it becomes

$$\psi(\mathbf{r}_1 + \delta\mathbf{r}, \mathbf{r}_2 + \delta\mathbf{r}, \dots) = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots) + \delta\mathbf{r} \sum_a \nabla_a \psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$$

or

$$\psi(\mathbf{r}_1 + \delta\mathbf{r}, \mathbf{r}_2 + \delta\mathbf{r}, \dots) = \left(1 + \delta\mathbf{r} \sum_a \nabla_a\right) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots).$$

Thus the operator

$$T = 1 + \delta\mathbf{r} \sum_a \nabla_a$$

is the operator the infinitesimally small spatial translation. Since the energy of isolated system does not change under spatial translation, it means

$$TH\psi = HT\psi.$$

Hence

$$\left(\sum_a \nabla_a\right)H - H\left(\sum_a \nabla_a\right) = 0.$$

As we have already mentioned, if operator commutes with the Hamiltonian, then the physical variable corresponding to this operator is conservative. In classical mechanics the physical variable, which is conservative due to the homogeneity of space, is the momentum. Hence the operator  $\sum_a \nabla_a$  is proportional to the momentum operator. The coefficient of proportionality can be found if, for example, we calculate the quantum mechanical average of operator  $\mathbf{p} = -i\hbar\nabla$  for free particle describing by plane wave  $\psi_{\mathbf{k}}(\mathbf{r}) = C \exp(i\mathbf{k}\mathbf{r})$

$$\int \psi_{\mathbf{k}}^* \mathbf{p} \psi_{\mathbf{k}} dV = \hbar \mathbf{k} \int \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} dV.$$



Thus, the operator

$$\mathbf{p} = -i\hbar\nabla$$

is the quantum mechanical momentum operator.

### 2.2.2 Space inversion and parity operator

The space inversion transformation consists in the replacement  $\mathbf{r} \rightarrow -\mathbf{r}$ . The operator  $P$  generating this transformation is called by the parity operator

$$P\psi(\mathbf{r}) = \psi(-\mathbf{r}).$$

Let us apply the parity operator to the Hamiltonian (2.7). The generalized momentum  $\mathbf{p}$  and vector potential  $\mathbf{A}$  are both polar vectors, therefore at the space inversion transformation we have  $P\mathbf{p} = -\mathbf{p}$  and  $P\mathbf{A} = -\mathbf{A}$ . Hence the kinetic energy remains invariable at the space inversion. If the potential energy is invariant with respect to the space inversion  $U(\mathbf{r}) = U(-\mathbf{r})$ , i.e. if the external potential is centrosymmetric, then the parity operator  $P$  commutes with the Hamiltonian (2.7)

$$[P, H] = 0.$$

The commuting operators have the common set of eigenfunctions. The eigenvalues of the parity operator can be found in the following way. On the one hand

$$P^2\psi(\mathbf{r}) = Pp\psi(\mathbf{r}) = p^2\psi(\mathbf{r}).$$

On the other hand

$$P^2\psi(\mathbf{r}) = P\psi(-\mathbf{r}) = \psi(\mathbf{r}).$$

Hence

$$p_{1,2} = \pm 1.$$

As a result the wave functions of the particle, moving in the centrosymmetrical potential  $\varphi(\mathbf{r}) = \varphi(-\mathbf{r})$ , either remain invariable or change the sign under the space inversion. The state in which the wave function does not change its sign is called by the even state, if the wave function changes its sign under the space inversion transformation then the corresponding state is called by the odd state.

Thus the invariance of the Hamiltonian with respect to the space inversion transformation manifests the parity conservation law: if an isolated ensemble of particles has a definite parity, then the parity remains invariable in the process of ensemble evolution.

The wave functions of the even states are the scalar functions, the wave functions of the odd states are the pseudoscalar functions.

### 2.2.3 Three-dimensional rotations and angular momentum operator

The rotation of an isolated ensemble of particles, as a whole, around an arbitrary axis does not change the relative positions of particles, hence, the state of the whole system should remain invariable. Let us consider infinitesimally small rotation  $\delta\varphi$  around the  $z$  axis. Under this rotation the particle coordinates are transformed in the following way

$$x' = x + \delta\varphi y, \quad y' = y - \delta\varphi x, \quad z' = z.$$

The transformation of wave function is

$$\begin{aligned} \psi(x', y', z') &= \psi(x, y, z) + \delta\varphi y \frac{\partial \psi}{\partial x} - \delta\varphi x \frac{\partial \psi}{\partial y} = \\ &= \left[ 1 + \delta\varphi \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \right] \psi(x, y, z). \end{aligned}$$

Hence the operator of infinitesimally small rotation around the  $z$  axis is

$$R_z(\delta\varphi) = 1 + \delta\varphi \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right).$$

Under the rotation around the arbitrary axis  $\delta\boldsymbol{\varphi}$  the rotation operator becomes

$$R(\delta\boldsymbol{\varphi}) = 1 - i\delta\boldsymbol{\varphi} \mathbf{l},$$

where the angular momentum operator  $\hbar \mathbf{l}$  is defined as

$$\hbar \mathbf{l} = [\mathbf{r}\mathbf{p}] = -i\hbar [\mathbf{r}\nabla]. \quad (2.14)$$

The components of the angular momentum operator

$$\hbar l_x = yp_z - zp_y, \quad \hbar l_y = zp_x - xp_z, \quad \hbar l_z = xp_y - yp_x$$

obey the following commutation relations

$$[l_\alpha, l_\beta] = ie_{\alpha\beta\gamma} l_\gamma, \quad (2.15)$$

where  $\alpha, \beta, \gamma = x, y, z$  and  $e_{\alpha\beta\gamma}$  is the completely antisymmetric tensor of the third order. The elements of this tensor are equal to zero if any two of its three indexes coincide. The non-zero elements of this tensor correspond to the three different indexes. It is usually assumed that  $e_{xyz} = 1$  and any other elements obtained by permutation of these indexes are equal to minus unity, if the number of permutations is odd, and unity, if the number of permutations is even.

The commutation relations for the angular momentum operator and operators of coordinate and generalized momentum are

$$[l_\alpha, r_\beta] = i e_{\alpha\beta\gamma} r_\gamma, \quad [l_\alpha, p_\beta] = i e_{\alpha\beta\gamma} p_\gamma. \quad (2.16)$$

The operator of the angular momentum square

$$\mathbf{l}^2 = l_x^2 + l_y^2 + l_z^2$$

commutes with each of the component of operator  $\mathbf{l}$ . Indeed

$$[l^2, l_\alpha] = l_\beta [l_\beta, l_\alpha] + [l_\beta, l_\alpha] l_\beta = -i e_{\alpha\beta\gamma} l_\beta l_\gamma + i e_{\alpha\gamma\beta} l_\gamma l_\beta = 0. \quad (2.17)$$

In the spherical set of coordinates the angular momentum square operator is

$$\mathbf{l}^2 = - \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right]. \quad (2.18)$$

It is seen that the operator (2.18) coincides with the angular part of the Laplace operator, written in the spherical coordinates

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \mathbf{l}^2. \quad (2.19)$$

As far as operators  $\mathbf{l}^2$  and  $l_z$  commute then they have the common set of eigenfunctions. With the help of commutation relations (2.15) it can be easily shown that the common eigenfunctions obey the equations

$$\mathbf{l}^2 \psi_{lm}(\mathbf{r}) = l(l+1) \psi_{lm}(\mathbf{r}), \quad l_z \psi_{lm}(\mathbf{r}) = m \psi_{lm}(\mathbf{r}), \quad (2.20)$$

where  $l$  is non-negative integer,  $l = 0, 1, 2, \dots$ , and the  $z$ -projection of angular momentum takes the values  $m = -l, -l+1, \dots, l$ . The solutions of the equations (2.20) are the spherical harmonics

$$Y_{lm}(\theta, \varphi) = (-1)^{\frac{m+|m|}{2}} i^l \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos \theta) \exp(im\varphi), \quad (2.21)$$

where  $P_l^m(\cos \theta)$  is the associated Legendre polynomial.

It can be easily shown that the Hamiltonian (2.2) for the case of particle motion in the spherically symmetric potential  $\varphi(\mathbf{r}) = \varphi(r)$  commutes with the angular momentum operator. Indeed the equation for the angular momentum operator in spherical coordinates is

$$\mathbf{l} = \mathbf{e}_\theta \frac{i}{\sin \theta} \frac{\partial}{\partial \varphi} - \mathbf{e}_\varphi i \frac{\partial}{\partial \theta}. \quad (2.22)$$

It is seen from (2.22) that the angular momentum operator commutes with  $U(r)$ . On the other hand, as it follows from the equations (2.17)–(2.19) the operator  $\mathbf{l}$  commutes with the Laplace operator. Thus when we deal with the eigenvalue problem on particle motion in the spherically symmetric potential  $\varphi(r)$ , we can always express the eigenfunctions in terms of the spherical harmonics (2.21).

It is evident that the angular momentum operator is invariant with respect of space inversion transformation, because both coordinate and generalized momentum operators change sign under the space inversion. Hence the eigenfunctions of the problem on the particle motion in the spherically symmetric potential have to have the definite parity. The parity of the different states are determined by the parity the spherical harmonics (2.21). By applying the parity operator to the spherical harmonics we get

$$PY_{lm}(\theta, \varphi) = Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l Y_{lm}(\theta, \varphi),$$

i.e. the parity of state is defined by

$$P_l = (-1)^l. \quad (2.23)$$

The angular momentum operator in the cylindrical set of coordinates is

$$\mathbf{l} = \mathbf{e}_\rho \left( i \frac{z}{\rho} \frac{\partial}{\partial \varphi} \right) + \mathbf{e}_\varphi \left[ -i \left( z \frac{\partial}{\partial \rho} - \rho \frac{\partial}{\partial z} \right) \right] + \mathbf{e}_z \left( -i \frac{\partial}{\partial \varphi} \right). \quad (2.24)$$

It is evident from this equation, that the angular momentum projection operator  $l_z$  commutes with the Hamiltonian (2.7) when  $U = U(\rho, z)$  and  $\mathbf{A} = \mathbf{e}_\varphi A(\rho, z)$ . In this case, as it follows from the equations (2.20) and (2.21), the angular part of the wave function is given by  $\exp(im\varphi)$ . Hence the parity of eigenstates for the problem of particle motion in the external fields of cylindric symmetry is defined by

$$P_m = (-1)^m. \quad (2.25)$$

### 2.3 Particle motion in the Coulomb field

Let us consider the problem on a particle motion in the attracting Coulomb field. In this case the potential energy of a particle is

$$U(r) = -\frac{Ze^2}{r} \quad (2.26)$$

and the equation (2.12) became

$$\left[ -\frac{\hbar^2}{2m_0} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l^2}{r^2} \right) - \frac{Ze^2}{r} \right] \psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}). \quad (2.27)$$

We have shown above, that the Hamiltonian of the equation (2.27) commutes with the operators of parity, angular momentum square, and projection of angular momentum. Therefore the wave function can be expressed in terms of the eigenfunctions of the parity, angular momentum, and projection of angular momentum operators. However, as we have seen, the parity of states in the spherically symmetric external field is unambiguously determined by the angular momentum, therefore to define the particle state we can use the following quantum numbers: energy  $E$ , angular momentum  $l$ , and projection of angular momentum  $m$ .

### 2.3.1 Discrete spectrum

As we have discussed above for the bound states of electron in the Coulomb field the boundary conditions require that the wave function should be finite at  $r = 0$  and turn to zero at  $r \rightarrow \infty$

$$\psi_E(\mathbf{r})|_{r \rightarrow \infty} = 0. \quad (2.28)$$

The analysis, given in the previous section, has shown that in the case of particle motion in the spherically symmetric potential the wave function can be taken in the form

$$\psi_E(\mathbf{r}) = R(r) Y_{lm}(\theta, \varphi).$$

By substituting the latter equation into the equation (2.27) we get the following equation for the radial part of the wave function

$$\left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2m_0 Z e^2}{\hbar^2} \frac{1}{r} + \frac{2m_0 E}{\hbar^2} \right) R(r) = 0. \quad (2.29)$$

Taking into account that the bound states are the states of the negative energy, it is convenient to introduce the following notation

$$\kappa = \sqrt{\frac{2m_0 |E|}{\hbar^2}}.$$

The general solution of the equation (2.29) is

$$R(r) = \left[ C_1 F(l+1-\gamma, 2l+2, 2\kappa r) + C_2 (2\kappa r)^{-2l-1} F(-l-\gamma, -2l, 2\kappa r) \right] r^l \exp(-\kappa r), \quad (2.30)$$

where  $F(a, b, z)$  is the confluent hypergeometric function,  $\gamma = Z/(\kappa a_B)$ . Here  $a_B$  is the Bohr radius

$$a_B = \frac{\hbar^2}{m_0 e^2}. \quad (2.31)$$

The asymptotic form of the confluent hypergeometric function  $F(a, b, z)$  at  $z = 0$  is

$$F(a, b, |z| \rightarrow 0) \rightarrow 1.$$

Hence we should assume that  $C_2 = 0$ , because the second term in the right-hand-side of the equation (2.30) does not obey the boundary condition at  $r = 0$ . The asymptotic form of confluent hypergeometric function  $F(a, b, z)$  at  $z \rightarrow \infty$  is

$$F(a, b, z) = \frac{\Gamma(b) \exp(i\pi a)}{\Gamma(b-a)} z^{-a} + \frac{\Gamma(b)}{\Gamma(a)} z^{a-b} \exp(z) + \dots$$

It is seen that the second term in this equation infinitely increases when  $r \rightarrow \infty$ . However, this term vanishes when the argument  $a$  of the confluent hypergeometric function  $F(a, b, z)$  is a non-positive integer. Thus the solution (2.30) satisfies the boundary conditions when  $C_2 = 0$  and

$$l + 1 - \gamma = -n_r, \quad (2.32)$$

where  $n_r$  is the non-negative integer.

The latter equation yields the following equation for the energy spectrum of bound states

$$E_n = -\frac{Z^2 \hbar^2}{2m_0 a_B^2 n^2} = -\frac{Z^2 e^4 m_0}{2\hbar^2 n^2}, \quad (2.33)$$

where

$$n = n_r + l + 1 = 1, 2, 3, \dots$$

Notice, that the energy spectrum (2.33), resulted from the solution of the quantum mechanical problem on the electron motion in the Coulomb field, coincides with the spectrum that was obtained with the help application of the Bohr–Sommerfeld quantization rules to the classical equations. The quantum number  $n_r$  is called by the radial quantum number. We shall see later that the radial quantum number determines the number of nodes of the radial wave function  $R(r)$ . The quantum number  $l$  is usually called by the azimuthal quantum number. The quantum number  $n$  is called by the principle quantum number.

Before the quantum mechanics was completely worked out, the spectroscopic notations were developed to describe the different hydrogen-like energy levels in an atom. Basically, the notation consisted of a number (representing the value of  $n$ ) followed by a letter (representing the value of  $l$ ). The letters originally described the characteristics of the spectral lines, like “sharp”, “principal”, etc. The correspondence between the values of  $l$  and letters is given in Tab. 2.1.

Table 2.1. Spectroscopic notation

$l$	=	0	1	2	3	4	5	...
letter	→	$s$	$p$	$d$	$f$	$g$	$h$	...

It can be easily shown that the ground state of the hydrogenlike atom is always the  $s$  state. Indeed, the substitution  $R(r) = f(r)/r$  transforms the equation (2.29) to the form

$$\left( \frac{d^2}{dr^2} + \frac{2m_0 E}{\hbar^2} - \frac{l(l+1)}{r^2} - U(r) \right) f(r) = 0.$$

It is seen that the last equation coincides with the Schrödinger equation for particle moving in the one-dimensional potential well of the form

$$U_{\text{eff}}(r) = U(r) + \frac{\hbar^2}{2m_0} \frac{l(l+1)}{r^2}.$$

The second term in the right-hand-side of this equation is the energy of centrifugal motion. This energy is definitely positive at  $l > 0$ . Hence, the energy of fundamental states at  $l > 0$  is always higher than the energy of the  $s$  state. It can also be stated that the energy of the fundamental state for a given  $l$  increases with the increase of  $l$ .

In the case when  $a$  is a non-positive integer, the confluent hypergeometric functions  $F(a, b, z)$  can be expressed in terms of the Laguerre polynomials:  $F(-n, b+1, z) = (\Gamma(b+1)n!/\Gamma(b+1+n))L_n^{(b)}(z)$ . Hence the radial wave function  $R(r)$  can be rewritten in the following equivalent form

$$R_{nl}(r) = Cr^l \exp(-\kappa_n r) L_{n-l-1}^{(2l+1)}(2\kappa_n r), \quad (2.34)$$

where  $\kappa_n = 1/na_B$ . By using the normalization condition

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1,$$

we get the following equation for the normalized wave function

$$\begin{aligned} R_{nl}(r) &= \sqrt{\frac{(2\kappa_n)^3 (n-l-1)!}{2n(n+l)!}} (2\kappa_n r)^l \exp(-\kappa_n r) L_{n-l-1}^{(2l+1)}(2\kappa_n r) = \\ &= \frac{2}{n^2} \sqrt{\frac{Z^3 (n-l-1)!}{a_B^3 (n+l)!}} \left( \frac{2Zr}{na_B} \right)^l \exp\left(-\frac{Zr}{na_B}\right) L_{n-l-1}^{(2l+1)}\left(\frac{2Zr}{na_B}\right) \end{aligned} \quad (2.35)$$

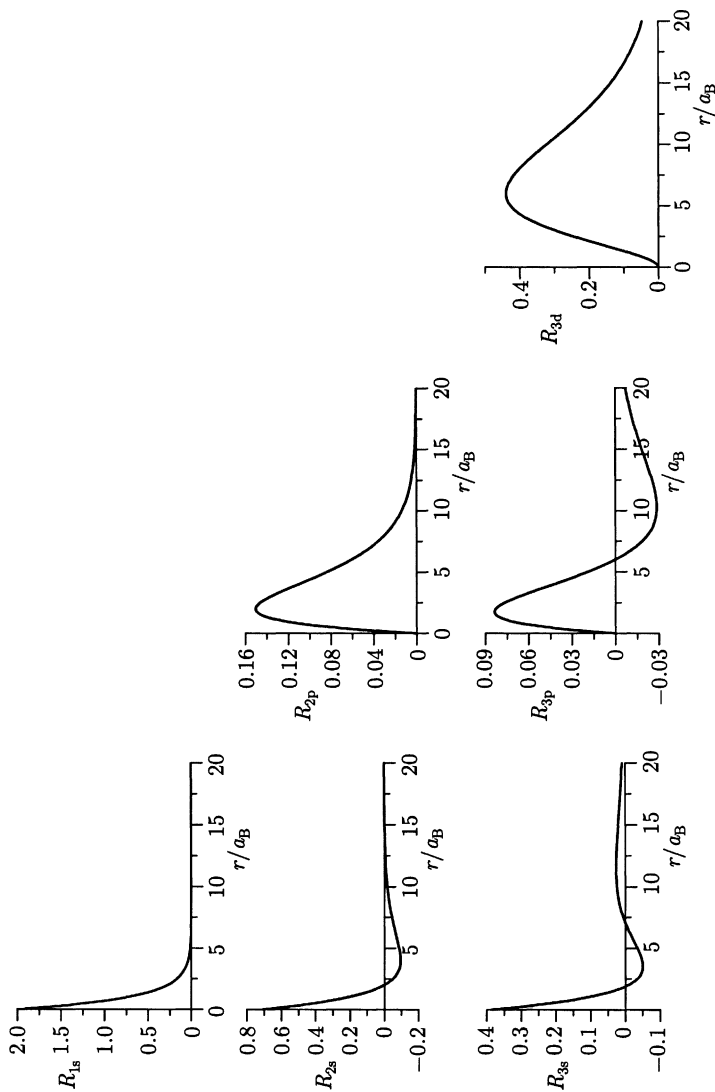


Figure 2.1. Radial wave functions of hydrogen atom



The explicit form of the wave functions for a number of states in hydrogen atom is given below:

1  $1s$  – state ( $n = 1, l = 0$ )

$$R_{1s}(r) = \frac{2}{\sqrt{a_B^3}} \exp\left(-\frac{r}{a_B}\right);$$

2  $2s$  – state ( $n = 2, l = 0$ )

$$R_{2s}(r) = \sqrt{\frac{1}{2a_B^3}} \exp\left(-\frac{r}{2a_B}\right) \left(1 - \frac{r}{2a_B}\right);$$

3  $2p$  – state ( $n = 2, l = 1$ )

$$R_{2p}(r) = \sqrt{\frac{1}{6a_B^3}} \exp\left(-\frac{r}{2a_B}\right) \frac{r}{2a_B};$$

4  $3s$  – state ( $n = 3, l = 0$ )

$$R_{3s}(r) = \frac{2}{3\sqrt{3a_B^3}} \exp\left(-\frac{r}{3a_B}\right) \left(1 - 2\frac{r}{3a_B} + \frac{2}{3}\left(\frac{r}{3a_B}\right)^2\right);$$

5  $3p$  – state ( $n = 3, l = 1$ )

$$R_{3p}(r) = \frac{2}{9}\sqrt{\frac{2}{3a_B^3}} \exp\left(-\frac{r}{3a_B}\right) \left(2 - \frac{r}{3a_B}\right) \frac{r}{3a_B};$$

6  $3d$  – state ( $n = 3, l = 2$ )

$$R_{3d}(r) = \frac{2}{9}\sqrt{\frac{2}{15a_B^3}} \exp\left(-\frac{r}{3a_B}\right) \left(\frac{r}{3a_B}\right)^2.$$

The graphs of the corresponding functions is shown in Fig. 2.1. By taking into account the definition of the principle quantum number  $n$ :

$$n = n_r + l + 1, \quad (2.36)$$

we can see that the number of zeros of the wave function is really determined by the radial quantum number  $n_r$ . The wave functions of the  $s$  states are maxima at  $r = 0$ , the wave functions of states with  $l > 0$  turn into zero at this point.

We have mentioned above that the product  $R^2(r)r^2$ , proportional to the probability for particle to be inside the spherical layer  $(r, r + dr)$ , is called by the charge density. The charge density distribution for the above states is shown in Fig. 2.2. It is seen that the maximum of charge density moves away from the center with the increase of the principle quantum number  $n$ .

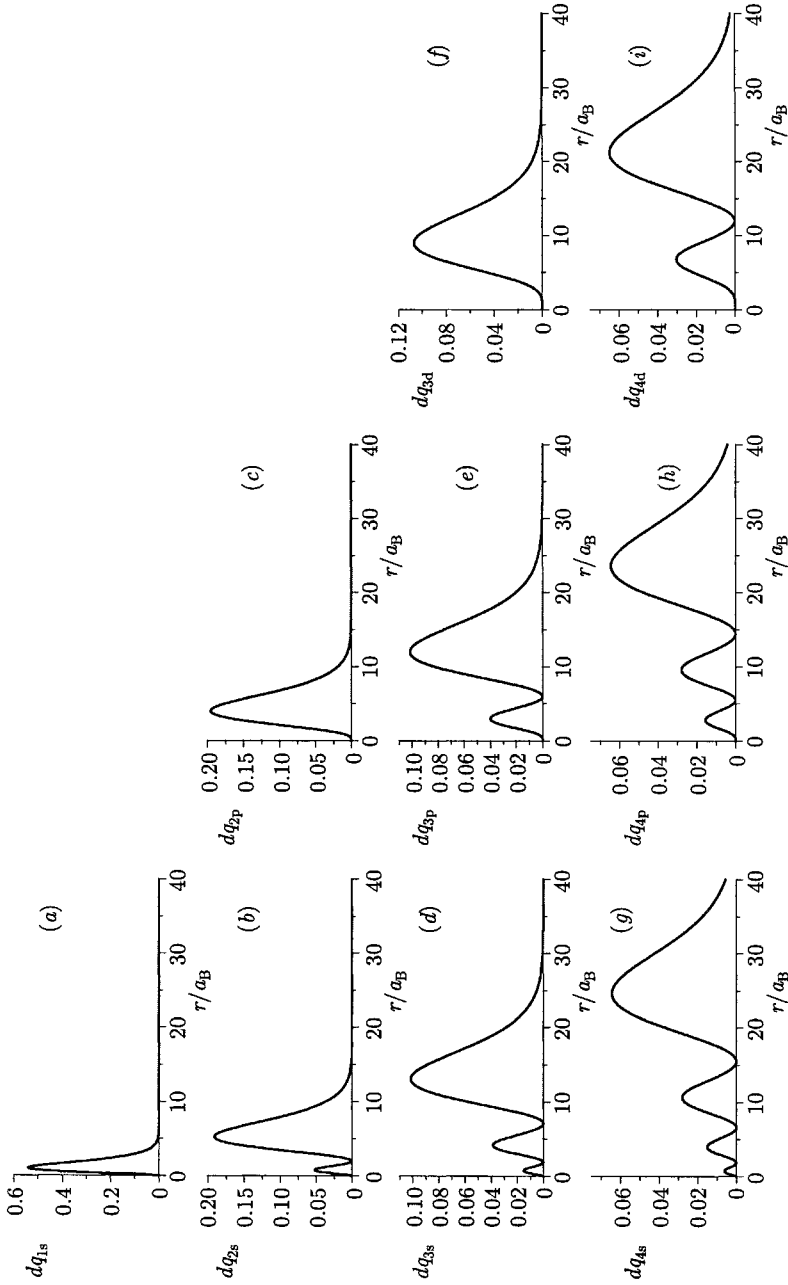


Figure 2.2. Density of charge distribution in hydrogen atom

### 2.3.2 Continuous spectrum

The continuous spectrum of the positive energy eigenvalues is stretched from zero up to infinity. Each energy eigenvalue is infinitely degenerated with respect to the angular momentum  $l$ , which runs all integers from zero up to infinity, and its projection  $m$ , taking all possible values,  $|m| \leq l$ , at given  $l$ .

The general solution is given by the equation (2.30), where we should again assume the coefficient  $C_2$  equal to zero in order to satisfy the boundary condition at  $r = 0$ :

$$R_{kl}(r) = C_{kl}(2kr)^l \exp(-ikr) F\left(l+1 + \frac{iZ}{ka_B}, 2l+2, i2kr\right), \quad (2.37)$$

where

$$k = \frac{\sqrt{2m_0 E}}{\hbar}.$$

The asymptotical form of the solution (2.37) at infinity is

$$R_{kl}(r) = C_{kl} \frac{\Gamma(2l+2) \exp\left(-\frac{\pi Z}{2ka_B}\right) \sin\left(kr + \left(\frac{Z}{ka_B}\right) \ln 2kr - \frac{\pi l}{2} + \delta_l\right)}{\left|\Gamma\left(l+1 + \frac{iZ}{ka_B}\right)\right| kr}, \quad (2.38)$$

where  $\delta_l = \arg \Gamma(l+1 - iZ/(ka_B))$ . By normalizing the wave function in accordance with the procedure discussed in subsection 2.1.2, we get the following equation for the normalization coefficient  $C_{kl}$ :

$$C_{kl} = \sqrt{\frac{8\pi k Z/a_B}{1 - \exp(-2\pi Z/(ka_B))}} \frac{1}{\Gamma(2l+2)} \prod_{s=1}^l \sqrt{s^2 + \left(\frac{Z}{ka_B}\right)^2}.$$

### 2.3.3 Matrix elements of transitions

The rate of the radiative transitions between the atomic states depends on the magnitude of the matrix elements of transitions

$$\langle n_1 l_1 m_1 | \mathbf{r} | n_2 l_2 m_2 \rangle = \int \psi_{n_1 l_1 m_1}^*(\mathbf{r}) \mathbf{r} \psi_{n_2 l_2 m_2} dV. \quad (2.39)$$

It is convenient to make the following transformation of the radius vector  $\mathbf{r}$ :

$$\mathbf{r} = \mathbf{e}_+ r \sin \theta \exp(i\varphi) + \mathbf{e}_- r \sin \theta \exp(-i\varphi) + \mathbf{e}_z r \cos \theta,$$

where  $\mathbf{e}_\pm = (\mathbf{e}_x \mp i\mathbf{e}_y)/2$ . In this case the right-hand-side of the equation (2.39) transforms into the product of integrals over the radial

and angular variables. The integrals over the angular variables give us the selection rules for the dipole allowed transitions. They are

$$\begin{aligned}
 \langle l_1 m_1 | \cos \theta | l_2 m_2 \rangle &= i \sqrt{\frac{(l_1 - m_1 + 1)(l_1 + m_1 + 1)}{(2l_1 + 1)(2l_1 + 3)}} \delta_{l_2, l_1 + 1} \delta_{m_2, m_1}, \\
 \langle l_1 m_1 | \cos \theta | l_2 m_2 \rangle &= -i \sqrt{\frac{(l_2 - m_2 + 1)(l_2 + m_2 + 1)}{(2l_2 + 1)(2l_2 + 3)}} \delta_{l_1, l_2 + 1} \delta_{m_1, m_2}, \\
 \langle l_1 m_1 | \sin \theta \exp(i\varphi) | l_2 m_2 \rangle &= \\
 &= i \sqrt{\frac{(l_1 - m_1 + 1)(l_1 - m_1 + 2)}{(2l_1 + 1)(2l_1 + 3)}} \delta_{l_2, l_1 + 1} \delta_{m_2, m_1 - 1}, \\
 \langle l_1 m_1 | \sin \theta \exp(i\varphi) | l_2 m_2 \rangle &= \\
 &= i \sqrt{\frac{(l_2 + m_2 + 1)(l_2 + m_2 + 2)}{(2l_2 + 1)(2l_2 + 3)}} \delta_{l_1, l_2 + 1} \delta_{m_1, m_2 + 1}.
 \end{aligned} \tag{2.40}$$

The matrix elements for the component ( $\mathbf{re}_-$ ) can be easily obtained from the last two equations in (2.40) with the help of the equality

$$\langle l_1 m_1 | \sin \theta \exp(-i\varphi) | l_2 m_2 \rangle = \langle l_2 m_2 | \sin \theta \exp(i\varphi) | l_1 m_1 \rangle^*.$$

Thus the selection rules for the dipole allowed transitions are:

a) linear polarized wave

$$\Delta l = l_1 - l_2 = \pm 1, \quad \Delta m = m_1 - m_2 = 0;$$

b) circular polarized wave

$$\Delta l = l_1 - l_2 = \pm 1, \quad \Delta m = m_1 - m_2 = \pm 1.$$

In the last case the signs plus and minus correspond to the right and left circular polarized waves, respectively.

The radial matrix elements are

$$\begin{aligned}
 \langle n_1 l_1 | r | n_2 l_2 \rangle &= \frac{a_B}{Z} \frac{2^{l_1 + l_2 + 2}}{n_1^{l_1 + 2} n_2^{l_2 + 2}} \sqrt{\frac{(n_1 - l_1 - 1)!(n_2 - l_2 - 1)!}{(n_1 + l_1)!(n_2 + l_2)!}} \times \\
 &\times \int_0^\infty x^{l_1 + l_2 + 3} \exp \left[ -x \left( \frac{1}{n_1} + \frac{1}{n_2} \right) \right] L_{n_1 - l_1 - 1}^{(2l_1 + 1)} \left( \frac{2x}{n_1} \right) L_{n_2 - l_2 - 1}^{(2l_2 + 1)} \left( \frac{2x}{n_2} \right) dx
 \end{aligned} \tag{2.41}$$

Particularly, for the transition  $1S \rightarrow nP$  we get

$$\langle nP | r | 1S \rangle = \frac{a_B}{Z} \sqrt{\frac{(n+1)!}{(n-2)!}} \frac{16n^3(n-1)^{n-3}}{(n+1)^{n+3}}. \tag{2.42}$$

Table 2.2. Radial matrix elements of transitions  $1S \rightarrow nP$

$\frac{Z}{a_B}$	$\langle nP r 1S\rangle$	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
$n$		1.29027	0.51669	0.30458	0.2087	0.15514	0.12142	0.0985
$\frac{Z}{a_B}$	$\langle nP r 1S\rangle$	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>
$n$		0.08205	0.06975	0.06026	0.05276	0.0467	0.04173	0.03758
$\frac{Z}{a_B}$	$\langle nP r 1S\rangle$	<b>16</b>	<b>17</b>	<b>18</b>	<b>19</b>	<b>20</b>	<b>21</b>	<b>22</b>
$n$		0.03408	0.03109	0.02852	0.02628	0.02432	0.02259	0.02106

Table 2.2 shows the numerical values of the matrix elements  $1S \rightarrow nP$  when  $n$  is varied in the range  $2 < n < 22$ .

The equation (2.42) enables us to find the asymptotic form of the matrix elements from the ground state to the high-lying quasiclassical  $nP$  states. In the case when  $n \gg 1$  we get from the equation (2.42) the following result

$$\langle nP|r|1S\rangle = \frac{a_B}{Z} \sqrt{\frac{(n+1)!}{(n-2)!}} \frac{16n^3(n-1)^{n-3}}{(n+1)^{n+3}} \xrightarrow{n \gg 1} \frac{C}{n^{3/2}}. \quad (2.43)$$

Thus, for these transitions, the oscillator force decreases with the increase of the principle quantum number as  $1/n^3$ . In Fig. 2.3 the matrix

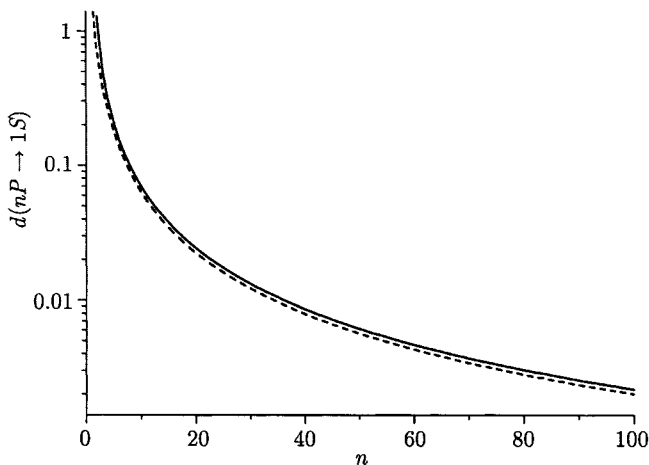


Figure 2.3. The magnitude of the matrix elements of  $nP \rightarrow 1S$  transitions in hydrogen as a function of the principle quantum number  $n$ . The solid curve is the exact function (2.42), the dashed curve is approximation (2.43). The dashed curve is shifted down for convenience

elements calculated on the basis of equations (2.42) and (2.43) are shown in comparison. For the illustration purposes we assume the coefficient  $C$  equal to  $C = 2$ , but at  $C = 2.2$  the two curves in Fig. 2.3 coincide almost completely in the region  $n \geq 7$ . There is some discrepancy in the region  $n < 7$ . But by comparing the equations (2.42) and (2.43) we can see that according to equation (2.42) in the region  $n < 7$  the decrease is more fast, therefore in this region the higher powers of  $1/n$  should be included in asymptotic equation (2.43).

## 2.4 Hydrogen atom

The hydrogenlike atom consists of the electron and nucleus. The atomic nucleus has the finite mass, therefore the nucleus of the hydrogen atom is also involved into the motion. Hence, the energy spectrum must depend on the nucleus mass. If the ratio of electron mass to nucleus mass (in the hydrogen atom this is the ratio of electron mass to proton mass  $m_e/m_n \approx 5 \cdot 10^{-4}$ ) is taken as a smallness parameter, then the energy spectrum of electron in the Coulomb field gives us only the zero order approximation for the hydrogen atom spectrum. The total energy of atom is the sum of the electron energy and nucleus energy. Similar the total momentum, and total angular momentum of atom are the sums of them for electron and nucleus. In the processes of absorption or emission of photons by an atom, the conservation laws hold for whole isolated system, therefore the motion of electron in the process of photon absorption or emission is always accompanied by the motion of nucleus. Therefore if we would like to increase the accuracy of calculated energy spectra for hydrogenlike atom we should take into account the motion of the atomic nucleus.

The account for the finite nucleus mass provides the simplest hydrogen atom model. The further development of this model will be given in the next chapters. Here, we start with the study of the influence of the finiteness of the nucleus mass on the energy spectra of hydrogenlike atoms.

### 2.4.1 Hamiltonian of two-particle problem

The Hamiltonian of system consisting of two charged particles with the Coulomb interaction is

$$H_0 = \frac{\mathbf{p}_a^2}{2m_a} + \frac{\mathbf{p}_b^2}{2m_b} + \frac{q_a q_b}{|\mathbf{r}_a - \mathbf{r}_b|}, \quad (2.44)$$

where  $q_a$  and  $q_b$  are the charges of particles. It is seen that the Hamiltonian (2.44) does not commute with momentum operators for each

individual particle, but it commutes with the total momentum operator

$$\mathbf{P} = \mathbf{p}_a + \mathbf{p}_b. \quad (2.45)$$

Indeed

$$[\mathbf{P}, H_0] = -i\hbar q_a q_b \left( \frac{\partial}{\partial \mathbf{r}_a} + \frac{\partial}{\partial \mathbf{r}_b} \right) \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} = 0.$$

It means that the variation in the electron momentum of free atom is always accompanied by the variation in the nucleus momentum. However, the coordinate of the atomic center of mass does not vary, because the total momentum is an integral of motion. Therefore it is convenient to introduce the center-of-mass coordinate,  $\mathbf{R}$ , and relative position coordinate,  $\mathbf{r}$ :

$$\mathbf{r} = \mathbf{r}_a - \mathbf{r}_b, \quad \mathbf{R} = \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b}. \quad (2.46)$$

Similar to the momentum operators, the operators of angular momentum of each individual particle do not commute with the Hamiltonian (2.44), but the total angular momentum operator

$$\hbar \mathbf{L} = \hbar \mathbf{l}_a + \hbar \mathbf{l}_b = [\mathbf{r}_a \mathbf{p}_a] + [\mathbf{r}_b \mathbf{p}_b] \quad (2.47)$$

commutes with the Hamiltonian (2.44). By taking into account that the angular momentum operators  $\mathbf{l}_a$  and  $\mathbf{l}_b$  commute with each other and both of them commute with the Laplace operators  $\Delta_{a,b}$  we get for the total angular momentum operator

$$[\mathbf{L}, H_0] = -iq_a q_b \left( \left[ \mathbf{r}_a \frac{\partial}{\partial \mathbf{r}_a} \right] + \left[ \mathbf{r}_b \frac{\partial}{\partial \mathbf{r}_b} \right] \right) \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} = 0.$$

Thus the total angular momentum operator  $\mathbf{L}$  is the integral of motion, while the angular momenta of the individual particles are not conserved.

If the transformations (2.46) are applied to the equation (2.47) we get

$$\hbar \mathbf{L} = [\mathbf{r} \mathbf{p}] + [\mathbf{R} \mathbf{P}], \quad (2.48)$$

where

$$\mathbf{p} = -i\hbar \frac{\partial}{\partial \mathbf{r}} = \frac{m_b}{m_a + m_b} \mathbf{p}_a - \frac{m_a}{m_a + m_b} \mathbf{p}_b, \quad \mathbf{P} = -i\hbar \frac{\partial}{\partial \mathbf{R}} = \mathbf{p}_a + \mathbf{p}_b. \quad (2.49)$$

Thus the total angular momentum  $\mathbf{L}$  is the sum of the angular momentum of center of mass and angular momentum of the relative motion of particles.

### 2.4.2 Reduced electron mass

If the transformations (2.46) and (2.49) are applied to the Hamiltonian (2.44), we get

$$H_0 = -\frac{\hbar^2}{2m_r}\Delta_r + \frac{q_a q_b}{r} - \frac{\hbar^2}{2(m_a + m_b)}\Delta_R, \quad (2.50)$$

where  $m_r$  is the reduced electron mass, defined as

$$m_r = \frac{m_a m_b}{m_a + m_b}. \quad (2.51)$$

If an atom is placed into the atomic trap, the potential of which possesses the central symmetry, then the total angular momentum of atom  $\mathbf{L}$  is still the integral of motion. Indeed, if the potential energy of a trap depends only on the magnitude of the radius vector  $\mathbf{R}$ , i.e.  $U_{\text{trap}} = U(R)$ , we get

$$\begin{aligned} [\mathbf{L}, U(R)] &= -i([\mathbf{r}_a \nabla_a] + [\mathbf{r}_b \nabla_b])U(R) = \\ &= -i \left[ \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b} \mathbf{R} \right] \frac{1}{R} \frac{\partial U}{\partial R} = -i[\mathbf{R}\mathbf{R}] \frac{1}{R} \frac{\partial U}{\partial R} = 0. \end{aligned}$$

The Hamiltonian for an atom, placed in the atomic trap, is

$$H = H_0 + U(R) = -\frac{\hbar^2}{2m_r}\Delta_r + \frac{q_a q_b}{r} - \frac{\hbar^2}{2(m_a + m_b)}\Delta_R + U(R). \quad (2.52)$$

Thus we can see that the Hamiltonian (2.52) is the sum of two terms. One of them depends on the relative position coordinate,  $\mathbf{r}$ , another term depends on the center-of-mass coordinate,  $\mathbf{R}$ . It is seen that the angular momentum operator of the relative motion of particles  $[\mathbf{r}\mathbf{p}]$  and angular momentum operator of center of mass  $[\mathbf{R}\mathbf{P}]$  commutes separately with the Hamiltonian (2.52). Hence, both angular momenta are the integrals of motion. In this case the two-particle wave function  $\psi(\mathbf{r}_a, \mathbf{r}_b)$  is factorized, i.e. it becomes a product of the wave functions depending on the coordinates  $\mathbf{r}$  and  $\mathbf{R}$  in separate

$$\psi(\mathbf{r}_a, \mathbf{r}_b) = f(\mathbf{r})g(\mathbf{R}).$$

The wave functions  $f(\mathbf{r})$  and  $g(\mathbf{R})$  obey the following equations

$$\left( -\frac{\hbar^2}{2m_r}\Delta_r + \frac{q_a q_b}{r} \right) f(\mathbf{r}) = E^{(1)} f(\mathbf{r}), \quad (2.53a)$$

$$\left( -\frac{\hbar^2}{2(m_a + m_b)}\Delta_R + U(R) \right) g(\mathbf{R}) = E^{(2)} g(\mathbf{R}). \quad (2.53b)$$



It is seen that the Hamiltonian of the equation (2.53a) will completely coincide with the Hamiltonian for the problem of electron motion in Coulomb field, if we substitute the electron mass in equation (2.29) by the reduced mass defined by the equation (2.51). Hence without any additional analysis, we can easily write the equation for the energy spectrum of the hydrogenlike atom, when  $q_a = -|e|$  and  $q_b = Z|e|$

$$E_n^{(1)} = -\frac{Z^2 e^4}{2\hbar^2 n^2} \frac{m_e m_n}{m_n + m_e}, \quad (2.54)$$

where  $m_e$  is the electron mass, and  $m_n$  is the nucleus mass.

### 2.4.3 Atom in trap

In the case of the free atom ( $U(R) = 0$ ) the solutions of the equation (2.53b) are the plain waves  $\psi(\mathbf{R}) = C_{\mathbf{K}} \exp(i\mathbf{K}\mathbf{R})$ . To find the wave function  $\psi(\mathbf{R})$  in the case of trapped atom, we need in the profile of the potential well of atomic trap. In the vicinity of its bottom, the potential energy of the atomic trap can be approximated by the parabolic potential well:

$$U(\mathbf{R}) = U(0) + \alpha R^2.$$

By accounting the spherical symmetry of the problem, the wave function of the equation (2.53b) can be taken in the following form

$$g(\mathbf{R}) = g_l(R) Y_{lm}(\theta_R, \varphi_R),$$

where the radial wave function  $g_l(R)$  obeys the following equation

$$\frac{d^2 g_l}{dR^2} + \frac{2}{R} \frac{dg_l}{dR} + \left( \frac{2ME}{\hbar^2} - \frac{l(l+1)}{R^2} - \left( \frac{M\Omega}{\hbar} \right)^2 R^2 \right) g_l = 0, \quad (2.55)$$

where

$$M = m_a + m_b, \quad \Omega^2 = 2\alpha/M.$$

The solutions of the equation (2.55) are again the confluent hypergeometric functions. By taking into account the boundary conditions that were discussed in the previous section, for eigenfunctions of the equation (2.53b) we get

$$g_{n_R l m}(\mathbf{R}) = \sqrt{\frac{2\beta^{l+3/2} n_R!}{(n_R + l + 1/2)!}} Y_{lm}(\theta_R, \varphi_R) \times \\ \times R^l \exp\left(-\frac{\beta R^2}{2}\right) L_{n_R}^{(l+1/2)}(\beta R^2), \quad (2.56)$$

where  $\beta = M\Omega/\hbar$ , and  $n_R$  is the non-negative integer. The spectrum of the energy eigenvalues is defined by

$$E_{n_R l}^{(2)} = \hbar\Omega \left( 2n_R + l + \frac{3}{2} \right). \quad (2.57)$$

Similarly to the electron motion in the Coulomb field, the spectrum (2.57) is degenerated with respect to the combination of the quantum numbers  $n_R$  and  $l$ . In this case, the combination is the sum of doubled radial quantum number and orbital quantum number,  $p = 2n_R + l$ .

#### 2.4.4 Interaction of trapped atom with electromagnetic field

Let us consider the interaction of the trapped atom with the electromagnetic field. For the hydrogenlike atom, we have  $q_a = -|e|$  and  $q_b = Z|e|$ , and the Hamiltonian of the problem can be written in the form

$$\begin{aligned} H = & \frac{1}{2m_a} \left( \mathbf{p}_a - \frac{q_a}{c} \mathbf{A}(\mathbf{r}_a) \right)^2 + \frac{1}{2m_b} \left( \mathbf{p}_b - \frac{q_b}{c} \mathbf{A}(\mathbf{r}_b) \right)^2 + U(r) + U(R) = \\ & = \frac{\mathbf{p}^2}{2m_r} + \frac{|e|}{c} \left( \frac{1}{m_a} \mathbf{A}(\mathbf{r}_a) + \frac{Z}{m_b} \mathbf{A}(\mathbf{r}_b) \right) \mathbf{p} + U(r) + \\ & + \frac{\mathbf{P}^2}{2(m_a + m_b)} - \frac{|e|}{Mc} (\mathbf{A}(\mathbf{r}_a) - Z\mathbf{A}(\mathbf{r}_b)) \mathbf{P} + U(R) + \\ & + \frac{1}{2c^2} \left( \frac{q_a^2}{m_a} \mathbf{A}^2(\mathbf{r}_a) + \frac{q_b^2}{m_b} \mathbf{A}^2(\mathbf{r}_b) \right). \end{aligned} \quad (2.58)$$

The characteristic spatial width of the potential well of atomic trap is significantly greater than the Bohr radius, i.e.  $\sqrt{\beta}a_B \ll 1$ , and we can use the following expansions

$$\begin{aligned} \mathbf{A}(\mathbf{r}_a) &= \mathbf{A}(\mathbf{R}) + \frac{m_b}{M} (\mathbf{r} \nabla) \mathbf{A}(\mathbf{R}) + \dots, \\ \mathbf{A}(\mathbf{r}_b) &= \mathbf{A}(\mathbf{R}) - \frac{m_a}{M} (\mathbf{r} \nabla) \mathbf{A}(\mathbf{R}) + \dots \end{aligned} \quad (2.59)$$

The leading term of both expansions is

$$\mathbf{A}(\mathbf{r}_{a,b}) \approx \mathbf{A}(\mathbf{R}),$$

Hence, the Hamiltonian (2.58) takes the form

$$\begin{aligned} H = & \frac{\mathbf{p}^2}{2m_r} + U(r) + \frac{|e|}{c} \left( \frac{1}{m_a} + \frac{Z}{m_b} \right) \mathbf{A}(\mathbf{R}) \mathbf{p} + \\ & + \frac{\mathbf{P}^2}{2M} + U(R) + \frac{|e|}{Mc} (1 - Z) \mathbf{A}(\mathbf{R}) \mathbf{P} + \frac{e^2}{2c^2} \left( \frac{1}{m_a} + \frac{Z^2}{m_b} \right) \mathbf{A}^2(\mathbf{R}). \end{aligned} \quad (2.60)$$

The last term in (2.60) is usually omitted, because its mean value over the period of optical oscillations does not depend on the coordinate. Therefore, for the hydrogen atom (when  $Z = 1$ ), we get

$$H = -\frac{\hbar^2}{2m_r}\Delta_r + U(r) + \frac{|e|\hbar}{m_r c}\mathbf{A}(\mathbf{R})\mathbf{p} - \frac{\hbar^2}{2M}\Delta_R + U(R). \quad (2.61)$$

By comparing the equations (2.60) and (2.61) we can see that in hydrogen atom, in contrast to the hydrogenlike ions, the transitions between the trap levels without change in the intra-atomic electron state are prohibited. However it should be noted that the energy distance between the states of atom in the atomic trap  $\hbar\Omega$  is usually much smaller than the energy distance between the different electron states in atom  $\hbar\Omega \ll E_n - E_m$ . Therefore, if the frequency of electromagnetic wave is close to the frequency of the intra-atomic electron transitions  $\omega_{nm} = (E_n - E_m)/\hbar \approx \omega$  and at the same time  $\Omega \ll \omega$ , then the probability of the above mentioned transitions is very low for ions too.

As already mentioned, the angular momenta  $\hbar\mathbf{l}_1 = [\mathbf{r}\mathbf{p}]$  and  $\hbar\mathbf{l}_2 = [\mathbf{R}\mathbf{P}]$  are both the integrals of motion. As a result the wave function of the trapped atom can be written as the following product

$$\psi(\mathbf{r}_a, \mathbf{r}_b, t) = f_{n_1 l_1 m_1}(\mathbf{r}) g_{n_2 l_2 m_2}(\mathbf{R}) \exp\left[-i\frac{E_1 + E_2}{\hbar}t\right],$$

where the values of  $E_{1,2}$  are defined by the equations (2.54) and (2.57), respectively:

$$E_1 = -\frac{Z^2 e^4 m_r}{2\hbar^2 (n_1 + l_1 + 1)^2}, \quad E_2 = \hbar\Omega \left(2n_2 + l_2 + \frac{3}{2}\right).$$

The probability amplitude for the transition between the trapped hydrogen atom states of energy  $E = E_1 + E_2$  and  $E' = E'_1 + E'_2$  is defined, in the frame of the first order approximation, by the following equation

$$a_{E'E}(t) = \frac{|e|\hbar}{m_r c} \langle n'_1 l'_1 m'_1 | \mathbf{p} | n_1 l_1 m_1 \rangle \times \\ \times \int_0^t \langle n'_2 l'_2 m'_2 | \mathbf{A}(\mathbf{R}, t') | n_2 l_2 m_2 \rangle \exp\left[i\frac{E' - E}{\hbar}t'\right] dt'. \quad (2.62)$$

It is convenient to express the matrix elements of the momentum operator in terms of the matrix elements of the coordinate operator. The commutator of the Hamiltonian (2.53a) and operator  $\mathbf{r}$  is

$$[H_{01}, \mathbf{r}] = -\frac{i\hbar}{m_r}\mathbf{p}.$$

Hence

$$\begin{aligned} \langle n'_1 l'_1 m'_1 | H_{01} \mathbf{r} - \mathbf{r} H_{01} | n_1 l_1 m_1 \rangle &= (E'_1 - E_1) \langle n'_1 l'_1 m'_1 | \mathbf{r} | n_1 l_1 m_1 \rangle = \\ &= -\frac{i\hbar}{m_r} \langle n'_1 l'_1 m'_1 | \mathbf{p} | n_1 l_1 m_1 \rangle. \end{aligned}$$

Now, we can use the matrix elements of the coordinate operator, that were calculated in the previous section.

Let atom interact with the plain wave

$$\mathbf{A}(\mathbf{R}, t) = \mathbf{A}_0 \sin(\omega t - \mathbf{kR}).$$

To calculate the matrix elements  $\langle n'_2 l'_2 m'_2 | \mathbf{A}(\mathbf{R}) | n_2 l_2 m_2 \rangle$  we shall use the following expansion of plain wave onto the spherical harmonics

$$\exp(ikZ) = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos \theta) j_l(kr),$$

where  $j_l(x)$  is the spherical Bessel functions. We have assumed that the wave vector  $\mathbf{k}$  of incident wave is directed along the  $z$  axis of the given reference frame. Thus, the required matrix elements are

$$\begin{aligned} \langle n'_2 l'_2 m'_2 | P_l(\cos \theta) j_l(kr) | n_2 l_2 m_2 \rangle &= \\ &= \int Y_{l'_2 m'_2}^*(\theta, \varphi) P_l(\cos \theta) Y_{l_2 m_2}(\theta, \varphi) \sin \theta d\theta d\varphi \times \\ &\times \int R^{l'_2 + l_2} \exp(-\beta R^2) L_{n'_2}^{(l'_2 + 1/2)}(\beta R^2) L_{n_2}^{(l_2 + 1/2)}(\beta R^2) j_l(kR) R^2 dR \end{aligned} \quad (2.63)$$

The first integral in (2.63) results in the following selection rules

$$l'_2 = l_2 + l, \quad m'_2 = m_2.$$

To calculate the second integral in (2.63) we can use the following formula

$$\begin{aligned} \int_0^{\infty} x^{\alpha-1} \exp(-px^2) J_{\nu}(cx) dx &= \\ &= \frac{c^{\nu}}{p^{(\alpha+\nu)/2}} \frac{\Gamma((\alpha+\nu)/2)}{2^{\nu+1} \Gamma(\nu+1)} F\left(\frac{\alpha+\nu}{2}, \nu+1, -\frac{c^2}{4p}\right), \end{aligned}$$

where  $F(a, b, z)$  is the confluent hypergeometric function.

As an example for the matrix elements of the transition between the initial state  $n_2 = 0, l_2 = 0, m_2 = 0$  and final state  $n'_2 = n, l'_2 = l, m'_2 = 0$  we get

$$\begin{aligned} \langle nl0 | \exp(ikZ) | 000 \rangle &= \\ &= \sqrt{\frac{\pi}{2}} \left(l + \frac{1}{2}\right) \frac{n! (n + l + 1/2)!}{(1/2)!} \exp\left(-\frac{k^2}{4\beta}\right) \cdot \left(\frac{k^2}{4\beta}\right)^{l/2} \times \\ &\quad \times \sum_{m=0}^n \frac{(-1)^m}{(n-m)! (l+m+1/2)!} L_m^{(l+1/2)} \left(\frac{k^2}{4\beta}\right). \end{aligned} \quad (2.64)$$

In particular

$$\begin{aligned} |\langle 000 | \exp(ikZ) | 000 \rangle|^2 &= \exp\left(-\frac{k^2}{2\beta}\right), \\ |\langle 010 | \exp(ikZ) | 000 \rangle|^2 &= \frac{k^2}{2\beta} \exp\left(-\frac{k^2}{2\beta}\right), \\ |\langle 100 | \exp(ikZ) | 000 \rangle|^2 &= \frac{1}{6} \left(\frac{k^2}{2\beta}\right)^2 \exp\left(-\frac{k^2}{2\beta}\right), \\ |\langle 110 | \exp(ikZ) | 000 \rangle|^2 &= \frac{1}{10} \left(\frac{k^2}{2\beta}\right)^3 \exp\left(-\frac{k^2}{2\beta}\right). \end{aligned} \quad (2.65)$$

The interpretation of the obtained equations becomes more obvious, if we substitute the parameter  $\beta$  in the last equations by its explicit expression:

$$\frac{k^2}{2\beta} = \frac{(\hbar k)^2}{2M} \frac{1}{\hbar\Omega} = \frac{E_k}{\hbar\Omega}. \quad (2.66)$$

Let atom be initially in the ground trap state. In the process of photon absorption the atom should accept the recoil momentum  $\hbar k$  and, hence, the recoil energy  $E_k = \hbar^2 k^2 / (2M)$ . Thus we can see from the equations (2.65) that the probability of atom transition from the ground to excited trap state, in the process of photon absorption, depends on the ratio of the recoil energy to the energy difference between the trap states.

Notice that the process of the emission or absorption of photons by the trapped atom is similar to the process of emission or absorption of gamma photons by nuclei in crystals (Mossbauer effect). In the latter case the probability of the recoilless emission depends on the ratio of the recoil energy to the phonon energy.

The time integration in the equation (2.62) results in the energy conservation law

$$E'_1 + E'_2 = E_1 + E_2 + \hbar\omega.$$

Thus the equations (2.62)–(2.64) determine completely the selection rules and the probabilities of the radiative transitions for the trapped hydrogen atom. In contrast to hydrogen atom, the hydrogenlike ions ( $Z > 1$ ) can make the transitions between the atomic trap levels without change in the intra-atomic electron state. This type of transitions is described by the two last terms of the Hamiltonian (2.60).

Atomic Spectroscopy

Introduction to the Theory of Hyperfine Structure

Andreev, A.V.

2006, XII, 274 p., Hardcover

ISBN: 978-0-387-25573-6