

Of the sciences which regard nature, it is
the glory of God to conceal the thing, but it
is the glory of the King to find it out.

Roger Bacon, “*The Great Instauration*”

1

Origin of Main Quantum Concepts

Strictly speaking, the title “*Quantum mechanics*” is out of date. Now, it would be more appropriate to speak of unified *quantum theory* that comprehends all sub-fields of exact science, from biophysics to high energy physics and cosmology, and constitutes, on one hand, a foundation of modern scientific *Weltanschauung*, and, on the other hand, a base of current technological progress (computers, quantum electronics, nanotechnology, nuclear and thermonuclear energy, superconductivity and so on). Contrary (or, maybe, owing) to its all-embracing character, quantum theory can be set forth in a pure axiomatic manner, similarly to formal thermodynamics. In this way, one could avoid reproducing the complicated and at times contradictory road of chronological development. However, at the very least, a brief acquaintance with the history of the main ideas of quantum theory is instructive and perhaps necessary.

1.1

Light: Waves or Particles?

The first quantum notions came out of the question of the nature of light.

In the nineteenth century, the *wave theory* dominated the minds of physicists. As early as 1802, *Young* explained the phenomena of optical interference using the principle of *superposition* of waves. With fixed phase relationships between the components, the superposition is *coherent*. This allows one to observe typical interference effects, as in a standard experiment, Figure 1.1, where we see primary and secondary maxima for the light transmitted through two slits.

The wave theory of light was definitively formulated as a consequence of the *Maxwell equations*, 1861. These equations allow for the propagation of electromagnetic waves in empty space (far away from the sources, charges or currents). Since the equations are *linear*, the superposition principle is valid, a sum of two solutions is also a possible solution. The diversity of *interference* and *diffraction* phenomena follows from this principle, along with the laws of light propagation through media (reflection, refraction, dispersion, scattering and so on).

On the other hand, *Newton* adhered to a *corpuscular* viewpoint concerning the nature of light. Apart from simple arguments related to the rectilinear propagation

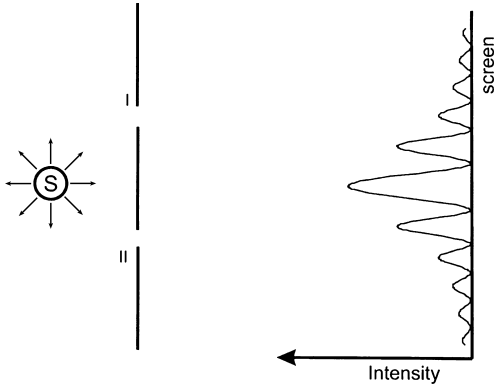


Figure 1.1 Two-slit interference.

of light (*geometric optics*), he was leaning for support on *monistic* concepts of nature: having agreed on the atomistic structure of matter, it would be strange to assume a completely different structure of light; it is much more natural to allow for the existence of the light corpuscles.

1.2

Planck Constant, Beginning of the Quantum Era

Only after two centuries of accumulated experimental knowledge, could this belief be transformed into a scientific hypothesis. First, the atomic structure of matter was strictly proven, then the data related to the black body radiation forced *M. Planck*, 1900, to rediscover the ideas of discreteness of light. Thus, the starting point of quantum physics coincided with the beginning of the twentieth century.

It is known that the electromagnetic field in a cavity can be represented by a set of harmonic oscillators for various frequencies that are present in the spectrum of the field. Planck showed that the correct (observed) distribution of energy in the spectrum of such equilibrium (“*black*”) radiation cannot be obtained in keeping with the view that the field oscillators gain and lose energy in a continuous way. It is necessary to accept that, for each oscillator of frequency ν , radiation and absorption processes can proceed only through *discrete* steps characterized by energy portions $\Delta E = h\nu$, where h – a new fundamental constant, *Planck constant* – is the *quantum of action*,

$$h = 6.6262 \cdot 10^{-34} \text{ J s} = 6.6262 \cdot 10^{-27} \text{ erg s} . \quad (1.1)$$

In classical mechanics, the action is the integral $\int \mathcal{L} dt$ of the Lagrangian \mathcal{L} along the trajectory of the system; it has dimension [energy \times time = momentum \times length], the same as angular momentum. The *quantization* of action will allow us later to bridge the gap between classical and quantum theory.

It is often more convenient to use the *cyclic frequency* $\omega = 2\pi\nu$ and write $h\nu = \hbar\omega$, where

$$\hbar = \frac{h}{2\pi} = 1.0546 \cdot 10^{-27} \text{ erg s} . \quad (1.2)$$

In quantum physics, the most appropriate energy unit is *electron-Volt*; with the elementary charge $e = 4.8032 \cdot 10^{-10}$ abs. units,

$$1 \text{ eV} = 1.6022 \cdot 10^{-19} \text{ C V} = 1.6022 \cdot 10^{-12} \text{ erg} . \quad (1.3)$$

In nuclear and particle physics, one uses prefixes *kilo*, *Mega*, *Giga*, *Tera*: $1 \text{ keV} = 10^3 \text{ eV}$, $1 \text{ MeV} = 10^6 \text{ eV}$, $1 \text{ GeV} = 10^9 \text{ eV}$, $1 \text{ TeV} = 10^{12} \text{ eV}$ (the same prefixes are used for quantifying the computer memory). To facilitate future estimates of the order of magnitude of physical quantities, we can notice that in many cases it is sufficient to combine the Planck constant with the speed of light c and remember that

$$\hbar c \approx 200 \text{ MeV fm} , \quad 1 \text{ fm} = 10^{-13} \text{ cm} = 10^{-15} \text{ m} . \quad (1.4)$$

We can use the following preliminary picture: the radiation field “consists” of elementary units, *quanta*, whereas the energy of each individual oscillator mode with frequency ω , $E = n\hbar\omega$ is defined by an integer number of quanta, n , each of them carrying the amount of energy $\hbar\omega$. It is unclear at this stage if this picture can be extended to other physical systems, are these quanta localized in space, and so on.

1.3 Photons

The next important step was made by *A. Einstein, 1905*. He showed that if we consider the equilibrium radiation as a gas of particles with energy $E = \hbar\omega$ and momentum $p = E/c = \hbar k$ where the wave vector $k = \omega/c$, the Planck formula for entropy of black radiation can be, at least for sufficiently large ω , derived in the same way as it is done for “normal” particles in the kinetic theory of gases. Empirical regularities of the *photoelectric effect* (knock-out of electrons from metals by the light, Figure 1.2), as, for example, the fact that by changing the light intensity we do not change the energy of knocked-out electrons, but just proportionally change their number, immediately follow from simple conservation laws of energy and momentum in every act of absorption or emission of the quantum.

Each metal is characterized by its *work function*, W , the minimum energy one needs to supply in order to knock out an electron from a solid which is an analog of the *ionization potential* in atoms or *separation energy* in nuclei. If an individual light quantum of frequency ω is absorbed by an electron in a metal, the maximum kinetic energy of the emitted electron is

$$K_{\max} = \hbar\omega - W , \quad (1.5)$$

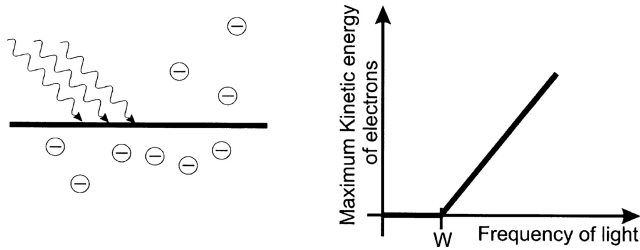


Figure 1.2 Photoelectric effect.

being fully determined by the elementary act of interaction rather than by the light intensity. The experimental confirmation of this relation (*Millikan, 1915*) was in fact one of the first direct measurements of the Planck constant.

Thus, we have a new elementary object – a light quantum, *photon* (the name was introduced much later). On the other hand, according to the relativity theory, energy E and momentum p of any free particle are related as

$$E^2 = c^2 p^2 + (mc^2)^2. \quad (1.6)$$

The validity of this rule when applied to the photon was tested in experiments on scattering of electromagnetic waves off electrons. The experiments (*Compton, 1923*) have shown that the photon behaves as a particle with $m = 0$ and $E = cp$. The experimental result agrees with the equation

$$\Delta\lambda = 4\pi \frac{\hbar}{mc} \sin^2\left(\frac{\theta}{2}\right) \quad (1.7)$$

for the increase of the wavelength of the photon, $\lambda = 2\pi c/\omega$, and therefore reduction of its frequency and energy, in the process of scattering by angle θ off a particle of mass m originally at rest, Figure 1.3. Equation (1.7) is a direct consequence of the relation $E = \hbar\omega$ and conservation laws of energy and momentum.

Problem 1.1

Derive (1.7); estimate the photon wavelength necessary for the measurement of the Compton effect with electrons.

Problem 1.2

A direct test of corpuscular properties of light can be performed with measuring the recoil of radiating atoms. In the experiment of *Frisch, 1933*, sodium atoms radiated light of the wavelength $\lambda = 589$ nm. Estimate the velocity of recoil atoms.

The result (1.7) obviously cannot be derived from classical equations that do not contain the Planck constant. By combining this knowledge with previous ideas, we see that light in different experimental conditions may reveal features of *both waves*

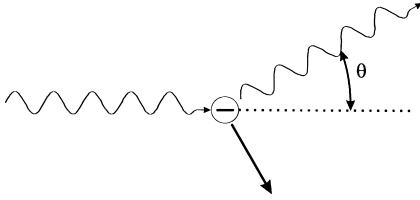


Figure 1.3 Compton effect.

and particles. The wave aspects follow from the Maxwell equations. The corpuscular effects demonstrate that the field not only carries energy and momentum, but in exchanging those with matter, behaves as a set of discrete projectiles. The dictionary for connecting between the corpuscular (energy and momentum) and wave (frequency and wave vector) languages reads, as we repeat here,

$$E = \hbar\omega; \quad \mathbf{p} = \hbar\mathbf{k}, \quad (1.8)$$

or, for the wavelength,

$$\lambda = \frac{c}{\nu} = \frac{2\pi c}{\omega} = \frac{2\pi}{k}; \quad (1.9)$$

frequently it is convenient to introduce

$$\bar{\lambda} = \frac{\lambda}{2\pi} = \frac{1}{k} = \frac{\hbar}{p}. \quad (1.10)$$

Thus, the Planck constant turns out to be just a *scale coefficient* to be applied in translating between the two languages.

1.4 Spectroscopy and Stability of Atoms

In the beginning of the twentieth century, physicists had already determined that matter has discrete atomic and molecular structure since the existence of elementary carriers of electric charge – electrons – and of neutral atoms as well as molecules composed of atoms had been firmly established. It was observed that an electron beam (*cathode rays*) in electromagnetic fields obeys classical rules of motion. However, this could not be the case for electrons localized in a finite spatial region, such as an atom of size 10^{-8} cm. The *Rutherford experiments* in 1911 discovered the presence of the heavy nucleus with the positive charge compensating the total electron charge, though having a very small size, $\sim 10^{-13}$ cm \equiv 1 fm. Classical physics was helpless in attempts to explain the stability of atoms. Any system of charges coupled only by *electrostatic* forces is unstable (*Earnshaw theorem*). An idea of a *dynamical* atomic structure analogous to a planetary system encounters an objection that the electrons moving along a Coulomb orbit (as in the *Kepler problem*

with gravitational forces) radiate energy as any accelerated charges. As a result of radiation, the electrons must lose their energy and eventually fall onto the nuclear center.

The atomic spectroscopy provided a key for solving this puzzle. Emission and absorption spectra of vapors of various chemical elements, in fact of individual atoms, display the groups of very narrow *spectral lines* characteristic for a given element and corresponding to discrete wavelengths. The empirical treatment of an enormous amount of spectroscopic data lead to the *Ritz combination principle*: for a given element, the observed values λ of the wavelengths can be expressed through differences of the *spectral terms* T_n labeled by *integer numbers* n' and n ,

$$\frac{1}{\lambda} = T_{n'} - T_n . \quad (1.11)$$

For example, the hydrogen atom produces the series of close wavelengths described by the *Balmer formula*

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) , \quad (1.12)$$

where the *Rydberg constant* is $R_H = 109\,678 \text{ cm}^{-1}$. Regularities (1.11) were found in many cases with the scale (analog of the coefficient R_H) increasing for heavier elements. The combination principle (1.11) differs from the typical rules known for classical radiators. A radiating vibrator (antenna) emits the wavelengths corresponding to the main vibrational frequency ω_0 and its overtones $n\omega_0$. In the planetary model of the atom, the frequency ω_0 would be the orbital revolution frequency.

1.5

Bohr Postulates

A revolutionary step that laid the foundation of quantum theory was made by *N. Bohr, 1913*. The Bohr postulates allowed one to build an atomic model that provided a way to explain the main empirical facts. The postulates, which can be seen as an embryonic formulation of future quantum mechanics, appeared alien in the context of classical physics.

According to Bohr, the atom (for simplicity, we have in mind the hydrogen atom, consisting of a heavy positively charged proton set at the origin and the electron on a bound orbit) is indeed reminiscent of the solar system. However, among all classical orbits, there exist special *stationary states* where the electron can move without radiating. The same should be valid for any classical system performing *finite periodic* motion. The stable orbits form a *discrete set (quantization)*. Referring to the quantum of action h , Bohr postulated that the orbits are singled out to be stable if their classical action over the period (recall classical mechanics, for example, [1, Section 49]) is equal to an integer number of quanta,

$$\oint p dq = nh = 2\pi n\hbar , \quad n = 1, 2, \dots \quad (1.13)$$

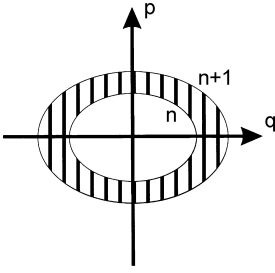


Figure 1.4 Quantization in phase space.

Note that for a circular orbit of radius r and constant speed v , this condition is equivalent to the quantization of the orbital momentum l :

$$p = mv, \quad \oint p dq = 2\pi r \rightarrow l = mvr = n\hbar. \quad (1.14)$$

Here, for the first time, a *quantum number* n emerges as a label of a stationary quantum state.

The *phase integral* $\oint p dq$, where p and q are *canonically conjugate* momentum and coordinate, respectively, is taken over the period of motion along the closed classical trajectory with given energy E . This integral is equal to the area of the phase space (p, q) enclosed by the trajectory, Figure 1.4. It is known from classical mechanics [1] that this quantity is an *adiabatic invariant*. If the parameters of the system are slowly (*adiabatically*) being changed, the adiabatic invariant stays constant. More precisely, it changes, though much slower than the external conditions; typically, if τ is the characteristic time of change of the parameters ($\tau \gg T$, where T is the period of motion), the change of the adiabatic invariant is proportional to $\exp(-\tau/T)$. Only such classical quantities can be quantized; otherwise, the condition (1.13) would be contradictory: a slow change of characteristics would not change the left-hand side, but cause a sudden jump of the quantum number in the right-hand side that can take only discrete values. Opposite to that, we see that by changing the parameters of the adiabatic invariant we do not change its discrete label n and the classification of quantized levels is stable.

Problem 1.3

Consider a particle performing small oscillations around the equilibrium point under the action of an elastic force, $F = -\kappa x$, where the coordinate x measures the deviation from the equilibrium. Such a *linear harmonic oscillator* system is classically described by the *Hamilton function*, in this case just as a sum of kinetic and potential energy,

$$H = K(p) + U(x) = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2. \quad (1.15)$$

Show that the quantized energy levels E_n form, according to the rule (1.13), the *equidistant spectrum*,

$$E_n = n\hbar\omega, \quad \omega = \sqrt{\frac{\kappa}{m}}. \quad (1.16)$$

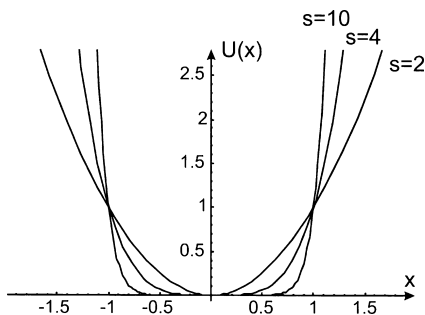


Figure 1.5 Potentials $U \sim |x|^s$.

Solution For a symmetric potential, $U(x) = U(-x)$, Figure 1.5, the quantization condition (1.13) takes the form

$$4 \int_0^{x_n} dx \sqrt{2m[E - U(x)]} = 2\pi n\hbar, \quad (1.17)$$

where x_n is the energy-dependent classical *turning point*, $U(x_n) = E$. To calculate this integral, introduce the variable $\gamma(x) = U(x)/E$. This leads to the integral $\int_0^1 d\gamma$ in fixed limits. Since $dx/d\gamma \propto 1/\sqrt{\gamma}$, we make a substitution $\gamma = \sin^2 \xi$ and come to the elementary integral $\int_0^{\pi/2} d\xi \cos^2 \xi = \pi/4$. In the case of the harmonic oscillator, one can avoid calculations, noticing that for the harmonic oscillator, the area inside the closed orbit of given energy E in the phase space (p, x) is an ellipse $x^2/a^2 + p^2/b^2 = 1$ with semi-axes $a = \sqrt{2E/m\omega^2}$ and $b = \sqrt{2mE}$. The area of the ellipse gives, $I = \pi ab = 2\pi E/\omega$. The amplitude of the oscillations with given energy is $A_n = \sqrt{n(2\hbar/m\omega)}$.

The Bohr postulate agrees with our dictionary (1.8). If a free electromagnetic field can be considered as a set of independent oscillator modes of different frequencies, the quantization (1.16) can be interpreted as ascribing a certain number of quanta of corresponding frequency to each stationary state of a given mode. This number is given by the integer n in the quantization postulate. The exact quantum-mechanical result for the harmonic oscillator is, as we will see in Chapter 11,

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right). \quad (1.18)$$

The lowest possible *ground state*, $n = 0$, no longer corresponds to $E = 0$, as it would be for a classical particle at rest in the equilibrium point. The *zero point vibrations* carry energy $\hbar\omega/2$. In the case of electromagnetic field, this shows that even the state with no photons, the *vacuum state*, has energy due to *quantum fluctuations*. The original form (1.13) of the quantization principle is approximately right for highly excited states, $n \gg 1$.

Problem 1.4

What is the n -dependence of the energy of the n -th level, E_n , for $n \gg 1$ in the potential field $U(x) = \alpha|x|^s$?

Solution With the same method as for Problem 1.3, we obtain the phase integral $\propto E^{(2+s)/2s}$ and

$$E_n \propto n^{2s/(2+s)}. \quad (1.19)$$

Important particular cases: $E_n \propto n$ (harmonic oscillator, $s = 2$ as in Problem 1.3); $E_n \propto n^{4/3}$ (quartic potential, $s = 4$), Figure 1.5; $E_n \propto n^2$ (potential box with vertical walls, Section 3.1, $s \rightarrow \infty$); $E_n \propto 1/n^2$ (Coulomb case, (1.26) below).

The *second Bohr postulate* is essentially a quantum formulation of the energy conservation in radiative transitions. The acts of emission and absorption of light proceed as transitions between the initial i and final f stationary states of the atom. Since the photon carries the energy $\hbar\omega$, the energy conservation law takes the form

$$E_f - E_i = \pm\hbar\omega, \quad (1.20)$$

where plus and minus correspond to absorption $E_f > E_i$ and emission $E_f < E_i$, respectively. The possibility of emission means that the discrete states found ignoring the possibility of radiation are in fact *quasistationary*, they have *finite lifetime*. But the quantization neglecting the radiation is still meaningful as long as the lifetime is much longer than the period of motion.

1.6**Hydrogen Atom**

Now, we apply the Bohr quantization to the hydrogen atom, Figure 1.6, a system of the heavy proton (charge $+e$) fixed at the origin and the electron (charge $-e$, mass m) on a bound Coulomb orbit, for simplicity, assumed to be circular. For an orbit of radius r and speed v , the acting force is, according to Newtonian mechanics,

$$F = \frac{e^2}{r^2} = \frac{mv^2}{r}. \quad (1.21)$$

The total electron energy, a sum of kinetic K and potential U parts, is *negative* in the bound state,

$$E = K + U = \frac{mv^2}{2} - \frac{e^2}{r} = -\frac{e^2}{2r} = \frac{U}{2}. \quad (1.22)$$

The quantization (1.13) can be written by virtue of (1.21) as

$$n^2\hbar^2 = (mvr)^2 = mre^2. \quad (1.23)$$

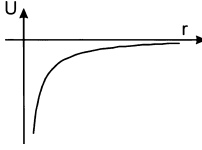


Figure 1.6 Attractive Coulomb potential.

This determines the radii of the stable orbits

$$r_n = \frac{\hbar^2}{m e^2} n^2 \equiv a n^2, \quad (1.24)$$

where the *Bohr radius* of the lowest hydrogen orbit is

$$a = \frac{\hbar^2}{m e^2} = 0.529 \text{ \AA} = 0.529 \cdot 10^{-8} \text{ cm} = 0.0529 \text{ nm}. \quad (1.25)$$

For large quantum numbers $n \gg 1$, the radius (1.24) becomes macroscopic, $R_n \approx 0.5 \text{ cm}$ for $n = 10^4$.

Equations (1.22), (1.24) and (1.25) determine the energies of stationary orbits (*energy levels* of the hydrogen atom),

$$E_n = -\frac{e^2}{2r_n} = -\frac{1}{2n^2} \frac{m e^4}{\hbar^2}. \quad (1.26)$$

The energy of the ground state $n = 1$, that is, with the reversed sign, the ionization energy of the hydrogen atom, equals

$$E_{\text{ion}} = -E_1 = \frac{m e^4}{2\hbar^2} \equiv 1 \text{ Ry} = 13.6 \text{ eV}. \quad (1.27)$$

It might be convenient to use a set of the so-called *atomic units* (a.u.) where $m = e = \hbar = 1$ and the atomic unit, a.u., for energy (sometimes called 1 Hartree) is 2 Ry (Rydberg), so that in the hydrogen atom $E_n = -1/(2n^2)$ a.u.

The characteristic energies in the hydrogen atom are small compared to the electron mass:

$$E_{\text{ion}} = \frac{1}{2} m c^2 \frac{e^4}{\hbar^2 c^2} \equiv \frac{1}{2} \alpha^2 m c^2 \ll m c^2, \quad (1.28)$$

where we used the dimensionless *fine structure constant*

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.06}. \quad (1.29)$$

Therefore, in atomic physics, relativistic effects are usually small. They however grow in heavy atoms. Going back to (1.21), it is easy to see that for a nucleus of charge Ze instead of the proton, we would have to substitute $e^2 \Rightarrow Ze^2$ in all equations. In (1.28), α would then be replaced by αZ which can be close to 1 for large Z . The estimate for the speed of the electron on the n -th orbit gives, according to (1.23) and (1.24),

$$v_n = \frac{Z e^2}{n \hbar} = c \frac{Z \alpha}{n}, \quad (1.30)$$

that is, $(v/c) \ll 1$, except for the heaviest atoms and decreases for remote orbits. Note that in atomic units $c = 1/\alpha \approx 137$.

Problem 1.5

For the lowest electron orbit in the hydrogen atom,

- estimate the magnitude of the electric field of the nucleus at the orbit (in V/cm);
- estimate the magnitude of the magnetic field created at the nucleus by the orbital motion of the electron (in Tesla);
- compare the Coulomb and gravitational forces between the electron and the proton.

Solution

- The electric field at the orbit can be expressed in terms of the ground state energy,

$$\mathcal{E} = \frac{e}{a^2} = \frac{2|E_{\text{g.s.}}|}{ea} = 5.14 \cdot 10^9 \text{ V/cm} = 1.7 \cdot 10^7 \text{ abs. unit/cm} , \quad (1.31)$$

where $|E_{\text{g.s.}}| = 13.6 \text{ eV}$, (1.27).

- The magnetic field of the linear element $d\mathbf{l}$ that carries the electric current I is given by the *Biot-Savart law*,

$$\mathbf{B} = \frac{I}{cR^3}[d\mathbf{l} \times \mathbf{R}] , \quad (1.32)$$

where \mathbf{R} is the distance from the current element to the observation point. An electron on the orbit of radius r with the period of motion T produces the current

$$I = \frac{e}{T} = \frac{ev}{2\pi r} . \quad (1.33)$$

By integrating (1.32) over this orbit, we obtain the magnetic field in the center of the orbit

$$B = \frac{2\pi I}{cr} = \frac{ev}{cr^2} . \quad (1.34)$$

For the ground state orbit, this gives:

$$r = a , \quad v = \frac{\hbar}{ma} , \quad B = \frac{m^2 e^7}{c\hbar^5} . \quad (1.35)$$

By introducing the fine structure constant (1.29), for the magnetic field (1.35) we obtain

$$B = \alpha\mathcal{E} = 1.3 \cdot 10^5 \text{ Gs} = 13 \text{ T} . \quad (1.36)$$

c) The ratio of forces equals

$$\frac{F_{\text{Coulomb}}}{F_{\text{grav}}} = \frac{e^2}{G m M} = 2.3 \times 10^{39}, \quad (1.37)$$

where

$$G = 6.67 \cdot 10^{-8} \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-2} \quad (1.38)$$

is the Newton gravitational constant, and m and M are masses of the electron and proton, respectively.

For future estimates, it is useful to note that the fine structure constant (1.29) defines a step in a sequence of lengths serving as milestones on the way into the depth of matter. The next stop after the Bohr radius (1.25) occurs at the *Compton wavelength*

$$\lambda_C = \alpha a = \frac{\hbar}{mc} = 3.862 \cdot 10^{-11} \text{ cm}, \quad (1.39)$$

where the mass numerical value is given for the electron. We already encountered this length in (1.7) for the Compton effect. Later, we will see in (5.85) that this length determines the best localization of a particle of mass m allowed by quantum theory and relativity. Going even further, we come to the *classical electron radius* that does not contain the Planck constant,

$$r_e = \alpha \lambda_C = \alpha^2 a = \frac{e^2}{mc^2} = 2.818 \cdot 10^{-13} \text{ cm}. \quad (1.40)$$

This quantity determines the limit of validity of classical electrodynamics; at smaller distances, the electrostatic energy e^2/r of the electron considered as a classical point charge would exceed its total mass.

After establishing a set of stationary orbits, we can apply the second Bohr postulate (1.20) and find the spectrum of radiation emitted by the atom in the transition between the orbits $n \rightarrow n'$, $n' < n$,

$$\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar}. \quad (1.41)$$

For the hydrogen atom, (1.26) and (1.41) give

$$\omega_{nn'} = \frac{me^4}{2\hbar^3} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right), \quad (1.42)$$

or, turning to the wavelengths,

$$\frac{1}{\lambda_{nn'}} = \frac{\omega_{nn'}}{2\pi c} = \frac{me^4}{4\pi c \hbar^3} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \quad (1.43)$$

This is nothing but the combination principle (1.11) with the prediction of the value for the Rydberg constant (1.12) denoted here as R_∞ ,

$$R_\infty = \frac{m e^4}{4\pi c \hbar^3} = 109\,737 \text{ cm}^{-1}. \quad (1.44)$$

With a classical expression for the intensity of radiation of the charged particle, $|dE/dt| \sim (e^2/c^3)(\text{acceleration})^2$, we can roughly estimate the lifetime of the electron on an excited orbit, for example for the transition ($n = 2$) \rightarrow ($n = 1$): the energy $\hbar\omega_{21}$ will be radiated during $\tau \sim (\hbar/mc^2)(1/\alpha^5)$. Since the period of classical rotation on the orbit is $T \propto (r_2/v_2)$, we obtain $T \sim (\hbar/mc^2)(1/\alpha^2)$. This means that $\tau/T \sim (1/\alpha^3) \sim 10^6$, the excited states are long-lived, *quasistationary*. The ground state is stable, contrary to classical images.

Problem 1.6

Show that the difference between R_∞ and the experimental value R_H , (1.12), is due to the assumption of the infinitely heavy nucleus, and taking into account a finite proton mass (nuclear *recoil*), we remove this discrepancy. Compare the atomic levels of the three isotopes: hydrogen, deuterium and tritium.

Solution The correct mass in the description of *relative motion* of the electron, mass m_e , and the nucleus, mass M , should be the *reduced mass*,

$$m \Rightarrow \mu = \frac{m_e M}{m_e + M}. \quad (1.45)$$

The idea that the ratio m_e/m_p can change with time on an astronomical scale is currently under discussion. This could be possibly discovered by precisely measuring the spectra of remote (old) stars.

The Bohr atom has an infinite sequence of bound states that becomes infinitely dense and converges from below to $E = 0$, with the *threshold* of unbound states corresponding to classical *infinite* motion. At $E > 0$, there is no analog of the

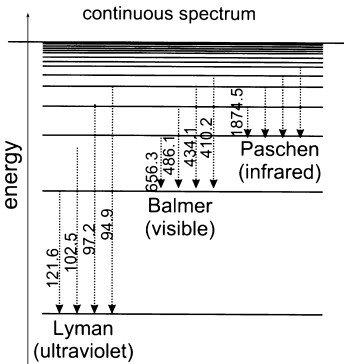


Figure 1.7 Spectrum of the Bohr atom.

Bohr postulate that would select quantized trajectories as all values of energy are allowed (*continuous spectrum*). Figure 1.7 shows the scheme of the low-lying energy spectrum. Since the spacings between the levels with adjacent values of n rapidly decrease as n increases, all spectral lines corresponding to the transitions from different initial states n to the same final state n' turn out to be close. They can be combined in the *spectral series* labeled by the quantum number n' . Historically, the series carry the personal names: $n' = 1$ – *Lyman series*, ultraviolet radiation with the largest wave length 1216 Å for the transition from $n = 2$; $n' = 2$ – *Balmer series*, visible light, and so on; observable lines with $n' > 2$ correspond to infrared radiation.

Problem 1.7

Many *hydrogen-like* systems exist where we can apply the same approach. Find the ground state energy and the largest Lyman-like wavelength of radiation for *positronium* (bound state of the electron and the *positron* that is the *antiparticle* of the electron with the same mass and the charge $+e$); *kaonic* and *pionic* mesoatoms [the nucleus of charge $+Ze$ and negatively charged kaons, $m(K^-) = 494 \text{ MeV}/c^2$, and pions, $m(\pi^-) = 140 \text{ MeV}/c^2$]; muonic atom [the nucleus of charge Ze and the negatively charged muon, a heavy analog of the electron, $m(\mu^-) = 106 \text{ MeV}/c^2$]; *protonium* (proton and antiproton).

Problem 1.8

In metals and plasmas with the presence of mobile electrons, the charge of a positively charged center (ion in plasmas or impurity in solids) is *screened* by the redistribution of the electrons. As a result, the electrostatic potential of the center ceases to be long-ranged and drops exponentially,

$$U(r) = -Ze^2 \frac{e^{-\mu r}}{r}, \quad (1.46)$$

where μ grows, and the attraction range, *Debye radius* $r_D = 1/\mu$, shrinks as the density of free electrons increases. A similar *Yukawa potential* arises in nuclear physics describing the interaction between the nucleons via exchange by mesons. In this case, instead of Ze^2 , one has a *coupling constant* f^2 and the radius $1/\mu$ is the Compton wavelength of the meson of mass M , $1/\mu = \hbar/Mc$. Show with the aid of the Bohr quantization that the exponentially screened potential has only a *finite* number of bound states. Estimate this number in terms of parameters f, μ and the mass m of the particle moving in this potential. This finiteness explains a gradual disappearance of spectral lines in plasmas as the density of free electrons grows.

Solution The quantization rule gives

$$Ze^2 m \mu \left(1 + \frac{1}{\mu r} \right) r^2 e^{-\mu r} = n^2 \hbar^2. \quad (1.47)$$

The left-hand side of (1.47) exponentially falls off for large distances, $\mu r \gg 1$. Therefore, there is no solutions for large values of n and the number of bound

states should be finite. The maximum allowed radius can be found from the maximum of the left-hand side that is given by the positive root of the equation

$$r^2 - \frac{r}{\mu} - \frac{1}{\mu^2} = 0 \rightsquigarrow r = \frac{1 + \sqrt{5}}{2\mu} . \quad (1.48)$$

Of course, one could guess with no calculations that the maximum radius of the orbit should be of the order $r_D = 1/\mu$. The maximum quantum number corresponding to the number of levels supported by the screened potential is now determined from

$$n_{\max}^2 \approx \frac{(3 + \sqrt{5})(1 + \sqrt{5})}{4} e^{-(1+\sqrt{5})/2} \frac{mZe^2}{\mu\hbar^2} \approx 0.84 \frac{r_D}{a} Z , \quad (1.49)$$

where $a/Z = \hbar^2/(me^2Z)$ is the Bohr radius of the lowest bound orbit in the pure Coulomb potential of the charge Z . Although the semiclassical quantization (1.13) is usually not accurate for the lowest orbit, nevertheless, we get a reasonable estimate that for a very low value of the Debye radius, $r_D < a/Z$, the screened potential does not support bound states, $n_{\max} < 1$.

In the Yukawa-type potential,

$$U(r) = -\frac{f^2}{r} e^{-(Mc/\hbar)r} , \quad (1.50)$$

the squared coupling constant f^2 has a dimension [energy · distance]. The meson exchange, according to the previous results, does not create a bound state of two particles, if the attraction is too weak, $(f^2/\hbar c) < 1.19(M/m)$ where m is the reduced mass of the interacting particles. This result is quite close to the exact one, $f_{\text{crit}}^2/(\hbar c) = 0.84(M/m)$, that can be obtained with the aid of a numerical solution of the full quantum Schrödinger equation for the Yukawa potential.

1.7

Correspondence Principle

The Bohr postulates give an *exact* result for the hydrogen atom (in the non-relativistic approximation). This is a lucky feature of the Coulomb potential. In general, by applying the same quantization, we obtain only an approximate solution. There remains also an uncertainty concerning the possibility to have the solution with $n = 0$. Being formally allowed, it would give the fall on the center ($l = 0$ according to (1.14)).

The Bohr theory was improved and refined by A. *Sommerfeld*. The orbital momentum and elliptical orbits were more consistently included in the formalism. This implies the presence of additional quantum numbers characterizing a shape of a stationary orbit. Apart from the *main quantum number* n , the orbit should be labeled by the quantum number l of *orbital momentum*, $l = 0, 1, \dots, n - 1$, and

the *magnetic quantum number* m that describes the orientation of the orbit in space. The level energy cannot depend on the orientation. Therefore, all sublevels with different m have the same energy (*degeneracy*). In addition, as a specific property of the Coulomb potential, the energy does not depend on l for given n . This so-called *accidental degeneracy* will be discussed within Chapters 7 and 18. The orbits with various values of l and fixed n form *atomic shells*. Explanation of the periodic table of chemical elements was a base for the main achievement of “*old quantum theory*”. By accounting for relativistic corrections, one was able to describe more details of atomic spectra.

The discreteness of atomic states was directly demonstrated in the experiments by *Franck and Hertz, 1913*. They observed minima of the electron current through a gas at such values of the accelerating potential which correspond to the electron energies sufficient for the excitation of quantized atomic states in the processes of electron-atom collisions. Thus, there was no doubt that the quantum theory caught up with some deep properties of nature. However, this was still not a consistent logical theory.

Starting with classical laws of motion and imposing the quantization rules, one should expect that under some conditions, the theory has to reproduce all classical results when the quantization does not influence the observables. Characteristic of science, the new development does not cancel old results, but just limits their domain of validity. Classical science (mechanics and electrodynamics) had to become a particular limiting case of more general theory. The requirement that quantum approach has to confirm correct classical results was one of the main criterion used by Bohr. This is his famous *correspondence principle*. In spite of all shortcomings of old quantum theory, this principle is satisfied. There exists an intermediate, *semi-classical* or *quasiclassical* domain where quantum conclusions gradually become indistinguishable from classical ones.

Consider highly excited Bohr orbits, $n \gg 1$. The orbit radii r_n rapidly grow with n and reach macroscopic values. Such *Rydberg orbits* are used, for example, in physics of mesoatoms, Problem 1.7. The pions born in particle or nuclear reactions with high energy are slowed down in a medium and can be captured on one of the Rydberg orbits with a large n . Then, they emit a cascade of photons and descend to the ground or one of the lowest states. At distances corresponding to large n , we can expect the validity of classical mechanics. If this is the case, the combination principle for radiation should be governed by classical rules.

A classical charge in periodic motion with frequency ω_0 radiates electromagnetic waves of the same frequency or its overtones, $\Delta n \cdot \omega_0$, with an integer Δn . This seemingly has nothing in common with the combination principle (1.12). However, under semiclassical conditions, the transitions satisfy

$$n \gg 1, \quad n' \gg 1, \quad \frac{n - n'}{n} \equiv \frac{\Delta n}{n} \ll 1. \quad (1.51)$$

Then, the quantum radiation frequency (1.42) can be approximately written as

$$\omega_{nn'} = \frac{me^4}{2\hbar^3} \frac{n^2 - n'^2}{(nn')^2} \approx \frac{me^4}{\hbar^3 n^3} \Delta n. \quad (1.52)$$

For the same region (1.51), the classical revolution frequency is

$$\Omega_n = \frac{v_n}{r_n} = \frac{m e^4}{\hbar^3 n^3} . \quad (1.53)$$

Thus, indeed in the semiclassical region the radiation frequency is a multiple of the revolution frequency,

$$\omega_{\text{rad}} = \Delta n \cdot \Omega_n . \quad (1.54)$$

This particular example confirms the general scientific rule that a more advanced theory should contain the previous results of a less general theory as a specific case valid under certain conditions.

Now, we can extend this result for motion in any binding potential. Taking the derivative of the equation that connects energy E_n and the classical momentum $p_n(x)$ along the same trajectory,

$$E_n = \frac{p_n^2(x)}{2m} + U(x) , \quad (1.55)$$

we find the Hamilton equation,

$$dE_n = \frac{p_n}{m} dp_n = v_n dp_n . \quad (1.56)$$

Consider the action integral taken from the turning point a_n to an arbitrary point x inside the potential. In the semiclassical region (1.51), this is a smooth function of n . To calculate its derivative with respect to n , one needs to only differentiate the integrand rather than the limits of the integral since the integrand $p_n(x)$ vanishes at the turning point:

$$\int_{a_n}^x dx \frac{\partial p_n(x)}{\partial n} = \int_{a_n}^x dx \frac{\partial p_n}{\partial E_n} \frac{\partial E_n}{\partial n} = \Delta_n \int_{a_n}^x \frac{dx}{v_n} = \Delta_n t_n(x) . \quad (1.57)$$

Here, we introduced $t_n(x)$ as a duration of classical motion with energy E_n from a_n to x and the distance between the neighboring levels

$$\Delta_n = E_n - E_{n-1} \approx \frac{dE_n}{dn} . \quad (1.58)$$

In order to find Δ_n , we differentiate the quantization condition (1.13):

$$\pi \hbar = \frac{\partial}{\partial n} \int_{a_n}^{b_n} p_n dx . \quad (1.59)$$

Similarly to (1.57), we obtain

$$\pi \hbar = \Delta_n \int_{a_n}^{b_n} \frac{dx}{v_n} , \quad (1.60)$$

which gives one half of the total period T_n of motion,

$$\pi\hbar = \Delta_n \frac{T_n}{2} = \Delta_n \frac{\pi}{\Omega_n}, \quad (1.61)$$

or, finally,

$$\Delta_n = \hbar\Omega_n. \quad (1.62)$$

For the harmonic oscillator, according to (1.16), $\Omega_n = \omega$ does not depend on the quantum number n (in classical mechanics, the period does not depend on the amplitude).

We came to a more specific form of the *correspondence principle*. The level spacing between the nearest semiclassical levels (divided by \hbar) is equal to the classical frequency of periodic motion with the same energy. In each small interval, the semiclassical spectrum of bound states is approximately equidistant as for a harmonic oscillator with frequency ω smoothly changing from one interval to another one. As discussed earlier, this is necessary in order to get a correct transition to the classical radiation theory: the frequency spectrum (1.54) of the semiclassical system contains the main revolution frequency and multiple harmonics, as it would be for a classical vibrator.

1.8

Spatial Quantization

The quantization rule cannot be limited to the bound states in the Coulomb field as it has a general character. Thus, the *magnetic moment* of an electron has to be quantized. A classical bound electron orbit is a spire carrying the electric current $I = e/T$, where T is the revolution period, $T = 2\pi/\omega$. Such a spire possesses a magnetic moment $\mu = IA/c$ where the area \mathcal{A} of the (elliptical) orbit is

$$\mathcal{A} = \int_0^{2\pi} d\varphi \frac{r^2}{2} = \frac{1}{2} \int_0^T dt r^2 \frac{d\varphi}{dt} = \frac{1}{2} \int_0^T dt r^2 \omega = \frac{1}{2m} \int_0^T l dt = \frac{lT}{2m}, \quad (1.63)$$

where l is the conserved orbital momentum quantized according to (1.14). Therefore, we obtain the quantization of the magnetic moment:

$$\mu = \frac{e}{cT} \frac{lT}{2m} = \frac{el}{2mc} = \frac{e\hbar}{2mc} n, \quad (1.64)$$

where we predict the value of the *orbital gyromagnetic ratio*

$$g_l \equiv \frac{\mu}{l} = \frac{e}{2mc}. \quad (1.65)$$

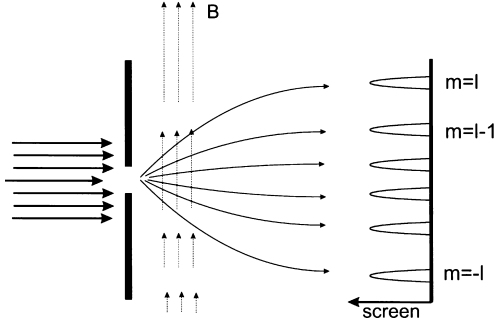


Figure 1.8 Spatial quantization.

The orbital magnetic moment is equal to a multiple of the elementary magnetic moment, *Bohr magneton*; for the electron

$$\begin{aligned} \mu &= n\mu_B, \quad 1\mu_B = g_l\hbar = \frac{e\hbar}{2mc} = 9.27 \cdot 10^{-21} \text{ erg/Gs} \\ &= 0.927 \cdot 10^{-23} \text{ J/T}. \end{aligned} \quad (1.66)$$

The quantization rule (1.64) does not contain any characteristic of the Coulomb field, and it is natural to assume that such a magnetic moment is associated with motion of any charged particle.

To make our arguments more precise, we need to recall that \mathbf{l} and $\boldsymbol{\mu}$ are *vectors*. The direct experiment by *Stern and Gerlach* in 1922 has shown that the quantized quantities are the *projections* of these vectors onto a direction that is singled out by the experiment, Figure 1.8, the direction of the nonuniform magnetic field in the Stern–Gerlach experiment. The atomic beam was deflected from the straight trajectory by a nonuniform magnetic field $B_z(z)$ that exerts a force $F = \mu_z \partial B_z / \partial z$. The classical electrodynamics would predict a formation on a registration plate of a broad band corresponding to all values of μ_z continuously changing from $-\mu$ to $+\mu$. The experiment instead forms a number of discrete narrow strips that are symmetric with respect to the original direction of motion. This means that, for a fixed absolute value of $|\boldsymbol{\mu}|$, only certain orientations of $\boldsymbol{\mu}$ and \mathbf{l} relative to the external field are allowed (*spatial quantization*). The split components of the beam correspond to all possible *integer* values of the projection l_z in the units of \hbar within the range restricted by the maximum projection l ,

$$l_z = m\hbar, \quad m = -l, -l+1, \dots, 0, \dots, l-1, l. \quad (1.67)$$

If the orbital momentum is $l\hbar$, the Stern–Gerlach experiment produces $(2l+1)$ components with various values of the magnetic quantum number m .

1.9 Spin

According to the rule (1.67), the number of the split components of the beam in the Stern–Gerlach device has to be *odd*. However, in some experiments, an *even* number of components, for example, a doublet, was observed. Atomic spectroscopy also gave examples of doublets not accounted for by theory. In 1925, *S. Goudsmith* and *J. Uhlenbeck* suggested a hypothesis of the existence of an intrinsic angular momentum of the electron. This additional momentum, *spin s*, is not connected with the orbital motion as the rotation of a planet around its own axis is not related to orbital motion.

All observations are consistent with the half-integer value of electron spin, $s = (1/2)\hbar$, so that the spatial quantization allows for only two orientations of the vector s relative to the field,

$$s_z = \pm \frac{\hbar}{2}. \quad (1.68)$$

The magnitude of the beam deviation in the experiment of Figure 1.8 gives the *spin gyromagnetic ratio* that turns out to be twice as large as its orbital counterpart (1.65),

$$g_s = \frac{\mu_s}{s} = \frac{e}{mc}. \quad (1.69)$$

Therefore, the magnetic moment of the electron at rest ($l = 0$) is again equal to the Bohr magneton,

$$\mu(l = 0) = \mu_s = g_s s = \frac{e\hbar}{2mc} = 1 \mu_B. \quad (1.70)$$

The elementary particles forming atomic nuclei, *neutrons* and *protons* as well as their constituents, *quarks*, also have spin $\hbar/2$. However, their gyromagnetic ratios differ from the simple result (1.69) because of the effects of *strong* (nuclear) forces on their intrinsic structure. The appropriate unit for the proton magnetic moment is, similarly to (1.66), the *nuclear magneton*,

$$\begin{aligned} 1 \text{ n.m.} &= \frac{e\hbar}{2m_p c} = 1 \mu_B \frac{m_e}{m_p} = \frac{1 \mu_B}{1836} = 5.05 \cdot 10^{-24} \text{ erg/Gs} \\ &= 0.505 \cdot 10^{-26} \text{ J/T}. \end{aligned} \quad (1.71)$$

However, for the proton and neutron, experiments give

$$\mu_p = 2.79 \text{ n.m.}, \quad \mu_n = -1.91 \text{ n.m.}; \quad (1.72)$$

the difference with the nuclear magneton is the so-called *anomalous magnetic moment*. Note that the neutron is electrically neutral, $e_n = 0$, but its magnetic moment does not vanish due to the non-vanishing contributions of quarks and *gluons*. The precision experiments also show that the electron magnetic moment is slightly

different from the simple value (1.70). The anomalous magnetic moment of the electron is, in contrast to the proton or neutron, small,

$$\mu_e = \left(1 + \frac{\alpha}{2\pi}\right) \mu_B, \quad (1.73)$$

where the fine structure constant α was introduced in (1.29); very precise measurements also show very small higher order corrections. This deviation is explained by the *quantum electrodynamics*, while the values (1.72) still cannot be theoretically obtained, although their ratio is understood in terms of quark structure.

For a general case of angular momentum that can have orbital or spin origin (or to be of a combined nature), we will use the generic notation \mathbf{J} if measured in units of \hbar . The dimensionless quantity J is quantized with an integer or half-integer value, and the projection J_z on a selected quantization direction can take $(2J + 1)$ values, $J_z = -J, -J + 1, \dots, +J$. As we will see in Chapter 16, this quantization is a geometric property of rotations in three-dimensional space. The magnetic moment of the system is proportional to its angular momentum,

$$\boldsymbol{\mu} = g\hbar\mathbf{J}, \quad (1.74)$$

where g is a gyromagnetic ratio specific for each system. In the weak static magnetic field $B = B_z$ imposed on a system at rest, the intrinsic structure of the system is unchanged. However, the magnetic interaction energy,

$$E_{\text{magn}} = -(\boldsymbol{\mu} \cdot \mathbf{B}) = -g\hbar B J_z, \quad (1.75)$$

appears, and $2J + 1$ components of a state with different J_z are equidistantly split in energy (*Zeeman effect*, Chapter 24).

1.10

De Broglie Waves

In spite of the success regarding the Bohr model and old quantum theory as a whole, many problems, especially those related to the radiation intensity and structure of complex atoms remained unsolved. The very recipe of quantization did not have a general character. Essentially, it was just a remarkable stroke of Bohr's genius. A new fundamental concept was needed in order to build a self-consistent new theory. The situation could be described by the table below.

The question marks in the table were substituted by *de Broglie waves*, 1923. In the spirit of the Newtonian idea of the monism of nature, we assume that to any experiment with particles of energy E and momentum \mathbf{p} , there corresponds a wave process with the wavelength λ and frequency ω such that

$$\lambda = \frac{h}{p}, \quad \omega = \frac{E}{\hbar}. \quad (1.76)$$

Note again that the Planck constant plays only the role of a scale factor used for translating between the wave and particle languages.

Under the assumption (1.76), the motion of particles has to be accompanied by the typical wave phenomena. For example, when skirting an obstacle of a size comparable with the wavelength (1.76) or being reflected from a periodic crystalline structure, a particle beam should display diffraction. In the experiments by *Davisson and Germer, 1927*, an electron beam produced a diffraction pattern similar to that for diffraction of X-rays in the reflection from a specially oriented crystal. In 1931, *Stern et al.*, showed that even complex objects, such as helium atoms, manifest diffraction from crystals. Recently, the interference and diffraction phenomena were observed on a *macroscopic* scale, even with large molecules as *Fullerenes C₆₀*. In all cases, the wavelength found in the experiment was in exact correspondence with the momentum of the particles in agreement with (1.76).

Problem 1.9

Estimate the electron energy needed for observing diffraction from a crystal. Find the wavelength and frequency of the de Broglie wavelength for electrons with velocity 1 cm/s; electrons with energy $E = 100$ MeV; thermal neutrons (energy $3T/2$ at room temperature T ; we always omit the Boltzmann constant and measure temperature in energy units, $1 \text{ eV} = 11\,600 \text{ K}$); for a football.

If the wave description is universal, we can apply a similar approach to atomic *bound* states (states of finite motion in classical mechanics). Here, we have to come to the picture of *standing waves*. Indeed, we immediately obtain the Bohr postulate (1.13): for a circular orbit of radius r , a stationary state appears if the length of the orbit equals an integer number of the wavelengths,

$$\lambda = \frac{2\pi r}{n}, \quad n = 1, 2, \dots, \quad (1.77)$$

from where we select the radii $r_n = n\lambda/2\pi$, or, in accordance with (1.76), $r_n = n\hbar/p$, and the orbital momentum $l = mvr_n = pr_n = n\hbar$, as in (1.14). It is clear from this simple argument that the quantization emerges as a consequence of the *boundary conditions* imposed onto the de Broglie waves. Here, we can recall a vibrating string or waves in the resonators where in the same way, the boundary conditions single out *normal modes* of the system.

For the wavelengths shorter than typical length parameters of a system, the wave aspects become less pronounced, the diffraction angle becomes smaller, and we come to the limit of *geometrical optics*. The wave propagation along the straight rays

	Light	Matter
Classical theory	Wave phenomena (Maxwell equations)	Corpuscular picture (Newton equations for $v \ll c$ or Einstein equations for $v \sim c$)
Quantum theory	Corpuscular picture (photons), (1.8) and (1.9)	???

is analogous to the straight motion of classical free particles. This situation is expected to be intermediate between quantum and classical mechanics, as discussed in relation to the correspondence principle.

Before establishing the quantum-mechanical formalism, we need to accumulate some experience concerning the behavior of quantum waves in various simple situations. Here, we will only use the definition of the de Broglie waves and the dictionary between the two languages. This experience will allow us to understand the operational interpretation of quantum waves.

