Theoretical and Quantum Mechanics

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Fundamentals for Chemists

by

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CONTENTS

PART ONE

SELECTED TOPICS OF THEORETICAL MECHANICS

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[*] These sections are more difficult and can thus be omitted at the first reading.

[+] These sections are considered in seminars.

PART TWO

BASICS OF QUANTUM MECHANICS

PHYSICAL CONSTANTS AND UNITS

Name	**Notation**	**Value**
Angstrom	Å	10^{-10} m
Atomic mass unit	amu	$1{,}660.10^{-27}$ kg
Avogadro's number	N_A	$6{,}022.10^{23}$ mol^{-1}
Boltzmann constant	k	$1{,}381.10^{23}$ J.K^{-1}
Bohr magneton	μ_B	$9{,}274.10^{-24}$ J.T^{-1}
Bohr radius	a_0	$0{,}529.10^{-10}$ m
Calorie	cal	4,19 J
Coulomb constant	$k_0 = 1/4\pi\varepsilon_0$	$8{,}99.10^{9}$ N.m^2/C^2
Electron charge	e	$1{,}602.10^{-19}$ C
Electron mass	m_e	$9{,}109.10^{-31}$ kg
Electronvolt	eV	$1{,}602.10^{-19}$ J
Fine-structure constant	$\alpha = e^2 k_0 / \hbar c$	$1/137{,}036 = 7{,}297.10^{-3}$
Gauss	Gs	10^{-4} T
Gravitational constant	G_0	$6{,}67.10^{-11}$ N.m^2.kg^{-2}
Permeability of vacuum	μ_0	$4\pi.10^{-7}$ N.s^2/C^2
Permittivity of vacuum	ε_0	$8{,}854.10^{-12}$ C^2/N.m^2
Planck's constant	h	$6{,}626.10^{-34}$ J.s
	$\hbar = h/2\pi$	$1{,}055.10^{-34}$ J.s
Rydberg constant	R	$1{,}097.10^{7}$ m^{-1}
	$\Re = ch$	$2{,}17.10^{-18}$ J $= 13{,}6$ eV
	$\mathscr{R} = Rc$	3,27.1015 s^{-1}
Speed of light	c	$2{,}998.10^{8}$ m/s
Universal gas constant	R	8,31 J/mol.K

LIST OF SYMBOLS

Notation	Quantity	Page
Latin		
A	amplitude of the displacement	94
$\mathbf{A}$	vector potential	19
A^l_{nk}	signed minor	101
$\widetilde{A}$	complex amplitude	97
a	semimajor axis of an ellipse	82
	amplitude of oscillation	95
	width of a potential well	285
$\mathbf{a}$	acceleration	5
a_0	radius of Bohr	82, 185, 355
$\mathbf{B}$	magnetic induction	18
$\widetilde{B}$	complex amplitude	97
b	semiminor axis of an ellipse	82
C	constant quantity	14, 52
C_i	superposition coefficients	218
$\widetilde{C}^i_k$	complex coefficients (amplitude of the oscillation of q_k with ω_l)	101
c	constant	94
d	constant	94
	distance between two point sources	170
$d, \mathbf{d}$	electrical dipole moment	401
dW	probability of finding object in an element of volume dV	207
$d\mathbf{r}$	element of the displacement (change of all co-ordinates)	53
ds	magnitude of the element of the displacement $d\mathbf{r}$	22
E	energy	21
E_n	energy of the state with quantum number n	186, 287, 319, 347
E_l	rotational energy	341
$\mathscr{E}$	intensity of the electrical field	18
$\mathcal{E}$	normalised (dimensionless) energy of a particle	297, 315, 343
e	charge of the electron	18
	eccentricity	60
$F, \mathbf{F}$	force	5
F_τ	tangential component of the force	37
F_n	normal component of the force	37
$\mathbf{F}_m$	magnetic force	79
F_α	force acting of the particle α	16
G	gravitational force	37
G_0	gravitational constant	52
g	Lande factor (gyromagnetic ratio)	85, 434

g_l	Lande factor for the orbital magnetic moment	434
g_s	Lande factor for the spin magnetic moment	434
g_j	Lande factor for the total magnetic moment	435
$H(q_j, P_j)$	Hamilton's function	123
$\hat{H}$	operator of Hamilton	255
$\hat{H}^0$	non-perturbed operator of Hamilton	392
$\hat{H}'$	in $\lambda\hat{H}'$, where $\lambda\hat{H}'$ is the operator of perturbation	392
$\mathscr{H}_n(\xi)$	Hermite polynomials	319
h	height	104
$\left.\begin{matrix} h \\ \hbar = h/2\pi \end{matrix}\right\}$	Planck's constant	162
I	current	85
$I(\nu, T_0)$	spectral distribution	152
J, $\mathbf{J}$	total angular momentum	421
j	probability flux	292
	total quantum number	421
j_{in}	probability flux of the impacting particles	292
j_r	probability flux of the reflected particles	292
j_{tr}	probability flux of the transmitted particles	292
K	rotational quantum number	365
k	coefficient of elasticity	105
	constant of Boltzmann	152
k_0	constant $(k_0 \equiv 1/4\pi\varepsilon_0)$	81
$\mathscr{L}$	Lagrangian function	6
$\mathbf{L}$	angular momentum	40
$\hat{\mathbf{L}}$	operator of the angular momentum	244
L_r, L_θ, L_φ	components of the angular momentum in spherical co-ordinates	139
$\hat{L}^2$	operator of the square of the angular momentum (of L^2)	244
$\hat{L}_x, \hat{L}_y, \hat{L}_z$,	operators of the Cartesian components of the angular momentum	244
$\mathrm{L}_{n-l-1}^{2l+1}$	polynomials of Laguerre	346
M	total mass of the particle system; mass of the molecule	37, 113
m	mass	5
	magnetic quantum number	249, 253
m_0	rest mass	80, 177
m_e	electron mass	51
m_j	total magnetic quantum number	422
m_s	spin magnetic quantum number	412
m_α	mass of the particle α	15
$\widetilde{m}$	reduced mass	50

N	number of the particles	6
$\mathbf{N}$	torque	41
n	quantum number	165, 184, 286, 319
	principal quantum number	348
n_f	quantum number of the final state	187
n_i	quantum number of the initial state	187
n_r	radial quantum number	346
$\mathbf{n}^0$	unit vector	85
$\mathbf{P}$	generalized momentum	131
P_i	i-component of the generalized momentum	21
P_φ	φ-component of the generalized momentum in polar system	53, 136, 139
P_r	r-component of the generalized momentum in spherical system	139
P_θ	θ-component of the generalized momentum in spherical system	139
P_ρ	ρ-component of the generalized momentum in polar system	136
$P_l^{\lvert m\rvert}$	Legendre polynomials	339
$\hat{\mathscr{P}}$	operator of the permutation	463
p	orbit parameter	60
$\mathbf{p}$	momentum	20
p_i	i-component of the momentum	20
p_τ	tangential component of the momentum	37
p_n	normal component of the momentum	37
$\hat{\mathbf{p}}$	operator of the momentum $\mathbf{p}$	241
$\hat{p}_x$, $\hat{p}_y$, $\hat{p}_z$	operators of the Cartesian component of the momentum $\mathbf{p}$	233, 241
Q_i	component of the generalized force	21
$\mathbf{q}$	electrical charge	52, 79
q_i	ith generalized co-ordinate	6
q_j	all generalized co-ordinates $q_1, q_2, q_3, ..., q_s$	6
$\widetilde{q}$	complex generalized co-ordinate	97
$\dot{q}_i$	ith generalized velocity	6, 7
$\dot{q}_j$	all generalized velocities $\dot{q}_1, \dot{q}_2, \dot{q}_3, ..., \dot{q}_s$	6, 7
R	universal gas constant	155
	Rydberg constant in m^{-1}	158
	reflection coefficient	292
$\Re$	Rydberg constant in eV	186
$\Re_{\tilde{m}}$	Rydberg constant taking into account the nucleus mass	190, 348
$\mathscr{R}$	Rydberg constant in s^{-1}	187
$\mathbf{R}$	radius vector of the centre of mass	37
$R(r)$, $R(\xi)$	radial wave function	340, 346
$\mathbf{r}$	radius vector	12
$\mathbf{r}^0$	unit vector along $\mathbf{r}$	53, 98
r_0, $\mathbf{r}_0$	radius of the particle orbit in Coulomb field	81
	equilibrium distance of the force centre (circle radius)	57

r_α	apogee radius	82
r_c	cyclotron radius	80
r_k	radius of the potential energy minimum of the molecule in *K*-state	366
r_ρ	perigee radius	82
r_α	radius-vector of the particle α	16
$\hat{r}$	operator of the radius-vector **r**	240
S	action	7
	spin	412
$\hat{S}_x, \hat{S}_y, \hat{S}_z$	operators of the Cartesian spin components	413
$\hat{S}^2$	operator of the square of the spin	413
s	degrees of freedom	6
	spin quantum number	412
T	kinetic energy	15
	coefficient of the transmission	292
T_0	temperature in K	152
$\hat{T}$	operator of the kinetic energy	254
$\hat{T}_r$	radial part of the operator of the kinetic energy	255
t	time	6
U	potential energy	15
U^*	generalized potential	18
$\widetilde{U}$	effective potential energy	55
$\mathbf{u}$	velocity	13
V	volume	129
v	vibrational quantum number	369
v, $\mathbf{v}$	velocity in the lab-frame	13
v', $\mathbf{v}'$	velocity in the moving frame	13
v_i	component v_x, v_y, v_z of the particle velocity	6
v_r	*r*-component of the velocity in spherical frame	138
v_α	velocity of the particle α	15
v_θ	θ-component of the velocity in spherical frame	138
v_ρ	ρ-component of the velocity in polar system	136
v_φ	φ-component of the velocity in polar and spherical systems	136, 138
v_x, v_y, v_z	Cartesian components of the velocity	135
w	work function	164
W	probability	209
X	Cartesian axis	13
$X(r)=R(r)r$	help function	342
$X(S_z)$	spin function	414
$X_+(S_z)$	spin function of the positive oriented spin	414
$X_-(S_z)$	spin function of the negative oriented spin	414

X_∞	asymptotic behaviour of the function $X(\xi)$ at $\xi \to \infty$	344
X_0	asymptotic behaviour of the function $X(\xi)$ at $\xi \to 0$	344
$\left.\begin{matrix}x_1\\x_2\end{matrix}\right\}$	displacement from the equilibrium of two oscillators	104
x_i	Cartesian co-ordinates x, y, z of the particle	6
x_0	normalised constant	315
$\hat{x}$	operator of the co-ordinate x	233, 240
$\left.\begin{matrix}\tilde{x}_1\\\tilde{x}_2\end{matrix}\right\}$	complex co-ordinates of two oscillators	106, 107
$\mathbf{x}^0$	unit vector along X-axis	16
Y	Cartesian axis	13
$Y_{lm}(\theta, \varphi)$	spherical functions	250
$\hat{y}$	operator of the co-ordinate y	240
$y'(x)$	the derivative of the function $y(x)$ with respect to x	9
$\mathbf{y}^0$	unit vector along Y-axis	16
Z	Cartesian axis	13
	charge number	184
$\hat{z}$	operator of the co-ordinate z	240
$\mathbf{z}^0$	unit vector along Z-axis	16

Greek

α	fine-structure constant	197
γ	relativistic factor	80
γ_{kl}	coefficient before the product in the energy expression	17
Δ	change of the quantity	114
δ	phase angle (initial phase)	95
$\delta(x)$	delta function (Dirac function)	222
$\boldsymbol{\varepsilon}$	infinitesimal vector quantity (velocity)	13
ε	infinitesimal quantity	13
ε_0	vacuum permittivity	52
$\eta(\xi)$	polynomial of the degrees of ξ	316
θ	azimuthal angle	25
κ	force constant	92
	coefficient in the expression (12.7)	283
κ_{ik}	coefficient in the expansion of U in the equilibrium state	99
$\mathbf{\Lambda}$	vector of the classical state	126
$\hat{\Lambda}$	operator of Legendre	248
λ	wavelength	153
	small parameter of the theory of the perturbation	392
	eigenvalue of the operator of the permutation $\hat{\mathscr{P}}$	463
λ_0	constant of the radioactive decay	307
$\mu, \boldsymbol{\mu}$	magnetic dipole moment	85, 87

μ_0	vacuum permeability	439
μ_B	Bohr magneton	433
$\mu_l, \boldsymbol{\mu}_l$	orbital magnetic dipole moment	433
$\mu_s, \boldsymbol{\mu}_s$	spin magnetic dipole moment	434
$\mu_j, \boldsymbol{\mu}_j$	total magnetic dipole moment	435
ν	linear frequency	95
ν^*	spectroscopic frequency	158, 351
ν_r^*	resonance (spectroscopic) frequency	353
ν_∞^*	threshold (spectroscopic) frequency	353
ξ	dimensionless co-ordinate	315, 343, 368
$\left.\begin{matrix}\xi_1\\ \xi_2\end{matrix}\right\}$	normal co-ordinates of the two pendulums	108
ξ_l	normal co-ordinate oscillating with natural frequency ω_l	102
ρ	linear polar co-ordinate	22
	probability density	
ρ_n	probability density of the state with quantum number n	288, 323, 355
ρ^{cl}	classical probability density	288, 324
σ	area of the phase space	128
$\hat{\boldsymbol{\sigma}}$	operator of Pauli	448
$\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$	Cartesian co-ordinates of the operator of Pauli	414
τ	period	81
Φ	functional	8
	scalar potential	19
φ	polar angle	22
ψ	wave function	206
ψ_a	antisymmetric wave function	464
ψ_{f_i}	wave function of the state with value f_i of the quantity f	215
ψ_n	wave function of the state with quantum number n	319
ψ_{nlm}	wave function of the state with quantum numbers n, l, m	347
$\psi_{\mathbf{p}}$	eigenfunction of the operator $\hat{\mathbf{p}}$	242
ψ_{p_x}	eigenfunction of the operator $\hat{p}_x$	242
ψ_s	symmetric wave function	464
ψ_∞	asymptotic behavior of the ψ-function on infinity	316
ω	angular frequency	101
ω, $\boldsymbol{\omega}$	angular velocity	77
ω_0	angular velocity of the particle in Coulomb field	81
	natural angular frequency	94
ω_a	angular frequency of antisymmetric oscillations	109
ω_c	cyclotron frequency	79
ω_L	Larmor frequency of the precession	84
ω_s	angular frequency of symmetric oscillations	110

Mathematical

δq	variation of the generalized co-ordinate	9
δy	variation of the function y	8
$\delta\Phi$	variation of the functional Φ	9
Σ	sum	5
∇	operator nabla	16
$\left.\begin{matrix}\Delta\\ \nabla^2\end{matrix}\right\}$	operator of Laplace	241
$\left.\begin{matrix}\Delta_{\theta,\varphi}\\ \nabla^2_{\theta,\varphi}\end{matrix}\right\}$	angular part of the operator of Laplace	248
Δ_r	radial part of the operator of Laplace	248
$\times$	sign for the vector product	18, 35
$\langle\varphi\vert\psi\rangle$	Dirac notation	219
$\langle\varphi\vert$	"bra" element	219
$\vert\psi\rangle$	"ket" element	219
$\{\ \}(\{F,G\})$	Poisson bracket (for the functions F and G)	131
$\{\ \}(\{\hat{A},\hat{B}\})$	quantum-mechanical Poisson bracket (for the operators $\hat{A}$ and $\hat{B}$)	274
$*(A*)$	sign for the complex conjugate quantity (A complex conjugate)	96
$^{-}(\bar{f})$	sign for a mean value (of the quantity f)	231
$^{\cdot}(\dot{x})$	time derivative (time derivative of x)	6
$^{\wedge}(\hat{f})$	sign for an operator (operator of the quantity f)	232
$\propto$	sign for proportionality	71
$\sim$	sign "in the order of"	84
$\approx$	sing "approximately equal"	50
$\div(2\div 7)$	sign "from to" (from 2 to 7)	31
$[\,]([\hat{A},\hat{B}])$	commutator (commutator for the operators $\hat{A}$ and $\hat{B}$)	235
$\lVert\ \rVert(\lVert N\rVert)$	matrix (matrix with the elements N_{ki})	390
$\lVert N\rVert*$	complex conjugate matrix of $\lVert N\rVert$	390
$\lVert\tilde{N}\rVert$	transposed matrix of $\lVert N\rVert$	390
$\lVert N\rVert^{+}$	adjoint matrix of $\lVert N\rVert$	390

To MARIYANA

PREFACE

This book has emerged from an undergraduate course as well as a graduate one, which I have taught for a number of years. Recently, many universities have experimented by bringing quantum theory forward in the curriculum and we follow their example. This book is intended to serve as an introduction to theoretical mechanics and quantum mechanics for chemists. I have included those parts of quantum mechanics which are of greatest fundamental interest and utility, and have developed those parts of classical mechanics which relate to and illuminate them. I try to give a comprehensive treatment wherever possible. The book would acquaint chemists with the quantum structure of the basic object of chemistry, the atom. My intention is to bridge the gap between classical physics, general and inorganic chemistry, and quantum mechanics.
For these reasons:

1. I present in one course the basics of theoretical mechanics and quantum mechanics, to emphasise the continuity between them;
2. I have chosen the topics of theoretical mechanics based upon two criteria:
    a) usefulness for chemical problems:
    - two-body problem;
    - rotational motion of a charged particles (free and in an atom);
    - interaction of a magnetic field with a magnetic dipole;
    - details of small oscillations and oscillations of molecules;

    b) the need for transition from classical to quantum mechanics:
    - basics of Lagrangian mechanics;
    - basics of Hamiltonian mechanics;
3. I give detailed explanation of an application of the quantum method to simple systems: one-dimensional potential, harmonic oscillator, hydrogen atom, and hydrogen-like atoms.
4. The basics of representation theory and elements of matrix mechanics are given;
5. Perturbation theory is developed;
6. The interaction of an atom with a magnetic field is explained physically;
7. The generalisation to many-particle systems is presented in the last two chapters.

The purpose is to give the student a manual for a self-learning course. My teaching experience during all these years gave me a reason to believe that the pedagogical features, the manner of introduction of the new concepts and phenomena, and the search of meaning in the different categories, make this book suitable for independent work.

I use widely the classical interpretation in my presentation of the phenomena, and I stress that this is only a presentation. Despite that the words "description", 'happens," and so on, refer to concepts of classical physics, such an interpretation helps the students very much to understand the meaning of the characteristics and/or phenomena, but it does not affect the university level of the course.

For every lecturer the axiomatic method of exposition of quantum mechanics is both tempting and elegant. But it is effective only for an audience which is well-grounded in mathematics and physics. Traditionally, students in chemistry have modest knowledge of physics and mathematics. Therefore, I have started quantum mechanics from the basics. This is partly compensated by a detailed explanation of the historical sources of quantum mechanics. Then again, because I could assume only minimal skills in mathematics, I chose to present the beginning of quantum mechanics by asking certain questions of about nature and answering through an experimental observation. It is shown how these observations logically lead to certain remarkable conclusions. In this manner, I introduce the wave function before the Schroedinger equation.

For the readers who would like to broaden their understanding of the subject:

— I point concrete chapters in the references at the beginning of every chapter;

— I give a list of references with brief comments at the end of the book.

I hope the book would be useful for

— chemistry undergraduate and graduate students;

— chemists in general (the matter is rigorously exposed and the book could be used also by professional chemists);

— other readers, especially engineering students;

— "specialists, who have not been taught or have been taught scanty quantum mechanics; for them the book is useful because the information from other disciplines, such as mathematics, general physics, electrodynamics, and so on, is given in a concentrated form, and they are not forced to make inquiries in other books" (an opinion of the referee to the Bulgarian edition of the book).

In my opinion, the most typical characteristics of this book are the following:

— theoretical mechanics and quantum mechanics are combined in one book (in the majority of classical mechanics books the level is too high or they are directed toward the technical disciplines and are not suitable for the introduction of quantum-mechanical principles);

— the different topics and parts of the book are connected with each other; the book, despite being a composite of two kinds of mechanics, is wholesome (I would mention here the words of Prof. Liboff in the preface of his book (R. L. Liboff, *Introductory of Quantum Mechanics*, Holden-day Inc., 1980) "Physics is not a sausage that one can cut into little pieces"); the material is presented rigorously and continuously; this is a university level course;

— it provides a necessary minimum of mechanics for chemists; obviously the introductory course on mechanics cannot cover the whole field, and my selection of problems was made according to their utility for chemists, their physical importance, pedagogical value, as well as historical impact on the development of the field.

— very often the mathematical manipulations obscure the physics of the matter; I tried to avoid this and to see the physics in every mathematical category and equation whenever possible;

— the pedagogical features of the book, some of which are not usually found in books at this level; they were proven to be very successful in the classroom; such a feature are:

— the detailed outlines at the beginning of each chapter (given in the contents of the chapters);

— each chapter ends with a summary;

— each chapter is followed by a quiz of self-assessment questions, the answers of which are in the text – they help the readers assess how well they have met the various objectives;

— a varied set of thoroughly tested problems is included at the end of each chapter; these problems form an integral part of the course (we solved these problems during seminars and I usually give some of them at exams);

— non-typical for mechanics topics are included (for example, interference and diffraction, magnetic dipole moment, mathematical information for the variation, different equations and mathematical functions, and so on) in order to have full and consistent explanation;

— the mathematical derivations and the solutions of the equations are given in detail and at the university level;

- there are many summary tables, vector interpretations, and diagrams of angular momenta (orbital, spin and total) and their coupling;
- "the book is useful to beginners with a felicitous selection and distribution of the material," according to the referee to the Bulgarian edition of the book.

The material of the classical mechanics has a fragmentary character. This choice is made because of the needs of both the chemistry students and quantum mechanics. The small volume and the desire for logical consistency impose an abstraction, to some extent.

At the number of some sections there are additional signs: with an asterisk are denoted the more complicated sections (they can be omitted at first reading) and with a plus - the sections which are considered in the seminars. The literature pointed in each chapter is cited with its number, and the literature at the end of the book - with the letter "R" and a number, both in square brackets.

Sofia Stefan Ivanov
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Chapter 1

LAGRANGIAN FUNCTION AND LAGRANGE'S EQUATIONS

1.1 Two Methods for Studying of the Mechanical Motion: Newtonian and Lagrangian
Basic objects in mechanics; particle, solid body and continuous medium; mechanical state and the problem of the mechanics; Newton method – a frame, motion equation, initial conditions; degrees of freedom, generalized co-ordinates and generalized velocities; configuration and phase space; Lagrangian method, advantages. 4

1.2 Hamilton's Principle and Lagrange's Equations
Action integral — Hamilton's principle; the conception of a functional and variation; Lagrange's equation; as consequence of Hamilton principle; characteristics of the Lagrangian function — additivity, product with a constant, derivative; Lagrange function and total derivative of the function of co-ordinates. 7

1.3 Lagrangian Function for a Free Particle
General properties of space and time (*homogeneity and isotropy of space and homogeneity of time*) *and the Lagrangian function; Galilean transformations; the function invariance at these transformations; Lagrangian function for a free particle and for a system of noninteracting particles.* 12

1.4 Lagrangian Function for a System of Interacting Particles
Conservative system; Langrangian function for a conservative system, kinetic and potential energy; the Lagrange's equation and the Newton's equation, potential and conservative force, potential energy and

SUGGESTED READING

1. Kibble, T. W., Classical mechanics, McGraw-Hill Book Co., 2nd ed., 1988, Section 1.2, Chapter 11.
2. Fetter, A. L., J. D. Walecka, Theoretical Mechanics of Particles and Continua, McGraw-Hill Book Co., 1980, Sections 13, 15 and 17.
3. Landau, L. D. and E. M. Lifshitz, Mechanics, Pergamon Press, 2nd ed., 1969, Chapter 1.

1.1 TWO METHODS FOR STUDYING OF THE MECHANICAL MOTION: NEWTONIAN AND LAGRANGIAN

The basic objects studied in mechanics are particles (particle points), solid states and continuous medium. *A particle is a body, whose dimensions can be neglected at a given level of description.* Of course this neglecting depends on the conditions of the problem. The molecules can be treated as particles while studied in their translational motion (e.g., in a solution), but not while analyzing their oscillations, which are defined by their constituent atoms and the distances between them. (Sometimes instead of a particle is used a material point.) *A group of particles, whose motion is free or constrained by some conditions, often defined as constraints, is called a mechanical system.* In particular, *if a group of particles is united by solid constraints such that the shape and volume of the system does not change, they form a solid state.* Most complicated for studying is *the continuous* *medium*, because it *is a system with infinite number of particles*. In this course we will limit ourselves to considerations of the motion of a particle and systems of finite number of particles. The problems of solid state and continuous medium won't be considered.

If we give the position and the velocities of all system particles in a fixed moment of time, we define the state of the system. The basic problem of classical mechanics is, knowing the state of the mechanical system in the initial moment of time and the laws to which the motion of the system obeys, to determine its state in any subsequent moment. For the solution of this problem in the approach of Newton, first it is necessary to have *a reference frame*. With it very often is associated a Cartesian co-ordinate system. Second, necessary are equations, in which the acceleration is related to the co-ordinates and velocities, i.e., *the equations of motion*. These equations are obtained from the Newton's laws. Since these laws are central to our subsequent work, we will briefly review them.

I law: There exist reference frames, in which if upon a body is not acted by another material object, i.e. a force (*a measure for an influence*) *such as another material body or a force field, the body remains in rest or in uniform motion. Such reference frames are called inertial frames.*

Newton's first law simply asserts that such inertial frames exist. We would like to underline that the first law of Newton introduces the term "inertial frame" and this law does not result from the second law (an error, which is often made).

II law: Under the action of the forces $\mathbf{F}_1, \mathbf{F}_2$, ..., $\mathbf{F}_\mathrm{n}$ *a particle of mass m gains an acceleration* $\mathbf{a}$ *with a direction of its resultant force* $\mathbf{F} = \sum_{i=1}^{n} \mathbf{F}_i$ *and a value equal to this resultant force divided by its mass:*

$$\mathbf{a} = \sum_{i=1}^{n} \frac{\mathbf{F}_i}{m} = \frac{\mathbf{F}}{m}. \tag{1.1a}$$

This relation is written for the case when the mass is conserved and constant in time. If this is not so (for example, in relativistic mechanics) we write instead of Eq. (1.1a) the following

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} = \frac{dm\mathbf{v}}{dt}. \tag{1.1b}$$

Here $\mathbf{p} = m\mathbf{v}$ is the momentum.

III law: To each action there is an equal and opposite reaction.

Or, *if particle 1 acts on particle 2 with a force* $\mathbf{F}_{12}$, *then particle 2 acts on particle 1 with a force* $-\mathbf{F}_{21}$ *and* $\mathbf{F}_{12} = -\mathbf{F}_{21}$.

For the description of a system of N particles are necessary $3N$ differential equations of second order. Hence, for the complete Newton description besides the reference frame and motion equations are necessary also $6N$ constants. These constants are determined by *the initial conditions*. Thus, *for the Newtonian method are necessary a reference frame, 3N equations and 6N initial constants - the values of the co-ordinates* x_i *and the velocities* $v_i = dx_i / dt \equiv \dot{x}$ *at* $t = 0$ $\left(i = 1, 2, ..., 3N\right)$.

The number of independent values necessary for the determination of a mechanical system's position is called the number of degrees of freedom. In the considered case we have $s = 3N$ degrees of freedom. In the presence of r constraints the degrees of freedom are $s = 3N - r$.

When $r = 0$ very often are used Cartesian co-ordinates. But this is not necessary. Depending on the conditions of the problem, it may appear that the choice of some other co-ordinates is more suitable. *Any s independent quantities,* $q_1, q_2, ..., q_i, ... q_s$, *which determine completely a system of s degrees of freedom, are called generalized co-ordinates. Their time derivatives* $\dot{q}_1, \dot{q}_2, ..., \dot{q}_i, ... \dot{q}_s$ *are called the generalized velocities of the system.*

The generalized co-ordinates allow a very useful representation. It consists in the following: an s-dimensional space is introduced, along the axes of which one plots the values of the generalized co-ordinates q_j (q_j stands for all co-ordinates, $q_j \equiv q_1, q_2, ..., q_s$). Such a space is called *a configuration space or q-space*. Naturally, taking into account everyday experience, it may be difficult to imagine such a space. But going from one-dimensional (linear space) to two-dimensional (plane) space and to three-dimensional (real) space, and remembering the four-dimensional space with three spatial co-ordinates and one time co-ordinate (which is so useful in relativity theory), it is not difficult to imagine the s-dimensional configuration space. By the way, the 4-dimensional space is also configuration space. By analogy with the configuration space, one can introduce the phase space. *It is 2s-dimensional space and a co-ordinate system is introduces in it, along the axes of which are plotted s generalized co-ordinates and s generalized momenta*, which we shall discuss later on (Section 6.2).

In the Lagrangian method, with every mechanical system one associates *a function of the generalized co-ordinates, the generalized velocities and time:*

$$\mathscr{L} = \mathscr{L}\left(q_1, q_2, ..., q_s, ... \dot{q}_1, \dot{q}_2, ..., \dot{q}_s, t\right) \tag{1.2}$$

or, briefly, $\mathscr{L} = \mathscr{L}(q_j, \dot{q}_j, t)$, where $\dot{q}_j \equiv \dot{q}_1, \dot{q}_2, ..., \dot{q}_s$. *This function is called Lagrangian function, or simply Lagrangian.*

Knowing the Lagrangian function, we can describe the motion of the system with the help of equations involving the partial derivatives of the function. These equations are called Lagrange's equations.

It is natural to ask, if we have the powerful method of Newton, why use another method, such as the Lagrangian method? The answer lies in the advantages of the Lagrangian method.

The number of Newton's equations necessary for the description of a system of *N* particles is 3*N*. The number of Lagrange's equations for the description of the same system is 3*N*-*r*, where *r* is the number of constraints. The constraints, which are unknown, don't enter in Lagrange's equations. In this case the solution gives information only for the motion of the system, without determining the action of the constraints. Under the action of a constraint we understand the force with which this constraint acts on the mechanical system. For most mechanical systems we are not interested in this action.

The Lagrangian function can be used not only for a system with finite number of degrees of freedom, but also for a system with infinite such number, such as the continuous medium. Moreover, it may be used with success for the description of nonmechanical medium, e.g., for electromagnetic and other fields. The method of Lagrange possesses greater generality and the significance of the Lagrangian function goes out of the frame of classical mechanics. This is so, because the Lagrange's equations can be obtained with the help of more general variational principle - the Hamiltoin's principle. In theoretical mechanics it has the role of Newton's law, i.e., it is taken as a fundamental statement of mechanics. Hamilton's principle is applied also to nonmechanical systems, e.g., for electromagnetic fields and for fields of elementary particles.

1.2 HAMILTON'S PRINCIPLE AND LAGRANGE'S EQUATIONS

Thus, according to the method of Lagrange every mechanical system is characterized by the function $\mathscr{L}(q_j, \dot{q}_j, t)$. *The time integral of the Lagrangian on the interval from time* t_1 *to time* t_2 *is called action:*

$$S = \int_{t_1}^{t_2} \mathscr{L}(q_j, \dot{q}_j, t)\,dt. \tag{1.3}$$

The integration is performed from the moment t_1, in which the position of the system is characterized with the values of the generalized co-ordinates $q_j(t_1)$ to the moment t_2, in which these values are $q_j(t_2)$.

According to Hamilton's principle the system moves in a way such that the functions $q_j(t)$ have a form, which ensures that the action (1.3) has the minimum possible value. In Fig. 1-1 is shown a system with one degree of freedom, for simplicity.

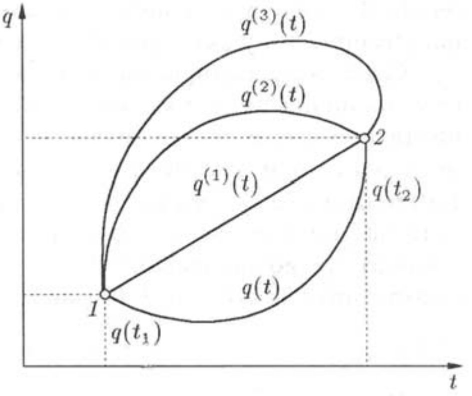


Figure 1-1. Hamilton principle.

The particle could move from the point *1* to the point *2* in different trajectories $q(t), q^{(1)}(t), q^{(2)}(t), q^{(3)}(t)$ with the corresponding action S, S_1, S_2, S_3 $(S < S_1 < S_2 < S_3)$. According to Hamilton's principle the particle will move along the trajectory of minimal action, i.e. along $q_j(t)$ with an action *S*.

The action is a functional. In order to see what this means, we shall briefly review some parts of functional analysis.

It is known that if to every number *x* of one group of numbers is associated another number *y*, this number *y* is a function of *x,* and we write $y = y(x)$. If to every function $y(x)$ from some group of functions is associated a number Φ, then Φ is a functional of $y(x)$ and we write $\Phi = \Phi\left[y(x) \right]$. In the functional the role of the argument is performed by the function. By the analogy to the increment $\Delta x = x - x_1$ (or to dx) of the function argument, we shall introduce the quantity

$$\delta y = y(x) - y_1(x). \tag{1.4}$$

The functions $y(x)$ and $y_1(x)$ are two functions of the considered class of functions. *The difference* (1.4) *of these functions is called the variation of the function* $y(x)$ *and is denoted as* $\delta y(x)$ *or* δy. The variation is a function of *x*. If we differentiate this function by *x*, then according to (1.4) we obtain:

$$(\delta y)' = y'(x) - y_1'(x). \tag{1.5}$$

Here y' stands for the derivative with respect to *x,* to distinguish it from the derivative with respect to *t, denoted as* $\dot{x}$. As the right-hand side represents the variation of the function $y'(x)$, from (1.4) we obtain:

$$(\delta y)' = \delta y'. \tag{1.6}$$

The derivative of the variation is equal to the variation of the derivative.

By analogy to the differential of a function $dy = y(x+dx) - y(x)$, we introduce the variation $\delta\Phi$ of the functional Φ:

$$\delta\Phi = \Phi\left[y(x) + \delta y\right] - \Phi\left[y(x)\right]. \tag{1.7}$$

Continuing with the analogy, we can say that as the differential becomes zero at the extremum of the function, so the variation becomes zero at the extremum of the functional. (The introduced term of a variation Φ (1.7) needs mathematical precision (see e.g., [2], Section 17); here we present only the concept of it.)

After these few concepts from functional analysis, let's return to Hamilton's principle. Suppose that in a one-dimensional system the function $q = q(t)$ is that for which *S* has a minimum. This means that *S* increases when $q(t)$ is replaced with the function of the form $q(t) + \delta q(t)$. The variation $\delta(t)$ is a small function in all intervals from time t_1 to time t_2. As we are interested in functions describing the motion from the position *1* (moment t_1) to the position *2* (moment t_2), the function $q(t)$ passes through the corresponding points *1* and *2* in Fig. 1-1, i.e.

$$\delta q(t_1) = \delta q(t_2) = 0. \tag{1.8}$$

The change of the action *S* when replacing *q* with $q + \delta q$, i.e. the variation δS of the functional, is determined by the difference

$$\delta S = \int_{t_1}^{t_2} \mathscr{L}(q + \delta q, \dot{q} + \delta\dot{q}, t)\,dt - \int_{t_1}^{t_2} \mathscr{L}(q, \dot{q}, t)\,dt. \tag{1.9}$$

We expand the Lagrangian of the first integral by δq and $\delta \dot{q}$ and reduce Eq. (1.9) to

$$\delta S = \int_{t_1}^{t_2} \left(\frac{\partial \mathscr{L}}{\partial q} \delta q + \frac{\partial \mathscr{L}}{\partial \dot{q}} \delta \dot{q} \right) dt. \tag{1.10}$$

Taking into account that from (1.6) it follows that $\delta \dot{q} = \frac{d}{dt} \delta q$, and integrating the second term by parts, we obtain

$$\int_{t_1}^{t_2} \frac{\partial \mathscr{L}}{\partial \dot{q}} \delta \dot{q} dt = \int_{t_1}^{t_2} \frac{\partial \mathscr{L}}{\partial \dot{q}} d\delta q = \frac{\partial \mathscr{L}}{\partial \dot{q}} \delta q \bigg|_{t_1}^{t_2} - \int_{t_1}^{t_2} \delta q \frac{d}{dt} \frac{\partial \mathscr{L}}{\partial \dot{q}} dt. \tag{1.11}$$

According to (1.8), the first term in the right-hand side of (1.11) is equal to zero. Substituting (1.11) in (1.10) and taking into account Hamilton's principle (the minimum action), we get

$$\delta S = \int_{t_1}^{t_2} \left(\frac{\partial \mathscr{L}}{\partial q} - \frac{d}{dt} \frac{\partial \mathscr{L}}{\partial \dot{q}} \right) \delta q dt = 0. \tag{1.12}$$

As δq is an arbitrary function, this ($\delta S = 0$) is possible only if

$$\frac{d}{dt} \frac{\partial \mathscr{L}}{\partial \dot{q}} - \frac{\partial \mathscr{L}}{\partial q} = 0. \tag{1.13}$$

If the system has *s* degrees of freedom with generalized co-ordinates q_j and generalized velocities $\dot{q}_j$, Eq. (1.13) can be easily generalized, as the generalized co-ordinates and velocities are independent and in (1.9) are varied *s* different functions $q_i(t)$ $(i = 1, 2, ..., s)$. Then we shall obtain *s* equations of the form (1.13).

$$\frac{d}{dt} \frac{\partial \mathscr{L}}{\partial \dot{q}_i} - \frac{\partial \mathscr{L}}{\partial q_i} = 0 \quad i = 1, 2, ..., s. \tag{1.14}$$

These equations are known as *Lagrange's equations. These are s equations of second order for unknown functions* $q_j(t)$ *and the general solution has 2s constants.* For their determination are necessary the initial conditions. Giving the values of all co-ordinates and velocities at $t=0$ they can be determined, which fully defines the motion of the mechanical system.

Let's summarize briefly the method of Lagrange. *For a system with s degrees of freedom we choose s generalized co-ordinates* q_j. *To this system we associate the Lagrangian function* $\mathscr{L}\left(q_j, \dot{q}_j, t\right)$ (*in the following sections we shall see how we can find it*). *Knowing this function, we can write Lagrange's equations* (1.14)*, which are the equations of motion. It is necessary to add to it the initial conditions - the values of the generalized co-ordinates and velocities at* $t=0$.

Here we shall consider some general properties of the Lagrangian. The Lagrangian possesses the property of *additivi*ty. If the system consists of two non-interacting parts *A* and *B,* each of which has its Lagrangian, then the $\mathscr{L}$ of the whole system is equal to the sum of the two Lagrangians:

$$\mathscr{L}=\mathscr{L}_A+\mathscr{L}_B. \tag{1.15}$$

From Lagrange's equations (1.14), it is obvious, that multiplying of the Lagrangian by a constant *C* does not change them. Hence, *for the description of motion, with the same success one can use the function* $C\mathscr{L}$. We note that when we consider a single isolated system we can multiply $\mathscr{L}$ by different constants. But when we consider different isolated parts of one mechanical system (or different isolated mechanical systems), their Lagrangian functions can not be multiplied by different constants but only with one and the same constant. This condition is imposed by the property of additivity. Only when we multiply the different parts of the system with one and the same constant *C*, we will obtain the Lagrangian function of the whole system as $C\mathscr{L}$, which leads to the same Lagrange's equations as $\mathscr{L}$. Multiplying of the Lagrangian function by one and the same constant is equivalent to an arbitrary choice of the measured units of the physical quantities. Finally, we shall prove one very important property of the Lagrangian function: if we add to the Lagrangian function the total time derivative of any function of the co-ordinates and time, the equations (1.14) remain unchanged.

Let's consider the function $\mathscr{L}(q, \dot{q}, t)$ and create from it the function $\tilde{\mathscr{L}}(q, \dot{q}, t)$ (it is read $\mathscr{L}$ tilde) by adding the total time derivative of some function $f\left(q,\ \mathrm{t})\right)$ of the co-ordinates and time, i.e.,

$$\tilde{\mathscr{L}}(q, \dot{q}, t)=\mathscr{L}(q, \dot{q}, t)+\frac{d}{dt} f\left[q(t), t\right]. \tag{1.16}$$

Let's find the action $\tilde{S}$, which corresponds to $\tilde{\mathscr{L}}(q, \dot{q}, t)$:

$$\begin{aligned}\tilde{S} &= \int_{t_1}^{t_2} \tilde{\mathscr{L}}(q, \dot{q}, t)\,dt = \int_{t_1}^{t_2} \mathscr{L}(q, \dot{q}, t)\,dt + \int_{t_1}^{t_2} \frac{d}{dt} f(q, t)\,dt \\ &= S + f[q(t_2),\, t_2] - f[q(t_1), t_1].\end{aligned} \tag{1.17}$$

The action $\tilde{S}$ differs from the action S, which corresponds to the function $\mathscr{L}(q, \dot{q}, t)$, by $f\left[q\left(t_2\right), t_2\right] - f\left[q\left(t_1\right), t_1\right]$. This difference disappears when the variation is taken, and, consequently, the variations δS and $\delta\tilde{S}$ coincide, from which it follows that the equations (1.14), being a consequence of the minimum of the action ($\delta S = \delta\tilde{S} = 0$), do not change. We have proved that the Lagrangian function is defined to within accuracy of adding to it the total time derivative of an arbitrary function of the coordinates and time.

1.3 LAGRANGIAN FUNCTION FOR A FREE PARTICLE

While studying the Lagranian function of a free particle we shall choose an inertial reference frame. Such a function could depend on the position, i.e. on the radius-vector **r,** and the time *t* of the particle, i.e. $\mathscr{L}(\mathbf{r}, \mathbf{v}, t)$. With respect to an inertial reference frame space is homogeneous and isotropic and time is homogeneous. For space this means that all points and directions are equivalent, and for time, that all instants are identical. These properties determine some properties of the sought Lagrangian function. The homogeneity of space means that the function does not depend on the distance *r,* and the isotropy means that it does not depend on the radius-vector **r**. The homogeneity of time means that $\mathscr{L}$ does not depend on *t.* The only remaining dependence is that on the velocity **v**. But since space is isotropic, the Lagrangian depends only on the value of the velocity, but not on its direction, i.e. it depends on the square of the velocity vector $\mathbf{v}^2 = v^2$. Thus, from the properties of space and time, we conclude that

$$\mathscr{L} = \mathscr{L}\left(v^2\right). \tag{1.18}$$

To proceed further we need to recall the transformation and principle of Galileo. If **r** and $\mathbf{r}'$ are respectively the radius-vectors of the particle in two inertial reference frames, a non-moving *K* and a system K', moving with velocity **u** with respect to *K* (Fig. 1-2), then

$$\begin{aligned}&\mathbf{r}=\mathbf{r}'+\mathbf{u}\mathbf{t},\\&\mathbf{v}=\mathbf{v}'+\mathbf{u},\\&t=t'.\end{aligned}\tag{1.19}$$

Here **v** and **v**', *t* and *t'* are the velocities and the times of the particle respectively in the systems *K* and *K'* (it is supposed that in the initial moment *O* and *O'* coincide). Formulae (1.19) are called *Galilean transformations*. Galileo's principle is the following:

The fundamental laws of mechanics are equally in form in arbitrary reference frames related through the Galilean transformations. In the system *K* the Lagrangian is given in (1.18) and in the system *K'* we will denote it as $\mathscr{L}'=\mathscr{L}'\left(v'^2\right)$. According to Galileo's principle, $\mathscr{L}'=\mathscr{L}\left(v'^2\right)$, and according to the properties of the Lagrangian function, $\mathscr{L}'$ can differ from the $\mathscr{L}$ by the total time derivative of any function of the co-ordinates **r** and the time *t*. With that the equations (the laws) of the motion do not change. Suppose that *K'* moves with infinitesimal velocity $\boldsymbol{\varepsilon}$ ($\mathbf{u}=\boldsymbol{\varepsilon}$) with respect to *K*. Then

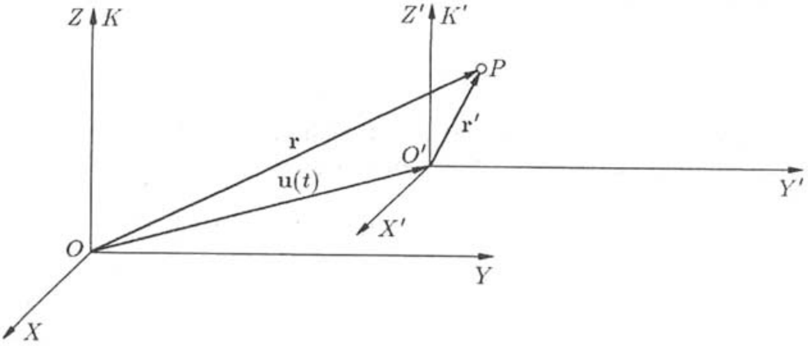


Figure 1-2. In the inertial reference frames *K* and *K',* the radius-vectors, velocities and times of the particle *P* are related through the Galileo's transformations and the fundamental laws have the same form.

$$\mathbf{v}=\mathbf{v}'+\boldsymbol{\varepsilon}\tag{1.20}$$

and for the Lagrangian function we obtain

$$\mathscr{L}=\mathscr{L}\left(v^2\right)=\mathscr{L}\left(v'^2+2\mathbf{v}'\boldsymbol{\varepsilon}+\varepsilon^2\right).\tag{1.21}$$

We expand the Lagrangian in a Taylor series about $\boldsymbol{\varepsilon}$, limiting ourselves with the linear terms:

$$\mathscr{L}\left(v^2\right)=\mathscr{L}\left(v'^2\right)+\frac{\partial\mathscr{L}\left(v'^2\right)}{\partial v'^2}2\mathbf{v}'\boldsymbol{\varepsilon}+0\left(\varepsilon^2\right). \tag{1.22}$$

In the left-hand side is the Lagrangian $\mathscr{L}$ in the system K and the first term in the right-hand side is $\mathscr{L}'$ in K'. The equations of motion (1.14) in both systems would not change, as the Galilean principle demands, if the second term in the right is the total time derivative of a function of the coordinates and the time. As $\boldsymbol{\varepsilon}$ is a constant quantity and $\mathbf{v}'$ is a time derivative of the position, this can be possible if $\partial\mathscr{L}\left(v'^2\right)/\partial v'^2$ does not depend on the velocity, i.e.,

$$\frac{\partial\mathscr{L}\left(v'^2\right)}{\partial v'^2}=C,\quad \mathscr{L}'=\mathscr{L}\left(v'^2\right)=Cv'^2. \tag{1.23}$$

Thus we proved that after a Galilean transformation with infinitesimal velocity the Lagrangian function for the free particle

$$\mathscr{L}=Cv^2 \tag{1.24}$$

satisfies Galileo's principle. The Lagrangian function is an invariant also at a finite velocity **u**. In fact

$$\begin{aligned}\mathscr{L}&=Cv^2=C\left(\mathbf{v}'+\mathbf{u}\right)^2=Cv'^2+2C\mathbf{v}'\mathbf{u}+Cu^2,\\ \mathscr{L}&=\mathscr{L}'+\frac{d}{dt}\left(2C\mathbf{r}'\mathbf{u}+Cu^2t\right).\end{aligned} \tag{1.25}$$

Since the second term in the right of the last equation is a total time derivative, it can be neglected and consequently $\mathscr{L}=\mathscr{L}'$.

The constant C is chosen such that $C=m/2$, where m is the mass of the particle (the choice is defined by the requirement that Lagrange's equations lead to the Newton's ones). This is possible according to the mentioned in Section 1.2 property of the function $\mathscr{L}$ that it can always be multiplied by an arbitrary constant. Finally, for the Lagrangian of a free particle we have

$$\mathscr{L}=\frac{mv^2}{2}. \tag{1.26}$$

The quantity $T = mv^2/2$ is called kinetic energy of the particle. We shall note that due to the additivity of the Lagrangian of a system of noninteracting particles, $\mathscr{L}$ has the form

$$\mathscr{L} = \sum_{\alpha} \frac{m_\alpha v_\alpha^2}{2}. \tag{1.27}$$

With the index $\alpha = 1, 2, 3 ...., N$ we denote the number of particles, and with i, j, k, l we denote the number of the generalized co-ordinates.

The sum $T = \sum_{\alpha} m_\alpha v_\alpha^2/2$ is the kinetic energy of the system.

1.4 LAGRANGIAN FUNCTION FOR A SYSTEM OF INTERACTING PARTICLES

We shall consider a closed system of particles. In such a system the particles may interact with one another, but they may not interact with other material objects outside the system. The interaction of the particles depends only on their mutual positions. This interaction can be described by a function, which depends on the particle co-ordinates. We shall denote this function as $U = U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$. It can be shown that such a mechanical system can be described by a Lagrangian function of the form (1.27) to which is added the function -*U*. Then for the Lagrangian function we have

$$\mathscr{L} = \sum_{\alpha} \frac{m_\alpha v_\alpha^2}{2} - U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N). \tag{1.28}$$

The term $\sum_{\alpha} m_\alpha v_\alpha^2/2$, as for the noninteracting particles, is called the kinetic energy and the function *U* is called the potential energy. Of course, we did not prove rigorously that the Lagrangian function has the form (1.28). We simply added the function –*U,* and from logical considerations it is evident that it has the dimension of the sum, i.e. the dimension of energy. From general physics, it is known what represents both terms in (1.28). But here we have began with Hamilton's principle and for the energy have mentioned in Section 1.3. Therefore, it is not accidental to call the term $\sum_{\alpha} m_\alpha v_\alpha^2/2$ kinetic energy and the function *U* - potential energy. The meaning of these terms and the reason to call them so will be explained in the following chapter. And the right to introduce the function U we shall illustrate by substituting $\mathscr{L}$ from (1.28) into Lagrange's equations and persuading ourselves that this Lagrangian correctly describes the motion of a closed system. Actually, by substituting the function $\mathscr{L}$ from (1.28) into the Lagrange's equations

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \mathbf{r}_\alpha} - \frac{\partial \mathscr{L}}{\partial \mathbf{r}_\alpha} = 0, \qquad \alpha = 1, 2, ..., N, \tag{1.29}$$

we obtain

$$m_\alpha \frac{d\mathbf{v}_\alpha}{dt} = -\frac{\partial U}{\partial \mathbf{r}_\alpha}, \tag{1.30}$$

i.e. the equation of motion in Newton's form.

The vector in the right, defined as a gradient of the function -U, is called the force, acting upon the particle α. We shall denote it with $\mathbf{F}_\alpha$:

$$\mathbf{F}_\alpha = -\frac{\partial U}{\partial \mathbf{r}_\alpha}. \tag{1.31}$$

Here we note that the derivative with respect to $\mathbf{r}_\alpha$ means gradient:

$$\frac{\partial U}{\partial \mathbf{r}} \equiv \mathrm{grad} U \equiv \nabla U. \tag{1.32}$$

We shall represent the force acting on the particle α through its components $F_{\alpha x}$, $F_{\alpha y}$ and $F_{\alpha z}$, along the axes X, Y, and Z:

$$\mathbf{F}_\alpha = \mathbf{x}^0 F_{\alpha x} + \mathbf{y}^0 F_{\alpha y} + \mathbf{z}^0 F_{\alpha z} = -\mathbf{x}^0 \frac{\partial U}{\partial x_\alpha} - \mathbf{y}^0 \frac{\partial U}{\partial y_\alpha} - \mathbf{z}^0 \frac{\partial U}{\partial z_\alpha}. \tag{1.33a}$$

Here $\mathbf{x}^0, \mathbf{y}^0$ and $\mathbf{z}^0$ stand for the unit vectors along the X, Y, Z axes, respectively. The components of the force are expressed through the function U in the following way:

$$F_{x_i} = -\frac{\partial U}{\partial x_i}, \quad i = 1, 2, 3, ..., 3N. \tag{1.33b}$$

The force, defined by the relation (1.31) (or (1.33)), is called a *potential force*. When such a force depends explicitly on time, it is called nonstationary, and when it does not depend on time, it is called a *stationary potential force or conservative force. Systems, in which only conservative forces act, are called conservative.*

We shall note one property of the potential energy *U*, which follows from the universality of Hamilton's principle: *the function U is defined to within an addition to it of an arbitrary constant.* Such addition does not violate Hamilton's principle, i.e. it does not influence the mathematical criterion for its validity - the variation of *S* to be equal to zero ($\delta S = 0$), and consequently it does not change the equations of motion. This property of the potential force is a partial case of the property (1.16) of the Lagrangian function.

We obtained the Lagrangian function in Cartesian co-ordinates. But as it was mentioned in Section 1.1, very often the generalized co-ordinates are more suitable for the motion analysis. It may be convenient to be able to express it in generalized co-ordinates q_j. It such a case it would be necessary to go from the $n = 3N$ variables x_i to the $s - r$ variables q_k. Let's consider the equations relating Cartesian and generalized co-ordinates:

$$x_i = x_i\left(q_1(t), q_2(t), ..., q_s(t)\right) \equiv x_i\left(q_j(t)\right), \quad i = 1, 2, 3, ..., n. \tag{1.34}$$

We shall begin with the transformation of the kinetic energy - the sum in the relation (1.28) for the function $\mathscr{L}$. Differentiating (1.34) by time, we shall express Cartesian velocities through generalized ones

$$\dot{x}_i = \sum_{k=1}^{s} \frac{\partial x_i}{\partial q_k} \dot{q}_k, \quad i = 1, 2, 3, ..., n. \tag{1.35}$$

Substituting (1.35) into the relation of the kinetic energy, we obtain

$$\begin{aligned} T &= \sum_{\alpha=1}^{N} \frac{m_\alpha \mathbf{v}_\alpha^2}{2} = \sum_{i=1}^{n} \frac{m_i \dot{x}_i^2}{2} = \sum_{i=1}^{n} \frac{m_i}{2} \left(\sum_{k=1}^{s} \frac{\partial x_i}{\partial q_k} \dot{q}_k \right)^2 \\ &= \sum_{i=1}^{n} \frac{m_i}{2} \left(\sum_{k=1}^{s} \frac{\partial x_i}{\partial q_k} \dot{q}_k \sum_{l=1}^{s} \frac{\partial x_i}{\partial q_l} \dot{q}_l \right) = \sum_{k,l} \dot{q}_k \dot{q}_l \sum_{i} \frac{m_i}{2} \frac{\partial x_i}{\partial q_k} \frac{\partial x_i}{\partial q_l} \end{aligned} \tag{1.36}$$

or

$$T = T\left(q_j, \dot{q}_j\right) = \sum_{k,l} \gamma_{kl}\left(q_j\right) \dot{q}_k \dot{q}_l, \tag{1.37}$$

where $\gamma_{kl}\left(q_j\right)=\sum_i^n \frac{m_i}{2}\frac{\partial x_i}{\partial q_k}\frac{\partial x_i}{\partial q_l}$, and γ_{kl} is a function of q_j since $x_i = x_i\left(q_j\right)$. We shall note also that under the summation by *i* of m_i we have $m_1 = m_2 = m_3 = m_{\alpha=1}$, $m_4 = m_5 = m_6 = m_{\alpha=2}$ and so on.

The transformation of the potential energy is trivial - we substitute (1.34) in $U\left(x_j\right)$ and obtain $U\left(q_j\right)$. Substituting in (1.28) the relations for $T\left(q_j, \dot{q}_j\right)$ and $U\left(q_j, t\right)$, we obtain the sought Lagrangian function

$$\mathscr{L}\left(q_j, \dot{q}_j\right)=T\left(q_j, \dot{q}_j\right)-U\left(q_j,\right). \tag{1.38}$$

The form of the Lagrangian function is the same when the energy depends explicitly on time:

$$\mathscr{L}\left(q_j, \dot{q}_j, t\right)=T\left(q_j, \dot{q}_j, t\right)-U\left(q_j, t\right). \tag{1.39}$$

We obtained $\mathscr{L} = T - U$ for conservative forces. But in the beginning it was underlined, that Lagrange's method is very general and it applies also to non-mechanical systems. Can we find $\mathscr{L}$ for the system in which the forces are non-conservative, e.g., depending on the velocities of the particles? It turns out that this is possible if the forces can be represented in the following form:

$$F_i = -\frac{\partial U^*}{\partial q_i} + \frac{d}{dt}\frac{\partial U^*}{\partial \dot{q}_i}. \tag{1.40}$$

In this case the "potential energy" U^* is a function of the generalized coordinates and velocities, $U^* = U^*\left(q_j, \dot{q}_j, t\right)$. The function U^* is called the generalized potential of the system.

1.5* LAGRANGIAN FUNCTION FOR A CHARGED PARTICLE IN ELECTROMAGNETIC FIELD

Consider a charged particle of charge *e* moving in an electric field $\mathscr{E}$ and a magnetic field **B**. The Lorentz force acts on the particle:

$$\mathbf{F} = e\mathscr{E} + e\mathbf{v}\times\mathbf{B}. \tag{1.41}$$

Its x-component has the following form:

$$F_x = e\mathscr{E}_x + e\left(\dot{y}B_z - \dot{z}B_y\right), \tag{1.42}$$

and the other two components are obtained by cyclic transformation of x, y, z. We shall show that this force can be written in the form (1.40). To do this, we shall use the known results from the theory of electromagnetic field, according to which it is always possible to find a scalar potential $\boldsymbol{\Phi}(\mathbf{r},t)$ and a vector potential $\mathbf{A}(\mathbf{r},t)$ through which the electric and magnetic fields are expressed:

$$\boldsymbol{\mathscr{E}} = -\nabla\boldsymbol{\Phi} - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla\times\mathbf{A}. \tag{1.43}$$

For the components $\mathscr{E}_x$ and B_x we get

$$\mathscr{E}_x = -\frac{\partial\boldsymbol{\Phi}}{\partial x} - \frac{\partial A_x}{\partial t}, \quad B_x = -\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}. \tag{1.44}$$

The other components of $\boldsymbol{\mathscr{E}}$ and $\mathbf{B}$ are expressed in a similar way. The potentials $\boldsymbol{\Phi}$ and $\mathbf{A}$ are not single valued and allow some arbitrariness. This permits the introduction of additional relation between them, the so called gauge condition of Lorentz:

$$\nabla\mathbf{A} + \frac{1}{c^2}\frac{\partial\boldsymbol{\Phi}}{\partial t} = 0. \tag{1.45}$$

And now, let us consider the function

$$\mathbf{U}^*(\mathbf{r},\dot{\mathbf{r}},t) = e\boldsymbol{\Phi}(\mathbf{r},t) - e\dot{\mathbf{r}}\mathbf{A}(\mathbf{r},t). \tag{1.46}$$

We shall prove that it is a generalized potential. From (1.46) we readily get

$$\begin{aligned}
-\frac{\partial U^*}{\partial x} &= -e\frac{\partial\boldsymbol{\Phi}}{\partial x} + e\left(\dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_y}{\partial x} + \dot{z}\frac{\partial A_z}{\partial x}\right),\\
\frac{d}{dt}\left(\frac{\partial U^*}{\partial\dot{x}}\right) &= -e\left(\frac{\partial A_x}{\partial t} + \frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial y}\dot{y} + \frac{\partial A_x}{\partial z}\dot{z}\right).
\end{aligned} \tag{1.47}$$

In the second relation we took into account that A_x depends on time also through the co-ordinates of the particle. Adding term by term in both relations and taking into account (1.44), we get

$$\begin{gathered}-\frac{\partial U^*}{\partial x}+\frac{d}{dt}\left(\frac{\partial U}{\partial \dot{x}}\right)=e\left(-\frac{\partial \Phi}{\partial x}-\frac{\partial A_x}{\partial t}\right)\\ +e\left[\dot{y}\left(\frac{\partial A_y}{\partial x}-\frac{\partial A_x}{\partial y}\right)+\dot{z}\left(\frac{\partial A_z}{\partial x}-\frac{\partial A_x}{\partial z}\right)\right]=\mathscr{E}_x+e\left(\dot{y}B_z-\dot{z}B_y\right).\end{gathered} \tag{1.48}$$

But this is the expression for F_x in the form of (1.42). Consequently, we are persuaded that the Lorentz force can be represented in the form (1.40) with the function $U^*=U^*(\mathbf{r},\dot{\mathbf{r}},t)$ (1.46). Then the Lagrangian function of a particle in electromagnetic field has the following form:

$$\mathscr{L}=\frac{1}{2}m\dot{\mathbf{r}}^2-e\Phi(\mathbf{r},t)+e\dot{\mathbf{r}}\mathbf{A}(\mathbf{r},t). \tag{1.49}$$

The second and the third terms represent the energy, which the particle has in the electric and magnetic fields, respectively.

1.6 SOME MECHANICAL VALUES AND THE LAGRANGIAN

Let us differentiate the Lagrangian function in Cartesian co-ordinates with respect to the components $\dot{x}_i$ of the αth particle:

$$\frac{\partial \mathscr{L}}{\partial \dot{x}_i}=m\dot{x}_i=p_i,\quad i=1,2,\ 3. \tag{1.50}$$

Or in a vector form

$$\frac{\partial \mathscr{L}}{\partial \dot{\mathbf{r}}}\equiv\frac{\partial \mathscr{L}}{\partial \mathbf{v}}=\mathbf{p}. \tag{1.51}$$

The momentum of the particle is equal to the derivative of the Lagrangian function with respect to its velocity.

When we differentiate the Lagrangian function with respect to x_i we obtain the component of the potential force F_i acting on the particle:

$$\frac{\partial \mathscr{L}}{\partial x_i} = -\frac{\partial U(x_j)}{\partial x_i} = F_i, \qquad i = 1, 2,\ 3. \tag{1.52}$$

By analogy with (1.51) and (1.52), we introduce the quantity P_i

$$P_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i}, \tag{1.53}$$

which is called *a generalized momentum*, and the quantity Q_i,

$$Q_i = \frac{\partial \mathscr{L}}{\partial q_i}, \tag{1.54}$$

which is called a generalized force.

With the help of the generalized momentum and the generalized force the Lagrange's equations (1.14) can be represented in Newton's form (compare with Eq. (1.1b)):

$$\frac{dP_i}{dt} = Q_i. \tag{1.55}$$

Using the Lagrangian function in Cartesian co-ordinates $\mathscr{L} = \sum_i^n \left(m_i \dot{x}^2\right)/2 - U\left(x_j\right)$, we can show that the total energy E is expressed by the function $\mathscr{L}$ in the following way:

$$E = \sum_{i=1}^{n} \frac{\partial \mathscr{L}}{\partial \dot{x}_i} \dot{x}_i - \mathscr{L}. \tag{1.56}$$

Actually

$$\sum_{i=1}^{n} \frac{\partial \mathscr{L}}{\partial \dot{x}_i} \dot{x}_i - \mathscr{L} = \sum_{i=1}^{n} m_i \dot{x}_i^2 - \sum_{i=1}^{n} \frac{m_i \dot{x}_i^2}{2} + U\left(x_j\right) = T\left(\dot{x}_j\right) + U\left(x_j\right) = E. \tag{1.57}$$

By analogy with (1.56), we shall express the total energy in generalized co-ordinates:

$$E = \sum_{i=1}^{s} \frac{\partial \mathscr{L}(q_j, \dot{q}_j)}{\partial \dot{q}_i} \dot{q}_i - \mathscr{L}(q_j\,,\, \dot{q}_j)\,. \tag{1.58}$$

It can be shown that in the same way we can express the energy E also for an open system, i.e. when the considered system interacts with another one or is in an external field:

$$E = \sum_{i=1}^{s} \frac{\partial \mathscr{L}(q_j,\, \dot{q}_j,\, t)}{\partial \dot{q}_i} \dot{q}_i - \mathscr{L}(q_j, \dot{q}_j,\, t)\,. \tag{1.59}$$

We shall take on the consideration of conservative laws in the next chapter. Here we shall only note that the relation (1.59) for the total energy is more general than the known from general physics $E = T + U$, and it can be used in cases when the energy can not be divided into kinetic and potential parts (e.g., in quantum mechanics).

1.7^+ LAGRANGIAN FUNCTION AND LAGRANGE'S EQUATIONS IN COMMONLY USED CO-ORDINATES

In order to find the Lagrangian function in concrete problems we proceed in the following way. We choose independent generalized co-ordinates for the system and maintain the form of the functions $x_i = x_i(q_j, t)$ and $\dot{x}_i = \dot{x}_i(q_j, \dot{q}_j, t)$. Substituting them in the relation of the Lagrangian function $\mathscr{L} = T(\dot{x}_j) - U(x_j)$, we get the function in generalized co-ordinates $\mathscr{L} = \mathscr{L}(q_j, \dot{q}_j, t) = T(q_j, \dot{q}_j, t) - U(q_j, t)$.

If in the obtained expression for $\mathscr{L}$ there are terms, which do not depend on q_i and $\dot{q}_i$ they are rejected since they do not contribute to the derivatives of $\mathscr{L}$ with respect to the generalized co-ordinates and velocities and consequently they do not influence Lagrange's equations. Finding $\mathscr{L}$ is substantially easier when we can relate the displacement element of the particle and the differential dq_j of the generalized co-ordinates.

In polar co-ordinates ρ, φ under the elementary change of ρ and φ by $d\rho$ and $d\varphi$ the particle moves from point P to point P' (Fig. 1-3). The displacement is a diagonal of the rectangle built upon $d\rho$ and $\rho d\varphi$, i.e.

$$(ds)^2 = (d\rho)^2 + \rho^2 (d\varphi)^2 . \tag{1.60}$$

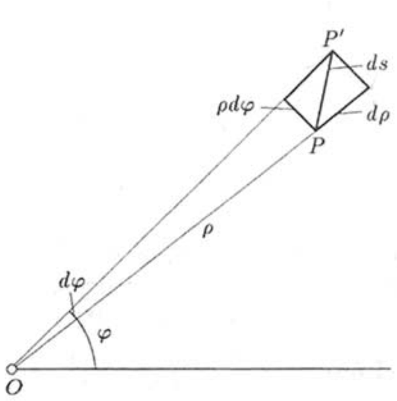


Figure 1-3. The displacement element *ds* in polar co-ordinates.

We divide by $(dt)^2$

$$\left(\frac{ds}{dt}\right)^2 = \left(\frac{d\rho}{dt}\right)^2 + \rho^2 \left(\frac{d\varphi}{dt}\right)^2 \tag{1.61}$$

and for the square of the velocity we obtain

$$v^2 = \dot{\rho}^2 + \rho^2 \dot{\varphi}^2 . \tag{1.62}$$

Thus, a particle of mass *m* has the kinetic energy

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\dot{\rho}^2 + \rho^2 \dot{\varphi}^2\right). \tag{1.63}$$

Consequently, if the particle is in a central field with a potential energy $U(\rho)$ its Lagrangian can be written as follows:

$$\mathscr{L}(\rho, \dot{\rho}, \dot{\varphi}) = \frac{1}{2} m \left(\dot{\rho}^2 + \rho^2 \dot{\varphi}^2\right) - U(\rho). \tag{1.64}$$

Substituting $\mathscr{L}(\rho, \dot{\rho}, \dot{\varphi})$ into (1.14) we obtain Lagrange's equations:

$$m\ddot{\rho} - m\rho\dot{\varphi}^2 + \frac{\partial U}{\partial \rho} = 0, \tag{1.65a}$$

$$m\frac{d}{dt}\left(\rho^2\dot{\varphi}\right) = 0. \tag{1.65b}$$

In a cylindrical co-ordinate system ρ, φ, z (Fig. 1-4), the displacement element ds_1 on the plane, which is a result of increasing ρ and φ by $d\rho$ and $d\varphi$, is the same as in polar co-ordinates. Due to this displacement, the particle moves from P_0 to P_1. Taking into account the increase dz in z-direction, the particle displaces into P_2, and the displacement is a diagonal of the rectangle, built on dz and ds_1. Hence,

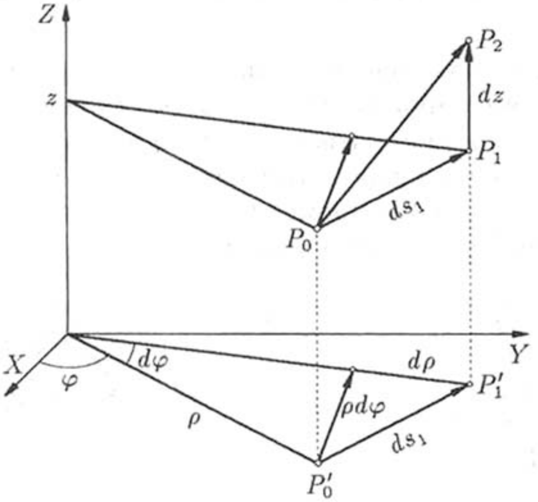


Figure 1-4. Displacement element in cylindrical co-ordinates.

$$(ds)^2 = (dz)^2 + (ds_1)^2 = (dz)^2 + \rho^2(d\varphi)^2 + (d\rho)^2. \tag{1.66}$$

We divide by $(dt)^2$ and obtain the velocity

$$v^2 = \dot{z}^2 + \rho^2\dot{\varphi}^2 + \dot{\rho}^2. \tag{1.67}$$

The Lagrangian function for the particle of mass m in a central field $U(\rho, z)$ has the following form:

$$\mathscr{L}(\rho, \dot{z}, \dot{\rho}, \dot{\varphi}) = \frac{m}{2}\left(\dot{z}^2 + \rho^2\dot{\varphi}^2 + \dot{\rho}^2\right) - U(\rho, z). \tag{1.68}$$

Deriving Lagrange's equations in this case I leave to the reader.

Finally, we consider spherical co-ordinates, r, φ, θ. Since later on we shall often encounter them, let us recall the connection between Cartesian and spherical co-ordinates (Fig. 1.5). From the figure it is obvious that

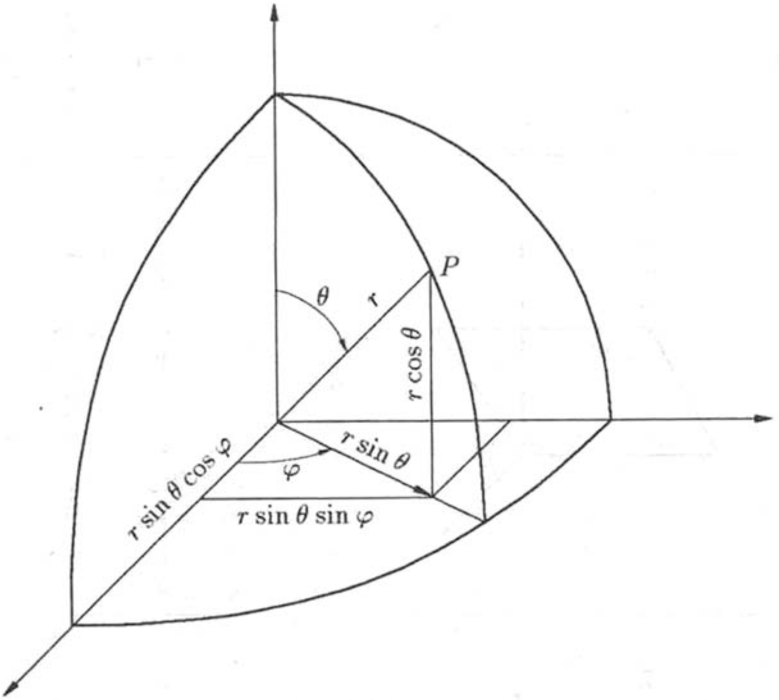


Figure 1-5. Cartesian (*x, y, z*) and spherical (*r, φ, θ*) co-ordinates of the point *P*.

$$x = r\sin\theta\cos\varphi, \tag{1.69a}$$
$$y = r\sin\theta\sin\varphi, \tag{1.69b}$$
$$z = r\cos\theta. \tag{1.69c}$$

To find *ds*, we shall take into account that with the change $d\theta$ of θ (Fig.1-6) the particle displaces with $rd\theta$, with the change $d\varphi$ of φ with $r\sin\theta d\varphi$, and with the change dr of r with dr. It is clear that the displacement element *ds* (P_0P_3) is a diagonal of the parallelepiped with sides equal to the displacement elements $rd\theta$ (P_0P_1), $r\sin\theta d\varphi$ (P_1P_2) and dr (P_2P_3). Hence

$$(ds)^2 = r^2(d\theta)^2 + r^2\sin^2\theta(d\varphi)^2 + (dr)^2. \tag{1.70}$$

(We would like to note that the volume element is $dV = r^2\sin\theta d\varphi d\theta dr$.) Dividing this relation by $(dt)^2$, we obtain the velocity in spherical co-ordinates:

$$v^2 = \dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\varphi}^2. \tag{1.71}$$

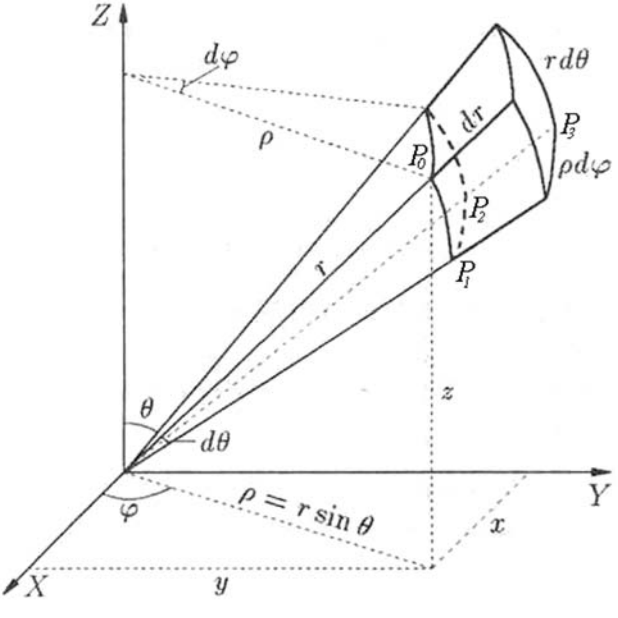


Figure 1-6. Displacement element in spherical co-ordinates.

Then, the Lagrangian function of a particle of mass m in the field with potential $U(r)$ is

$$\mathscr{L}\left(r,\theta,\dot{r},\dot{\theta},\varphi\right)=\frac{m}{2}\left(\dot{r}^2+r^2\dot{\theta}^2+r^2\sin^2\theta\dot{\varphi}^2\right)-U\left(r\right). \tag{1.72}$$

Knowing $\mathscr{L}\left(r,\theta,\dot{r},\dot{\theta},\varphi\right)$, we can readily obtain Lagrange's equations, which are given in Table 1-1.

Here we shall note an error, which is often made by students. The value of the radius-vector **r** of the particle in polar co-ordinates is equal to the linear co-ordinate ρ, i.e. $|\mathbf{r}|=r=\rho$. Therefore ρ,φ and r,φ are equivalent. In a cylindrical system (ρ,φ,z) the value r of the vector **r** differs from ρ, $r\neq\rho$, and the use of the co-ordinates r,φ,z is not correct in the case when the radius-vector of the particle position is denoted as **r.**

SUMMARY

In Lagrangian mechanics for a system of s degrees of freedom we choose s physical quantities $q_1,q_2,...,q_i,...q_s$, which are called generalized co-ordinates and their derivatives - generalized velocities. To every mechanical system is associated a Lagrangian function $\mathscr{L}\left(q_j,\dot{q}_j,t\right)$, the generalized co-ordinates and velocities being independent. According to Hamilton's principle the mechanical system moves in such a way that the action S is minimal, i.e.

$$\delta S=\int_{t_1}^{t_2}\mathscr{L}\left(q_j,\dot{q}_j,t\right)dt=0.$$

The Lagrange's equations, which are the equations of motion, follow from here, and read:

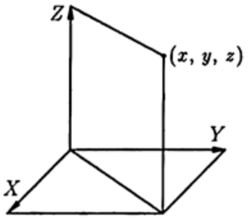
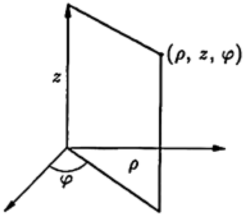
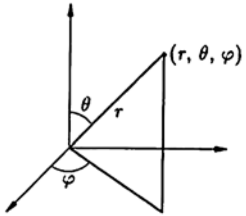
$$\frac{d}{dt}\frac{\partial\mathscr{L}}{\partial\dot{q}_i}-\frac{\partial\mathscr{L}}{\partial q_i}=0,\quad i=1,2,...,s.$$

The Lagrangian function is an additive one. Also, we can multiply it by a constant and add $\frac{d}{dt}f\left(q_j,t\right)$ ($f\left(q_j,t\right)$ is an arbitrary function) without changing the equations of motion.

The Lagrangian functions of a free particle and a system of noninteracting particles are, respectively

$$\mathscr{L}=\frac{mv^2}{2},\qquad \mathscr{L}=\sum_\alpha\frac{m_\alpha v_\alpha^2}{2}.$$

Table 1-1. Lagrangian and Lagrange's equations for a particle of mass m in an external field

	Cartesian co-ordinates	Cylindrical co-ordinates	Spherical co-ordinates
Frames			
Co-ordinates	x, y, x	ρ, φ, z	r, θ, φ
Potential energy	$U(x, y, x)$	$U(\rho, z)$	$U(r)$
Lagrangian	$\mathscr{L} = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - U(x, y, z)$	$\mathscr{L} = \frac{m}{2}(\dot{\rho}^2 + \rho^2\dot{\varphi}^2 + \dot{z}^2) - U(\rho, z)$	$\mathscr{L} = \frac{m}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\varphi}^2) - U(r)$
Lagrange's equations	$m\ddot{x} + \frac{\partial U}{\partial x} = 0$ $m\ddot{y} + \frac{\partial U}{\partial y} = 0$ $m\ddot{z} + \frac{\partial U}{\partial z} = 0$	$m\ddot{\rho} - m\rho\dot{\varphi}^2 + \frac{\partial U}{\partial \rho} = 0$ $m\frac{d}{dt}(\rho^2\dot{\varphi}) = 0$ $m\ddot{z} + \frac{\partial U}{\partial z} = 0$	$m\ddot{r} - mr\sin^2\theta\dot{\varphi}^2 - mr\dot{\theta}^2 + \frac{\partial U}{\partial r} = 0$ $m\frac{d}{dt}(r^2\dot{\theta}) - mr^2\sin\theta\cos\theta\dot{\varphi}^2 = 0$ $m\frac{d}{dt}(r^2\sin^2\theta\dot{\varphi}) = 0$

For particles interacting with potential energy $U\left(r_j\right)$, the Lagrangian function in Cartesian co-ordinates is

$$\mathscr{L} = \sum_{\alpha} \frac{m_\alpha v_\alpha^2}{2} - U\left(r_j\right)$$

and in generalized co-ordinates,

$$\mathscr{L}\left(q_j, \dot{q}_j, t\right) = T\left(q_j, \dot{q}_j\right) - U\left(q_j, t\right) = \sum_{k,l} \gamma_{kl}\left(q_j\right)\dot{q}_k \dot{q}_l - U\left(q_j, t\right).$$

The Lagrangian function of a charged particle in electromagnetic field depends on the scalar and vector potential of the field:

$$\mathscr{L} = \frac{1}{2} m\dot{\mathbf{r}}^2 - e\Phi\left(\mathbf{r}, t\right) + e\dot{\mathbf{r}}\mathbf{A}\left(\mathbf{r}, t\right).$$

In commonly used co-ordinate systems: Cartesian, cylindrical and spherical, the Lagrangian functions and Lagrange's equations are given in Table 1-1.

The momentum and energy of a system are expressed through $\mathscr{L}$ in the following way

$$\mathbf{p} = \sum_{\alpha} \frac{\partial \mathscr{L}}{\partial \dot{\mathbf{r}}_a}, \qquad E = \sum_{i=1}^{s} \frac{\partial \mathscr{L}}{\partial \dot{q}_i} \dot{q}_i - \mathscr{L}.$$

QUESTIONS

1. What is necessary for the description of the mechanical motion in Newtonian mechanics?
2. What represents the method of Lagrange?
3. What do represent: the generalized co-ordinates and velocities; the configuration and phase spaces?
4. What are the advantages of the method of Lagrange over the Newtonian method?
5. Why can the Lagrangian function be multiplied by the constant without changing the equations of motion?
6. Why can we add to the Lagrangian a function $\dfrac{df(\mathbf{r},\mathrm{t})}{dt}$, without changing the equations of motion?
7. Why can we add any constant to the potential energy of a system and how does this affect the Lagrangian function and Lagrange's equations?

8. Why does the Lagrangian function of a free particle depend only on v^2 but not on $\mathbf{v}$ and $\mathbf{r}$?
9. What does it mean that the Lagrangian function is an invariant with respect to the Galilean transformation? Give an example.
10. What is a potential? Can the Lagrangian function for a system of nonpotential forces be found?
11. What is a generalized potential? What is the generalized potential for the electromagnetic field?
12. What are the displacement elements and the volume elements in cylindrical and spherical co-ordinates?

PROBLEMS

1. Find the Lagrangian function and Lagrange's equations for a particle of mass *m* in a potential field $U(r)$.
2. Find the Lagrangian function and Lagrange's equations for a particle of mass *m* in a potential field $U(\rho)$ in polar co-ordinates.
3. Find the Lagrangian function and Lagrange's equations for a particle of mass *m* in a potential field $U(r)$ in cylindrical co-ordinates.
4. Find the Lagrangian function and Lagrange's equations for a particle of mass *m* in a potential field $U(r)$ in spherical co-ordinates.
5. Find the Lagrangian function, Lagrange's equations and the generalized co-ordinates of the electron in the hydrogen atom, assuming that the proton is immobile $(m_p \to \infty)$.
6. Find the Lagrangian function, Lagrange's equations and the generalized co-ordinates of a simple pendulum of mass *m* and length *l*, using the declination angle φ as a generalized co-ordinate.
7. Find the Lagrangian function, Lagrange's equations and the generalized co-ordinates for a particle of mass *m*, attached to the spring of negligible mass with a force constant κ (the system lies on a frictionless horizontal table).
8. The Lagrangian function of a charged particle moving with a relativistic velocity $v \sim c$ in an electromagnetic field has the following form: $\mathscr{L} = -mc^2\sqrt{1-\dot{r}^2/c^2} - e\Phi(\mathbf{r},t) + e\dot{\mathbf{r}}\mathbf{A}(\mathbf{r},t)$. Show that in the nonrelativistic case, $v \ll c$, this function has the form (1.49).

Chapter 2

CONSERVATION LAWS

SUGGESTED READING

1. Landau, L. D. and E. M. Lifschitz, Mechanics, Pergamon Press, 2nd ed., 1969, Sections 6÷9.
2. Kittel, Ch., W. D. Nayt, M. Ruderman, Mechanics, Berkeley Physics Course, vol. I, McGraw-Hill Book Co., 2nd ed., 1973, Chapters 5, 6.
3. Savelev, I. V., Fundamental of Theoretical Physics, Mir Publishing House, 1982.
4. Fetter, A. L., J. D. Walecka, Theoretical Mechanics of Particles and Continua, McGraw-Hill Book Co., 1980, Section 1.

2.1 CONSERVATION OF ENERGY

The state of a mechanical system is completely defined by s generalized co-ordinates q_j and s generalized velocities $\dot{q}_j$, i.e. by $2s$ quantities. During the motion of the system they are changed. But for the different systems some of these quantities and/or functions of them remain constants, which are determined by the initial conditions. *They are called constants of the motion.*

Some constants of the motions can be found from the form of the Lagrangian function. If it does not depend explicitly on some of the generalized co-ordinates, e.g., on q_i, from the Lagrange's equations (1.14) it is obvious that

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{q}_i} = 0. \tag{2.1}$$

Consequently the generalized momentum P_i is a constant of the motion

$$P_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i} = \text{const.} \tag{2.2}$$

Such co-ordinates, on which the Lagrangian function does not depend, are called cyclic.

Particularly important role in mechanics plays those constants of the motion whose constancy follows from *the basic properties of space and time - homogeneity and isotropy*. These constants are known as basic conservation laws of the corresponding quantities. Their general characteristic is their additivity. *The energy conservation is connected with the homogeneity of time*, *the momentum* conservation - *with space homogeneity*, and *the angular-momentum conservation - with space isotropy*. We shall note that homogeneity means equal properties in any point and the isotropy means equal properties in any direction. Because of their generality the conservation laws are powerful means in mechanics. They do not depend on the form of the trajectory and on the character of the acting forces and can be used even when these forces are unknown.

We shall consider the motion constant, originating from time homogeneity. The Lagrangian function of a closed system according to this can not depend on time. Actually, time homogeneity means an equality of all instants of time. Therefore, the mechanical properties of the system do not change: if we replace one instant of time with another without changing the co-ordinates and the velocities of the particles, the Lagrangian function remains the same.

For a closed system the Lagrangian function does not depend on time and therefore the total derivative with respect to time can be written in the following way:

$$\frac{d\mathscr{L}}{dt}=\sum_{i=1}^{s}\frac{\partial\mathscr{L}}{\partial q_i}\dot{q}_i+\sum_{i=1}^{s}\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\ddot{q}_i. \tag{2.3}$$

From Lagrange's equation (1.14) we express $\frac{\partial\mathscr{L}}{\partial q_i}$ through $\frac{d}{dt}\frac{\partial\mathscr{L}}{\partial\dot{q}_i}$ and replace it in Eq. (2.3) to obtain

$$\frac{d\mathscr{L}}{dt}=\sum_{i=1}^{s}\left(\frac{d}{dt}\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\right)\dot{q}_i+\sum_{i=1}^{s}\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\ddot{q}_i, \tag{2.4}$$

or

$$\sum_{i=1}^{s}\frac{d}{dt}\left(\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\dot{q}_i\right)-\frac{d\mathscr{L}}{dt}=\frac{d}{dt}\sum_{i=1}^{s}\left(\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\dot{q}_i-\mathscr{L}\right)=0. \tag{2.5}$$

The quantity in the brackets remains unchanged and it is a constant of the motion. By definition this quantity is called energy:

$$E=\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\dot{q}_i-\mathscr{L}=\text{const.} \tag{2.6}$$

We shall prove that the energy can be represented as the sum of the functions $T(q_j,\dot{q}_j)$ and $U(q_j)$, introduced in the previous section. For this purpose we shall determine the sum $\sum_i\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\dot{q}_i$ for the Lanragian function of the form (1.38):

$$\begin{aligned}\sum_i\frac{\partial\mathscr{L}}{\partial\dot{q}_i}\dot{q}_i&=\sum_i\frac{\partial}{\partial\dot{q}_i}\left(\sum_{k,l}\gamma_{kl}\dot{q}_k\dot{q}_l-U(q_j)\right)\dot{q}_i=\sum_i\left(\sum_l\gamma_{il}\dot{q}_l\dot{q}_i\right.\\&\left.+\sum_k\gamma_{ki}\dot{q}_k\dot{q}_i\right)=\sum_i\left(\sum_l\gamma_{il}\dot{q}_i\dot{q}_l+\sum_l\gamma_{il}\dot{q}_i\dot{q}_l\right)=2\sum_{i,l}\gamma_{il}\dot{q}_i\dot{q}_l=2T.\end{aligned} \tag{2.7}$$

Replacing (2.7) and (1.38) into (2.6), we get

$$E = 2T\left(q_j, \dot{q}_j\right) - T\left(q_j, \dot{q}_j\right) + U\left(q_j\right) = T\left(q_j, \dot{q}_j\right) + U\left(q_j\right). \quad (2.8)$$

We proved that the energy of the system consists of two different terms - kinetic energy $T(q_j, \dot{q}_j)$ and potential energy $U(q_j)$. In Cartesian co-ordinates the kinetic energy depends only on the velocities of the particles, $T(v_1, v_2, ..., v_N) = \sum m_\alpha v_\alpha^2 / 2$, and the potential energy depends on their co-ordinates, $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$. We shall underline that this analysis relates to mechanical energy.

We have persuaded ourselves *that the conservation of energy is valid for a closed system* - in the derivation we used a Lagrangian function, which does not depend on time. This condition is also valid for a system in a constant (with respect to time) external potential field. Hence the conservation law is valid also for such a system. *The acting forces in such systems are conservative.*

Because of the importance of the conservative systems in chemistry we shall consider with more detail the rate of change of the energy and the character of the acting forces in such systems. We shall underline once more that this is a system in a constant field, depending only on the co-ordinates. Consider a particle in an external field with kinetic energy $T = m\dot{\mathbf{r}}^2/2 = m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)/2$ and potential energy $U(x, y, z)$. The rate of change of the kinetic energy is

$$\dot{T} = m\left(\dot{x}\ddot{x} + \dot{y}\ddot{y} + \dot{z}\ddot{z}\right) = m\dot{\mathbf{r}}\ddot{\mathbf{r}} = \dot{\mathbf{r}}\mathbf{F} \quad (2.9)$$

where we used Newton's second law, $m\ddot{\mathbf{r}} = \mathbf{F}$. Here **F** is the acting conservative force and the quantity $\dot{\mathbf{r}}\mathbf{F}$ defines the rate of change of the kinetic energy. The change dT of the kinetic energy on the interval dt is defined by the work element of the force **F** under the displacement $d\mathbf{r}$:

$$dT = d\mathbf{r}\mathbf{F} = dA. \quad (2.10)$$

The conservative force $\mathbf{F}(\mathbf{r})$ depends only on the particle position. This fact is not sufficient to ensure energy conservation. But the last is guaranteed for a conservative system. Therefore, we shall find the sufficient condition $\mathbf{F}(\mathbf{r})$ to be a conservative force. Let us find the rate of change of the potential energy:

$$\dot{U}\left(x, y, z\right) = \frac{\partial U}{\partial x}\dot{x} + \frac{\partial U}{\partial y}\dot{y} + \frac{\partial U}{\partial z}\dot{z}. \quad (2.11)$$

Remembering that $\mathrm{grad}U = \nabla U$ is a vector

$$\nabla U = \frac{\partial U}{\partial x}\mathbf{x}^0 + \frac{\partial U}{\partial y}\mathbf{y}^0 + \frac{\partial U}{\partial z}\mathbf{z}^0, \tag{2.12}$$

we can represent (2.11) as a scalar product:

$$\dot{U} = \dot{\mathbf{r}}\nabla U. \tag{2.13}$$

Differentiating the equation $E = T + U = \mathrm{const}$ (the law of energy conservation) and taking into account (2.9) and (2.13), we obtain

$$\dot{\mathbf{r}}\left(\mathbf{F} + \nabla U\right) = 0\,. \tag{2.14}$$

This condition is valid for any velocity of the particle and hence

$$\mathbf{F}\left(\mathbf{r}\right) = -\nabla U\,. \tag{2.15}$$

In terms of components, this reads

$$F_x = -\frac{\partial U}{\partial y},\quad F_y = -\frac{\partial U}{\partial z},\quad F_x = -\frac{\partial U}{\partial z}\,. \tag{2.16}$$

The force **F** is a conservative, if it is stationary (it does not depend on time) and can be represented as a gradient of a function, depending on the co-ordinates, (2.15). For any scalar function $f(\mathbf{r})$ we have $\mathrm{curl}[\mathrm{grad}f(\mathbf{r})] \equiv \nabla \times \nabla f = 0$, and hence, according to (2.15), we can write for the force $\mathbf{F}(\mathbf{r})$

$$\nabla \times \mathbf{F}(\mathbf{r}) \equiv \mathrm{curl}\mathbf{F}(\mathbf{r}) = 0. \tag{2.17}$$

Thus, the necessary and sufficient condition to ensure the force $\mathbf{F}(\mathbf{r})$ to be a conservative force is its curl to vanish. In this case such a function $U(x, y, z)$ of the co-ordinates can always be found, so that $\mathbf{F}\left(\mathbf{r}\right) = -\nabla U$.

2.2 CONSERVATION OF MOMENTUM

The law of conservation of momentum in a closed system originates from the homogeneity of space. Consider a translation $\delta\mathbf{r}$ of all particles of the system. Because of the homogeneity of space such translation can not change the mechanical properties of the system, i.e. the Lagrangian function should retain its form. (Here we shall note that we write $\delta\mathbf{r}$, but not $d\mathbf{r}$, because $\mathbf{r}$ is a function of time, $\mathbf{r}=\mathbf{r}(t)$.) Such a displacement by $\delta\mathbf{r}$ in an open system would cause a change in the particles' positions with respect to interacting with them bodies and/or fields. Hence, the translation $\delta\mathbf{r}$ does not cause a change of the Lagrangian function $\mathscr{L}$, i.e. $\delta\mathscr{L}=0$, only in a closed system:

$$\delta\mathscr{L}=\sum_{\alpha}\frac{\partial\mathscr{L}}{\partial\mathbf{r}_{\alpha}}\delta\mathbf{r}_{\alpha}=\delta\mathbf{r}\sum_{\alpha}\frac{\partial\mathscr{L}}{\partial\mathbf{r}_{\alpha}}=0. \tag{2.18}$$

For an arbitrary function of time $\delta\mathbf{r}(t)$, Eq. (2.18) is satisfied if

$$\sum_{\alpha}\frac{\partial\mathscr{L}}{\partial\mathbf{r}_{\alpha}}=0. \tag{2.19}$$

Using Lagrange's equation (1.14), we get

$$\sum_{\alpha}\frac{\partial\mathscr{L}}{\partial\mathbf{r}_{\alpha}}=\sum_{\alpha}\frac{d}{dt}\frac{\partial\mathscr{L}}{\partial\mathbf{v}_{\alpha}}=\text{const}. \tag{2.20}$$

Hence, the quantity $\partial\mathscr{L}/\partial\mathbf{v}_{\alpha}$ does not change

$$\mathbf{p}=\sum_{\alpha}\frac{\partial\mathscr{L}}{\partial\mathbf{v}_{\alpha}}=\text{const}, \tag{2.21}$$

or substituting the Lagrangian function in Cartesian co-ordinates, we get

$$\mathbf{p}=\sum_{\alpha}m_{\alpha}\mathbf{v}_{\alpha}=\sum_{\alpha}\mathbf{p}_{\alpha}=\text{const}. \tag{2.22}$$

Thus, originating from the homogeneity of space, we have reached the following law: *the momentum of particles in a closed system does not change, i.e. it is a constant of motion.* Separate components of the momentum can conserve also in an external field (respectively, an external interaction), if the potential energy does not depend on the corresponding Cartesian co-ordinates. In other words, if along the co-ordinate x_i the corresponding component of the resultant force **F** is zero, $F_{x_i} = 0$, then $p_{x_i} = \text{const}$. For example, if the system of particles is near the Earth surface, the tangential component of the external component F_τ along this surface is zero and the law of the momentum conservation is valid for the component p_τ, but is not valid for the normal component p_n, because $F_n = -G \neq 0$ (where G is a gravity force).

We shall obtain the rate of change of the momentum of the system particles by differentiating with respect to time:

$$\dot{\mathbf{p}}_\alpha = \frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \mathbf{v}_\alpha} = \frac{\partial \mathscr{L}}{\partial \mathbf{r}_\alpha} = \mathbf{F}_\alpha . \tag{2.23}$$

There is a change in both the particles' momentum and the total momentum of the open system only when the applied force is different from zero.

In a mechanical system there exists a point, which always, independently of the form of the system motion, moves with such a velocity **u** *that multiplying* **u** *by the total mass of the system* $M = \sum m_\alpha$, *we get the momentum of the system. This point is called the centre of mass or the centre of gravity.* The definition of the radius-vector of the centre of mass is:

$$\mathbf{R} = \frac{\sum m_\alpha \mathbf{r}_\alpha}{\sum m_\alpha} = \frac{\sum m_\alpha \mathbf{r}_\alpha}{M}. \tag{2.24}$$

It moves with a velocity

$$\mathbf{u} = \dot{\mathbf{R}} = \frac{\sum m_\alpha \dot{\mathbf{r}}_\alpha}{M} = \frac{\sum m_\alpha \mathbf{v}_\alpha}{M}. \tag{2.25}$$

Multiplying by M, we obtain

$$M\mathbf{u} = \sum m_\alpha \mathbf{v}_\alpha = \mathbf{p}, \tag{2.26}$$

i.e., the introduced in (2.24) point in fact moves with such a velocity, which multiplied by the mass M of the system gives its momentum.

For a system of two particles the centre of mass is shown in Fig. 2-1.

The centre of mass possesses a very useful property: in the absence of external forces its velocity in any inertial reference frame is constant. Actually, for a closed system we have

$$\mathbf{u} = \dot{\mathbf{R}} = \frac{\sum m_\alpha \dot{\mathbf{r}}_\alpha}{M} = \frac{\sum \mathbf{p}_\alpha}{M} = \frac{\mathbf{p}}{M} = \text{const.} \tag{2.27}$$

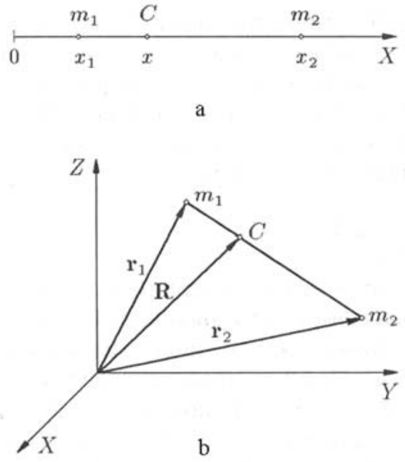


Figure 2-1. The centre of mass of a system of two particles of mass m_1 and m_2: a) two particles with co-ordinates x_1 and x_2 have a centre of mass with a co-ordinate $x = (m_1 x_1 + m_2 x_2)/(m_1 + m_2)$; b) two particles, whose positions are determined by the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ have the position of the centre of mass $\mathbf{R} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)/(m_1 + m_2)$.

If we choose *the frame K' with an origin at the centre of mass* (*so called CM-frame*) and moving with the system, the momentum $\mathbf{p}'$ of the mechanical system in it would be equal to zero, i.e. $\mathbf{p}' = 0$. This is so, for example, for a freely moving nucleus at the radioactive α-decay. The properties of the centre of mass make the reference frame connected with it very useful for the solution of many problems. For example, the problem of elastic and inelastic collision of two bodies (see Chapter 3), and so on.

2.3 CONSERVATION OF ANGULAR MOMENTUM

This law originates from space isotropy. As a result of this isotropy, the mechanical properties of a closed system of particles do not change under an arbitrary rotation of the system in space, and the Lagrangian function remains constant. Thus, after an infinitesimal rotation its variation is equal to zero, i.e., $\delta \mathscr{L} = 0$.

Let us rotate by an infinitesimal angle a particle with co-ordinates r, θ, φ, (Fig. 2-2). We shall represent this angle as a vector $\boldsymbol{\delta\varphi}$, directed along the axis of a rotation, so that the rotation, looked from its top, is in the positive direction, i.e. the rotation is counter-clockwise. Let's find the displacement $\delta\mathbf{r}$ due to such a rotation. It is seen from Fig. 2-2 that

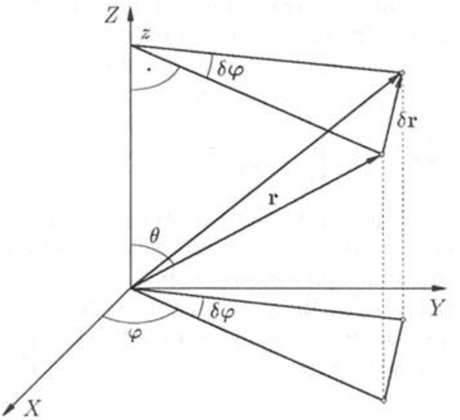


Figure 2-2. Under the rotation of a particle with co-ordinates r, θ, φ by an infinitesimal angle $\delta\varphi$, its position changes by $|\delta\mathbf{r}| = r\sin\theta\delta\varphi$.

$$|\delta\mathbf{r}| = r\sin\theta\delta\varphi. \tag{2.28}$$

But as $\mathbf{r}$ and $\boldsymbol{\delta\varphi}$ are vectors, we can write (2.28) in a vector form (right-handed co-ordinate system):

$$\delta\mathbf{r} = \boldsymbol{\delta\varphi}\times\mathbf{r}\,. \tag{2.29}$$

We have shown that any vector, whose beginning is on the rotation axis, changes under the rotation $\boldsymbol{\delta\varphi}$ according to (2.29).

The dependence (2.29) is valid also for a vector arbitrarily located on the axis of a rotation (for a proof see, e.g., Appendix VI in [2]). So, the change of the velocity has the same form:

$$\delta\mathbf{v} = \boldsymbol{\delta\varphi}\times\mathbf{v}\,. \tag{2.30}$$

Under the rotation by an angle $\delta\varphi$ the Lagrangian function does not change, i.e.,

$$\delta \mathscr{L} = \sum_{\alpha} \left(\frac{\partial \mathscr{L}}{\partial \mathbf{r}_{\alpha}} \delta \mathbf{r}_{\alpha} + \frac{\partial \mathscr{L}}{\partial \mathbf{v}_{\alpha}} \delta \mathbf{v}_{\alpha} \right) = 0. \tag{2.31}$$

In this equation we take into account that $\partial \mathscr{L} / \partial \mathbf{r}_{\alpha} = \dot{\mathbf{p}}_{\alpha}$, $\partial \mathscr{L} / \partial \mathbf{v}_{\alpha} = \mathbf{p}_{\alpha}$ and use the Eqs. (2.29) and (2.30):

$$\begin{aligned} \delta \mathscr{L} &= \sum_{\alpha} (\dot{\mathbf{p}}_{\alpha} \delta \mathbf{r}_{\alpha} + \mathbf{p}_{\alpha} \delta \mathbf{v}_{\alpha}) = \sum_{\alpha} \left[\dot{\mathbf{p}}_{\alpha} (\boldsymbol{\delta\varphi} \times \mathbf{r}_{\alpha}) + \mathbf{p}_{\alpha} (\boldsymbol{\delta\varphi} \times \mathbf{v}_{\alpha}) \right] \\ &= \boldsymbol{\delta\varphi} \sum_{\alpha} (\mathbf{r}_{\alpha} \times \dot{\mathbf{p}}_{\alpha} + \mathbf{v}_{\alpha} \times \mathbf{p}_{\alpha}) = \boldsymbol{\delta\varphi} \frac{d}{dt} \sum_{\alpha} (\mathbf{r}_{\alpha} \times \mathbf{p}_{\alpha}) = 0. \end{aligned} \tag{2.32}$$

Since $\boldsymbol{\delta\varphi} \neq 0$, $\delta \mathscr{L} = 0$ is equivalent to

$$\frac{d}{dt} \sum_{\alpha} (\mathbf{r}_{\alpha} \times \mathbf{p}_{\alpha}) = 0. \tag{2.33}$$

Under the motion of the closed system the vector quantity

$$\mathbf{L} = \sum_{\alpha} (\mathbf{r}_{\alpha} \times \mathbf{p}_{\alpha}). \tag{2.34}$$

remains constant. This quantity is called angular momentum (sometimes a moment of the momentum). It is obvious that $\mathbf{L} = \sum \mathbf{L}_{\alpha}$, i.e. the quantity **L** is additive.

The vector product (2.34), which defines the angular momentum, can be conveniently represented in the form of a matrix. For a particle it is the following

$$L = \begin{vmatrix} \mathbf{x}^0 & \mathbf{y}^0 & \mathbf{z}^0 \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}. \tag{2.35}$$

Its components, the angular momenta about the *X*-, *Y*- and *Z*-axes, are

$$\begin{aligned} L_x &= y p_z - z p_y, \\ L_y &= z p_x - x p_z, \\ L_z &= x p_y - y p_x. \end{aligned} \tag{2.36}$$

In order to find the rate of change of the angular momentum of a particle, we differentiate (2.34) with respect to time:

$$\dot{\mathbf{L}} = m\frac{d}{dt}(\mathbf{r}\times\dot{\mathbf{r}}) = m(\dot{\mathbf{r}}\times\dot{\mathbf{r}} + \mathbf{r}\times\ddot{\mathbf{r}}). \tag{2.37}$$

The first vector product in the right is zero because it is a product of the vector $\dot{\mathbf{r}}$ with itself. The second product is *the moment of* acting on the particle *force* **F** (it is called *torque*):

$$m\mathbf{r}\times\ddot{\mathbf{r}} = \mathbf{r}\times\mathbf{F} = \mathbf{N}. \tag{2.38}$$

Thus we obtain the important result that the rate of change of the angular momentum is equal to the moment of the applied force:

$$\dot{\mathbf{L}} = \mathbf{N}. \tag{2.39}$$

It is useful to compare it with the rate of change of the momentum $\dot{\mathbf{p}} = \mathbf{F}$ (the quantity **L** in the rotation motion plays the same role as **p** in the translational motion, thus the reason to call **L** an angular momentum is obvious). Since the definition of the vector product depends on the choice of right- or left-handed co-ordinate system, the directions of **L** and **N** also depend of this choice. They will be reversed in the left-handed system. Vectors of this type are known as *axial vectors* in contrast with the ordinary, or *polar vectors*, whose directions are defined independently of the choice of the co-ordinate system. Axial vectors are often associated with a rotation about a given axis. The direction of rotation around the axis (clockwise or counter clockwise) has physical meaning, but the direction of the vector along the axis has no physical meaning.

Thus, using space isotropy, we obtain the following conservation law: *the angular momentum of a closed system of particles remains constant.*

The law of conservation of angular momentum (of all its components) with respect to the origin of a co-ordinate system is valid in a closed system. We proved this result, since under a rotation the properties of a closed system do not change. But this is possible also in an external field, i.e. in an open system, if the field possesses a symmetry axis. Then, under a rotation about this axis the mechanical properties of the system won't change. Therefore, the projection of an angular momentum on this axis, defined with respect to any axis point, remains constant. Example of such partial conservation of angular momentum is the fields of central or axial symmetries. In the first case we have a field in which the potential energy depends only on the distance to a fixed point, called the centre of the field. An arbitrary rotation of the mechanical system does not change its mechanical properties, since the positions of the particles with respect to the centre remain unchanged. Hence, the angular momentum remains constant with respect to the centre of the field, but not with respect to any point. And the mechanical moment has only a component along the rotational axis. According to the previous paragraph, the conservative component in a field with axial symmetry along the Z-axis is L_z, the beginning of the co-ordinate system can be any point on the Z-axis.

Finally, we can summarize the results: *originating from the basic properties of time* (*homogeneity*) *and space* (*homogeneity and isotropy*)*, we obtained seven constants of motion: energy, three components of the linear momentum, and three components of the angular momentum.*

SUMMARY

The functions of the generalized co-ordinates and generalized velocities, which remain unchanged during the system's motion, are called constants of motion. Constants of motion are generalized momenta, corresponding to the cyclic co-ordinates (those on which the Lagrangian function does not depend explicitly).

The energy of a closed system and of a system in a constant force field, remains unchanged because of the homogeneity of time:

$$E = \frac{\partial \mathscr{L}}{\partial \dot{q}_i}\dot{q}_i - \mathscr{L} = T\left(q_j, \dot{q}_j\right) + U\left(q_j\right) = \text{const.}$$

Such systems are called conservative. Conservative forces act in them. The rate of change of the kinetic energy is determined by the rate of change of the work of the acting force $T = \dot{\mathbf{r}}\mathbf{F}$, i.e. by the power. The force acting on the particle α is conservative if it can be represented in the form $\mathbf{F}_\alpha(\mathbf{r}_\alpha) = -\nabla U(\mathbf{r}_\alpha)$ (in this case the total energy $T + U$ is constant). Necessary and sufficient condition for the existence of such a function $U(\mathbf{r}_\alpha)$, is $\nabla \times \mathbf{F}(\mathbf{r}_\alpha) = 0$.

The momentum of the closed mechanical system remains constant as a consequence of homogeneity of space:

$$\mathbf{p} = \sum_\alpha \frac{\partial \mathscr{L}}{\partial \mathbf{v}_\alpha} = \sum_\alpha m_\alpha \mathbf{v}_\alpha = \sum_\alpha \mathbf{p}_\alpha = \text{const.}$$

In an open system the total force determines the rate of change of the momentum $\dot{\mathbf{p}} = \mathbf{F}$. In such a system the separate components of the momentum p_i remain constant if the components of the force in the corresponding co-ordinates x_i are zero: $F_i = 0$. The momentum of a mechanical system in the reference frame of the centre of mass, whose radius-vector is by definition $\mathbf{R} = \sum m_\alpha \mathbf{r}_\alpha / M$, is zero. In any reference frame (an inertial one) the centre of mass moves with a constant velocity $\dot{\mathbf{R}}$, and the momentum of the system is $\mathbf{p} = \sum m_a \dot{\mathbf{r}}_\alpha = M\dot{\mathbf{R}}$.

The angular momentum $\mathbf{L} = \sum(\mathbf{r}_\alpha \times \mathbf{p}_\alpha)$ of a closed system remains constant, because of isotropy of space. The rate of change of the angular momentum of an open system is equal to the torque of the applied forces: $\dot{\mathbf{L}} = \mathbf{N}$. If in a given direction the components of the torque $N_i = 0$, then the corresponding components of the angular momentum in this direction are also conserved in open systems. These are systems with different types of symmetry (central or axial) and the components of the angular momentum with respect to the centre or to the symmetry axis remain constant.

QUESTIONS

1. What does homogeneity of time and homogeneity and isotropy of space mean?
2. Why the law of conservation of energy, which has been proved for a closed system, is true also in an external constant potential field?
3. In which cases is the law of momentum conservation valid in an open system?
4. In what reference frame is the momentum of a mechanical system equal to zero?
5. Suppose that two atoms with equal masses and equal but reversed velocities, are collided. Will the velocities of the atoms remain equal after the collision, if:
   a) before and after the collision the atoms are excited;
   b) as a result of the collision one or both atoms are excited;
   c) before the collision one or both atoms were excited?
6. When can the law of angular-momentum conservation be applied in an open system?
7. A charged particle is in the field of an unlimited charged plane XY. Which components of its momentum and angular momentum are conserved under its motion?
8. Which components of the momentum and the angular momentum of a charged particle are conserved under its motion in the field of an infinite solenoid?
9. Which component of the angular momentum of the electron of a hydrogen atom is conserved under its motion in the field of the proton?

PROBLEMS

1. Find the Cartesian components L_x, L_y, L_z and the square L^2 of the angular momentum in cylindrical co-ordinates ρ, φ, z.
2. Find the cylindrical components L_ρ, L_φ, L_z and the square L^2 of the angular momentum in Cartesian co-ordinates x, y, z.
3. Knowing the Lagrangian function in cylindrical co-ordinates (see Table 1-1), prove that $L_z = \partial\mathscr{L}/\partial\dot{\varphi}$.
4. Find the Cartesian components L_x, L_y, L_z and the square L^2 of the angular momentum in spherical co-ordinates.
5. Find the spherical components L_r, L_θ, L_φ and the square L^2 of the angular momentum in Cartesian co-ordinates x, y, z.
6. A proton of energy $m_p v_0^2/2$ moves toward a heavy nucleus of charge Ze. The impact parameter is equal to *b*. What is the minimal distance of the proton from the nucleus?

Chapter 3

CENTRAL CONSERVATIVE FORCES

SUGGESTED READING

1. Landau, L. D. and E. M. Lifshitz , Mechanics, 2nd ed., Pergamon Press, 1969, Chapters 3, 4.
2. Kibble, T. W., Classical mechanics, McGraw-Hill Book Co., 1973, 2nd ed., Chapter 4.
3. Kittel, Ch., W. D Knight, M. A. Rudermam, Berkeley Physics Course, Vol. I, Mechanics, McGraw-Hill Book Co., 1965, Section 6.1, Chapter 9.

3.1 ONE-DIMENSIONAL MOTION

One-dimensional motion is motion of a system with one degree of freedom. The general form of the Lagrangian function is already known:

$$\mathscr{L}=\gamma(q)\dot{q}^2-U(q)\,. \tag{3.1}$$

In Cartesian co-ordinates (3.1) transforms into

$$\mathscr{L}=\frac{m\dot{x}^2}{2}-U(x)\,. \tag{3.2}$$

We could write the corresponding Lagrange's equation, which is of second order. This equation of motion can be integrated in general. But we already know its first constant of motion, expressed by the conservation law

$$\frac{m\dot{x}^2}{2}+U(x)=E. \tag{3.3}$$

This differential equation is integrated by the method of separation:

$$\frac{dx}{dt}=\sqrt{\frac{2}{m}\left[E-U(x)\right]} \qquad \text{or} \tag{3.4}$$

$$t=\sqrt{\frac{2}{m}}\int\frac{dx}{\sqrt{E-U(x)}}+\text{const.} \tag{3.5}$$

We integrated an equation of motion of second order and, therefore, obtained two constants, *E* and const.

Although the relation (3.5) is obtained in a general form, it allows us to make some conclusions about the character of motion. Suppose that $U(x)$ has the form, shown in Fig. 3-1. Since the kinetic energy is positive, the motion is possible only if $U(x)<E$, i.e. in the interval x_1x_2 and $x>x_3$. The regions $x<x_1$ and x_2x_3 are forbidden. At the points *A, B* and *C,* $U(x)=E$ and the velocity of the particle is equal to zero. These points are called turning points. If the motion is limited by two such points, it is called finite motion and is confined to a given region. If the region is unlimited or is limited only from one side the motion is infinite ($x>x_3$).

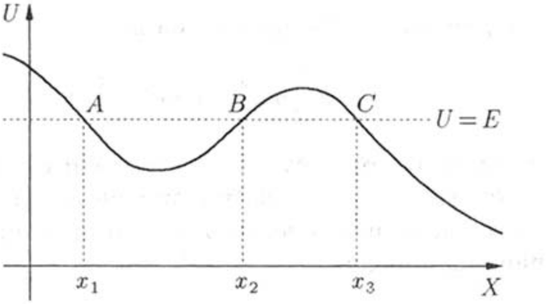


Figure 3-1. The motion is possible if $U(x)<E$, i.e. in the intervals $x_1<x<x_2$ and $x>x_3$, but not possible if $U(x)>E$ ($x_2<x<x_3$). In the points *A, B* and *C* (turning points), $U(x)=E$.

As an illustration, we shall consider two cases of the given form of the potential-energy curve. The first is the potential well, which corresponds to an attractive force, directed to the centre of the well. (We shall note that since $U(x)$ is determined to within an a constant, it is convenient to choose that constant such that $U(x)\to 0$ at $x\to\infty$, as shown in Figs. 3-2 and 3-3.) Two types of motion are possible. If *E* is negative ($E=E_1$ in Fig. 3-2), the motion is finite and is confined to a finite region - the particle oscillates between the two boundary points x_1 and x_2 in which $U(x)=E_1$. When the energy of the particle is equal to the depth of the well $-U_0$, it is at rest at the point $x=0$. If the particle starts its motion far out to the left with velocity v its energy is $E=E_2=mv^2/2$ and its motion is infinite. The particle accelerates when it moves to the centre of the well and decelerates further from the centre. Far from the centre it reaches the initial velocity v.

The second case is the potential barrier (Fig. 3-3). It illustrates a repulsive force directed outward from the centre. There are also two types of motion.

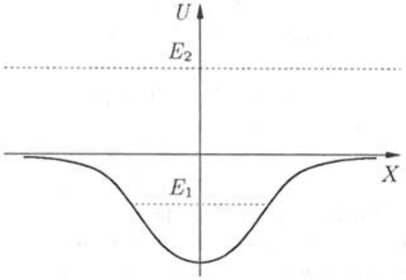


Figure 3-2. Potential well.

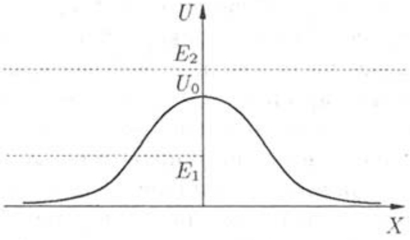


Figure 3-3. Potential barrier.

If the motion starts far out to the left with velocity v_1, such that $E = E_1 = mv_1^2/2 < U_0$ (U_0 is the barrier height), the particle will reach the point $E_1 = U(x)$, then it will reverse its direction and will continue to move towards $-\infty$, finally reaching velocity $-v_1$. If $E = E_2 = mv_2^2/2 > U_0$ the particle will have enough energy to overcome the barrier and in the far right it will reach velocity v_2.

The one-dimensional finite motion has a periodic character. Because of time isotropy (replacing t with $-t$ does not change the Lagrangian function (3.2) and the equation of motion) the motion is reversible. Therefore the time for the motion from x_1 to x_2 equals the time for the motion from x_2 to x_1. The period is equal to twice the time of the transition of the interval $x_1 x_2$, or

$$\tau = \sqrt{2m}\int_{x_1}^{x_2} \frac{dx}{\sqrt{E - U(x)}}, \tag{3.6}$$

where x_1 and x_2 are the solutions of the equation $U(x) = E$ and both τ and x_1 and x_2 are functions of the energy E.

3.2 THE TWO-BODY PROBLEM

The two-body problem takes a very important place both in physics and chemistry. We shall consider a system of two interacting particles of masses

m_1 and m_2. Suppose that in the laboratory frame (Lab-frame) the positions of the particles are given with the radius-vectors $\mathbf{R}_1$ and $\mathbf{R}_2$, and of the centre of mass, with **R** (Fig. 3-4a).

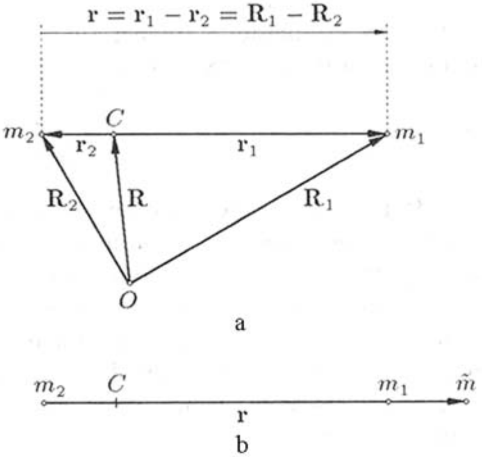


Figure 3-4. Two-body problem:

a) Origin of the laboratory reference frame (Lab-frame) *O*, and the position vectors of the particles of masses m_1 and m_2, $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, and the position of the centre of mass *C*, **R**; $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the particles in the centre-of mass frame (CM-frame) with an origin in the point *C*; **r** is the relative-position vector (|**r**| is the particle separation) - it begins from m_2 and is directed to m_1;

b) the relative-position vector **r** determines the position of the reduced mass $\tilde{m}$ in CM-frame.

We shall perform analysis in CM-frame with an origin at point *C*. In it, the positions of particles with masses m_1 and m_2 are $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. The separation of particles is determined by the value of the relative position vector **r**, which is the difference between their position vectors in both frames (see Fig. 3-4a). In CM-frame we have

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{3.7}$$

Since the potential energy of two interacting particles depends only on their separation, the Lagrangian function may be written as

$$\mathscr{L} = \frac{m_i \dot{\mathbf{r}}_1^2}{2} + \frac{m_2 \dot{\mathbf{r}}_2^2}{2} - U\left(\left|\mathbf{r}_1 - \mathbf{r}_2\right|\right). \tag{3.8}$$

According to (2.24) (in the CM-frame **R**=0), we obtain

$$m_1\mathbf{r}_1 + m_2\mathbf{r}_2 = 0. \tag{3.9}$$

From (3.7) and (3.9), we relate the positions of both particles with the relative vector **r**:

$$\mathbf{r}_1 = \frac{m_2}{m_1 + m_2}\mathbf{r}, \quad \mathbf{r}_2 = -\frac{m_1}{m_1 + m_2}\mathbf{r}. \tag{3.10}$$

Substitution into (3.8) yields for the Lagrangian function

$$\mathscr{L} = \frac{\tilde{m}\dot{\mathbf{r}}^2}{2} - U(r), \tag{3.11}$$

where

$$\tilde{m} = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_1 m_2}{M}, \qquad \left(\frac{1}{\tilde{m}} = \frac{1}{m_1} + \frac{1}{m_2}\right) \tag{3.12}$$

is called a reduced mass (the sigh ~ is read tilde). The Lagrange's equation is

$$\tilde{m}\frac{d^2\mathbf{r}}{dt^2} = -\frac{\partial U(r)}{\partial \mathbf{r}}. \tag{3.13}$$

Thus, the two-body problem reduces to the problem of motion of an imaginary body with a mass $\tilde{m}$ and a position vector **r**, which is the relative vector of the first particle with respect to the second one (Fig. 3-4b).

Thus to find the trajectories of two bodies it is enough to solve the problem of motion of one body, which has the reduced mass of both bodies. The reduced mass is smaller than any of the two masses. For a diatomic molecule, for which the masses of atom are $m_1 = m_2 = m$, the reduced mass is

$$\tilde{m} = m/2. \tag{3.14}$$

If we have a light and a heavy particle, so that $m_1 << m_2$, then the reduced mass is

$$\tilde{m} = \frac{m_1 m_2}{m_1 + m_2} = m_1 \frac{1}{1 + \frac{m_1}{m_2}} \approx m_1\left(1 - \frac{m_1}{m_2}\right). \tag{3.15}$$

If m_e stands for the electron mass and $m_p = 1836 m_e$ for the proton mass, the reduced mass of the hydrogen atom is

$$\tilde{m} = m_e\left(1 - \frac{1}{1836}\right) \approx m_e. \tag{3.16}$$

It is evident that in the case of a light and a heavy particle, the reduced mass is very close to the light particle's mass.

The function (3.11) and Lagrange's equation (3.1) describe the motion of a body with mass $\tilde{m}$ in the potential field $U(r)$. Our problem is to find the vector $\mathbf{r}$ as a function of time. The Lagrangian function leads to two equations for the determination of the two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ as functions of time. We reduced the problem of two bodies to the problem of one body. This problem is readily solved, but in order to interpret correctly the motion of both particles we have to remember the following:

First, from the Eq. (3.13) we can determine $\mathbf{r}(t)$. Recall that $\mathbf{r}$ is a vector pointed from particle m_2 to particle m_1. Thus we shall determine the motion of m_1 with respect to m_2, as m_2 is fixed at rest in the inertial reference frame. However, Eq. (3.13) does not contain the mass m_1, but the reduced mass $\tilde{m}$, and in the right side the term $-\partial U/\partial \mathbf{r}$ is the force, acting on the mass m_1, but not on the reduced mass (according to the third Newton's law the force $\partial U/\partial \mathbf{r}$ acts on mass m_2).

Second, after having found $\mathbf{r}$, we can determine the motion of both particles m_1 and m_2 in the CM-frame, using Eq. (3.10). In other words, we shall obtain the radius-vectors $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t)$, which define the trajectories with respect to the immobile centre of mass. Once again, recall that $\mathbf{r}(t)$ determines the trajectory of m_1 with respect to m_2, i.e. the particle of m_2 would be immobile.

Third, the Lagrangian function (3.11) is written in CM-frame and contains only the relative motion of the particles. Since the system of two particles is a conservative one, the centre of mass moves with a constant velocity $\dot{\mathbf{R}}$, which according to (2.24) is determined by the initial condition $\dot{\mathbf{R}}_1(0)$ and $\dot{\mathbf{R}}_2(0)$. In the Lab-frame the positions of m_1 and m_2 are determined by the vectors $\mathbf{R} + \mathbf{r}_1$ and $\mathbf{R} + \mathbf{r}_2$ and their velocities with $\dot{\mathbf{R}} + \dot{\mathbf{r}}_1$ and $\dot{\mathbf{R}} + \dot{\mathbf{r}}_2$, respectively. Or, in Lab-frame the trajectories of m_1 and m_2 are determined by the vectors $\mathbf{R} + \frac{m_2}{m_1 + m_2}\mathbf{r}$ and $\mathbf{R} - \frac{m_1}{m_1 + m_2}\mathbf{r}$.

3.3 CENTRAL CONSERVATIVE FORCES

*A force **F** is said to be central if is directed towards or away from a fixed point.* In this course we shall mainly deal with central forces acting according to the law of inverse squares:

$$F = -\frac{C}{r^2}. \tag{3.17}$$

The electrostatic and gravitational forces, acting between two immobile particles has such form. If one of the particles is positioned at the origin of the co-ordinate system and the other at a distance r, these central forces are always directed along the radius-vector $\mathbf{r}$:

$$\mathbf{F} = -\frac{C}{r^2}\mathbf{r}^0 = -\frac{C}{r^2}\frac{\mathbf{r}}{r}. \tag{3.18}$$

For the gravitational force between two particles of masses m_1 and m_2, we have $C = G_0 m_1 m_2$, where $G_0 = 6{,}67.10^{-11}\ \mathrm{N.m^2/kg^2}$ is the gravitational constant, and for the electrostatic force between two charges $\mathbf{q}_1$ and $\mathbf{q}_2$, $C = \mathbf{q}_1\mathbf{q}_2/4\pi\varepsilon_0$, where ε_0 is the permittivity of the vacuum. These forces are conservative and can be expressed through the potential energy

$$\mathbf{F} = -\frac{\partial U(r)}{\partial \mathbf{r}}, \quad U(r) = -\frac{C}{r}. \tag{3.19}$$

We have chosen the arbitrary constant of U so that $U(\infty) = 0$. It is preferable to deal with the scalar $U(r)$ than with the vector $\mathbf{F}(\mathbf{r})$.

We shall note that $C > 0$ corresponds to attractive forces (a gravitational force or an electrostatic one between charges of opposite signs) and $C < 0$ corresponds to repulsive forces (an electrostatic force between charges of equal signs). In atomic physics another central force plays a basic role – the nuclear force. From experiments on scattering of elementary particles, it is known that the nuclear force acts on a small distance between two nucleons (protons or neutrons) with a potential energy

$$U(r) = -\frac{C\exp(-r/r_0)}{r}. \tag{3.20}$$

Here $r_0 \approx 2.10^{-15}$ m, $C \approx 10^{-27}$ J.m. It is easy to see evaluate that at $r \le r_0$ the nuclear force between two protons dominates the Coulomb force of their repulsion. We shall note that (3.20) is an approximation.

Since central forces are always collinear to the radius-vector **r,** their torque is zero

$$\mathbf{N} = \mathbf{r} \times \mathbf{F} = 0. \tag{3.21}$$

According to (2.39) this means that the angular momentum is constant

$$\mathbf{L} = \mathbf{r} \times \tilde{m}\dot{\mathbf{r}} = \text{const}, \tag{3.22}$$

where $\tilde{m}$ is the reduced mass of the particles interacting with the force (3.18). This is the law of conservation of angular momentum and it contains two statements: that its direction is constant and that its magnitude is constant. The angular momentum is perpendicular to the plane of motion - the vector **L** is along the normal to the plane of **r** and $\dot{\mathbf{r}}$. Hence the statement that the direction of **L** is constant implies that **r** and $\dot{\mathbf{r}}$ must always lie in a fixed plane, which is perpendicular to **L**. From here it is evident that the orbit of the particle lies entirely in one plane. The description of such motion requires only two variables, which may be taken as the polar co-ordinates r and φ. Then the Lagrangian function can be written as

$$\mathscr{L} = \frac{\tilde{m}}{2}\left(\dot{\mathbf{r}}^2 + \mathbf{r}^2\dot{\varphi}^2\right) - U(r). \tag{3.23}$$

The co-ordinate φ is a cyclic co-ordinate (see Section 2.1) and the generalized momentum $P_\varphi = \partial\mathscr{L}/\partial\dot{\varphi}$ is a constant of the motion:

$$P_\varphi = \tilde{m}r^2\dot{\varphi} = \text{const}. \tag{3.24}$$

We shall verify that this quantity is equal to the angular momentum. The velocity $\dot{\mathbf{r}}$ (3.22) has components in the directions of the unit vectors $\mathbf{r}^0$ and $\boldsymbol{\varphi}^0$. Indeed, as it is shown in Fig. 3-5 the displacement $d\mathbf{r}$ of the particle, due to the increments of the elements dr and $d\varphi$, can be represented as

$$d\mathbf{r} = dr\mathbf{r}^0 + rd\varphi\,\boldsymbol{\varphi}^0 \tag{3.25}$$

and dividing by dt, we obtain

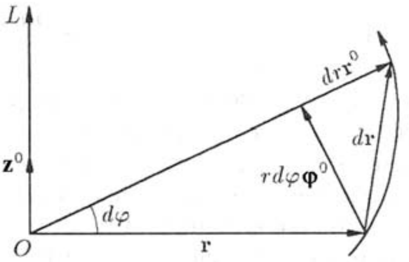


Figure 3-5. The motion of a particle of a reduced mass $\tilde{m}$ in a central field with a centre O is performed in a plane, normal to **L** and is described with the polar co-ordinates r and φ ($\mathbf{r}^0$ and $\boldsymbol{\varphi}^0$ are corresponding unit vectors). At the elementary change of the co-ordinates with dr and $d\varphi$ the particle displaces with $d\mathbf{r}$.

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \dot{r}\mathbf{r}^0 + r\dot{\varphi}\boldsymbol{\varphi}^0. \tag{3.26}$$

The substitution of (3.26) into the expression for **L** (3.22) yields

$$\mathbf{L} = \mathbf{r} \times \tilde{m}\mathbf{v} = r\mathbf{r}^0 \times \tilde{m}\left(\dot{r}\mathbf{r}^0 + r\dot{\varphi}\boldsymbol{\varphi}^0\right) = 0 + \tilde{m}r^2\dot{\varphi}\left(\mathbf{r}^0 \times \boldsymbol{\varphi}^0\right) = \tilde{m}r^2\dot{\varphi}\mathbf{z}^0. \tag{3.27}$$

The magnitude of **L** is $L = L_z = \tilde{m}r^2\dot{\varphi}.$ We proved that under the motion in central-force field the generalized momentum P_φ has a meaning of angular momentum:

$$L = L_z = P_\varphi = \tilde{m}r^2\dot{\varphi}. \tag{3.28}$$

The law of conservation of angular momentum has an interesting geometrical interpretation. When the angle φ changes by an amount $d\varphi$ the position vector **r** sweeps out an area dS (Fig. 3-5):

$$dS = r^2 d\varphi/2. \tag{3.29}$$

The rate of change of this area, which is called an area velocity or a sector velocity, is

$$\frac{dS}{dt} = \frac{1}{2}r^2\dot{\varphi} = \frac{L}{2\tilde{m}} = \text{const}. \tag{3.30}$$

*For equal intervals of time the radius-vector sweeps equal surfa*ce. This law is known as *second Kepler's law* of the motion of the planets. As we saw, it is valid for any central force, not only for a gravitational one.

The forces acting according to the inverse-square law are central and conservative ones. Besides the law of angular-momentum conservation, the law of the conservation of energy is also valid:

$$E=\frac{\tilde{m}}{2}\left(\dot{r}^2+r^2\dot{\varphi}^2\right)+U\left(r\right). \tag{3.31}$$

We have found two constants of motion (3.28) and (3.31), which express the laws of conservation of angular momentum and energy. (These constants of motion are very often called first integrals of the motion, as they contain first derivatives of the co-ordinates.) Important information can be obtained directly from these equations, without solving them to determine r and φ as functions of time. Eliminating $\dot{\varphi}$ in (3.31) with the help of (3.28), we obtain an equation for r and $\dot{r}$ only:

$$E=\frac{1}{2}\tilde{m}\dot{r}^2+\frac{L^2}{2\tilde{m}r^2}+U(r). \tag{3.32}$$

Often this is called a radial equation, underlying that it indicates the energy balance only under the change of the distance r to the centre. Comparing this equation with (3.3), we see that it has the same form as the equation of energy for one-dimensional motion with "potential energy" $\tilde{U}(r)$:

$$\tilde{U}\left(r\right)=\frac{L^2}{2\tilde{m}r^2}+U(r). \tag{3.33}$$

This energy is called effective potential energy.

It is easy to explain the physical meaning of the additional term $L^2/2\tilde{m}r^2$ in $\tilde{U}\left(r\right)$. Taking the value of L from (3.28), it can be represented as $\tilde{m}r^2\dot{\varphi}/2$. This term is different from zero only for motion along φ, i.e. rotation. This is the reason to call the additional energy $L^2/2\tilde{m}r^2$ a centrifugal energy. Despite that in (3.32) the motion is represented as one-dimensional (radial), the motion along φ, i.e. the rotation, is present non-explicitly in the term $\propto L^2$. The angular momentum is a constant, but it exists as a consequence of the motion along φ, i.e., of the fact that $\dot{\varphi}\neq 0$. The effective potential energy can be used for qualitative analysis, just as $U(x)$ can be used in a one-dimensional motion. When

$$\tilde{U}(r) = \frac{L^2}{2\tilde{m}r^2} + U(r) \le E \,. \tag{3.34}$$

and $\tilde{U}(r') = \tilde{U}(r'') = E$ the motion is finite and is bounded in the region $r' \le r \le r''$. Both solutions of the equation determine the minimal and maximal distance from the centre, and the orbit lies between them. Under the conditions (3.34) and $\tilde{U}(r') = E$, the motion is semi-infinite in the region $r \ge r'$ with the turning point r'. If $\tilde{U}(r)$ has a minimum and E is equal to $\tilde{U}_{\min}$, then $\dot{r}$ is always zero (see (3.32)) and r is fixed at the position of the minimum. In this case the particle moves along a circle around the centre.

3.4* ORBITS OF THE MOTION

In order to determine the character of motion we have to know the form of the function $\tilde{U}(r)$ in (3.33). The centrifugal energy is always positive. In the case of a repulsive force, the function of the potential $U(r) = -C/r$ $(\mathrm{C} < 0)$ is positive for any r. Then the effective potential energy $\tilde{U}(r)$ decreases monotonically from $+\infty$ at $r = 0$ to 0 at $r = \infty$ (Fig. 3-6). There is no minimum and the circular motion is not possible. For any (positive) value of E there is a minimal distance $r = r_{\min}$ (the distance of closest approach) which is the only solution of the equation $\tilde{U}(r) = E$, but there is no maximal distance. If the radial velocity is such that the particle approaches the centre, it will move with an orbit in which the value radius-vector r will decreased to $r_{\min}$ and after that it will increases to infinity. It is known (and later on will be proved) that such an orbit is a hyperbola (Fig. 3-6b). If the force is attractive $(C > 0)$ the effective potential energy takes the form

$$\tilde{U}(r) = \frac{L^2}{2\tilde{m}r^2} + U(r) = \frac{L^2}{2\tilde{m}r^2} - \frac{C}{r}. \tag{3.35}$$

From the summation of the potential and centrifugal energy we obtain the curve $\tilde{U}(r)$, which possesses a minimum (Fig. 3-7). Equating the derivative $d\tilde{U}(r)/dr$ to zero, we determine r_0, at which $\tilde{U}(r)$ is minimal

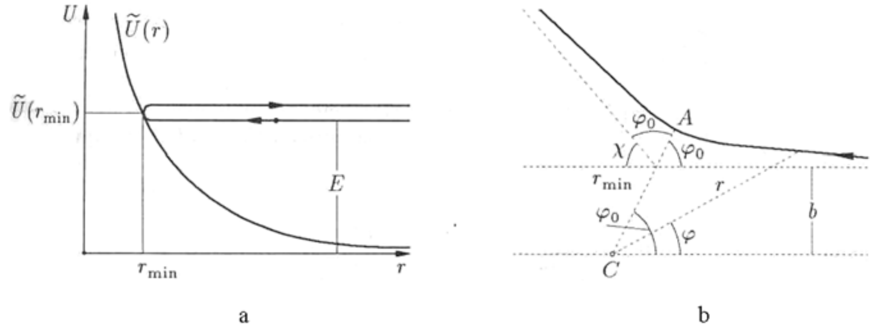


Figure 3-6. Repulsive central conservative force:

a) the effective potential energy is monotonically decreasing function;

b) the orbit of the particle is hyperbola; *b* is the impact factor; the angle χ, determining the deflection from the initial particle direction, is a scattering angle, $r_{\min}$ is the minimal distance of the centre to the orbit, which is symmetrical with respect to the line defining $r_{\min}$.

$$\frac{d\tilde{U}(r)}{dr} = -\frac{L^2}{2\tilde{m}r^3} + \frac{C}{r^2} = 0, \quad r_0 = \frac{L^2}{C\tilde{m}}, \quad \tilde{U}_{\min} = -\frac{C^2\tilde{m}}{2L^2} = \frac{U(r_0)}{2}. \qquad (3.36)$$

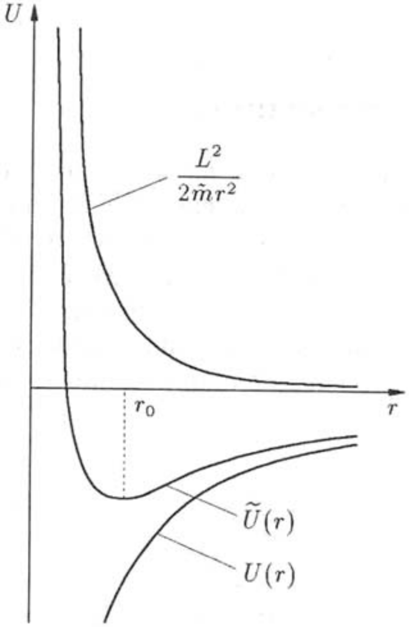


Figure 3-7. The effective potential energy $U(r)$ is a sum of the potential energy $U(r)$ and the centrifugal energy $L^2/2\tilde{m}r^2$, and it possesses a minimum $\tilde{U}_{\min} = U(r_0)/2$ at $r = r_0$.

The form of the curve $\tilde{U}(r)$ allows the determination of the character of the motion. We shall note that the curve is symmetrical with respect to the force centre *O* (Fig. 3-8a).

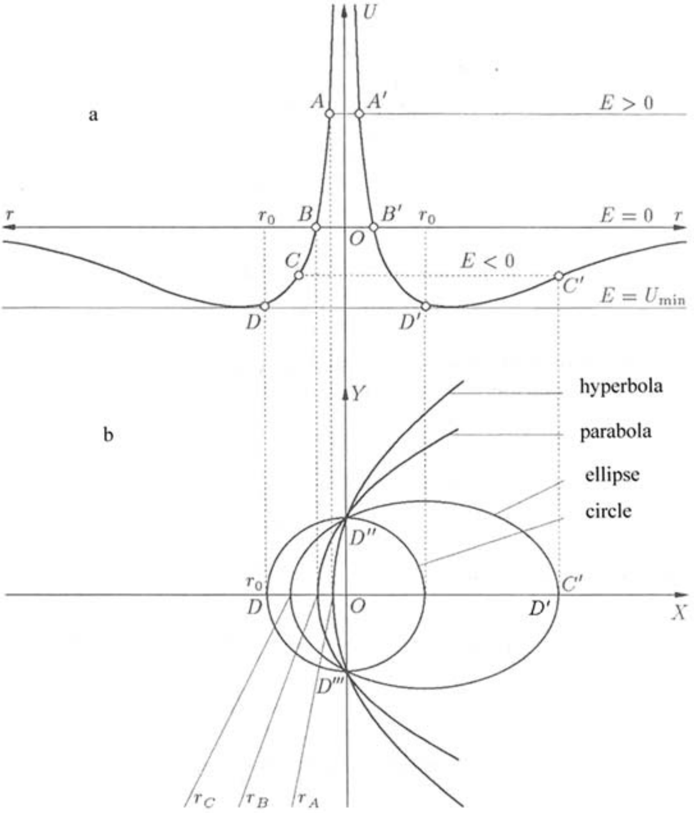


Figure 3-8. a) View of the effective potential energy $\tilde{U}(r)$ for bodies with equal reduced masses and angular moment **L**, but different energies *E*. The corresponding orbits are: $E > 0$ - a hyperbola, *E*=0 - a parabola, *E*<0 - an ellipse, $E = \tilde{U}_{\min}$ - a circle. All orbits go through the points *D″* and *D‴*.

At $E > 0$ the motion is unbounded and the minimal distance to the centre *O* is $r_{\min} = r_A$. The orbit is a hyperbola.

At $E = 0$ the motion is unbounded and the minimal distance to the centre *O* is $r_{\min} = r_B$. The orbit is a parabola.

At $E < 0$ the motion is finite and holds in the region $r_{\min} \le r \le r_{\max}$, where $r_{\min} = r_C$ and $r_{\max} = r_{C'}$. The orbit is an ellipse.

At $E=\tilde{U}_{\min}$ the motion is finite with a constant minimal distance $r=r_0$. The orbit is a circle.

And now, let us show that the orbits are indeed such. In order to find the equation of the orbit, we have to eliminate the time from the constants of motion (3.28) and (3.32), and obtain the equation which relates r and φ. From (3.32) at $U(r)=-C/r$ we readily find

$$\dot{r}\equiv\frac{dr}{dt}=\sqrt{\frac{2}{\tilde{m}}\left(E+\frac{C}{r}-\frac{L^2}{2\tilde{m}r^2}\right)}. \qquad (3.37).$$

We rewrite (3.28) as $dt=d\varphi\tilde{m}r^2/L$. Substituting it into the last equation, we get

$$\varphi=\int\frac{L/r^2}{\sqrt{2\tilde{m}\left(E+\frac{C}{r}\right)-\frac{L^2}{r^2}}}dr+\text{const.} \qquad (3.38)$$

This equation relates r and φ, i.e., it is the equation of the orbit. We rewrite it in the form

$$\varphi=\int\frac{L/r^2}{\sqrt{2\tilde{m}E+\left(\frac{C\tilde{m}}{L}\right)^2-\left(-\frac{C\tilde{m}}{L}+\frac{L}{r}\right)^2}}dr+\text{const.} \qquad (3.39)$$

and use the substitutions

$$2\tilde{m}E+\left(\frac{C\tilde{m}}{L}\right)^2=a^2,\quad \left(-\frac{C\tilde{m}}{L}+\frac{L}{r}\right)=u,\quad \frac{-Ldr}{r^2}=du. \qquad (3.40)$$

This yields

$$\varphi=-\int\frac{du}{\sqrt{a^2-u^2}}=\arccos\frac{u}{a}+\text{const.} \qquad (3.41)$$

Returning to the initial variable r we represent the relation between r and φ in the following form

$$\varphi = \arccos\frac{-\dfrac{C\tilde{m}}{L}+\dfrac{L}{r}}{\sqrt{2\tilde{m}E+\left(\dfrac{C\tilde{m}}{L}\right)^2}} = \arccos\frac{-1+\dfrac{L^2}{C\tilde{m}}\dfrac{1}{r}}{\sqrt{1+\left(\dfrac{2El^2}{C^2\tilde{m}}\right)^2}} = \arccos\frac{-1+\dfrac{p}{r}}{e}, \quad (3.42)$$

where we substituted $L^2/C\tilde{m} = r_0 \equiv p$ (see (3.36)) and $\sqrt{1+2L^2E/C_2\tilde{m}} = e$. We set the initial angle $\varphi_0 = 0$ (it determines the orientation of the orbit). The final form of the equation of the orbit is

$$p/r = 1 + e\cos\varphi. \quad (3.43)$$

This is the conventional representation of a conic section with the focus in the centre of the field; the quantity p is called the parameter of the orbit and e is called eccentricity. The parameter determines the size of the conic section and the eccentricity - its form. Depending on the values of e we obtain the four types of orbits:

$e > 1$ - a hyperbola,
$e = 1$ - a parabola,
$0 < e < 1$ - an ellipse,
$e = 0$ - a circle.

Taking into account (3.36) we can write for the eccentricity

$$e = \sqrt{1-\frac{E}{\tilde{U}_{\min}}} = \sqrt{1+\frac{E}{\left|\tilde{U}_{\min}\right|}}, \quad (3.44)$$

from where it is evident that the conditions for *e*, which determine different types of orbits precisely coincide with the conditions for *E* in Fig. 3-8.

We shall note that the obtained orbits are the orbits of a body moving around another immobile body. In order to find the real orbits around the centre of mass (Fig. 3-9), we have to return to the equations (3.10).

The radius-vector value of the reduced mass changes as (see (3.43))

$$r = \frac{p}{1 + e\cos\varphi}. \quad (3.45)$$

According to (3.10), $\mathbf{r}_1$ has the same direction and its magnitude is

$$r_1 = \frac{pm_2}{m_1+m_2}\frac{1}{1+e\cos\varphi} = \frac{p_1}{1+e\cos\varphi}. \tag{3.46}$$

The particle moves along an ellipse and the direction of its radius-vector $\mathbf{r}_1$ coincides with the direction of **r.**

In any moment the vector $\mathbf{r}_2$ is opposite to **r** (3.10). Therefore, when **r** is oriented at an angle φ, the vector $\mathbf{r}_2$ is oriented at an angle $\varphi_2 = \pi + \varphi$. Then from (3.10) and (3.45) we get

$$r_2 = \frac{m_2}{m_1+m_2}\frac{1}{1+e\cos(\pi+\varphi)} = \frac{p_2}{1-e\cos\varphi}. \tag{3.47}$$

The orbit is also an ellipse and m_2 moves so that both particles are on the line passing through the centre of mass at any moment (Fig. 3-9).

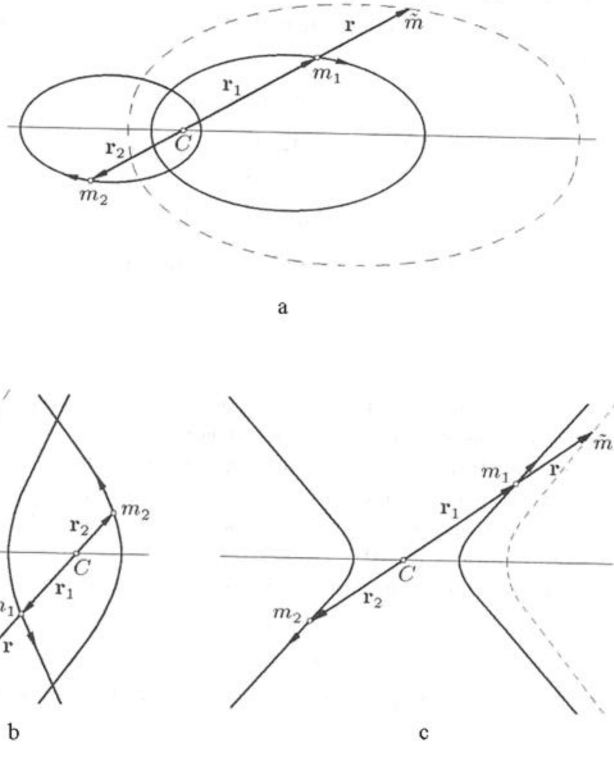


Figure 3-9. The orbits of particles with masses $\tilde{m}, m_1$ and m_2 $(m_1 : m_2 = 2:3)$ in CM-frame with an origin at the point *C*: a) ellipses (if $m_1 \ll m_2$, the ellipses are contained in one another!); b) hyperbolas (an attractive force); c) hyperbolas (a repulsive force). $\mathbf{r}_1$ and $\mathbf{r}_2$ are radius-vectors of the particles m_1 and m_2, **r** is a radius-vector of the reduced mass $\tilde{m}$.

3.5* ELASTIC COLLISIONS

One of the most important ways to obtain information about very small bodies is to bombard them and measure the number of particles reflected in a given direction. The angular distribution of scattered particles depends on the target form and the nature of the force between it and the particles. In order to interpret the results of similar experiments, it is necessary to know how to calculate the angular distribution when the force is known.

We shall first analyse the case of a single act, when only one particle impacts on a target (also a particle). In the next section we will introduce the characteristic of a scattering of a particle flow by a central field, and will consider the important case of scattering by a Coulomb potential field.

The collision is a process, described by a special case of the two-body problem. In the beginning the particles are far from each other, as a result of which their motion is uniformly linear. As they approach each other, the interaction $U(r)$ influences strongly their motion, and it becomes non-uniformly curvilinear. After that, they go to infinity, moving uniformly and linearly, or remain at a finite distance from each other. In the first case we speak about scattering, and in the second about the capture of a particle. We shall underline that the collision does not necessarily mean a mechanical contact between the particles, but change of direction and/or the motion character due to their interaction.

We shall consider an elastic collision between two particles. The collision is elastic when it is not accompanied by a change of the internal energy of the particles. Hence, there is not a kinetic-energy loss due to the collision.

In the problem of scattering we have to use two reference frames simultaneously: Lab-frame, in which the initial values $\mathbf{p}_1$ and $\mathbf{p}_2$ of the momenta are given, and their values $\mathbf{p}'_1$ and $\mathbf{p}'_2$ after the collision are sought, and CM-frame, which is suitable for the analysis. In the last frame we shall denote the quantities with index "$_0$" (e.g., $\mathbf{v}_{10}$ is the velocity of the first particle in the CM-frame before the collision) and with prime, the quantities after the collision.

In the Lab-frame let the second particle before the collision to be at rest, i.e. $\mathbf{v}_2 = 0$. Thus, according to (2.25) and (3.10), the velocities of the centre of mass $\mathbf{u}$ in the Lab-frame, and of the particles in the CM-frame are, respectively,

$$\mathbf{u} = \frac{m_1}{m_1 + m_2}\mathbf{v}_1, \quad \mathbf{v}_{10} = \frac{m_2}{m_1 + m_2}\mathbf{v}_1, \quad \mathbf{v}_{20} = -\frac{m_1}{m_1 + m_2}\mathbf{v}_1. \tag{3.48}$$

For the momenta of both particles after multiplying their velocities by m_1 and m_2 we have

$$\mathbf{p}_{10} = \tilde{m}\mathbf{v}_1, \quad \mathbf{p}_{20} = -\tilde{m}\mathbf{v}_1. \tag{3.49}$$

The total momentum of the particles in the CM-system, as expected, is zero. From the conservation of momentum law, it follows that after the collision the momenta of the particles will also differ by sign, $\mathbf{p}'_{10} = -\mathbf{p}'_{20}$. Due to energy conservation, unchanged remain also their magnitudes $|\mathbf{p}'_{10}| = |\mathbf{p}'_{20}|$. Hence, the momenta of the particles in the CM-frame are only turned off to the angle χ without changing their values. (Fig. 3-10). Denoting with $\mathbf{e}^0$ a unity vector of the velocity of the particle m_1 after the collision, we can write the velocities of both particles in the following form:

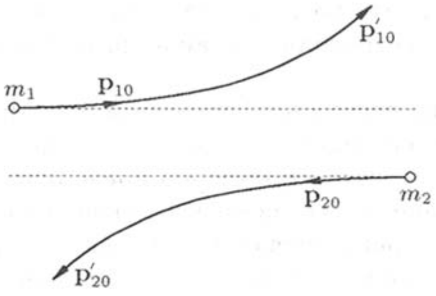


Figure 3-10. Scattering of the particles in CM-frame: the momenta before the collision $\mathbf{p}_{10}$ and $\mathbf{p}_{20}$ are equal and opposite $\mathbf{p}_{10} = -\mathbf{p}_{20}$; the momenta after the collision remain the same but they are turned off to the angle χ.

$$\mathbf{v}'_{10} = \frac{m_2}{m_1 + m_2} v_1 \mathbf{e}^0, \quad \mathbf{v}'_{20} = -\frac{m_1}{m_1 + m_2} v_1 \mathbf{e}^0. \tag{3.50}$$

Adding to these velocities the velocity **u** of the centre of mass, we shall obtain the particles' velocities after the collision in the Lab-frame. The corresponding expressions for the momenta have the following form

$$\begin{aligned} \mathbf{p}'_1 &= \frac{m_1}{m_1 + m_2}\mathbf{p}_1 + \frac{m_2}{m_1 + m_2} p_1 \mathbf{e}^0, \\ \mathbf{p}'_2 &= \frac{m_1}{m_1 + m_2}\mathbf{p}_1 - \frac{m_2}{m_1 + m_2} p_1 \mathbf{e}^0, \end{aligned} \tag{3.51a}$$

or

$$\begin{aligned}\mathbf{p}_1' &= \frac{m_1}{m_1+m_2}\mathbf{p}_1 + p_{10}\mathbf{e}^0 = \frac{m_1}{m_1+m_2}\mathbf{p}_1 + \mathbf{p}_{10}',\\ \mathbf{p}_2' &= \frac{m_2}{m_1+m_2}\mathbf{p}_1 - p_{10}\mathbf{e}^0 = \frac{m_2}{m_1+m_2}\mathbf{p}_1 - \mathbf{p}_{10}'.\end{aligned} \tag{3.51b}$$

The obtained relations become very clear, when they are shown graphically. Then they are called momentum diagrams. Let's represent the vector $\mathbf{p}_1$ by the line AB as the sum of $AO = \frac{m_1 p_1}{m_1+m_2}$ and $OB = \frac{m_2 p_1}{m_1+m_2}$ (Fig. 3-11a). We shall draw a circle with a centre in point O and radius

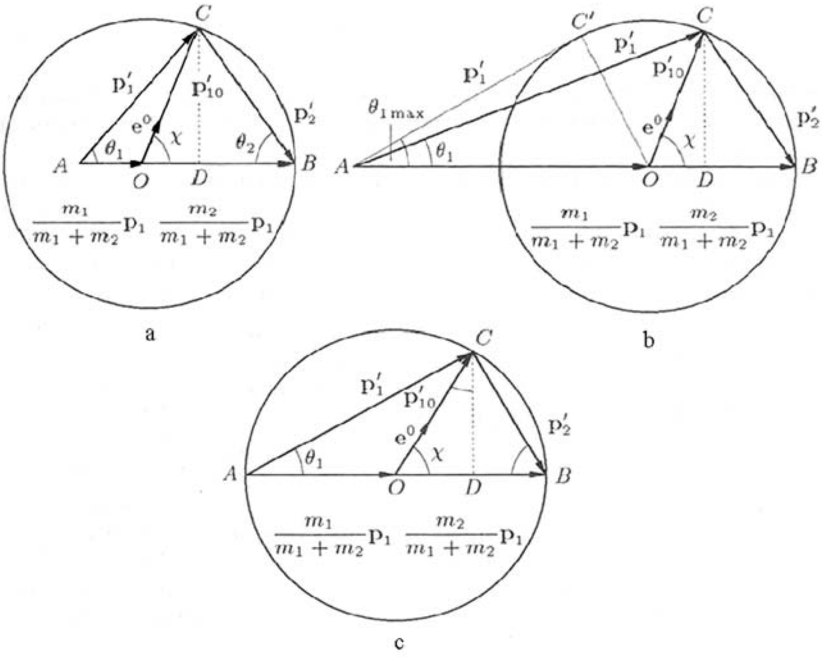


Figure 3-11. Momentum diagram of an elastic collision between the particles m_1 and m_2 : a) $m_1 < m_2$, b) $m_1 > m_2$, c) $m_1 = m_2$. Here $\mathbf{p}_1$ and $\mathbf{p}'_1$ are the momenta of m_1 in Lab-frame before and after the collision; $\mathbf{p}'_2$ is the momentum of m_2 in Lab-frame after the collision; $\mathbf{p}'_{10}$ is the momentum of m_1 in CM-frame after the collision and $\mathbf{e}^0$ is the unity vector in its direction; $m_2\mathbf{p}_1/(m_1+m_2) = \mathbf{p}_{10}$ is the momentum of m_1 in CM-frame before the collision $(\mathbf{p}_{10} \parallel \mathbf{p}_1)$; χ is the scattering angle of m_1 and m_2 in CM-frame; θ_1 and θ_2 - scattering angles of m_1 and m_2 in Lab-frame.

$\frac{m_2 p_1}{m_1+m_2}$. If $m_1 < m_2$, the point *A* is in the circle (Fig. 3-11a), but if $m_1 > m_2$, the point *A* is outside of it (Fig. 3-11b). From the point *O,* at an angle χ with respect of $\mathbf{p}_1$ we plot a unity vector, along which direction the first particle moves after the collision (in the CM-frame). Then *OC* will represent the vector $\frac{\mathbf{e}_0 p_1 m_2}{m_1+m_2}$, the line *AC* - the vector $\mathbf{p}'_1$ and *CB* - the vector $\mathbf{p}'_2$ in full agreement with formulae (3.51).

Let's find the scattering angles. They are determined by the deflection of the particles after the collision. In the Lab-frame the scattering angle of particle m_1 is θ_1, between the vectors $\mathbf{p}_1$ and $\mathbf{p}'_1$, and of particle m_2 is θ_2, between the vectors $\mathbf{p}_2$ and $\mathbf{p}'_2$. The scattering angle χ in the CM-frame is the angle between the vectors $\mathbf{p}'_{10} = m_1 \mathbf{v}'_{10}$ and $\mathbf{p}_1$ $(\mathbf{p}_1 \parallel \mathbf{p}_{10})$. The sum $\theta_1 + \theta_2$ determines the angle between both particles after the collision. The scattering angles θ_1 and θ_2 can be expressed through χ. For the determination of χ we have to know both the law of interaction between the particles and the initial conditions. For the angle θ_1 from ΔADC and ΔODC we obtain

$$\tan\theta_1 = \frac{CD}{AD} = \frac{OC\sin\chi}{AO+OD} = \frac{\frac{p_1 m_2}{m_1+m_2}\sin\chi}{\frac{p_1 m_1}{m_1+m_2} + \frac{p_1 m_2}{m_1+m_2}\cos\chi}, \tag{3.52}$$

and after dividing the nominator and the denominator by $p_1/(m_1+m_2)$, we have

$$\tan\theta_1 = \frac{m_2\sin\chi}{m_1 + m_2\cos\chi}. \tag{3.53}$$

For the scattering angle θ_2 from the isosceles ΔBOC triangle we obtain

$$\theta_2 = \frac{\pi-\chi}{2}. \tag{3.54}$$

Since the scattering angle χ in the CM-frame can change from 0 to π, the scattering angle of the particle m_2 in Lab-frame can change from $\pi/2$ to 0.

More complex is the case of the scattering angle θ_1 of particle m_1 - from the diagram it is seen that the cases $m_1 < m_2$ and $m_1 > m_2$ lead to different pictures. In the first case θ_1 is equal to zero at $\chi = 0$, then monotonically increases with an increase of χ (remaining always less than χ) up to a value $\theta_1 = \pi$ at $\chi = \pi$. At the same time the difference between θ_1 and χ is as small as the relation m_1 / m_2 is smaller - when $m_1 / m_2 \to 0$, then $\theta_1 \to \chi$.

If $m_1 > m_2$, for small χ the angle θ_2 grows when χ increases, but to some limited value, corresponding to χ, at which the vector $\mathbf{p}'_1$ becomes tangent to the circle. Further increase of χ leads to the decrease of θ_1, and at $\chi = \pi$ it becomes zero. Consequently, for the scattering of a heavier particle, the scattering angle θ_1 can not be bigger than $\theta_{1\max}$ (the point *C′* in Fig. 3-11b correspond to this case):

$$\sin\theta_{1\max} = \frac{m_2}{m_1}. \tag{3.55}$$

In the particular case when the masses of the particles are equal, $m_1 = m_2$, formula (3.53) is substantially simplified:

$$\tan\theta_1 = \frac{\sin\chi}{1+\cos\chi} = \tan\frac{\chi}{2} \tag{3.56}$$

and, hence,

$$\theta_1 = \frac{\chi}{2}, \quad \theta_2 = \frac{\pi}{2} - \frac{\chi}{2}. \tag{3.57}$$

In other words, in Lab-frame, in the case of equal masses, the angle between particles after the scattering is $\pi/2$.

3.6* SCATTERING OF PARTICLES. FORMULA OF RUTHERFORD

In Section 3.2 we showed that the problem of the motion of two interacting particles reduced to the problem of the motion of a particle with reduced mass $\tilde{m}$. Knowing the trajectory of the reduced particle, we can calculate the trajectories of both particles. We shall use this method for an investigation of the scattering of two particles m_1 and m_2. Let us return to Fig. 3-6b. The scattering angle χ is a function of the impact parameter *b*, $\chi = \chi(b)$. In the experiment with microparticles the impact parameter *b* can not be determined. Therefore, we must use a statistical approach to scattering.

Let us suppose that a beam of particles impinges on the force centre. We shall characterise the beam through its incident flux *n* - the number of particles crossing unit transverse area per unit time (here *n* is the particle-flux density). The number of particles dN_χ, scattered under an angle lying between χ and $\chi + d\chi$ (Fig 3-12) can be found experimentally. These are particles with an impact parameter lying within *b* and $b + bdb$ and their number is equal to the number of particles, passing through the ring of radius *b* and width *db*, i.e.

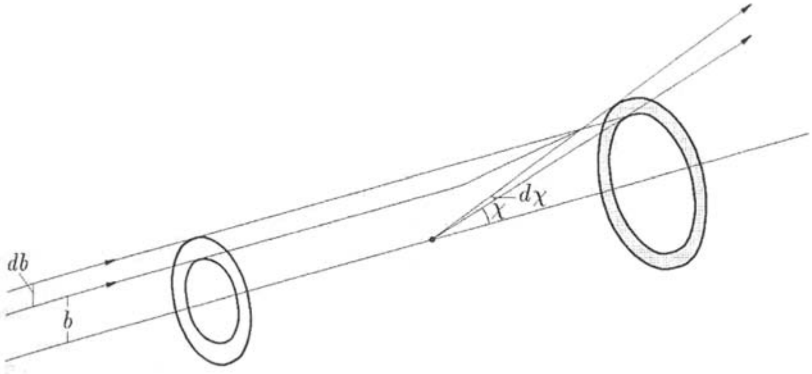


Figure 3-12. Particles with an impact parameter lying between *b* and *b*+*db* will be scattered under an angle lying between χ and $\chi+d\chi$.

$$dN_\chi = n2\pi bdb. \tag{3.58}$$

This number is not convenient for the scattering characterisation, as it depends on the flux density. Therefore we introduce the relation

$$d\sigma(\chi) \equiv \frac{dN_\chi}{n} 2\pi b db, \tag{3.59}$$

which determines the relative number (fraction) of particles, scattering at an angle $\chi \div \chi + d\chi$. *This relation has dimension of area and is called differential cross section.* It is an important characteristic of the scattering process and uniquely determines the type of scattering field.

The total cross section σ is defined as the ratio of the particle number N, scattered per unit time under any angle, to the density flux of the incident particles:

$$\sigma = \frac{N}{n} = \int d\sigma = \int \frac{d\sigma}{d\chi} d\chi. \tag{3.60}$$

The scattering angle is a function only of the impact parameter *b* and, which is the same, the impact parameter *b* is the function only of the angle χ. Hence,

$$d\chi = \frac{d\chi(b)}{db} db \text{ or } db = \frac{db(\chi)}{d\chi} d\chi. \tag{3.61}$$

Changing variables from *b* (3.58) to χ, we shall write the differential cross section in the following form:

$$d\sigma = 2\pi b(\chi)\left|\frac{db}{d\chi}\right| d\chi. \tag{3.62}$$

The absolute value sign is needed because $db/d\chi$ is typically negative (the particles with large *b* are less deflected, as can be seen in Fig. 3-12).

Very often it is more convenient to use the solid angle $d\Omega$ instead of $d\chi$ (Fig. 3-13). For this transformation we shall return to the quantity dN_χ, and we shall note that it can be seen as the number of particles flowing in a solid angle $d\Omega = 2\pi \sin\chi d\chi$ (such is the value of the solid angle between the cones with angles χ and $\chi + d\chi$). Substituting in (3.61) $2\pi d\chi$ with $d\Omega/\sin\chi$, we express $d\sigma$ through $d\Omega$:

$$d\sigma = \frac{b(\chi)}{\sin\chi}\left|\frac{db}{d\chi}\right| d\Omega. \tag{3.63}$$

We remind to the reader that this is the differential cross section in the CM-frame (the centre-of-mass frame) of the particle with $\tilde{m}$.

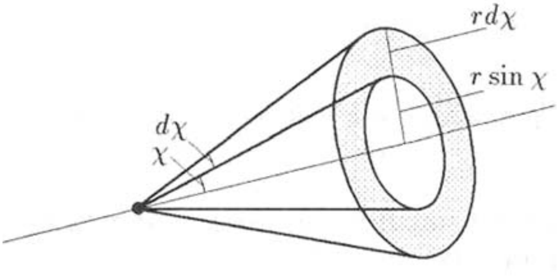


Figure 3-13. The differential cross section is defined as the fraction of particles scattered for unit time at angles from χ to $\chi+d\chi$ (or, which is the same, in the solid angle $d\Omega=2\pi\sin\chi d\chi$ between the cones of angles χ and $\chi+d\chi$) to the flux density of the incident beam.

The most important case for determination of a cross section in classical mechanics is the scattering of charged particles in a Coulomb field.

In this case the cross section is obtained in the form of elementary functions and it is most interesting that the obtained classical cross section preserves its form during the transition to quantum mechanics.

For the determination of the scattering angle we shall use the results from Section 3.4. We shall consider the repulsive potential field $U(r)=-C/r$ (where $C<0$). The scattering angle χ can be expressed by the angle $2\varphi_0$ between the asymptotes of the trajectory (Fig.3-6b):

$$\chi=\pi-2\varphi_0. \tag{3.64}$$

The angle φ_0 is the polar angle of the nearest to the centre point, point *A*. For the determination of the angle φ_0 we use Eqs. (3.38) and (3.42):

$$\varphi_0=\int\limits_{r_{\min}}^{\infty}\frac{\frac{L}{r^2}}{\sqrt{2\tilde{m}\left(E+\frac{C}{r}\right)-\frac{L^2}{r^2}}}dr=\arccos\left.\frac{-\frac{C\tilde{m}}{L}+\frac{L}{r}}{\sqrt{2\tilde{m}E+\left(\frac{C\tilde{m}}{L}\right)^2}}\right|_{r_{\min}}^{\infty}. \tag{3.65}$$

The minimal distance $r_{\min}$ is the positive solution of Eq. (3.34). We substitute this solution into (3.65) and take into account the conservation laws of energy and angular momentum:

$$E = \frac{\tilde{m} v_\infty^2}{2}, \quad L = \tilde{m} v_\infty b. \tag{3.66}$$

Here v_∞ is the unperturbed particle velocity (the initial or the final one), i.e. at $r \to \infty$ (see Fig. 3-6). For the angle φ_0 we obtain

$$\varphi_0 = \arccos \frac{1}{\sqrt{1 + \left(\frac{\tilde{m} v_\infty^2 b}{C} \right)^2}} . \tag{3.67}$$

Using the trigonometry formula $\arctan x = \arccos \left(1 \big/ \sqrt{1 + x^2} \right)$ (for $x \geq 0$) we easily determine the impact parameter *b* as a function of φ_0:

$$b = \frac{|C|}{\tilde{m} v_\infty^2} \tan \varphi_0 . \tag{3.68}$$

Changing φ_0 with $|\pi - \chi| / 2$ and squaring it, we get

$$b^2 = \frac{C^2}{\tilde{m}^2 v_\infty^4} \cot^2 \frac{\chi}{2} . \tag{3.69}$$

We differentiate with respect to χ and substitute the result into (3.62) or (3.63). Finally, for the differential cross section we obtain

$$d\sigma = \pi \left(\frac{C}{\tilde{m}^2 v_\infty^2} \right)^2 \frac{\cos \frac{\chi}{2}}{\sin^3 \frac{\chi}{2}} d\chi, \quad \text{or} \quad d\sigma = \left(\frac{C}{\tilde{m}^2 v_\infty^2} \right)^2 \frac{d\Omega}{\sin^4 \frac{\chi}{2}} d\chi . \tag{3.70}$$

Formulae (3.70) are the celebrated Rutherford formulae, used by him to analyse the experimental results of α-particle scattering by heavy nuclei. With these experiments was established the planetary model of the atom. As can be seen from (3.67), at the constant solid angle $d\Omega = \text{const}$ the quantity $d\sigma \sin^4 (\chi/2) = \text{const}$, which was verified experimentally.

The experiments also verified that the number of scattered particles (i.e. the differential cross section) quickly decreases with both the increase of the scattering angle (as $1/\sin^4(\chi/2)$) and with the magnitude of the α-particle energy (as $1/E^2$). For small angles the differential cross section is large. This is due to the Coulomb field, which is weak far from the centre, but decreases sufficiently slowly. Therefore it acts on many particles, which exhibit small deflections due to this action. The cross section does not depend on the sign of the coefficient C $\left(d\sigma \propto C^2\right)$, so the obtained result is valid for both Coulomb repulsion and Coulomb attraction between the particles m_1 and m_2. The experiment verified also that $d\sigma$ is proportional to the square of the charge of the nucleus.

Formulae (3.70) give the differential cross section in the CM-frame. The transformation to the Lab-frame is done with formulae (3.53) and (3.54). Finding $d\sigma(\theta_2)$ is trivial, but the determination of $d\sigma(\theta_1)$ is difficult. For the most interesting case of a scattering of light particle by a heavy one $(m_1 << m_2)$, when $\tilde{m} \approx m_1$ and $\chi \approx \theta_1$, we obtain from (3.70) the differential cross section of the light particle

$$d\sigma = \left(\frac{C}{4E}\right)^2 \frac{d\Omega}{\sin^4 \frac{\theta_1}{2}}, \tag{3.71}$$

where $E = m_1 v_\infty^2/2$ is the energy of the incident particle.

SUMMARY

One-dimensional motion in a potential field $U(x)$ of a particle of energy E is bounded in a region x_1x_2 by the conditions $E > U(x), U(x_1) = E$ and $U(x_2) = E.$

Central conservative forces of interaction between two bodies are directed along the line connecting their centres and depend only on the distance between them. Such forces are the gravitational, Coulomb and nuclear forces.

The two-body problem, in which the interaction is determined by the central conservative forces, can be reduced to the problem of one particle (with a reduced mass $\tilde{m} = m_1 m_2/(m_1 + m_2)$ and a relative radius-vector of a particle with respect to another, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$) in the field of the central conservative force. The motion of a particle in such a field occurs in a plane and both the energy and angular momentum are conserved. The angular momentum, which is this case is an orbital one (It is due to the orbital motion, but not to a spin, for instance) is normal to the plane of the motion: $L = \tilde{m}r^2\varphi$. A two-dimensional problem (a motion in a plane) can be reduced to a one-dimensional radial motion in a field of an effective potential energy $\tilde{U}(r)$:

$$\tilde{U}(r) = \frac{L^2}{2\tilde{m}r^2} + U(r).$$

The additional term $L^2/2\tilde{m}r^2$ is called a centrifugal energy and is due to the rotation along φ. The effective potential energy for the one-dimensional radial motion plays a role analogous to $U(r)$ for one-dimensional motion. For repulsion $U(r) > 0$ and the motion is infinite, and for attraction $U(r) < 0$ and the character of the motion depends on the relation of the total particle energy to the effective potential energy. The orbits (curves of second order) are the following:

$E > 0$ - a hyperbola,
$E = 0$ - a parabola,
$\tilde{U}_{\min} < E < 0$ - an ellipse,
$E = \tilde{U}_{\min}$ - a circle.

Knowing the orbit of a particle of reduced mass allows the determination of the real orbit of the particle in the CM-frame (centre-of-mass frame). The motion has a constant area velocity, i.e. for equal time intervals the radius-vector sweeps equal areas:

$$\frac{dS}{dt} = \frac{1}{2} r^2 \dot{\varphi} = \text{const.}$$

Hence, the angular velocity along a circle is constant, but along other trajectories it changes, approaching its maximum in the perigee (the minimal distance to the focus).

As two particles approach each other, interacting by a central force, they scatter, and the light particle can scatter at any angle, while for the heavy one the scattering angle has a maximum. As a characteristic of the scattering we use the differential cross section, which for the Coulomb field is determined by the Rutherford's formula.

We have persuaded ourselves that the two-body problem (including scattering) in CM-frame is substantially simplified. This concerns more complex systems. Therefore it is better to solve the problem in the CM-frame and after that to do a transformation to the desired frame.

QUESTIONS

1. What are the conditions for finite/infinite motion?
2. Why the one-dimensional motion is a periodic one?
3. What is a character of motion if a particle of energy E approaches: a) a potential well of depth $U(x)$; b) a potential barrier of height $U(x)$?
4. For interaction between a light and a heavy particle of masses m_1 and m_2 $(m_1 << m_2)$, respectively, which mass determines the reduced mass?
5. The two-body problem is reduced to the motion of the reduced mass $\tilde{m}$ with radius-vector **r** (Eq. (3.3). What is the physical meaning of: a) the vector **r**; b) the force $-\partial U(r)/\partial \mathbf{r}$?
6. How will you find the Lagrangian function of two particles in Lab-frame, knowing it in CM-frame?
7. Knowing the radius-vector of a particle with a reduced mass, how will you determine the position of the masses m_1 and m_2 in: a) CM-frame; b) Lab-frame?
8. Why does the particle trajectory, moving due to the action of a central force, lie in a plane?
9. What is the physical meaning of the generalized momentum P_φ of the particle in the central force field?
10. Which is the direction of the angular momentum in the central force field?
11. The radial equation of the energy (3.2) is one-dimensional (it depend only on *r*). Is the particle motion, described by this equation, also one-dimensional?
12. Why is the additional term $L^2/2\tilde{m}r^2$ in the effective potential energy called centrifugal energy?
13. How will you explain physically that due to the repulsion from the force centre, the particle can not move along a closed curve (in particular, along a circle), but as a result of an attraction it can do so?
14. Explain graphically why are different orbits obtained when the particles have different values of the total energy with respect to the effective potential energy?
15. If you know the instant position of one of the particles and the centre of mass, can you show where is found: a) the second particle; b) the particle of the reduced mass?

16. How is the momentum of the particles changed as a results of an elastic collision in the CM-frame?
17. What are the scattering angles in the CM- and the Lab-frames, when the light particle of mass m_1 impinges on the heavy one of mass m_2 $(\mathrm{m}_1 << m_2)$?

PROBLEMS

1. A particle of mass m and a velocity v moves in the central field $U(r) = \kappa r^2/2.$
   a) What is its effective potential? Plot it together with its components.
   b) What condition satisfies the effective potential at the circle motion?
   c) Find the radius and the angular velocity of the circular motion.
2. An electron of velocity v_P passes through a point *P* at a distance *b* from an atomic nucleus *O* (here $v_P \perp PO$). Through the relation of v_P to the velocity v_0 of the circle motion through this point, find at which value of β is the orbit a closed or an open curve. For the orbits, which are an ellipse, a circle and a hyperbola, plot the curve for the effective potentials and show the position of the point *P* on them.
3. Alfa-particle of energy 2.10^{-15} J is scattered off an Al atom at an angle $\theta_1 = \pi/2$. Find the minimal distance *b* between the particle and the nucleus?

Chapter 4

ROTATING MOTION OF A CHARGED PARTICLE

SUGGESTED READING

1. Kibble, T. W., Classical mechanics, McGraw-Hill Book Co., 2nd ed., 1988, Sections 5.1, 5.2, 5.5, 5.6
2. Kittel, Ch., W. D. Knight, M. A. Ruderman, Berkeley Physics Course, Vol. I, Mechanics, McGraw-Hill Book Co., 2nd ed., 1973, Sections 4.1, 4.2.
3. Spolsky, E. V., Atomic Physics, Vol. 1, Mir Publishing House, 1963, Section 76.

4.1* ROTATING FRAMES

Up till now we used only the inertial reference frame, in which the laws of motion take on a simple form, expressed in Newton's law. However, many problems are solved much easier in non-inertial frame. (Here we shall consider only a rotating about a fixed axis.) Namely, they represent an interest from the point of view of this course. Applying the rotational motion, we shall consider a charged-particle motion in a constant magnetic field and simultaneously in such a field and an electric field of a point charge. These problems are very important for our further presentation.

Consider two reference frames with a common origin *O*: an inertial frame *K* and a non-inertial frame *K'*, rotating with an angular velocity $\omega = \text{const}$ with respect to *K*. For the sake of definiteness we shall assume that the angular velocity is directed along the axis *Z* (Fig. 4-1). The values in K' we shall denote with prime.

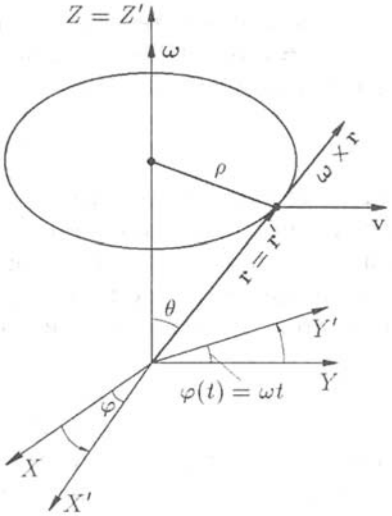


Figure 4-1. The co-ordinate frame *K'* (*x',y',z'*) rotates around the inertial co-ordinate frame *K*(*x,y,z*) with an angular frequency *ω*, directed along the *Z*-axis. When both frames have a common origin *O*, the radius-vectors of the particle coincide, $\mathbf{r} = \mathbf{r}'$. Its velocity in *K'* is $\mathbf{v}'$ and in *K* it is $\mathbf{v} = \mathbf{v}' + \boldsymbol{\omega} \times \mathbf{r}$.

The radius-vectors of a fixed point $\mathbf{r}$ and $\mathbf{r}'$ in the frames *K* and *K'* coincide:

$$\mathbf{r} = \mathbf{r}'. \tag{4.1}$$

If in the *K′* frame **r'** is a fixed vector, i.e. it does not change with time, and therefore, $\mathbf{v}' = \dot{\mathbf{r}}' = 0$, the velocity v in the *K* frame is determined by the rotation of the non-inertial frame (Fig.4-1):

$$v = \omega\rho = \omega r \sin\theta, \tag{4.2a}$$

or in a vector form

$$\mathbf{v} = \boldsymbol{\omega}\times\mathbf{r}. \tag{4.2b}$$

If $\mathbf{r}' = \mathbf{r}'(t)$, the particle moves with a velocity $\mathbf{v}'$. Then, in the inertial frame *K* its velocity is a sum of the velocity **v**' in K' and the velocity of the rotating frame $\boldsymbol{\omega}\times\mathbf{r}$:

$$\mathbf{v} = \mathbf{v}' + \boldsymbol{\omega}\times\mathbf{r}. \tag{4.3}$$

To analyse the rotating motion we must know the motion equation in the rotating frame. This equation we could obtain from Lagrange's equation for the function $\mathscr{L}$. It is readily found, as in the Lagrangian function of a particle (3.23) we replace **r** and **v** with **r**' and **v**' according to (4.1) and (4.3). We shall use another way, which is not so consistent, but is easier - it avoids a straightforward but long vector calculation.

First, we shall note that when any vector, whose origin coincides with the origin of the frames and is the same in both frames, changes in *K* and K' differently. If in the rotating frame **b** is a vector and, hence, its change is zero, $d'\mathbf{b}' = d'\mathbf{b} = 0,$ then in the immobile system *K* its change is

$$d\mathbf{b} = \mathbf{d}\boldsymbol{\varphi}\times\mathbf{b}. \tag{4.4}$$

Here the angle by which the frame *K′* changes for the interval *dt* is represented by the vector $\mathbf{d}\boldsymbol{\varphi}$. (We shall note that the elementary infinitesimal rotations can be assigned both a magnitude and a direction along the axis of rotation, i.e. they are vectors; at the same time the angle is a scalar - for details, see e.g., [R2], Section 7. There is a total analogy with the variation $\delta\mathbf{r}$ in Section 2.3 (see (2.29) and Fig. 2-2.)

Dividing by *dt*, we shall obtain in the inertial system *K* the rate of change of any fixed in the K' frame vector **b:**

$$\frac{d\mathbf{b}}{dt} = \boldsymbol{\omega}\times\mathbf{b}. \tag{4.5}$$

If in the *K′* frame the vector **b** is not fixed and its change is $d'\mathbf{b} \neq 0$, then in the immobile frame *K* its change will be:

$$d\mathbf{b} = d'\mathbf{b} + \mathbf{d\varphi} \times \mathbf{b}. \tag{4.6}$$

After dividing by dt, we obtain the rate of change of the vector **b** in the *K* frame:

$$\frac{d\mathbf{b}}{dt} = \frac{d'\mathbf{b}}{dt} + \boldsymbol{\omega} \times \mathbf{b}. \tag{4.7}$$

It can be proved that the same dependence is valid also for a vector which does not pass trough the origin of both frames. When $\mathbf{b} = \mathbf{r}$, we obtain the dependence (4.3), which can be written in the following form:

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \frac{d'\mathbf{r}}{dt} + \boldsymbol{\omega} \times \mathbf{r}. \tag{4.8}$$

We apply formula (4.7) to the vector **v:**

$$\frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{r}}{dt^2} = \frac{d'\mathbf{v}}{dt} + \boldsymbol{\omega} \times \mathbf{v}. \tag{4.9}$$

We shall find the derivative of vector **v** (4.8) in the *K′* frame:

$$\frac{d'\mathbf{v}}{dt} = \frac{d'^2\mathbf{r}}{dt^2} + \boldsymbol{\omega} \times \mathbf{v}'. \tag{4.10}$$

On the other hand, multiplying (4.8) vectorially by **ω** we obtain

$$\boldsymbol{\omega} \times \mathbf{v} = \boldsymbol{\omega} \times \mathbf{v}' + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}). \tag{4.11}$$

Substituting of (4.10) and (4.11) in (4.9) leads to the following result:

$$\frac{d^2\mathbf{r}}{dt^2} = \frac{d'^2\mathbf{r}}{dt^2} + 2(\boldsymbol{\omega} \times \mathbf{v}') + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}). \tag{4.12}$$

On the left-hand side we have the acceleration in the inertial frame *K* and on the right-hand side - the acceleration in the non-inertial frame *K′*. Hence, the acceleration, as seen by an inertial observer, differs from that seen by an observer in the rotating frame. Two additional terms in the right (the second and the third ones) owe to the inertial forces, originating from the uniform rotating of *K'*. The second term is called *Coriolis acceleration and the third one - centrifugal* (*normal*) *acceleration.* The Coriolis acceleration vanishes unless the particle moves in the rotating frame along a direction different from $\boldsymbol{\omega}$, but in contrast, the centrifugal acceleration remains even when the particle is at rest in *K'*. Multiplying the right- or left-hand side by the particle mass and equating it to the acting force, we obtain the equation of motion in *K* and *K'* frames, respectively.

4.2 PARTICLE IN A UNIFORM MAGNETIC FIELD

A charge $\mathbf{q}$, which moves with a velocity $\mathbf{v}$ in a magnetic field **B**, is acted upon by a magnetic Lorentz force, proportional to its velocity and perpendicular to it:

$$\mathbf{F}_m = \mathbf{q}\mathbf{v}\times\mathbf{B}. \tag{4.13}$$

This formula is written in the SI system (in CGSE (Gauss') system it has the form $\mathbf{F}_m = \frac{\mathbf{q}}{c}\mathbf{v}\times\mathbf{B}$). The equation of motion is

$$m\frac{d\mathbf{v}}{dt} = \mathbf{q}\mathbf{v}\times\mathbf{B}. \tag{4.14}$$

In a constant and a uniform magnetic field the relation (4.14) has exactly the form of (4.5):

$$\frac{d\mathbf{v}}{dt} = \boldsymbol{\omega}\times\mathbf{v}, \tag{4.15}$$

where

$$\boldsymbol{\omega} \equiv \boldsymbol{\omega}_c = -\frac{\mathbf{q}}{m}\mathbf{B}. \tag{4.16}$$

In the Gauss' system $\boldsymbol{\omega}_c = -\mathbf{q}\mathbf{B}/mc$. Consequently, according to the conclusions of the preceding section, the vector of *the velocity of the charge* $\mathbf{q}$ *rotates around the direction **B** with a constant angular velocity* $\boldsymbol{\omega}_c$, which is called a cyclotron frequency or gyrofrequency. Sometimes it is called the Larmor frequency of rotation, in contrast to the Larmor frequency of precession, which will be considered in the next section.

We shall note that at relativistic velocities the cyclotron frequency decreases

$$\omega_c = \frac{B\mathbf{q}}{m_0 \gamma}, \qquad \gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}, \tag{4.17}$$

where m_0 is the mass of the particle at rest.

From Eq. (4.16) it is obvious that for positively charged particle **ω** and **B** are antiparallel, but for negatively charged particle they are parallel (Fig. 4-2a).

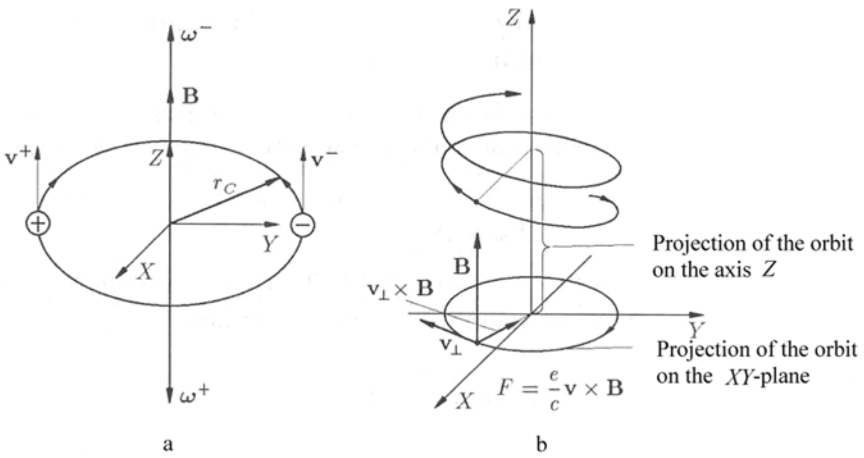


Figure 4-2. Motion of a charged particle in constant uniform magnetic field: a) $\mathbf{v} \perp \mathbf{B}$ - the particle moves along the circle of a radius $r_c = mv/\mathbf{q}B$ with an angular frequency $\omega_c = \mathbf{q}B/m$, the positively and the negatively charged particles rotating in opposite directions; b) **v** has a longitudinal component along **B** - the particle moves along the spiral line.

When the particle velocity is perpendicular to **B**, the particle motion is along a circle of radius r_c, called cyclotron radius:

$$r_c = \frac{v}{\omega_c} = \frac{mv}{\mathbf{q}B}. \tag{4.18}$$

When **v** has both perpendicular, $v_\perp$, and parallel, $v_\parallel$, components (Fig 4.2b), the motion is along a spatial curve - a helix (spiral). The motion along the *Z*-axis is uniform and the projection on the plane is a circle of radius $r_c = v_\perp / \omega_c$.

4.3 LARMOR EFFECT

Consider the influence of the magnetic field on the charged particle of mass m_1 and charge $-\mathbf{q}_1$ in the Coulomb field of a point charge $\mathbf{q}_2$ ($m_2 \to \infty$ and consequently $\tilde{m} \approx m_1$). In essence, this is the problem of the influence of a magnetic field on the electron in an atom, which moves in the Coulomb field of the nucleus.

Before considering this problem we shall analyze the motion of the charge $-\mathbf{q}_1$ in the Coulomb field of $\mathbf{q}_2$. Using the results of Sections 3.3 and 3.4 we shall consider the more interesting case of a bounded motion. Then, the orbit of the charged particle is an ellipse or a circle. These are the classical trajectories of an electron in the field of the nucleus. The motion is periodic, and integrating (3.30), we readily obtain the period τ:

$$\tau = \frac{2m_1 S}{L}. \tag{4.19}$$

We recall that L stands for the angular momentum, and S - for the area, swept by the radius vector for one period, i.e. the area, bounded by the orbit. For a motion along a circle the area is $S = \pi r_0^2$ and along an ellipse - $S = \pi ab$, where *a* and *b* are respectively semimajor and semiminor axes (Fig. 4-3). According to (3.36) for a motion along a circle $L^2 = C\tilde{m}r_0$ and in the considered case of a Coulomb field for $m_2 \to \infty$ we obtain

$$L^2 = k_0 \mathbf{q}_1 \mathbf{q}_2 m_1 r_0$$
$$\left(k_0 \equiv \frac{1}{4\pi\varepsilon_0} = 9.10^9\,\mathrm{N.m^2/C^2}, \quad \varepsilon_0 = 8{,}85.10^{-12}\,\mathrm{C^2}/\left(\mathrm{N.m^2}\right) \right). \tag{4.20}$$

Substituting L into (4.19) we determine the angular velocity:

$$\omega_0^2 = \left(\frac{2\pi}{\tau} \right)^2 = \frac{L^2}{m_1^2 r_0^4} = k_0 \frac{\mathbf{q}_1 \mathbf{q}_2}{m_1 r_0^3}. \tag{4.21}$$

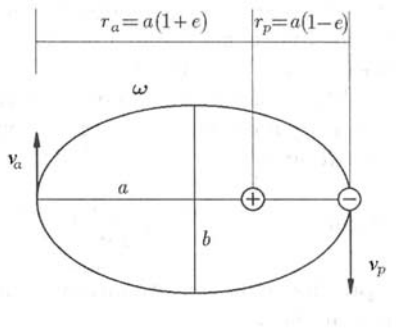


Figure 4-3. The motion of a charged particle along an ellipse in the field of a point opposite charge: a and b are, respectively, the semimajor and the semiminor axes of the ellipse, e - the eccentricity, v_a and v_p - the velocities in the apogee and the perigee.

For an H atom the angular frequency, estimated for the radius of Bohr $r = a_0 \approx 5.10^{-11}\,\mathrm{m}$ is on the order $\omega_0 \approx 4.10^{16}\,\mathrm{s}^{-1}$ (at $\mathbf{q}_1 = \mathbf{q}_2 = |e| = 1{,}6.10^{-19}$ C, $m_1 = m_2 = 9{,}1.10^{-31}$ kg).

For a motion along an ellipse according to the law of the area velocity, the angular velocity is not constant - it approaches a minimum in the apogee (the furthest point from $\mathbf{q}_2$) and a maximum in the perigee (the nearest point to $\mathbf{q}_2$). It is given by the same relation (4.21) replacing r_0 in the perigee with $r_p = a(1-e)$ and in the apogee with $r_a = a(1+e)$ (Fig. 4-3).

Let us now turn on a weak magnetic field $\mathbf{B} = B\mathbf{z}^0$ (later on we will determine more accurate how weak). The equation of the motion, including the electrical and the magnetic force is

$$m_1 \frac{d^2\mathbf{r}}{dt^2} = -k_0 \frac{\mathbf{q}_1\mathbf{q}_2}{r^3}\mathbf{r} - \mathbf{q}_1 \frac{d\mathbf{r}}{dt} \times \mathbf{B}. \tag{4.22}$$

Let us write this equation in the rotating frame, whose angular frequency is ω. According to (4.8) and (4.12), we get

$$\frac{d'^2\mathbf{r}}{dt^2} + 2\boldsymbol{\omega} \times \frac{d'\mathbf{r}}{dt} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}) = -k_0 \frac{\mathbf{q}_1\mathbf{q}_2}{m_1 r^2}\frac{\mathbf{r}}{r} - \frac{\mathbf{q}_1}{m_1}\left(\frac{d;\mathbf{r}}{dt} + \boldsymbol{\omega} \times \mathbf{r}\right) \times \mathbf{B}. \tag{4.23}$$

If we choose the angular frequency

$$\boldsymbol{\omega} = -\frac{-\mathbf{q}_1}{2m_1}\mathbf{B} = \frac{\mathbf{q}_1}{2m_1}\mathbf{B}, \tag{4.24}$$

the Eq. (4.23) is simplified a lot. The terms $\propto d'r/dt$ are cancelled and the last terms on the right and left are added. Thus, we get

$$\frac{d'^2\mathbf{r}}{dt^2} = -k_0\frac{\mathrm{q}_1\mathrm{q}_2}{m_1 r^3}\mathbf{r} - \left(\frac{\mathrm{q}_1 B}{2m_1}\right)^2 \mathbf{z}^0\times\left(\mathbf{r}\times\mathbf{z}^0\right). \tag{4.25}$$

We have taken into account that $\mathbf{B} = B\mathbf{z}^0$ and changed the sign before the term $2\boldsymbol{\omega}\times\left(d'\mathbf{r}/dt\right)$ due to the exchange of the positions of both vectors and before $\boldsymbol{\omega}\times\left(\boldsymbol{\omega}\times\mathbf{r}\right)$ due to the exchange of the positions of the vectors $\boldsymbol{\omega}$ and $\mathbf{r}$ in the brackets. We shall also note that the second term in the last equation contains the vector **r**: $\mathbf{z}^0\times\left(\mathbf{r}\times\mathbf{z}^0\right) = \mathbf{r}$.

For a weak magnetic field the term with the square of *B* can be neglected in comparison to the term determined by the electrical field. For this it is necessary that

$$\left(\frac{\mathrm{q}_1 B}{2m_1}\right)^2 = \omega^2 << k_0\frac{\mathrm{q}_1\mathrm{q}_2}{m_1 r_\alpha^3} \le k_0\frac{\mathrm{q}_1\mathrm{q}_2}{m_1 r_0^3}. \tag{4.26a}$$

For a motion along a circle this condition, after taking into account (4.21), reduces to

$$\omega << \omega_0. \tag{4.26b}$$

Thus, from (4.25) we obtain the approximate equation

$$m_1\frac{d'^2\mathbf{r}}{dt^2} = -k_0\frac{\mathrm{q}_1\mathrm{q}_2}{m_1 r^3}\mathbf{r}. \tag{4.27}$$

This is the equation of motion of a particle in a central Coulomb field (3.13). As we have shown in Section 3.4, the orbit of the bounded motion of a particle under the action of a central force is an ellipse (a partial case of it is a circle).

Consequently, the orbit in the rotating frame is an ellipse. In an inertial frame this ellipse slowly precesses with an angular frequency *ω*, because according to (4.26) the frequency of the ellipse precession, i.e. the angular frequency of the rotation of the frame *K'*, is negligibly small compared to the angular velocity of the particle motion along the orbit. In Fig. 4-4 is shown the orbit precession in Lab-frame in the partial case when the **B** is normal to the plane of the orbit. In the general case, when **B** is inclined, the plane of the orbit precesses around the direction of **B** (see Section 4.4). According to (4.26) the ellipse axis will turn only by a small angle for one turnover.

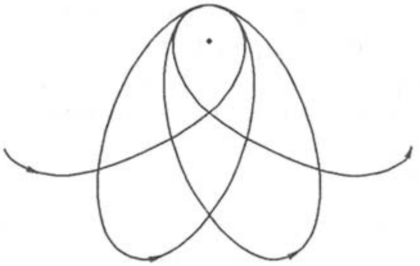


Figure 4-4. Precession of an orbit of a charged particle, moving in a Coulomb field of a point charge and a weak magnetic field **B**, normal to the plane of the orbit.

This phenomenon is known as *Larmor effect* and the angular frequency of the precession,

$$\boldsymbol{\omega}_L = -\frac{\mathbf{qB}}{2m_1}. \tag{4.28}$$

is called *Larmor frequency of precession*, or simply Larmor frequency. We shall note that it is two times smaller than the cyclotron frequency ω_c (4.16).

The Larmor precession is a basis for the observable changes in the spectra emitted by atoms in the presence of a magnetic field. The changes in the spectrum are known as the Zeeman effect.

The Larmor precession of atomic systems is of great interest. Let us see if the condition $\mathbf{q}_1 B/2m_1 << \omega_0$ (4.26) is valid. Written for the magnetic field, it reads $B << |2m_1\omega_0/\mathbf{q}_1|$. Then, for the hydrogen atom we have $m_1 = m_e = 9{,}2.10^{-31}$ kg, $\mathbf{q}_1 = \mathbf{q}_2 = |e| = 1{,}6.10^{-19}$ C, $\omega_0 \approx 4.10^{16}$ s^{-1} (see the estimate after (4.21)). Thus, we get $B << 4.10^5$ T. Field of $B \sim 10^3$ T are record ones and the condition (4.26) is satisfied.

4.4* INTERACTION OF A MAGNETIC DIPOLE WITH A MAGNETIC FIELD

We would like to find out what would the motion be, if the vector **B** was inclined with respect to the plane of the motion of the charged particle. It is logical to expect a change of the angular momentum in this case. Actually, the magnetic force $\mathbf{F}_m$ (4.13), which creates a force moment, acts on the charge $-\mathbf{q}_1$ and according to Eq. (2.39) the moment changes as follows:

$$\frac{d\mathbf{L}}{dt} = \mathbf{N} = \mathbf{r} \times \mathbf{F}_m = -\mathbf{r} \times (\dot{\mathbf{r}} \times \mathbf{B}). \tag{4.29}$$

It is necessary for the analysis to recall some results from electrodynamics. We note that the motion of the charge along a close curve (for the sake of simplicity we shall consider the motion along a circle of radius r_0) is equivalent to the circular current loop $I = -\mathbf{q}_1 / \tau = -\mathbf{q}_1 / (2\pi r_0 / v)$. It is well known that such a current has a magnetic dipole moment

$$\boldsymbol{\mu} = IS\mathbf{n}^0, \tag{4.30}$$

where S is the area, closed by the loop current and $\mathbf{n}^0$ is a unit vector normal to this area. So, for the magnetic moment of a moving charge $-\mathbf{q}_1$ we have

$$\boldsymbol{\mu} = -\frac{v\mathbf{q}_1 r_0}{2}\mathbf{n}_0. \tag{4.31}$$

Hence, the atom in which the electron $(-\mathbf{q}_1 = -e)$ moves in the electrical field of the nucleus, is equivalent to a magnetic dipole.

The angular moment of the charge is

$$\mathbf{L} = (\mathbf{r} \times m_1\mathbf{v}) = m_1 r_0 v \mathbf{n}^0. \tag{4.32}$$

Then, we can express the magnetic moment $\boldsymbol{\mu}$ through the mechanical moment $\mathbf{L}$:

$$\boldsymbol{\mu} = -\frac{\mathbf{q}_1}{2m_1}\mathbf{L}. \tag{4.33}$$

We have concluded that the magnetic moment $\boldsymbol{\mu}$ corresponds to the orbital angular momentum $\mathbf{L}$. This is a part of a more general statement that *to any rotary motion of a charged particle correspond both a mechanical moment and a magnetic moment. They are always proportional*, but the coefficient of proportionality g between them,

$$\boldsymbol{\mu} = -g\mathbf{L}, \tag{4.34}$$

depends on the type of the rotation. A circular current loop is equivalent to a magnetic dipole. It is known that in the uniform magnetic field the torque **N** influences such a dipole

$$\mathbf{N} = \boldsymbol{\mu} \times \mathbf{B}, \quad \text{or} \quad N = \mu B \sin\theta, \tag{4.35}$$

where the angle θ is shown in Fig. 4-5.

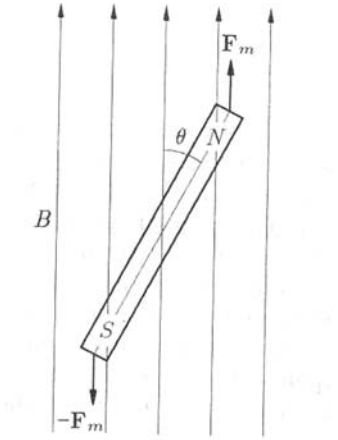


Figure 4-5. Magnetic dipole (a permanent magnet), which is equivalent to an electron in an atom, in external uniform magnetic field **B**. The dipole is acted upon by a torque **N**, which is created by the pairs of magnetic forces $\mathbf{F_m}$ and $-\mathbf{F_m}$.

Then, according to (4.33) and (4.35), for the angular momentum we have

$$\frac{d\mathbf{L}}{dt} = \mathbf{N} = \boldsymbol{\mu} \times \mathbf{B} = \frac{-\mathbf{q}_1}{2m_1}(\mathbf{L} \times \mathbf{B}), \tag{4.36}$$

or

$$\frac{d\mathbf{L}}{dt} = \frac{\mathbf{q}_1}{2m_1}(\mathbf{B} \times \mathbf{L}). \tag{4.37}$$

Taking into account (4.24) we can write for the change of the angular moment the following:

$$\frac{d\mathbf{L}}{dt} = (\boldsymbol{\omega}_L \times \mathbf{L}). \tag{4.38}$$

But this, remembering (4.5), denotes that the vector **L** rotates with an angular velocity $\boldsymbol{\omega}_L$. Since the vector of the angular velocity is directed along the magnetic field, it is obvious that **L** rotates around the vector **B**. With this its magnitude does not change. In fact, taking the dot product of **L** with (4.37) we get

$$\mathbf{L}\frac{d\mathbf{L}}{dt} = \frac{1}{2}\frac{d\mathbf{L}^2}{dt} = 0, \quad |\mathbf{L}| = \text{const.} \tag{4.39}$$

*Thus, when a charged particle with an angular momentum **L** is placed in an external uniform magnetic field, the vector **L** starts to precess with a permanent angular velocity around the axis of the magnetic field* exactly in the same way as a mechanical top precesses in the gravitational field of the Earth (for details see [1], Section 11.3).

At this precession the particle receives an additional potential energy *U*. Let's turn to the magnetic analogue of Fig. 4-5. If the torque **N**, originating from the pair of magnetic forces, did not act, the magnetic dipole would be in the state with minimal energy, i.e. it would orient at an angle $\theta = 90°$ - and $U = 0$. In order to determine the angle θ, we have to calculate the work, which is necessary to turn the dipole from $90°$ to the angle θ:

$$U = \int_{90^0}^{\theta} N d\theta = \int_{90^0}^{\theta} \mu B \sin\theta d\theta = \mu B \int_{90^0}^{\theta} \sin\theta d\theta = -\mu B \cos\theta, \quad \text{or} \quad U = -\boldsymbol{\mu}\mathbf{B}. \tag{4.40}$$

Let us summarise what we have written up to here. *A charged particle* $-\mathbf{q}_1$ *moves under the action of a central force* (*the Coulomb interaction force with the charge*). *Its orbital angular momentum is constant and perpendicular to the orbit plane. The particle motion is equivalent to the circular current loop, which creates a magnetic dipole in the direction of **L*** (*Fig. 4-6*). *The magnetic field at an angle* θ *to the angular moment gives rise to a torque **N**. Under the influence of this torque the magnetic dipole changes its orientation. As a consequence, the vector **L** precesses around **B** with Larmor frequency* ω_L *and simultaneously with it and the "nailed on" by the law of angular-momentum conservation orbit.*

From the point of view of mechanics, the Larmor effect is a partial case of a more general and important phenomenon - the precession of the axis of rotation under the action of a weak force. The best-known example of such a motion is the precession of the gyroscope.

Finally, let us see what happens with a magnetic dipole, i.e. with an atom, in nonuniform magnetic field. In this case the force is determined by the dipole moment and the gradient of the field acting on it:

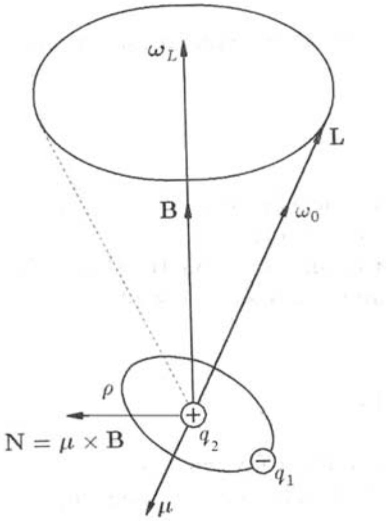


Figure 4-6. Larmor precession of a particle $-\mathbf{q}_1$, moving along the circular orbit ρ in uniform magnetic field **B.** The vector **L** describes a reversed cone, as its generating line, and the base of this cone is described by the arrow of **L** ($\boldsymbol{\mu}$ is the magnetic moment, **N** - the torque, ω_L - the frequency of the precession); **N** is perpendicular to the plane of the vectors $\boldsymbol{\mu}$ and **B**.

$$\mathbf{F} = (\boldsymbol{\mu}\mathrm{grad})\mathbf{B} \equiv (\boldsymbol{\mu}\nabla)\mathbf{B}. \tag{4.41}$$

For example, if the inhomogeneity of the magnetic field is in the direction of the axis *Z,* then only in this direction will the force influence the atom: $F_x = 0,\ F_y = 0,\ F_z = \mu_z\, \partial B_z / \partial z$. By studying the atom motion in an external magnetic field, we can determine its magnetic moment.

SUMMARY

If an inertial frame and a rotating frame with an angular velocity $\boldsymbol{\omega}$ have common origin, then the vectors, starting at this point and coinciding in both frames change, in general, differently. The relation determining the rate of change of a vector **b** in an inertial frame K is

$$\frac{d\mathbf{b}}{dt}=\frac{d'\mathbf{b}}{dt}+\boldsymbol{\omega}\times\mathbf{b},$$

where $d\mathbf{b}/dt$ is the rate of change of the vector in the rotating frame K'. It is clear from here that when the radius-vectors of the particle coincide in both frames, its velocities and accelerations differ. In the rotating frame the acceleration has two additional terms (the centrifugal and the Coriolis accelerations), due to the inertial forces.

A charge in a uniform constant magnetic field, normal to its velocity, moves along a circle with an angular frequency equal to the cyclotron frequency

$$\boldsymbol{\omega}_c=-\frac{\mathbf{q}}{m}\mathbf{B}.$$

When the velocity of the charge has a longitudinal component (along the external magnetic field), the orbit is a helix, the projection of the orbit normal to the plane of **B** is cyclotron circumference.

The magnetic field normal to the plane of the charge motion causes a precession of the orbit with an angular frequency

$$\boldsymbol{\omega}_L=-\frac{\mathbf{qB}}{2m},$$

known as Larmor precession frequency. The Larmor precession leads to the observable Zeeman effect.

If the magnetic field is inclined with respect to the plane of the motion, then the orbit plane, the angular momentum and the magnetic moment precess with the same frequency $\boldsymbol{\omega}_L$. Physically, the precession is due to the interaction between the external magnetic field and the magnetic moment of the circular current loop. (A mechanical analogue of the Larmor precession is the precession of a gyroscope.) The vector of the mechanical moment describes a cone and its arrow - the circumference with a frequency equal to the Larmor one.

QUESTIONS

1. Is it true that all vectors in an inertial frame and a rotating frame, which have common origin, coincide?
2. If two vectors in the K- and K'-frames coincide, are their changes equal?

3. Are equal or different the radius-vectors, the velocities and the accelerations of a particle in an inertial and a rotating frames?
4. How does a charge move in a uniform magnetic field when its velocity:
   a) is perpendicular to the magnetic field;
   b) has a component along the magnetic field?
5. Is the motion of a charged particle uniform along a closed line in the field of a fixed charge?
6. What is Larmor precession?
7. What is the difference between the cyclotron frequency and the Larmor frequency of the precession, physically and mathematically?
8. Explain physically why does the plane of the orbit of a charge in a Coulomb field precesses in an external weak magnetic field?
9. What is the cone of the precession?
10. Do the angular frequencies of a charge rotation and of an arrow of the vector **L** in an external magnetic field differ (see Fig. 4-6)?
11. Does the vector of the angular momentum **L** change at Larmor precession? If it does, how and why?

PROBLEMS

1. Determine the cyclotron frequency of an electron in a magnetic field $B = 10^4$ Cs. Find the frequency of the periodical motion and the corresponding wavelength in space. What is the cyclotron radius of an electron moving with velocity 10^8 cm/s normal to such a field?
2. What will the change of the angular frequency ω and the linear one v of the electron of a hydrogen atom in an external magnetic field B? Do the calculation for $B = 10^3$ T.
3. Calculate the magnetic moment μ, the gyromagnetic rate g, the velocity and the Larmor frequency of precession ω_L, of an electron in a hydrogen atom, moving along the circumference of the Bohr radius $r = a_0 = 0{,}5.10^{-10}$ m in a magnetic field $B = 10^4$ T.
4. The average magnetic moment of Fe is $\mu = 2.10^{-23}$ J/T.
   a) Assuming that this moment is due to the circular current loop of one electron, moving along a circumference, find the electron velocity.
   b) Find the total magnetic moment of all electrons in 1 cm^3 metal, assuming that they are oriented in one direction.

Chapter 5

SMALL HARMONIC OSCILLATIONS

SUGGESTED READING

1. Landau, L. D. and E. M. Lifshitz, Mechanics, Pergamon Press, 2nd ed., 1969, Sections 21÷24.
2. Kibble, T. W., Classical mechanics, McGraw-Hill Book Co., 2nd ed., 1988, Sections 12.2÷12.4.
3. Spolsky, E. V., Atomic Physics, Vol. 1, Mir Publishing House, 1963, Sections 46, 47.
4. Fetter, A. L., J. D. Walecka, Theoretical Mechanics of Particles and Continua, McGraw-Hill Book Co., 1980, Section 21.

5.1 ONE-DIMENSIONAL HARMONIC OSCILLATIONS

Consider the motion of a system with one degree of freedom around its equilibrium position. The system is in equilibrium if the resultant force acting on it is equal to zero. For a conservative force, according to (1.31), this means that the potential energy $U(q)$ has a minimum or a maximum at this point - $\partial U/\partial q = 0$. Suppose that the system now undergoes *a small displacement from equilibrium*. Let us choose the co-ordinate q at the point of equilibrium such that $q=0$. We expand $U(q)$ in Taylor series:

$$U(q)=U(0)+U'(0)q+\frac{1}{2}U''(0)q^2+... \tag{5.1}$$

where with primes we denote differentiation with respect to q. In the extremum we have $U'(0)=0$. We choose the arbitrary constant in $U(q)$ such that $U(0)=0$. Then, around the equilibrium point we can write approximately

$$U(q)=\frac{\kappa q^2}{2}, \quad \kappa=U''(0). \tag{5.2}$$

The kinetic energy in a one-dimensional system according to (1.37) has the following form:

$$T=\gamma(q)\dot{q}^2. \tag{5.3}$$

For a small displacement from equilibrium we can expand in Taylor series the coefficient $\gamma(q)$:

$$\gamma(q)=\gamma(0)+\gamma'(0)q+\frac{1}{2}''(0)q^2+\ldots\approx\gamma(0)\equiv\frac{m}{2}. \tag{5.4}$$

Then, for the kinetic energy we can write

$$T=\frac{m\dot{q}^2}{2}. \tag{5.5}$$

We shall note that in the case of a linear co-ordinate the constant *m* is the mass.

Knowing the potential and kinetic energies, we can determine the Lagrangian function $\mathscr{L}=m\dot{q}^2/2-\kappa q^2/2$. Its corresponding equation (see Eq. (1.13)) is:

$$m\ddot{q}+\kappa q=0\,. \tag{5.6}$$

Although this equation is elementary, we shall discuss the solution in detail, for similar methods also apply to more complex systems of many degrees of freedom. It is *a linear differential equation*, i.e. it contains only linear terms in the variable *q* and its derivatives. Such equations have an important property - their solutions satisfy the superposition principle: if $q_1(t)$ and $q_2(t)$ are solutions, then so is any linear combination of them:

$$q(t)=a_1q_1(t)+a_2q_2(t). \tag{5.7}$$

Here a_1 and a_2 are constants. Moreover, if $q_1(t)$ and $q_2(t)$ are linearly independent (i.e. $q_2(t)\neq C_1q_1(t)+C_2$; C_1 and C_2 are constants), then (5.7) is a general solution. Our aim is to find two independent solutions $q_1(t)$ and $q_2(t)$.

Consider first the case $\kappa<0$, which means that $U(q)$ has a maximum at $q=0$ (this is unstable equilibrium). Then, Eq. (5.6) can be written as

$$\ddot{q}-\beta^2q=0,\quad \beta^2=-\frac{\kappa}{m}. \tag{5.8}$$

The partial solutions of this equation are $q_1=e^{\beta t}$ and $q_2=e^{-\beta t}$. The general solution is a linear combination of these functions

$$q = \frac{1}{2} A e^{\beta t} + \frac{1}{2} B e^{-\beta t}. \tag{5.9}$$

We introduced the factor 1/2 - it is up to us whether to use the arbitrary constants A, B or $A/2, B/2$. The solution shows that a small displacement leads to exponential increase of q with time. In other words, the equilibrium is unstable, as expected when $U(q)$ has a maximum.

Now, let us consider the case $\kappa > 0$. The potential energy has a minimum at $q = 0$, and, consequently, this is a stable equilibrium. Then Eq. (5.6) becomes

$$\ddot{q} + \omega_0^2 q = 0, \quad \omega_0^2 = \frac{\kappa}{m}. \tag{5.10}$$

The functions $\sin \omega_0 t$ and $\cos \omega_0 t$ are partial solutions of this equation (substituting them in Eq. (5.10), we see that the equality is maintained). Therefore, the general solution is

$$q = c \cos \omega_0 t + d \sin \omega_0 t, \tag{5.11}$$

in which the arbitrary constants c and d are obtained from the initial conditions. If at $t = 0$ the initial generalized co-ordinate is $q(0) = q_0$ and the initial generalized velocity is $\dot{q}(0) = \dot{q}_0$, then

$$c = q_0, \quad d = \frac{\dot{q}_0}{\omega_0}. \tag{5.12}$$

For Cartesian co-ordinates we have $c = x_{0,}\ d = \dot{x}_0 / \omega_0$.

To obtain an alternative form of (5.11) we rewrite it in the form

$$q = c\left(\cos \omega_0 t + \frac{d}{c} \sin \omega_0 t \right), \tag{5.13}$$

and set $d/c = \tan \delta$. Then we have

$$\begin{aligned} q &= c\left(\cos \omega_0 t + \tan \delta \sin \omega_0 t\right) = \frac{c}{\cos \delta} \cos\left(\omega_0 t - \delta\right) \\ &= \sqrt{c^2 + d^2} \cos\left(\omega_0 t - \delta\right). \end{aligned} \tag{5.14a}$$

Introducing the notation $\sqrt{c^2+d^2}=a$, we finally get

$$q=a\cos\left(\omega_0 t+\delta\right). \tag{5.14b}$$

The new arbitrary constants a, δ are related to c, d by

$$c=\cos\delta, \quad d=-a\sin\delta. \tag{5.15}$$

The constant *a is called the amplitude* and it defines the maximum displacement of the co-ordinate *q*. The motion is an oscillation with a *period* τ:

$$\tau=\frac{2\pi}{\omega_0}. \tag{5.16}$$

The quantity δ is called *phase angle* (or simply *phase*) and ω_0 - *angular or cyclic frequency*. The subscript "0" is to denote that this is *natural frequency*, underlying that it depends only on the system parameter (see (5.10)). The periodic motion has such an angular velocity when the system is in a stable equilibrium state, without any external influence. The system can undergo also other oscillations with frequency ω imposed by an outer force. These are forced oscillations, unlike the natural ones with frequency ω_0. The *linear frequency* ν is the number of oscillations per unit time:

$$\nu=\frac{1}{\tau}=\frac{\omega_0}{2\pi}. \tag{5.17}$$

When q is a linear co-ordinate (e.g., r) we can determine the force, which acts on the one-dimensional system:

$$F=-\frac{\partial U\left(r\right)}{\partial r}=-\kappa r. \tag{5.18}$$

It always points to the centre of the stable equilibrium, and depends only on the displacement from it. It is obvious that when *q* is a Cartesian co-ordinate, this is a central potential force (Section 3.4). The quantity κ is called a force constant.

We have analysed the motion of a one-dimensional system around a stable equilibrium when the displacement is small. This is harmonic motion, i.e., a cosine (5.13) or sine law ($\delta=\pi/2$ in (5.14b)).

A one-dimensional system which moves around a stable equilibrium position at a small displacement from it, with a force proportional to this displacement and directed always to the equilibrium position while the displacement changes according to the harmonic law, is called a harmonic oscillator. Eq. (5.10) is an equation of the oscillator.

The solution of this equation (5.10), except in the form (5.11) or (5.13), can be represented also in a complex form:

$$q = \frac{1}{2}\tilde{A}e^{i\omega_0 t} + \frac{1}{2}\tilde{B}e^{-i\omega_0 t}. \tag{5.19}$$

Here and later on with the sigh "~" (tilde) we will denote a complex number. Substituting (5.19) in Eq. (5.10), we readily confirm that it is really a solution. Of course, q must be a real number. The sum of two complex numbers is real when they are complex conjugates. Hence $\tilde{A}$ and $\tilde{B}$ are complex conjugates. Let us set

$$\tilde{A} = c - id, \quad \tilde{B} = \tilde{A}^* = c + id. \tag{5.20}$$

Here the sign "*" (it is read asterisk) means complex conjugate.

Recalling Euler's formula $e^{\pm i\omega t} = \cos\omega t \pm i\sin\omega t$, we get from (5.19) and (5.20) Eq. (5.11):

$$\begin{aligned} q &= \frac{1}{2}(c - id)(\cos\omega_0 t + i\sin\omega_0 t) + \frac{1}{2}(c + id)(\cos\omega_0 t - i\sin\omega_0 t) \\ &= c\cos\omega_0 t + d\sin\omega_0 t. \end{aligned} \tag{5.21}$$

Of course (5.19) can also be transformed into (5.14b). But then we must represent the complex constants in a polar form:

$$\tilde{A} = ae^{i\delta}, \quad \tilde{B} = ae^{-i\delta}. \tag{5.22}$$

We shall note that $\tilde{A} = \tilde{B}^*$. Substituting into (5.19) we get

$$q = \frac{1}{2}ae^{i(\omega_0 t + \delta)} + \frac{1}{2}ae^{-i(\omega_0 t + \delta)} \tag{5.23}$$

and taking into account Euler's formula we obtain (5.14b), i.e. $q = a\cos(\omega_0 t + \delta)$.

Another useful representation can be obtained by noting that the sum of two complex conjugate numbers is equal to twice the real part of one of them, i.e.

$$q = 2\,\mathrm{Re}\left(\frac{1}{2}\tilde{A}e^{i\omega_0 t}\right) = \mathrm{Re}\left(\tilde{A}e^{i\omega_0 t}\right). \tag{5.24}$$

Here $\tilde{A} = ae^{i\delta}$ *is called complex amplitude*. Very often it is written

$$\tilde{q} = \tilde{A}e^{i\omega_0 t}. \tag{5.25}$$

Moreover, the sign for the complex number ~ is omitted, i.e.

$$q = Ae^{i\omega_0 t}, \tag{5.26}$$

where q and A are complex numbers, and it is implicit that the real quantity is $q = \mathrm{Re}\left(Ae^{i\omega_0 t}\right)$.

Example: Consider the oscillation of a diatomic molecule. Two atoms of masses m_1 and m_2, connected in a stable molecule, interact via Coulomb forces of attraction. The motion can be described by the two-body problem (Section 3.2), which is reduced to the motion of one particle of reduced mass in a potential field with an effective energy. The effective potential energy (Fig. 3-7) has a minimum. At small displacement from it we have harmonic oscillations. We shall show this. The potential energy in the equilibrium can be presented according to (5.1) and (5.2), as a quadratic function of the difference $\mathbf{r} - \mathbf{r}_0$ between the real distance $\mathbf{r}$ and the equilibrium distance $\mathbf{r}_0$:

$$U\left(\left|\mathbf{r} - \mathbf{r}_0\right|\right) = \frac{\kappa}{2}\left(\left|\mathbf{r} - \mathbf{r}_0\right|\right)^2. \tag{5.27}$$

Of course, this is valid only for small displacement from equilibrium: $\left|\mathbf{r} - \mathbf{r}_0\right| << r_0$. Then we shall obtain the motion equation of the particle with mass equal to the reduced mass $\tilde{m}$ of the molecule ($\left(\tilde{m} = m_1 m_2 / \left(m_1 + m_2\right)\right)$ from Eq. (3.13), replacing the force $\partial U/\partial r$ with the corresponding potential force $\mathbf{F} = -\partial U/\partial\left(\mathbf{r} - \mathbf{r}_0\right)$:

$$\tilde{m}\frac{d^2}{dt^2}\left(\mathbf{r} - \mathbf{r}_0\right) = -\frac{\partial U}{\partial\left(\mathbf{r} - \mathbf{r}_0\right)}. \tag{5.28}$$

Since the atoms are rotated around the centre of mass (see Section 3.4), for the determination of this force in the general case we must take into account also the change of direction of $\mathbf{r}-\mathbf{r}_0$. But this leads to an equation of the type (3.32), which includes also the centrifugal energy:

$$\frac{1}{2}\tilde{m}\left(\frac{d}{dt}(\mathbf{r}-\mathbf{r}_0)\right)^2+\frac{L^2}{2\tilde{m}(\mathbf{r}-\mathbf{r}_0)^2}+U(|\mathbf{r}-\mathbf{r}_0|)=E. \tag{5.29}$$

Fortunately, things in a molecule are simpler. As we shall see in the Second part (Section 14.6) the rotational energy is much smaller than the oscillation energy (it is called also vibrational energy). This means that a full turn (an ellipse or a circumference) occurs much more slowly than a full oscillation. The oscillation of the two atoms is a quick process and for a period the change of the direction $\mathbf{r}-\mathbf{r}_0$ is negligibly small. Then the force, corresponding to the potential (5.27) is determined by the relationship

$$F=-\frac{dU}{d(r-r_0)}=-\kappa(r-r_0). \tag{5.30}$$

This force is directed along the line, connecting the two atoms. Now, it is easy to write the motion equation of the particle with reduced mass $\tilde{m}$:

$$\tilde{m}\frac{d^2}{dt_2}(\mathbf{r}-\mathbf{r}_0)\equiv\tilde{m}\frac{d^2}{dt_2}(r-r_0)\mathbf{r}^0=-\kappa(r-r_0)\mathbf{r}^0, \tag{5.31a}$$

or

$$\tilde{m}\frac{d^2}{dt_2}(r-r_0)=-\kappa(r-r_0). \tag{5.31b}$$

We recall that $\mathbf{r}^0$ is unit vector along the direction of $\mathbf{r}$ and $\mathbf{r}_0$ is the equilibrium radius-vector. We obtained the equation of motion of a harmonic oscillator with frequency

$$\omega_0=\left(\frac{\kappa}{\tilde{m}}\right)^{\frac{1}{2}}. \tag{5.32}$$

We recall that κ is the force constant.

5.2* OSCILLATIONS OF A SYSTEM OF PARTICLES

Consider the motion of a system of s degrees of freedom around equilibrium. Let us choose the origin of the co-ordinate system of generalized co-ordinates in the centre of equilibrium, i.e. the origin of the co-ordinate system is at the point $q_j = 0$. By analogy with the preceding section, we shall expand the energy in Taylor series:

$$U(q_i) = U(0) + \sum_i \left.\frac{\partial U}{\partial q_i}\right|_0 q_i + \frac{1}{2}\sum_i \left.\frac{\partial^2 U}{\partial q_i \partial q_k}\right|_0 q_i q_k + \ldots \tag{5.33}$$

Here we also choose the arbitrary constant such that $U(0) = 0$; the second term is equal to zero because of the equilibrium. Then for the potential energy at small displacement we obtain

$$U(q_i) = \frac{1}{2}\sum_{i,k} \kappa_{ik} q_i q_k, \quad \kappa_{ik} = \kappa_{ki} = \left.\frac{\partial^2 U}{\partial q_i \partial q_k}\right|_0 . \tag{5.34}$$

To obtain (5.4) and (5.5), we write the series of γ_{ik} and the kinetic energy:

$$\begin{aligned} \gamma_{ik}(q_i) &= \gamma_{ik}(0) + \sum_i \left.\frac{\partial \gamma_{ik}}{\partial q_l}\right|_0 q_i + \ldots \approx \gamma_{ik}(0) \equiv \frac{m_{ik}}{2}, \\ T_{ik}(q_j) &= \frac{1}{2}\sum_{i,k} m_{ik} q_i q_k . \end{aligned} \tag{5.35}$$

Thus, U and T allow us to write the Lagrangian function in the form

$$\mathscr{L} = \frac{1}{2}\sum_{i,k} m_{ik} q_i q_k - \frac{1}{2}\sum_{i,k} \kappa_{ik} q_i q_k . \tag{5.36}$$

To obtain the motion equation we need the derivatives $\partial\mathscr{L}/\partial q_i$ and $\partial\mathscr{L}/\partial\dot{q}_i$. For this we must find the ordinary differential of the function $\mathscr{L}$:

$$d\mathscr{L} = \frac{1}{2}\sum_{i,k} m_{ik}\dot{q}_i d\dot{q}_k + \frac{1}{2}\sum_{i,k} m_{ik} d\dot{q}_i \dot{q}_k - \frac{1}{2}\sum_{i,k} \kappa_{ik} q_i dq_k - \frac{1}{2}\sum_{i,k} \kappa_{ik} dq_i q_k . \tag{5.37}$$

Here i and k are subscripts, which go from 1, 2, ... to s. Changing the subscript letters does not change the sum. Hence, we can change the places of the subscripts in (5.37) to obtain

$$d\mathscr{L}=\sum_{i,k} m_{ik}d\dot{q}_i\dot{q}_k-\sum_{i,k}\kappa_{ik}dq_iq_k, \tag{5.38a}$$

or

$$d\mathscr{L}=\sum_{i}\left(d\dot{q}_i\sum_{\kappa}m_{ik}\dot{q}_k\right)-\sum_{i}\left(dq_i\sum_{\kappa}\kappa_{ik}q_k\right). \tag{5.38b}$$

We divide by $d\dot{q}_i$ and dq_i and obtain the sought derivatives:

$$\frac{\partial\mathscr{L}}{\partial\dot{q}_i}=\sum_{k}m_{ik}\dot{q}_k,\quad \frac{\partial\mathscr{L}}{\partial q_i}=\sum_{k}\kappa_{ik}q_k, \tag{5.39}$$

which allows us to obtain Lagrange's equation

$$\sum_{k=1}^{s}m_{ik}\ddot{q}_k+\sum_{k=1}^{s}\kappa_{ik}q_k=0\quad i=1,2,...,s. \tag{5.40}$$

This a system of s homogeneous differentiation equations with constant coefficients. Its solution in complex form reads:

$$\tilde{q}_k=\tilde{C}_ke^{i\omega t},\quad k=1,2,...,s. \tag{5.41}$$

This is a partial solution. After substituting it into the system (5.40) we obtain

$$\sum_{k=1}^{s}\left(\kappa_{ik}-\omega^2m_{ik}\right)\tilde{C}_k=0\quad i=1,2,...,s, \tag{5.42}$$

i.e. we obtained s homogeneous algebraic equations for the unknown constant $\tilde{C}_j$. A system of homogeneous equations has a nonzero solution if its determinant is equal to zero:

$$\left|\kappa_{ik}-\omega^2m_{ik}\right|=0, \tag{5.43a}$$

or in explicit form

$$\begin{vmatrix} \kappa_{11}-\omega^2 m_{11} & \kappa_{12}-\omega^2 m_{12} & \dots & \kappa_{1s}-\omega^2 m_{1s} \\ \kappa_{21}-\omega^2 m_{21} & \kappa_{22}-\omega^2 m_{22} & \dots & \kappa_{2s}-\omega^2 m_{2s} \\ \dots & \dots & \dots & \dots \\ \kappa_{s1}-\omega^2 m_{s1} & \kappa_{s2}-\omega^2 m_{s2} & \dots & \kappa_{ss}-\omega^2 m_{ss} \end{vmatrix} = 0. \tag{5.43b}$$

This is the so-called characteristic equation. It is an algebraic equation of sth order with respect to the unknown quantity ω^2 and has s roots $\omega_1^2, \omega_2^2, \omega_3^2, \dots \omega_s^2$. The angular frequencies ω_l^2 $(l=1,2,\dots,s)$ are natural frequencies of the considered system of s degrees of freedom. Substituting every one of these roots into Eq. (5.40), we find the unknown coefficient $\tilde{C}_k$, obtaining each ω_l as a combination of the $\tilde{C}_k^l$'s.

The solution of the system (5.42) for the unknown $\tilde{C}_k$'s can be written in the following form

$$\tilde{C}_k^l = \tilde{c}_l A_{nk}^l, \quad k, l, n = 1, 2, \dots, s., \tag{5.44}$$

where $\tilde{c}_l$ is an arbitrary complex constant and A_{nk}^l is the signed minor of the element $\kappa_{nk} - \omega_l^2 m_{nk}$ in the determinant of the system

$$\sum_k \left(\kappa_{ik} - \omega^2 m_{ik}\right)\tilde{C}_k^l = 0 \quad i, l = 1, 2, \dots, s. \tag{5.45}$$

We shall note that n is chosen arbitrary, but such that at least one of the signed minors A_{nk}^l is different than zero.

Returning to $\tilde{q}_k$ (5.41) and taking into account the found values of ω_l^2 and C_k^l, we write the solution of the sought co-ordinate as follows:

$$\tilde{q}_k = \sum_k \tilde{q}_k^l = \sum_l \tilde{c}_l A_{nk}^l e^{i\omega_l t}, \quad k = 1, 2, \dots, s. \tag{5.46}$$

This is the solution in complex form. We use the results of the preceding section to determine the real values. Since all the terms of the system determinant (5.43) are real, then A_{nk}^l is also real. Hence, writing $\tilde{c}_k$ in a polar form

$$\tilde{c}_l = c_l e^{i\delta_l}, \tag{5.47}$$

we finally obtain the real solution of the motion equation of the system with s degrees of freedom around equilibrium:

$$q_k = \mathrm{Re}\sum_l \tilde{c}_l A_{nk}^l e^{i\omega_l t} = \sum_l A_{nk}^l \,\mathrm{Re}\, c_l e^{i(\omega_l t+\delta_l)} = \sum_l A_{nk}^l c_l \cos(\omega_l t + \delta_l). \quad (5.48)$$

From this solution follows a very important conclusion:

The change of each generalized co-ordinate represents a superposition of all s harmonic oscillations, whose frequencies are the natural frequencies of the system.

5.3 NORMAL CO-ORDINATES AND NORMAL MODES

It is natural to raise the question: can we not choose the generalized co-ordinates in such a way, that each of them undergoes only one simple oscillation?

Let us present the solution for the co-ordinate q_k (5.48) as follows:

$$q_k = \sum_l A_{nk}^l \xi_l. \quad (5.49)$$

We can consider the ξ_l as new generalized co-ordinates. Each of them undergoes a harmonic oscillation with a frequency ω_l :

$$\ddot{\xi}_l = c_l \cos(\omega_l t + \delta_l). \quad (5.50)$$

and hence it satisfies the equation

$$\ddot{\xi}_l + \omega_l^2 \xi_l = 0, \quad l = 1, 2, .., s. \quad (5.51)$$

This is the answer to our question. By a convenient choice we can define such generalized co-ordinates, which at the small displacement of the system from equilibrium undergo simple harmonic oscillations. Such co-ordinates are called *normal co-ordinates* and the corresponding oscillations - *normal oscillations* (*normal modes*). *Any periodic motion of the system can be represented as linear combination* (*superposition*) *of normal oscillations* (*normal modes*). (Sometimes (especially in the old books) the normal co-ordinates (oscillations) are called also principal ones.)

Let us turn to mathematics. We know that the potential energy is a quadratic function of the generalized co-ordinates:

$$U = \frac{1}{2}\sum_{i,k} \kappa_{ik}\dot{q}_i\dot{q}_k, \tag{5.52}$$

and the kinetic energy is a quadratic function of the generalized velocities

$$T = \frac{1}{2}\sum_{i,k} m_{ik}\dot{q}_i\dot{q}_k. \tag{5.53}$$

Also, $q_i = q_i(\xi_j)$. We pass to the new variables ξ_j, each of which is a function of the q_j, i.e. $\xi_l(q_j)$.

It can be proven (see, e.g., [4], Section 22) that this conversion can be done by a linear transformation:

$$\xi_l = \sum_k b_{ik}q_k, \tag{5.54}$$

for which the quadratic forms of T and U of the new variables have diagonal form (without mixed products $\xi_i\xi_k$ and $\dot{\xi}_i\xi_k$):

$$T = \frac{1}{2}\sum \xi_l^2, \quad U = \frac{1}{2}\sum \lambda_l\xi_l^2. \tag{5.55}$$

Then, for the Lagrangian function and the corresponding equation we have

$$\mathscr{L} = \frac{1}{2}\sum \ddot{\xi}_l^2 - \frac{1}{2}\sum \lambda_l\xi_l^2, \tag{5.56}$$

$$\ddot{\xi}_l + \lambda_l\xi_l = 0, \tag{5.57}$$

where $\lambda_l = \omega_l^2$ and ω_l are the natural frequencies of the system. These equations give the normal oscillations $\ddot{\xi}_l = c_l\cos(\omega_l t + \delta_l)$ (5.50).

On the base of the Eqs. (5.57) and (5.54) we can do two important conclusions:

1. *in each normal mode one normal co-ordinate only is oscillating*;
2. *in each normal mode all co-ordinates* q_j (*see Eq.* (5.54)) *are oscillating with the same frequencies.*

5.4* COUPLED OSCILLATORS

The classical problem of the coupled pendulums is a very good illustration of the results of the preceding section for a system of two degrees of freedom, $s=2$. One encounters many physical systems, which may be described as two harmonic oscillators which are approximately independent, but with some kind of relatively weak coupling between them.

Here we shall consider the system, shown in Fig. 5-1, which consists of two identical pendulums, each of them with mass m and a length l, coupled by a weak spring of elasticity k. When the spring is neither expanded nor contracted its natural length is equal to the distance between the pendulums, which are in equilibrium

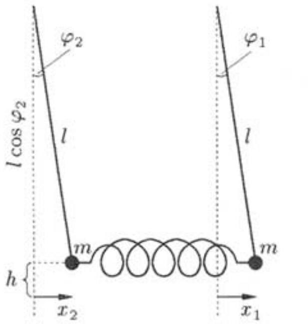


Figure 5-1. Two identical pendulums of mass m and a length l coupled through a weak spring of elasticity k. The potential energy of each of them is determined by their height relative to the equilibrium position, and by the expansion or compression of the spring: x_1-x_2, where x_1 and x_2 are the displacements from equilibrium.

We shall first solve the problem in arbitrary generalized co-ordinates and after that in normalized co-ordinates. We choose for generalized co-ordinates the displacements x_1 and x_2 from equilibrium.

The potential energy of each of the pendulums is a sum of two terms - the potential energy in the gravitational field, *mgh* (h stands for the height through which it is raised), and the potential energy of the spring

$k\left(x_1 - x_2\right)^2 / 2$ arising from its compression and extension. We shall write the potential energy U of the system, assuming that $U = 0$ at equilibrium:

$$\begin{aligned} U &= mgh_1 + mgh_2 + \frac{1}{2}k\left(x_1 - x_2\right)^2 \\ &= mgl(1-\cos\varphi_1) + mgl(1-\cos\varphi_2) + \frac{k}{2}\left(x_1 - x_2\right)^2. \end{aligned} \tag{5.58}$$

The inspection of Fig. 5-1 shows that $\sin\varphi = x/l$ and for small displacement $x/l = \sin\varphi \approx \tan\varphi << 1$, we can set $\cos\varphi = \left(1-\sin^2\varphi\right)^{1/2} = \left(1-\left(\dfrac{x}{l}\right)^2\right)^{1/2}$ $\approx 1-\left(1/2\right)\left(x^2/l^2\right)$. Substituting this into (5.58) yields:

$$U = \frac{1}{2}(\frac{mg}{l}+k)x_1^2 + \frac{1}{2}(\frac{mg}{l}+k)x_2^2 - kx_1x_2. \tag{5.59}$$

The kinetic energy at small displacement is as follows:

$$T = \frac{1}{2}m\dot{x}_1^2 + \frac{1}{2}m\dot{x}_2^2. \tag{5.60}$$

Thus, the Lagrangian for the system of coupled pendulums undergoing small displacements takes the form

$$L = T - U = \frac{1}{2}m\left(\dot{x}_1^2 + \dot{x}_2^2\right) - \frac{1}{2}\left(\frac{mg}{l}+k\right)\left(x_1^2 + x_2^2\right) + \frac{1}{2}2kx_1x_2. \tag{5.61}$$

To obtain the Lagrange's equation we use the results of the preceding section. The comparison of L with (5.36) gives the following results for the coefficients m_{ik} and κ_{ik}:

$$\begin{aligned} &m_{11} = m_{22} = m, \quad \kappa_{11} = \kappa_{22} = \frac{mg}{l} + k, \\ &m_{12} = m_{21} = 0, \quad \kappa_{12} = \kappa_{21} = -k. \end{aligned} \tag{5.62}$$

Substituting them in the motion equation (5.40) yields:

$$
\begin{aligned}
&m\ddot{x}_1+\left(\frac{mg}{l}+k\right)x_1-kx_2=0,\\
&m\ddot{x}_2+\left(\frac{mg}{l}+k\right)x_2-kx_1=0.
\end{aligned}
\tag{5.63}
$$

We see that the co-ordinate x_2 enters in the equation for the change of x_1 and the co-ordinate x_1 enters in the equation for x_2. So we need to solve a system of two coupled equations. Before doing this we shall recall the physical significance of the terms of the system (5.63). The first term $m\ddot{x}$ is the resultant force, acting on the pendulum. The second term, $(mg/l)x$, is the normal component of the gravitational force, i.e. the force, defining the oscillation of the uncoupled pendulum. The third (kx_1) and the fourth terms define the elastic force of the spring, acting, correspondingly, to the first pendulum $(k(x_1-x_2))$ and to the second pendulum $(-k(x_1-x_2))$. The opposite signs before $k(x_1-x_2)$ in both equations reflect the evident fact that the extended or compressed spring acts in different directions on both pendulums.

We shall pass to complex variables and shall seek the solution of the system (5.63) in the following form (compare with (5.61)):

$$
\tilde{x}_1=\tilde{C}_1e^{i\omega t},\quad \tilde{x}_2=\tilde{C}_2e^{i\omega t}.
\tag{5.64}
$$

We substitute in (5.63), cancel of the common factor $\exp(i\omega t)$ and obtain the system of equations for $\tilde{C}_1$ and $\tilde{C}_2$:

$$
\begin{aligned}
&\left(\frac{mg}{l}+k-m\omega^2\right)\tilde{C}_1-k\tilde{C}_2=0,\\
&-k\tilde{C}_1\left(\frac{mg}{l}+k-m\omega^2\right)\tilde{C}_2=0.
\end{aligned}
\tag{5.65}
$$

This system possesses nontrivial solution only if its determinant vanishes:

$$\begin{vmatrix} \left(\frac{mg}{l}+k-m\omega^2\right) & (-k) \\ (-k) & \left(\frac{mg}{l}+k-m\omega^2\right) \end{vmatrix} = 0. \tag{5.66}$$

Or, the characteristic equation for ω is as follows:

$$\omega^4 - 2\left(\frac{g}{l}+\frac{k}{m}\right)\omega^2 + \frac{g^2}{l^2} + 2\frac{kg}{lm} = 0. \tag{5.67}$$

The roots of this equation are

$$\omega_1^2 = \frac{g}{l}, \qquad \omega_2^2 = \frac{g}{l} + 2\frac{k}{m}. \tag{5.68}$$

We obtained two natural frequencies for the coupled oscillator. We replace ω^2 in (5.65) with ω_1^2 and the system for $\tilde{C}_1$ and $\tilde{C}_2$ takes the form:

$$\begin{aligned} k\tilde{C}_1^{(1)} - k\tilde{C}_2^{(1)} &= 0, \\ -k\tilde{C}_1^{(1)} + k\tilde{C}_2^{(1)} &= 0. \end{aligned} \tag{5.69}$$

The evident solution is

$$\tilde{C}_1^{(1)} = \tilde{C}_2^{(1)} = c_1 e^{i\delta_1}, \tag{5.70}$$

where c_1 is the module and δ_1 is the argument of an arbitrary complex constant. Then the partial solutions $\tilde{x}_1$ and $\tilde{x}_2$ of (5.64), corresponding to the natural frequency ω_1, take the form

$$\tilde{x}_1^{(1)} = c_1 e^{i(\omega_1 t + \delta_1)}, \quad \tilde{x}_2^{(1)} = c_1 e^{i(\omega_1 t + \delta_1)}. \tag{5.71}$$

The real part of this solution will give the displacements x_1 and x_2 of the pendulum

$$x_1^{(1)} = c_1 \cos(\omega_1 t + \delta_1), \quad x_2^{(1)} = c_1 \cos(\omega_1 t + \delta_1). \tag{5.72}$$

Now, replacing ω^2 in (5.65) with ω_1^2, i.e. with the square of the second natural frequency, we get

(5.73)

This syste $\begin{array}{l} -k\,C_1^{(2)} - k\,C_2^{(2)} = 0, \\ -k\,\tilde{C}_1^{(2)} - k\,\tilde{C}_2^{(2)} = 0. \end{array}$ m is satisfied if

$$\tilde{C}_1^{(2)} = -\tilde{C}_2^{(2)} = c_2 e^{i\delta_2}. \tag{5.74}$$

The corresponding to ω_2^2 complex solutions (5.64) are

$$\tilde{x}_1^{(2)} = c_2 e^{i(\omega_2 t+\delta_2)}, \quad \tilde{x}_2^{(2)} = -c_2 e^{i(\omega_2 t+\delta_2)} \tag{5.75}$$

and their real parts are

$$x_1^{(2)} = c_2 \cos(\omega_2 t + \delta_2), \quad x_2^{(2)} = -c_2 \cos(\omega_2 t + \delta_2). \tag{5.76}$$

The sum of the solutions (5.71) and (5.75) will give the general solution of the original system of differentiation equation (5.63):

$$\begin{aligned} x_1 &= x_1^{(1)} + x_1^{(2)} = c_1 \cos(\omega_1 t + \delta_1) + c_2 \cos(\omega_2 t + \delta_2), \\ x_2 &= x_2^{(1)} + x_2^{(2)} = c_1 \cos(\omega_1 t + \delta_1) - c_2 \cos(\omega_2 t + \delta_2). \end{aligned} \tag{5.77}$$

We obtained what we had proven in Section 5.2 for the general case - the change of each of the two generalized co-ordinates is a linear superposition of the natural oscillations with frequencies ω_1 and ω_2 (5.68).

Now, let us to pass to the normal co-ordinates ξ_1 and ξ_2. According to (5.54) they are expressed as a linear combination of x_1 and x_2 so that U and T have diagonal form. We choose

$$\begin{aligned} \xi_1 &= x_1 + x_2 , \\ \xi_2 &= x_1 - x_2 , \end{aligned} \tag{5.78}$$

and substituting $x_1 = (1/2)(\xi_1 + \xi_2)$ and $x_2 = (1/2)(\xi_1 - \xi_2)$ into (5.59) and (5.60) we verify that U and T take the form (5.55):

$$U=\frac{1}{2}\left(\frac{mg}{2l}\right)\xi_1^2+\frac{1}{2}\left(\frac{mg}{2l}+|\,k\right)\xi_2^2,$$
$$T=\frac{1}{2}\frac{m}{2}\dot{\xi}_1^2+\frac{1}{2}\frac{m}{2}\dot{\xi}_2^2. \tag{5.79}$$

In normal co-ordinates, instead of the system of equations (5.63) we analogously obtain two independent equations:

$$m\ddot{\xi}_1+\frac{mg}{l}\xi_1=0,$$
$$m\ddot{\xi}_2+\left(\frac{mg}{l}+2k\right)\xi_2=0. \tag{5.80}$$

Unlike (5.63), each of these equations describes different harmonic oscillators. By analogy with (5.13), we write the solutions as follows:

$$\xi_1=c_1\cos(\omega_1 t+\delta_1),\quad \xi_2=c_2\cos(\omega_2 t+\delta_2). \tag{5.81}$$

To understand the physical significance of the oscillations, described by equations (5.80), we shall consider the case when one of the normal co-ordinates does not change with time. If for any moment of time $\xi_2=0$, i.e. $x_1=x_2$, then the motion is described by the first equation of (5.80). In this case the frequency of the oscillation is that of a single free pendulum. Fig.5-2 illustrates this motion, which oscillates with the frequency of the free pendulum, because the spring has a fixed length (it is neither extended nor compressed) and plays no role, whatsoever. As we expect for the normal co-ordinates, both pendulums swing with equal frequency. They always oscillate in phase. *These "in phase" oscillations are also called antisymmetric, because the displacements with respect to the position of the centre of mass are antisymmetric - when one pendulum approaches the centre, but the other moves away with a frequency*

$$\omega_a=\omega_1=\sqrt{\frac{g}{l}}. \tag{5.82}$$

If $\xi_1=0$ at all time, i.e. $x_1=-x_2$, the motion is completely described by the second equation of (5.80). The frequency of these oscillations

$$\omega_s = \omega_2 = \sqrt{\omega_a + \frac{2k}{m}}. \tag{5.83}$$

depends on the elasticity of the spring, because at all time it is either extended or compressed. The pendulums swing "out of phase" (Fig. 5-3). *"Out of phase" oscillations are called symmetric, because the displacements with respect to the position of the centre of mass are symmetric - the pendulums either approach the centre or move away from it at the same time.*

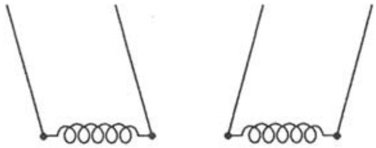


Figure 5-2. In phase or antisymmetric (with respect to the equilibrium position of the centre of mass) oscillations with frequency $\omega_a = \sqrt{g/l}$ are described by the Eq. $\ddot{\xi}_1 + (g/l)\xi_1 = 0$ for the normal co-ordinate $\xi_1 = x_1 + x_2$.

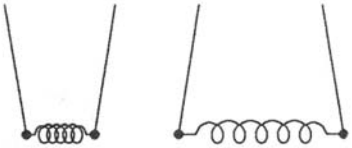


Figure 5-3. Out of phase or symmetric (with respect to the equilibrium position of the centre of mass) oscillations with frequency $\omega_s = \sqrt{g/l + 2k/m}$ are described by the Eq. $\ddot{\xi}_2 + (g/l + 2k/m)\xi_2 = 0$ for the normal co-ordinate $\xi_2 = x_1 - x_2$.

In the considered system of coupled oscillators there are two normal modes – *antisymmetric and symmetric* with frequency respectively ω_a and ω_s. *At the excitation of the given normal mode all system components oscillate with its own frequency. The normal modes are independent and they do not exchange energy. At the normal oscillation the pendulums also do not exchange energy.*

This however does not mean that the same pendulums can not exchange energy. On the contrary the spring ensures their active coupling and any change of the co-ordinates x_1 and x_2 can be represented as a superposition of these two normal oscillations. We shall analyse this with a concrete example.

We choose the initial conditions such that $c_1 = c_2 = 2a$ and $\delta_1 = \delta_2 = 0$. Then, for the displacements x_1 and x_2 we obtain

$$x_1 = \frac{1}{2}(\xi_1 + \xi_2) = a\cos\omega_\alpha t + a\cos\omega_s t = 2a\cos\frac{\omega_s - \omega_a}{2}t\cos\frac{\omega_s + \omega_a}{2}t, \tag{5.84a}$$

$$x_2=\frac{1}{2}(\xi_1-\xi_2)=a\cos\omega_\alpha t-a\cos\omega_s t=2a\sin\frac{\omega_s-\omega_a}{2}t\sin\frac{\omega_s+\omega_a}{2}t. \quad (5.84b)$$

Now, let us set the system in motion by displacing the first pendulum (the right hand one) at a distance $x_1=2a$ and releasing it. Fig. 5-4 demonstrates that the initial displacement of the coupled oscillators ($x_1=2a$, $x_2=0$) may be considered as a superposition of the "in phase" mode ($x_1=x_2=a$ so that $x_1+x_2=\xi_1=2a$) and the "out of phase" mode ($x_1=-x_2=a$ so that $x_1-x_2=\xi_2=2a$). The motion of the first pendulum is described by (5.84a) and of the second - by (5.84b).

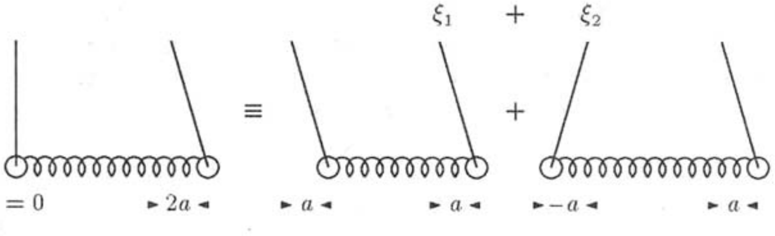


Figure 5-4. The displacement of one pendulum by a distance $2a$ is shown as a superposition of the two normal modes, i.e. the sum of the two normal co-ordinates, $x_1=(1/2)(\xi_1+\xi_2)$, so that their values in the initial moment, in which they are shown, are respectively $\xi_1=2a$ and $\xi_2=2a$.

In Fig. 5-5 are shown the curves of the dependencies $x_1(t)$ and $x_2(t)$.

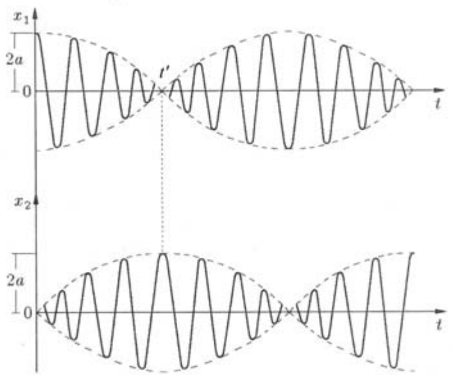


Figure 5-5. The change of the displacements of each pendulum with time: with decreasing of the amplitude of the displacement x_1 from $2a$ to 0, the amplitude of the displacement x_2 increases from 0 to $2a$, and at this moment the second pendulum acquires all the energy of the first pendulum (the last is shown by the dash line).

Both displacements oscillate with a frequency $(\omega_s + \omega_a)/2$ and with a slow amplitude modulation. We see that after releasing the first pendulum x_1 follows a cosine law, (5.84a). Its amplitude varies also as a cosine, but with a low frequency, which is half the difference between the normal mode frequencies, $((\omega_s - \omega_a)/2)$. After the initial moment the amplitude decreases. At the same time the displacement $x_2(t)$ vibrates as a sine function, but its amplitude builds up to $2a$ and then decays with low frequency $(\omega_s - \omega_a)/2$. The new state (see dashed line in Fig. 5-5) has a maximal amplitude of $x_2(t)$ (i.e. $x_2 = 2a$) and a minimal amplitude of $x_1(t)$ (i.e. $x_1 = 0$), and it may be also shown as a superposition of the normal modes (Fig. 5-6). At this state the first pendulum has come momentarily to rest, and the second is oscillating with an amplitude of $2a$. Thus, the first pendulum (with a displacement $x_1(t)$) transmits all its energy to the second one (with a displacement $x_2(t)$) and stops, when the amplitude of $x_2(t)$ reaches $2a$. The situation then reverses and the energy of the second pendulum returns to the first one. The whole process is then repeated indefinitely. The phenomenon of slow variation of the amplitude is known as *beats*, which occur between two oscillations of nearly equal frequencies. When the coupling is very weak, $k/m << g/l$, the normal-mode frequencies differ insignificantly and the beats have frequency $(\omega_s - \omega_a)/2 << \omega_a$, but the pendulums swing with frequency $(\omega_s + \omega_a)/2 \approx \omega_a$, almost equal to the frequency of an independent pendulum.

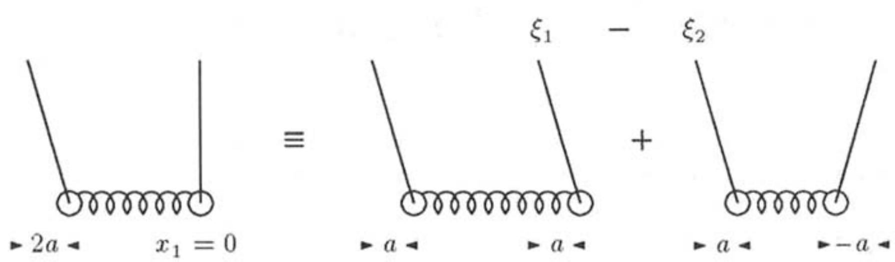


Figure 5-6. The displacement x_2 at the moment t' in Fig. 5-5 is shown as a superposition of the two normal modes, i.e. as the difference between the normal co-ordinates $x_2 = (1/2)(\xi_1 - \xi_2)$, whose values at the moment t' are $\xi_1 = 2a,\ \xi_2 = -2a$.

5.5 VIBRATIONS OF MOLECULES

In this section we deal with the classical theory of molecular oscillations. The total energy of a molecule can be considered as a sum of different parts corresponding to the different molecular motions: translational, associated with the translation of the whole molecule; vibrational, defined by the periodic changes of the relative positions of the nuclei; rotational, due to the periodic changes of the orientation of the whole molecule; electronic, which includes the electron motion of the electrons in the individual atoms. In quantum mechanics it is proven that it is possible to divide the total energy into such parts, since the interaction between the different motions is weak. Here we shall consider the atoms as stable particles, i.e. we won't be interested in electron motion.

We shall first define the number and type of the degrees of freedom of an N-atom molecule. Generally, it has $3N$ degrees of freedom. Three of them belong to the translational motion, which can be described by the three co-ordinates of the centre of mass. The degrees of freedom of the rotational motion are also three, one per rotation around each axis. Consequently, the degrees of freedom of the vibrational motion remain $3N-6$. They are called vibrational degrees of freedom.

For a linear molecule the rotation around its line is negligibly small (the size of the nuclei (almost all mass is in them) is essentially smaller than the distance between the atoms), and the vibrational degrees are $3N-5$. It is convenient to consider separately the longitudinal and transverse oscillations. For the longitudinal motion (along the molecular axis) the degrees of freedom are N, one of which is translational and $N-1$ are vibrational. From all these $3N-5$ degrees of freedom, the degrees of the transverse vibrations (to the molecular axis) are $(3N-5)-(N-1)=2N-4$. Since a linear molecule has an axis of symmetry, the transverse oscillations are in mutually perpendicular directions, which differ only by orientation. Therefore, $N-2$, i.e. twice less, natural frequencies correspond to the $2N-4$ degrees of freedom.

For the analysis it is convenient to eliminate the translational and rotational motions, so that the motion equation describes only the oscillations. To eliminate the translational motion we go to the frame in which the molecular momentum is zero. This is a CM-frame (see Section 3.2)), in which the centre of mass is at rest:

$$\mathbf{p}=M\dot{\mathbf{R}}=0, \quad \left(M=\sum_{\alpha} m_{\alpha}, \quad \mathbf{R}=\sum_{\alpha} m_{\alpha}\mathbf{r}_{\alpha}/M=\text{const}\right). \tag{5.85}$$

Since we consider small displacement $\Delta\mathbf{r}_\alpha$ from the equilibrium position $\mathbf{r}_{0\alpha}$ of each atom, its radius-vector may be seen as $\mathbf{r}_\alpha = \mathbf{r}_{\alpha 0} + \Delta\mathbf{r}_\alpha$. The condition $\mathbf{p} = 0$ means that $\mathbf{R}$ is constant and, hence,

$$\sum_\alpha m_\alpha \mathbf{r}_\alpha = \text{const} = \sum_\alpha m_\alpha \mathbf{r}_{\alpha 0}. \tag{5.86}$$

It is evident from this relationship that the condition for the elimination of the translational motion can be written as follows:

$$\sum_\alpha m_\alpha \Delta\mathbf{r}_\alpha = 0. \tag{5.87}$$

The elimination of the rotational motion means that the angular momentum is zero ($\mathbf{L} = 0$), i.e.,

$$\begin{aligned} \mathbf{L} &= \sum m_\alpha \left(\mathbf{r}_\alpha \times \mathbf{v}_\alpha\right) = \sum m_\alpha \left(\mathbf{r}_{\alpha 0} \times \Delta\mathbf{r}_\alpha\right) \times \Delta\dot{\mathbf{r}}_\alpha \\ &\approx \sum m_\alpha \left(\mathbf{r}_{\alpha 0} \times \Delta\dot{\mathbf{r}}_\alpha\right) = \frac{d}{dt} \sum m_\alpha \left(\mathbf{r}_{\alpha 0} \times \Delta\mathbf{r}_\alpha\right) = 0. \end{aligned} \tag{5.88}$$

Going from the equality to the approximate equality we neglected the quadratic term $\propto \Delta\mathbf{r}_\alpha \times \Delta\dot{\mathbf{r}}_\alpha$. From (5.88) it is obvious that the condition $\mathbf{L} = 0$ means that the sum under the sign of differentiation is constant. In the initial moment, $t = 0$, this constant is zero $\left(\delta\mathbf{r}_a = 0\right)$ and, hence, the condition of the elimination of the rotational motion is the following:

$$\sum m_\alpha \left(\mathbf{r}_{\alpha 0} \times \Delta\mathbf{r}_\alpha\right) = 0. \tag{5.89}$$

For the equation of the vibartional motion of a given molecule we need, except for the conditions (5.87) and (5.89), also the kinetic and the potential energy of the atoms. To determine the potential energy of the longitudinal oscillation we recall the problem of Section 5.1 for a diatomic molecule. The acting force there is analogous to the elastic force of a spring of elasticity k. Therefore, the diatomic molecule can be represented as a system of two particles of masses equal to the masses of the atoms and connected with a spring. The maximal and minimal distances between the atoms correspond to the maximal extension and the maximal compression of the spring (Fig. 5-7). The potential energy is

$$U(\Delta r)=\frac{1}{2}\kappa(\Delta r)^2, \tag{5.90a}$$

where the force constant is determined by

$$\kappa=\left.\frac{d^2U}{d(\Delta r)^2}\right|_{\Delta r=0}. \tag{5.90b}$$

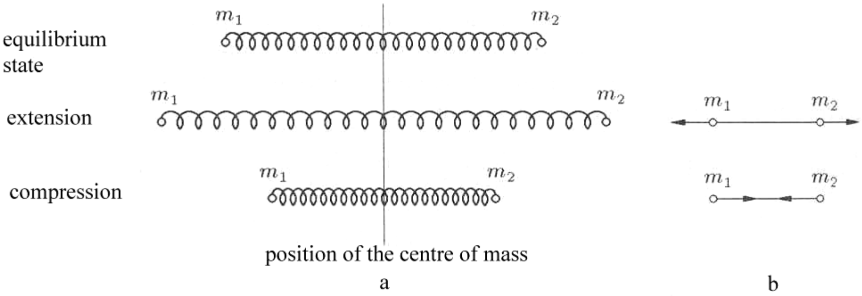


Figure 5-7. The oscillation of a diatomic molecule: a) analogy between the oscillations of a molecule of atoms of masses m_1 and m_2 and particles, connected with a spring. In both cases the potential energy has the form $U=\kappa(\Delta r)^2/2$; b) conditional notation of the oscillations.

Similarly, we can interpret a three-atomic molecule. In that case we represent the three atoms of the molecule connected by two springs. The oscillations will obey the laws of two coupled oscillators, studied in the preceding section. We observe two types of longitudinal oscillations - "in phase" (antisymmetric) and "out of phase" (symmetric) (Fig. 5-8).

For the potential energy of these oscillations we can write

$$U=\frac{\kappa}{2}\left[(r_1-r_2)^2+(r_2-r_3)^2\right], \tag{5.91}$$

where r_1, r_2 and r_3 stand for the displacements of the corresponding atoms from the equilibrium position.

For the transverse oscillations of a linear molecule the potential energy is defined by “bending" of the molecule. Similarly to the plate lamina, the potential energy of a three-atomic molecule *ABA,* at a given distance *l* between the atoms, depends on the angle of the displacement from the line (Fig. 5-9):

$$U = U(\beta) = \frac{\kappa'}{2}(\beta l)^2 . \tag{5.92}$$

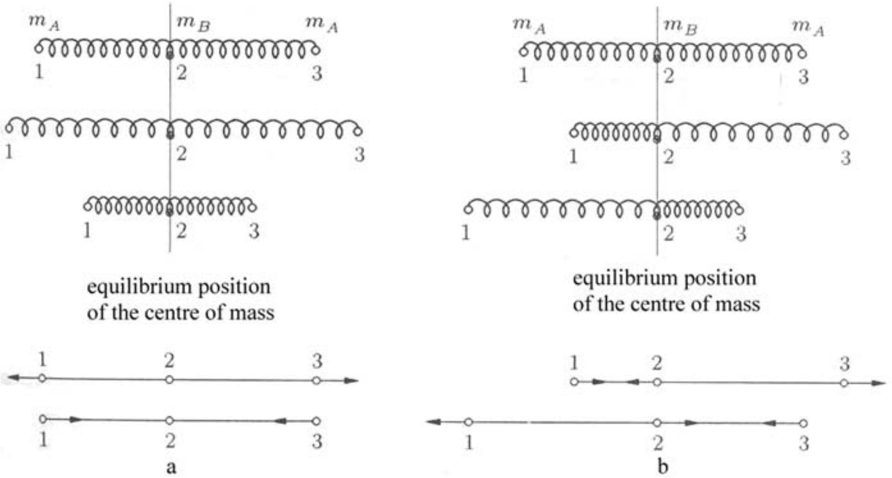


Figure 5-8. Analogy between the longitudinal oscillations of a linear symmetric molecule *ABA* and particles connected with springs, with conditional notation of the oscillations: a) *symmetric* oscillations; b) *antisymmetric* oscillations.

The analogy with the potential energy of a shearing strain in the solid state is evident.

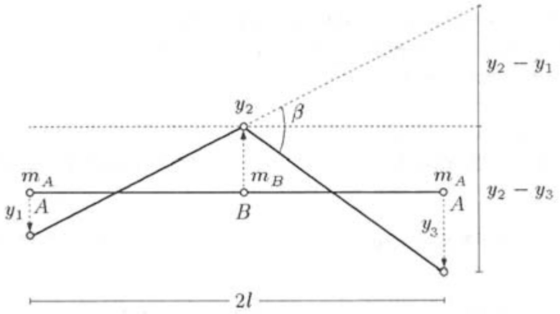


Figure 5-9. The potential energy of the transverse oscillations of a linear three-atomic molecule depends on the degree of its strain, i.e. on the angle β, as a measure of the displacement of the angle *ABA* from π: $U = (\kappa'/2)(\beta l)^2 = (\kappa'/2)\left[(y_2 - y_1)^2 + (y_2 - y_3)^2\right]^2$; m_A and m_B are the masses of the atoms; l is the distance between them; y_1, y_2, y_3 are the transverse co-ordinates of the atoms.

The atoms of multiatomic molecules oscillate as the masses of coupled oscillators. The normal oscillations of two three-atomic molecules (CO_2 and H_2O) and their frequencies are shown in Fig. 5-10.

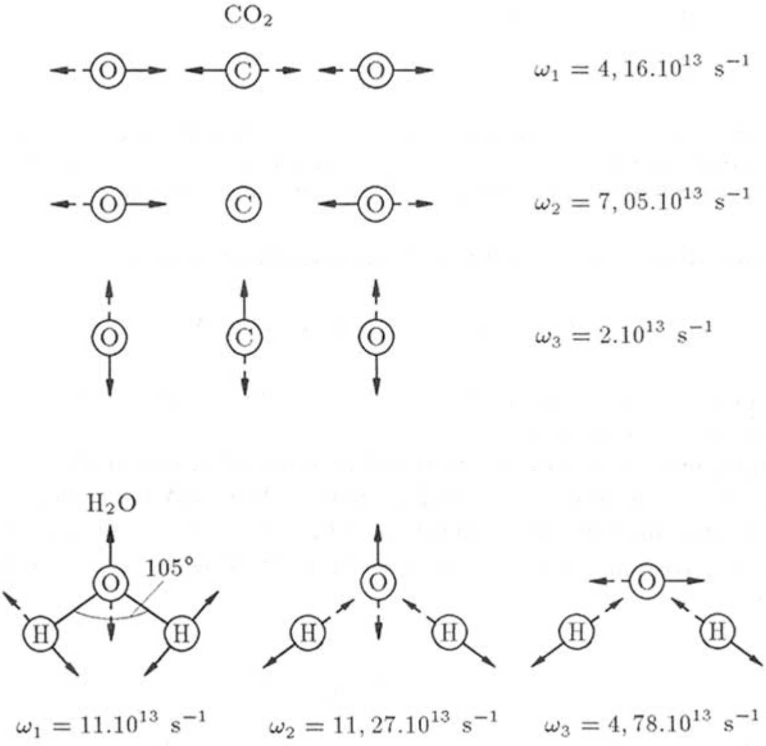


Figure 5-10. Normal oscillations of the three-atomic molecule of CO_2 and H_2O .

SUMMARY

At small displacement of a mechanical system of one degree of freedom from its stable equilibrium position, its kinetic and potential energies are quadratic functions:

$$T = \frac{m\dot{q}^2}{2}, \qquad U(q) = \frac{\kappa q^2}{2},$$

and the equation of motion

$$\ddot{q} + \omega_0^2 q = 0, \quad \omega_0^2 = \frac{\kappa}{m}.$$

has the harmonic solution

$$q = a\cos\left(\omega_0 t + \delta\right) .$$

This is called harmonic oscillator with a natural angular frequency ω_0. The displacement from the equilibrium distance between the atoms of a molecule changes harmonically. Very often it is used the complex form of the harmonic-oscillations, writing

$$\tilde{q} = \tilde{A}e^{i\omega_0 t},$$

where $\tilde{A} = ae^{i\delta t}$ is a complex amplitude, and the quantity q is the real part of $\tilde{q}$, i.e. $q = \mathrm{Re}\tilde{q} = \mathrm{Re}\left(\tilde{A}e^{i\omega_0 t}\right)$.

In a system of s degrees of freedom of arbitrary generalized co-ordinates, the change of each co-ordinate is a superposition of s harmonic oscillations with their corresponding natural frequencies. But we can choose such co-ordinates so that their change can be described by simple harmonic oscillations. They are called normal co-ordinates and normal oscillations. In normal co-ordinates both the kinetic and potential energy have diagonal form. When in a system a normal oscillation is excited, all particles of the system oscillate with equal frequency. Moreover when a fixed normal oscillation is excited, one normal co-ordinate only is oscillating.

Two coupled pendulums, similarly to the longitudinal oscillations of a three-atomic molecule, have two normal co-ordinates:

$$\xi_1 = x_1 + x_2, \qquad \xi_2 = x_1 - x_2$$

and two normal oscillations, antisymmetric and symmetric. Any periodic motion of the coupled pendulums (molecules) can be described as a superposition of the normal oscillations.

While doing the analysis of the oscillations of a molecule, by using the conditions

$$\sum_\alpha m_\alpha \Delta\mathbf{r}_\alpha = 0, \qquad \sum m_\alpha\left(\mathbf{r}_{\alpha 0} \times \Delta\mathbf{r}_\alpha\right) = 0$$

one can eliminate the translational and rotational motions.

QUESTIONS

1. What is the change of the co-ordinate q of a system of one degree of freedom for a displacement from an equilibrium, which is: a) stable; b) unstable?
2. What is a harmonic oscillator?
3. What is a natural frequency of the oscillation? What is natural oscillation?
4. Why for a small displacement r of the electron in a hydrogen atom can we represent the force acting on the electron in the form $F \propto r$, while the interaction force between the electron and the proton is a Coulomb force $F \propto 1/r^2$?
5. An atom of a positron is hydrogen-like atom, in whose nucleus instead of a proton there is a positron: a particle of electron mass, but of the positive charge e. Hence the force constants of the hydrogen and the positron are equal. Are the spectra of the radiation (the absorption) of both atoms equal? Why?
6. What is understood under complex amplitude?
7. What can be said about the quantities x and A, when the distance between the atoms of a diatomic molecule obeys the law $x = Ae^{i\omega t}$?
8. What is the change for small displacement from equilibrium of the generalized co-ordinate of a system with s degrees of freedom?
9. What is the difference between ordinary and normal co-ordinates?
10. How can a periodic motion be described if the normal co-ordinates are known?
11. What does define the potential energy of two coupled pendulums?
12. Do the forces, acting on two coupled oscillators differ by their: a) magnitude; b) directions?
13. Does the elastic force of the coupling influence the frequencies of the antisymmetric and symmetric oscillations?
14. Can the energy of a coupled oscillator be transmitted from one normal mode to another? And from one pendulum to another?
15. How many vibrational degrees of freedoms has a linear three-atomic molecule? How many of them are longitudinal and how many transverse? How many are the natural frequencies of the oscillations?
16. How many vibrational degrees of freedom has a diatomic molecule?
17. How can the translational motion of a molecule be eliminated?
18. How is determined the potential energy of a three-atomic molecule for: a) longitudinal oscillations; b) transverse oscillations?

PROBLEMS

1. Find the oscillation law for a particle of mass m and potential energy $U(x)=\kappa x^2/2$. Express the amplitude and initial phase of the oscillation through the initial values x_0 and v_0 of the co-ordinate and the velocity.
2. Find the ratio between the oscillation frequencies of diatomic molecules with atoms of different isotopes. The masses of the isotopes are: m_1, m_2 and m_1', m_2'.
3. Find the kinetic and potential energies of a harmonic oscillator as a function of time. Find their mean values and verify that $\overline{T}=\overline{U}$.
4. Find the laws and frequencies of oscillation of two identical pendulums of mass m and a length l, coupled by a spring of elasticity k at a distance b from the hanging points? Use the displacements x_1 and x_2 as the generalized co-ordinates.
5. Solve the fourth problem, using normal co-ordinates.
6. From spectral measurements it is known that the frequencies of oscillation of the molecules of HF and HCl are, respectively,
   $\nu_{\mathrm{HL}}=\omega/2\pi=1{,}202.10^{14}$ s^{-1} and $\nu_{\mathrm{HCl}}=\omega/2\pi=0{,}8.10^{14}$ s^{-1}.
   Find the force constants κ_{HF} and κ_{HCL} of both molecules and their ratio. Knowing that the length of the molecule HF is 1Å and its energy of dissociation is 6 eV, try to evaluate the correctness of the obtained force constant.
7. Find the frequencies of the longitudinal oscillations of a linear three-atomic molecule ABA, whose potential energy depends only on the distances AB and BA.
8. Find the frequencies of the transverse oscillations of a linear three-atomic molecule ABA. Suppose that its potential energy depends only on the angle ABA.
9. Find the frequencies of the antisymmetric oscillations of a linear three-atomic molecule ABA. Suppose that its potential energy depends on the distances AB, BA and the angle ABA.

Chapter 6

HAMILTONIAN MECHANICS

SUGGESTED READING

1. Landau, L. D. and E. M. Lifshitz, Mechanics, Pergamon Press, 2nd ed., 1969, Sections 6÷9.
2. Kittel, Ch., W. D. Nayt, M. Ruderman, Mechanics, Berkeley Physics Course, vol. I, McGraw-Hill Book Co., 2nd ed., 1973, Chapters 5, 6.
3. Fetter, A. L., J. D. Walecka, Theoretical Mechanics of Particles and Continua, McGraw-Hill, Book Co., 1980, Sections 1.

6.1 HAMILTONIAN FUNCTION AND HAMILTON’S EQUATIONS

Up till now we have got acquainted with the Lagrangian function and Lagrange's equation, satisfied by it. In Lagrange’s method a mechanical system is described by s equations of second order. Solving them, we determine the generalized co-ordinates, from which, trivially by differentiation, we get the generalized velocities. Thus, in Lagrangian mechanics, the mechanical system is described by the generalized co-ordinates and generalized velocities, which in Lagrange's equation are assumed to be independent.

This is not the only possible description. Hamilton obtained the equations of motion, in which independent variables are the generalized co-ordinates and the generalized momenta. It appears that such a description has some advantages, especially for problems of transition from classical to quantum mechanics.

Hamilton’s equations can be obtained from the principle of least action. Not only do they give possibilities to solve specific problems in mechanics, but they are also very useful in supplying fundamental postulates in such fields as quantum mechanics, statistical mechanics and celestial mechanics. They are differential equations of first order and are more "transparent" than Lagrange’s equations. On the other hand, their number necessary to describe a system with s degrees of freedom is $2s$, which is greater than the number of Lagrange's equations.

We shall obtain Hamilton's equations, starting from the Lagrangian function and Lagrange's equations. Let us determine the exact differential of the Lagrangian as a function of the co-ordinates and velocities (it is supposed that $\mathscr{L}$ does not depend explicitly on time):

$$d\mathscr{L} = \sum_i \frac{\partial \mathscr{L}}{\partial q_i} dq_i + \sum_i \frac{\partial \mathscr{L}}{\partial \dot{q}_i} d\dot{q}_i. \qquad (6.1)$$

Recalling the definition of the generalized momentum (1.53) and Lagrange's equation, we express P_i and $\dot{P}_i$ through the Lagrangian:

$$P_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i}, \quad \dot{P}_i = \frac{\partial \mathscr{L}}{\partial q_i}. \tag{6.2}$$

Then we substitute the derivative in the exact differential $d\mathscr{L}$ and instead of (6.1) obtain:

$$d\mathscr{L} = \sum_i \dot{P}_i dq_i + \sum_i P_i d\dot{q}_i = \sum_i \dot{P}_i dq_i + d\left(\sum_i P_i \dot{q}_i \right) - \sum_i \dot{q}_i dP_i. \tag{6.3}$$

After some simple mathematical procedures, we obtain:

$$d\left(\sum_i P_i d\dot{q}_i - \mathscr{L} \right) = \sum_i \dot{q}_i dP - \sum_i \dot{P}_i dq_i. \tag{6.4}$$

The function in the brackets is defined as *Hamilton's function or Hamiltonian*:

$$H\left(q_j, P_j\right) = \sum_i P_i \dot{q}_i - \mathscr{L}\left(q_j, \dot{q}_j\right) . \tag{6.5}$$

Here $\dot{q}_i = \dot{q}_j\left(q_j, P_j\right)$ and the Hamiltonian is a function of generalized coordinates q_j and generalized momenta P_j. It plays a central role in theoretical mechanics. If time does not appear explicitly in Eqs. (1.34), then the *Hamiltonian is the total energy* of the system (see Eq. (1.58). (This corresponds to a time-independent potential and time-independent constraints - for details and proof see [2], Section 20.) Here, an example of a Hamiltonian of a particle in a potential field $U(x, y, z)$ is the following:

$$H\left(x_j, P_j\right) = \frac{1}{2m}\left(P_x^2 + P_y^2 + P_z^2\right) + U\left(x, y, z\right) . \tag{6.6}$$

Taking into account (6.5), the exact differential (6.4) becomes:

$$dH = \sum_i \dot{q}_i dP - \sum_i \dot{P}_i dq_i . \tag{6.7}$$

On the other hand, we can write for the exact differential of the function H

$$dH = \sum_i \frac{\partial H}{\partial P_i} dP_i - \sum_i \frac{\partial H}{\partial q_i} dq_i, \tag{6.8}$$

and comparing (6.7) and (6.8), we obtain

$$\dot{q}_i = \frac{\partial H}{\partial P_i}, \quad \dot{P}_i = -\frac{\partial H}{\partial q_i}. \tag{6.9}$$

We have obtained $2s$ equations of motion of first order for the variables q_j and P_j. These equations are called *Hamilton's equations.* They allow the determination of the unknown $q_j(t)$'s and $P_j(t)$'s, i.e. the generalized co-ordinates and generalized momenta.

For their formal simplicity and symmetry these equations are called *canonical equations* and their generalized co-ordinates and the relative generalized momenta - *canonical conjugates.* In the most general case the Hamilotian can depend on time, i.e. $H = H(q_j, P_j, t)$. Then its total derivative with respect to time is

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \sum_i \frac{\partial H}{\partial q_i}\dot{q}_i + \sum_i \frac{\partial H}{\partial P_i}\dot{P}_i . \tag{6.10}$$

Substituting the values of q_j and P_j from Hamilton's equations (6.9), we get

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} . \tag{6.11}$$

From here we can make a very important conclusion: *if the function of Hamilton does not depend explicitly on time, it is a constant of the motion.* We shall note that this is not obvious since H depends implicitly on time through the q_j's and P_j's. However, this is expected - the Hamiltonian is the energy of the system, i.e. if the energy does not depend explicitly on time, the system is conservative and dH/dt represents the law of conservation of energy.

We shall underline one more peculiarity of the Hamiltonian. The result from the second equations of (6.2) and (6.9) is

$$\frac{\partial H}{\partial q_i} = -\dot{P}_i = -\frac{\partial \mathscr{L}}{\partial q_i}, \quad \text{or} \quad \frac{\partial H}{\partial q_i} = -\frac{\partial \mathscr{L}}{\partial q_i}, \quad i = 1, 2, ..., s. \tag{6.12}$$

It is obvious that the generalized co-ordinates which are cyclic for the Lagrangian $\mathscr{L}$ *, are also cyclic for the Hamiltonian* H *. This means that the respective generalized momenta are constants of the motion:* $\dot{P}_k = 0$, $P_k = \text{const}$, *when* $\partial H/\partial t = 0$.

6.2 CONCEPT OF CANONICAL TRANSFORMATIONS, PHASE SPACE AND LIOUVILLE'S THEOREM

We derived Lagrange's equations from the principle of least action (Section 1.2) using arbitrary generalized co-ordinates q_j. We recall that q_j stands for the set of all the generalized co-ordinates $q_1, q_2, ..., q_s$. In Lagrange's method the generalized co-ordinates q_j and the generalized velocities $\dot{q}_j$ are independent variables. Since the choice of the q_j's is arbitrary, Hamilton's principle would have physical meaning only if its consequences do not depend on this choice. Indeed, the general form of Lagrange's equations does not change for an arbitrary transformation from generalized co-ordinates to other co-ordinates, i.e., for a transformation of the form

$$q_i' = q_i'(q_i), \quad i = 1, 2, ..., s. \tag{6.13}$$

For such a transformation the function $\mathscr{L}(q_j, \dot{q}_j)$ transforms in $\mathscr{L}'(q_j', \dot{q}_j')$ and the new generalized velocities are functions of the original generalized co-ordinates and generalized velocities:

$$\begin{array}{l} q_j \longrightarrow \dot{q}_j \longrightarrow \mathscr{L}(q_j, \dot{q}_j), \\ \downarrow \\ q_j' \longrightarrow \dot{q}_j' \longrightarrow \mathscr{L}'(q_j', \dot{q}_j'), \; \left(q_i' = q_i'(q_i), \; \dot{q}_i' = \dot{q}'(q_j, \dot{q}_j)\right). \end{array} \tag{6.14}$$

The same, of course, is valid for Hamilton's equations - they remain invariant for a transformation (6.13). Independent variables in Hamilton's equations are the generalized co-ordinates and generalized momenta (unlike the generalized velocities in Lagrange's equations). For such transformations, (6.13), the Hamiltonian $H(q_j, P_j)$ is transformed in

$H'(q'_j, P'_j)$, and the new generalized momenta P'_i are functions of the original generalized co-ordinates and generalized momenta:

$$\begin{array}{l} q_j \xrightarrow{\dot{q}_j,\ \mathscr{L},\ \partial\mathscr{L}/\partial\dot{q}_i} P_j \rightarrow H\left(q_j, P_j\right), \\ \downarrow \\ q'_j \xrightarrow{\dot{q}'_j,\ \mathscr{L}',\ \partial\mathscr{L}'/\partial\dot{q}'_i} P'_j \rightarrow H'\left(q'_j, P'_j\right),\ \left(q'_i = q'_i\left(q_j\right),\ P'_i = P'_i\left(q_j, P_j\right)\right). \end{array} \tag{6.15}$$

It appears that Hamilton's equations allow a much wider class of transformations - they remain invariant with respect to some (but not all) transformations "mixing" the co-ordinates q_j and momenta P_j (compare with $q'_i(q_j)$):

$$\begin{array}{l} q_j, P_j \longrightarrow H\left(q_j, P_j\right), \\ \downarrow \\ q'_j, P'_j \longrightarrow H'\left(q'_j, P'_j\right), \qquad \left(q'_i = q'_i\left(q_j, P_j\right),\quad P'_i = P'_i\left(q_j, P_j\right)\right). \end{array} \tag{6.16}$$

These transformations are called canonical transformations. We shall emphasize once more that for them Hamilton's equations retain their form. Here, both the original generalized co-ordinates q_j and theirs corresponding momenta P_j, and q'_j and P'_j, are canonical conjugate co-ordinates.

The canonical transformations are transformations of the generalized co-ordinates and generalized momenta into new variables - the generalized co-ordinates and generalized momenta q'_j and P'_j, each of them being a function of the original variables, and Hamilton's equations remain invariant. Below, the term "state of the system" will be very important for us. To know the state of a system in classical mechanics at a given instant of time, is to know, at that instant, so many dynamical variables, that the values of all dynamical variables may be predicted uniquely. Knowing the values of the generalized co-ordinates at a given moment, is to know the location and orientation of the system at that moment. These dynamical variables are not enough for the description of the system. This is because in the following instant of time these quantities will be determined by the motion of the system. In classical mechanics the location and orientation, and the motion, of a system at a given instant specify its state at that instant.

For a particle in three-dimensional space the classical state $\mathbf{\Lambda}$ is given by six quantities. Conditionally we can write:

$$\mathbf{\Lambda} = \left(x, y, z, \dot{x}, \dot{y}, \dot{z}\right), \tag{6.17}$$

or in terms of momenta (Fig. 6-1)

$$\mathbf{\Lambda} = \left(x, y, z, p_x, p_y, p_z\right) . \tag{6.18}$$

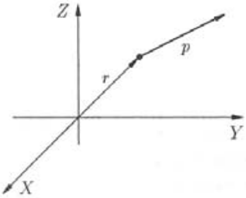


Figure 6-1. The classical state of a free particle is determined by 6 quantities (x, y, z, p_x, p_y, p_z) .

The state of a system of two particles moving in a plane is determined by eight quantities:

$$\mathbf{\Lambda} = \left(x_1, y_1, x_2, y_2, p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}\right) . \tag{6.19}$$

The set of generalized co-ordinates of a given system is not unique. So, the description of the system state $\mathbf{\Lambda}$ is also not unique. For instance, the state $\mathbf{\Lambda}$ (6.17) in Cartesian representation can be written as

$$\mathbf{\Lambda} = \left(x, y, z, p_x, p_y, p_z\right), \tag{6.20a}$$

and in spherical-polar representation, as

$$\mathbf{\Lambda} = \left(r, \theta, \varphi, P_r, P_\theta, P_\varphi\right) . \tag{6.20b}$$

However, all representations of the state of a fixed system contain equal number of variables. The canonical transformations lead to a change of the representation of the state:

$$\begin{aligned} q_j, P_j \quad &\rightarrow \quad q'_j, P'_j \,, \\ \mathbf{\Lambda} = \left(q_j, P_j\right) \quad &\rightarrow \quad \mathbf{\Lambda} = \left(q'_j, P'_j\right) . \end{aligned} \tag{6.21}$$

Getting ahead of our exposition, we shall mention that in quantum mechanics for the description of the state of an electron in an atom are necessary four quantities:

$$\mathbf{\Lambda} = \left(E, L^2, L_z, S\right) . \tag{6.22}$$

Here E stands for the total energy, L^2 and L_z - for the square and the *z*-component of the angular momentum, S - for the electron spin.

In classical mechanics we can represent the state Λ of the system of s degrees of freedom as a $2s$-dimensional vector (i.e. a vector with 2s components). It is natural for such representations to use $2s$-dimensional space with mutually perpendicular axes on which we plot the variables q_j and P_j. A fixed point in this $2s$-dimensional space corresponds to any given state of the system, i.e., to any set of the canonical variables. Conversely, a fixed state, that is the values of co-ordinates and momenta, corresponds to a point in this space. The introduced $2s$-dimensional space, called *phase space* (the configuration space is s-dimensional one - see Section 1.1), is such that unique and reversible correspondence exists between its points and the system state. To the motion of a mechanical system we correspond a line in phase space, which is called *phase trajectory.*

Example: Consider the phase space of a harmonic oscillator (for instance a simple pendulum, (Fig. 6-2)). In Fig. 6-2c is shown its phase trajectory in the phase space x, p.

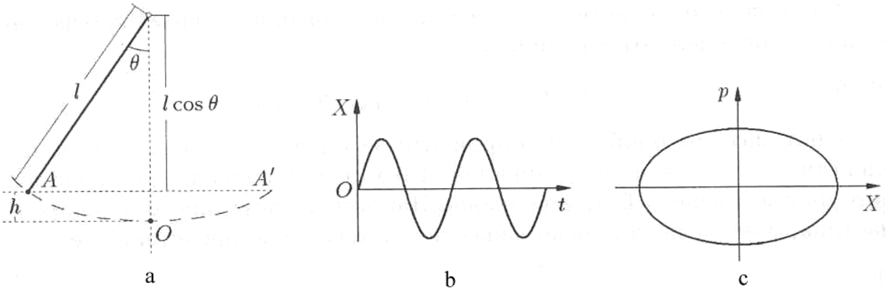


Figure 6-2. Phase trajectory of a simple pendulum: a) the real trajectory is a part of a circumference (the arc *AA′*); b) the co-ordinate x changes according to a harmonic law $x=x_0\cos\omega t$; c) the trajectory in the phase space (in this case $2s$-dimensional phase space - a phase plane) is an ellipse.

Analogous to the volume element in the Cartesian space, here the product of differentials

$$dV = dq_1 dq_2 \dots dq_s dP_1 dP_2 \dots dP_s \tag{6.23}$$

represents the volume element in the phase space. The integral $\int dV$ in a given region of the phase space represents the volume of this region. Every point of a given region σ of the phase space moves according to the motion equation of the considered mechanical system. If at the instant t the phase volume of the region σ (Fig. 6-3) is

$$V = \int_{\sigma} dxdP = \int_{x_1}^{x_2} \int_{P_1}^{P_2} dxdP, \tag{6.24}$$

then at the instant t' the points of s will occupy a new region σ', whose volume is

$$V' = \int_{\sigma'} dxdP = \int_{x_1'}^{x_2'} \int_{P_1'}^{P_2'} dxdP, \tag{6.25}$$

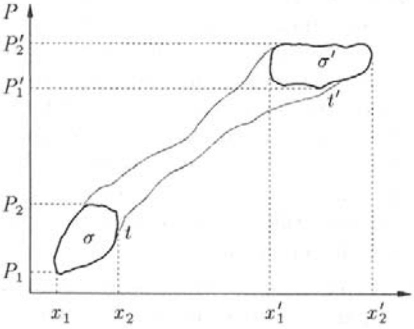


Figure 6-3. Phase volume: at the instant of time t the region σ occupies the volume $\int_{\sigma} dxdP$, and at the instant t' - it occupies the volume $\int_{\sigma'} dxdP$; according to the Liouville's theorem these two volumes are equal.

During the motion, the region volume does not change. It can be proven (see [R3], Section 8.8) that the phase volume is a constant quantity. This is the content of Liouville's theorem, which can be formulated as follows: *The volume of a phase-space region, which is determined by the points depicting the different states of identical mechanical systems* (*an ensemble of systems*), *is constant.* In other words, during the motion of the systems of the ensemble, its volume does not change.

6.3* HAMITONIAN OF A CHARGED PARTICLE IN AN ELECTROMAGNETIC FIELD

As an example of Hamilton's function, we shall obtain the Hamiltonian of a charged particle of mass m and charge e, using the definition (6.5) for H. To do this we need the Lagrangian and the generalized momentum of the particle. In Section 1.5 we obtained Lagrange's function (1.49):

$$\mathscr{L} = T - e\Phi + e\mathbf{vA}. \tag{6.26}$$

We recall that $\mathbf{\Phi}$ and $\mathbf{A}$ are the scalar and vector potentials of the electromagnetic field. The components P_i of the momentum of the particle can be found by differentiating the Lagrangian with respect to the generalized velocities $\dot{x}_i$:

$$P_i = \frac{\partial \mathscr{L}}{\partial \dot{x}_i} = \frac{\partial T}{\partial \dot{x}_i} + e\frac{\partial (\mathbf{vA})}{\partial \dot{x}_i}. \tag{6.27}$$

As $\mathbf{vA} = \sum_k \dot{x}_k A_k$ then $\partial(\mathbf{vA})/\partial \dot{x}_i = A_i$, and substituting it in (6.27), we obtain for the generalized momentum

$$P_i = \frac{\partial T}{\partial \dot{x}_i} + eA_i = m_e \dot{x}_i + eA_i. \tag{6.28}$$

We substitute this momentum, (6.28), and the Lagrangian (6.28) in the definition (6.5), and get:

$$\begin{aligned} H &= \sum_i \dot{x}_i P_i - \mathscr{L}, \\ H &= \sum_i \left(\frac{\partial T}{\partial \dot{x}_i} + eA_i \right) \dot{x}_i - (T - e\Phi + e\mathbf{vA}). \end{aligned} \tag{6.29}$$

But according to (2.7), $\sum_i (\partial T/\partial \dot{x}_i)\dot{x}_i = 2T$, and after substituting it in (6.29), the Hamitonian takes the form

$$H = T - e\Phi = T(x, y, z, P_x, P_y, P_z) + e\Phi(x, y, z). \tag{6.30}$$

Thus, the Hamiltonian of a charged particle is a sum of its kinetic and potential energies, expressed by the co-ordinates and momenta.

Now, we shall obtain the explicit form of $T(\mathbf{P})$. From (6.28) we determine the component of the mechanical momentum $p_i = m_e \dot{x}_i$ through the corresponding components P_i of the generalized momentum:

$$m_e \dot{x}_i = P_i - eA_i \tag{6.31a}$$

or

$$\mathbf{p} = \mathbf{P} - e\mathbf{A}. \tag{6.31b}$$

We substitute $\dot{x}_i$ from (6.31a) in the expression of the kinetic energy $T = \sum m_e \dot{x}_i^2 / 2$ and as a result we get:

$$T = \sum_i \frac{(P_i - eA)^2}{2m_e} = \frac{(\mathbf{P} - e\mathbf{A})^2}{2m_e}. \tag{6.32}$$

Taking into account (6.32) in (6.30), we finally obtain the Hamiltonian of the charged particle in an electromagnetic field:

$$H == \frac{(\mathbf{P} - e\mathbf{A})^2}{2m_e} + e\Phi. \tag{6.33}$$

We shall note that the conjugate to the co-ordinate x canonical momentum does not coincide with the usual mechanical momentum $p_x = m_e v_x$ of the particle. The generalized momentum $\mathbf{P}$ is the mechanical momentum plus an electromagnetic contribution $-e\mathbf{A}$. The difference between $\mathbf{P}$ and $m_e\mathbf{v}$ is due to the field, so $-e\mathbf{A}$ has a field character. In this sense we could say that $m_e\mathbf{v}$ has a material character.

6.4. POISSON BRACKET

Consider the two functions $F(q_j, P_j, t)$ and $G(q_j, P_j, t)$ of the canonical variables and the time. *The Poisson bracket* $\{F, G\}$ *of two functions F and G is defined as*

$$\{F, G\} = \sum_i \left(\frac{\partial F}{\partial P_i} \frac{\partial G}{\partial q_i} - \frac{\partial F}{\partial q_i} \frac{\partial G}{\partial P_i} \right). \tag{6.34}$$

Where do we meet these and why are they necessary? To answer these questions, let us take the function $F(q_j, P_j, t)$ and find its total time-derivative:

$$\frac{dF}{dt}=\frac{\partial F}{\partial t}+\sum_{i}^{s}\left(\frac{\partial F}{\partial q_i}\dot{q}_i+\frac{\partial F}{\partial P_i}\dot{P}_i\right). \tag{6.35}$$

After substitution of $\dot{q}_i$ and $\dot{P}_i$ from Hamilton's equations (6.9), the total derivative takes the form:

$$\frac{dF}{dt}=\frac{\partial F}{\partial t}+\sum_{i}^{s}\left(\frac{\partial F}{\partial q_i}\frac{\partial H}{\partial P_i}-\frac{\partial F}{\partial P_i}\frac{\partial H}{\partial q_i}\right), \tag{6.36}$$

or according to the definition (6.34) of the Poisson bracket,

$$\frac{dF}{dt}=\frac{\partial F}{\partial t}+\{H,F\}. \tag{6.37}$$

For an arbitrary dynamical variable, i.e. for an arbitrary function F of the generalized co-ordinates and momenta, and of time, the total time derivative is equal to its partial derivative plus the Poisson bracket of the Hamiltonian and the function F.

If the dynamical quantity is a constant of the motion, i.e. $dF/dt=0$, then

$$\frac{\partial F}{\partial t}=-\{H,F\}. \tag{6.38}$$

We can consider (6.38) as a condition for F to be a constant of the motion. If a constant of the motion F does not depend explicitly on time, then

$$\{H,F\}=0, \tag{6.39}$$

i.e., its Poisson bracket with the Hamiltonian is equal to zero.

The Poisson bracket allows writing Hamilton's equations in an elegant and symmetric way. Actually, for any function F and the canonical variables from (6.34), taking into account $\partial q_i/\partial P_i=0$ and $\partial P_i/\partial q_i=0$, we can write

$$\{F,q_i\}=\frac{\partial F}{\partial P_i},\quad \{F,P_i\}=-\frac{\partial F}{\partial q_i}. \tag{6.40}$$

Replacing F with H, and comparing with (6.9), we can write Hamilton's equations through the Poisson bracket:

$$\dot{q}_i = \{H, q_i\}, \quad \dot{P}_i = \{H, P_i\}. \tag{6.41}$$

The following properties are characteristic for the Poisson bracket:

1. antisymmetry

$$\{F, G\} = -\{G, F\}, \tag{6.42a}$$

and as a consequence,

$$\{F, F\} = 0; \tag{6.42b}$$

2. equality to zero of the bracket of a function and a constant

$$\{F, C\} = 0; \tag{6.43}$$

3. linearity with respect to both arguments (functions), e.g.,

$$\{F_1 + F_2, G\} = \{F_1, G\} + \{F_2, G\}, \quad \{CF, G\} = C\{F, G\}; \tag{6.44}$$

4. a distributive property with respect to a multiplication, similarly to the rule of product differentiation

$$\begin{aligned} &\{F_1 F_2, G\} = F_1\{F_2, G\} + F_2\{F_1, G\}, \\ &\{F_1, G_1 G_2\} = G_1\{F\ , G_2\} + G_2\{F, G_1\}; \end{aligned} \tag{6.45}$$

5. the partial derivative with respect to time is taken according to the rule of differentiation of a product

$$\frac{\partial}{\partial t}\{F, G\} = \left\{\frac{\partial F}{\partial t}, G\right\} + \left\{F, \frac{\partial G}{\partial t}\right\}; \tag{6.46}$$

6. when we take as an argument of the Poisson bracket the canonical variables, besides (6.40) and (6.41), we have the following dependencies:

$$\{q_i, q_k\} = 0, \; \{P_i, P_k\} = 0, \; \{q_i, P_k\} = \delta_{ik}, \; \delta_{ik} = \begin{cases} 0, & i \neq k, \\ 1, & i = k, \end{cases} \qquad (6.4$$

where δ_{ik} is the symbol of Kronecker;

7. the Poisson bracket is invariant with respect to the canonical transformation from the variables q_j, P_j to q'_j, P'_j

$$\{F, C\}_{q_j, P_j} = \{F, C\}_{q'_j, P'_j}. \qquad (6.48)$$

(This paragraph can be omitted at first reading). The Hamiltonian method is extremely powerful tool in classical mechanics. Moreover, it provides the most direct transition between classical mechanics and quantum mechanics. In this course we shall see that the Hamiultonian function is of great importance in quantum mechanics. The first attempts to explain the quantization of the periodic system were connected with the canonical variables (see Sections 8.2 and 8.3). To address the quantization of quantum objects Schroedinger, Dirac and others, developed subsequently a canonical quantization procedure (see interesting details of this development in [R32] Section 24). The canonical prescription is to replace the classical Poisson bracket with a quantum-mechanical Poisson bracket $\{A, B\} \to \{\hat{A}, \hat{B}\} = \frac{1}{i\hbar}[\hat{A}, \hat{B}]$ (here $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator of the operators $\hat{A}$ and $\hat{B}$); for details see sections 10.2, 11.3 and 11.4, this is only an illustration. For example, replacing the Poisson bracket in (6.47) we obtain $[\hat{q}_i, \hat{q}_k] = [\hat{P}_i, \hat{P}_k] = 0$, $[\hat{q}_i, \hat{P}_k] = i\hbar\delta_{ik}$, which in Cartesian co-ordinates are exactly the Eqs. (10.60)÷(10.63) (Chapter 10 of this course). The relationship between the canonical conjugate pairs is of central importance in quantum mechanics. There is an "uncertainty principle" in it (Section 10.9), according to which it is impossible to measure both terms of such a pair simultaneously with arbitrary accuracy.

6.5^+ HAMILTONIAN AND HAMILTON'S EQUATIONS IN CARTESIAN, CYLINDRICAL AND SPHERICAL CO-ORDINATES

Energy, Hamiltonian, and angular momentum take an important place not only in classical mechanics, but also in quantum mechanics. We shall consider these for a free particle of mass m in three often used co-ordinate systems: Cartesian, cylindrical and spherical.

a) Cartesian co-ordinate system

1. Co-ordinates: x, y, z.
2. Generalized velocities: $\dot{x}, \dot{y}, \dot{z}$.
3. Components of the velocity $\mathbf{v}$ and the momentum $\mathbf{p} = m\mathbf{v}$:

$$\begin{aligned} &v_x = \dot{x}, \quad && v_y = \dot{y}, \quad && v_z = \dot{z}, \\ &p_x = m\dot{x}, \quad && p_y = m\dot{y}, \quad && p_z = m\dot{z}. \end{aligned} \tag{6.49}$$

4. Kinetic energy and Lagrangian:

$$T = \frac{m}{2}v^2 = \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right), \qquad \mathscr{L} = \mathrm{T}. \tag{6.50}$$

5. Generalized momenta:

$$P_x = \frac{\partial \mathscr{L}}{\partial \dot{x}} = m\dot{x}, \quad P_x = \frac{\partial \mathscr{L}}{\partial \dot{y}} = m\dot{y}, \quad P_x = \frac{\partial \mathscr{L}}{\partial \dot{z}} = m\dot{z}. \tag{6.51}$$

6. Physical significance of the generalized momenta:

$$P_x = p_x, \quad P_y = p_y, \quad P_z = p_z. \tag{6.52}$$

7. Function of Hamilton:

Since we consider a free particle, $H = T + U = T$. Expressing the velocity through the momentum we obtain

$$H\left(x, y, z, P_x, P_y, P_z\right) = \frac{P^2}{2m} = \frac{1}{2m}\left(P_x^2 + P_y^2 + P_z^2\right). \tag{6.53}$$

8. Cyclic co-ordinates: x, y, z.

The Hamiltonian does not depend on x, y, z and the corresponding canonical conjugate momenta are constants of the motion:

$$P_x = p_x = \text{const}, \quad P_y = p_y = \text{const}, \quad P_z = p_z = \text{const}. \tag{6.54}$$

9. Hamilton's equations:

$$\begin{aligned} &\frac{\partial H}{\partial x} = -\dot{p}_x, \quad && \frac{\partial H}{\partial y} = -\dot{p}_y, \quad && \frac{\partial H}{\partial z} = -\dot{p}_z, \\ &\frac{\partial H}{\partial p_x} = \dot{x}, \quad && \frac{\partial H}{\partial p_y} = \dot{y}, \quad && \frac{\partial H}{\partial p_z} = \dot{z}. \end{aligned} \tag{6.55}$$

b) Cylindrical co-ordinate system

1. Co-ordinates: ρ, φ, z.
2. Generalized velocities: $\dot{\rho}, \dot{\varphi}, \dot{z}$.
3. Components of the velocity $\mathbf{v}$ and the momenta $\mathbf{p} = m\mathbf{v}$:

The components v_ρ and v_z are determined trivially. Changing the co-ordinate φ by $d\varphi$ the position of the particle changes by $\rho d\varphi$ (Fig. 6-4) and, consequently, we can write for the velocity and the momentum

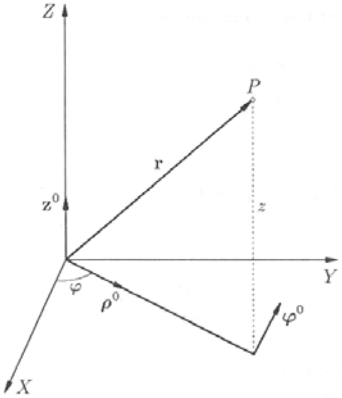


Figure 6-4. In a cylindrical co-ordinate system the radius-vector $\mathbf{r}$ of a given point lies on the plane, defined by the unit vectors $\boldsymbol{\rho}^0$ and $\mathbf{z}^0$; the third unit vector $\boldsymbol{\varphi}^0$ is normal to this plane, and $\mathbf{r}$ has no component along it.

$$\begin{aligned} v_\rho &= \dot{\rho}, & v_\varphi &= \rho\dot{\varphi}, & v_z &= \dot{z}, \\ p_\rho &= m\dot{\rho}, & p_\varphi &= m\rho\dot{\varphi}, & p_z &= m\dot{z}. \end{aligned} \tag{6.56}$$

4. Kinetic energy and Lagrangian:

$$T = \frac{m}{2}v^2 = \frac{m}{2}\left(\dot{\rho}^2 + \rho^2\dot{\varphi}^2 + \dot{z}^2\right), \qquad \mathscr{L} = \mathrm{T}. \tag{6.57}$$

5. Generalized momenta:

$$P_\rho = \frac{\partial \mathscr{L}}{\partial \dot{\rho}} = m\dot{\rho}, \quad P_\varphi = \frac{\partial \mathscr{L}}{\partial \dot{\varphi}} = m\rho^2\dot{\varphi}, \quad P_z = \frac{\partial \mathscr{L}}{\partial \dot{z}} = m\dot{z}. \tag{6.58}$$

6. Physical significance of the generalized momenta:

The components P_ρ and P_z coincide with the corresponding components p_ρ and p_z of the momentum $\mathbf{p}$, but P_φ is equal to the projection L_z of the angular momentum along the Z-axis.

We shall verify this. As it is seen in Fig. 6-4, the radius-vector **r** of a particle whose position is at the point P, has components only along two axes of the cylindrical co-ordinate system, ρ and z:

$$\mathbf{r} = \rho\boldsymbol{\rho}^0 + z\mathbf{z}^0. \tag{6.59}$$

However the velocity of the particle has three components (see (1.66)):

$$\mathbf{v} = \dot{\mathbf{r}} = \dot{\rho}\boldsymbol{\rho}^0 + \rho\dot{\varphi}\boldsymbol{\varphi}^0 + \dot{z}\mathbf{z}^0. \tag{6.60}$$

For the vector **L** we have

$$\mathbf{L} = \mathbf{r}\times m\mathbf{v} = m\begin{vmatrix} \boldsymbol{\rho}^0 & \boldsymbol{\varphi}^0 & \mathbf{z}^0 \\ \rho & 0 & \mathrm{z} \\ \dot{\rho} & \rho\dot{\varphi} & \dot{z} \end{vmatrix}, \tag{6.61}$$

from where we readily determine

$$L_z = m\rho^2\dot{\varphi}, \quad \text{i.e.} \quad L_z = P_\varphi. \tag{6.62}$$

We have verified that the generalized momentum P_φ is equal to the z-component of the angular momentum **L**.

Finally, for the generalized momenta we can write

$$P_\rho = m\dot{\rho} = p_\rho, \quad P_\varphi = m\rho^2\dot{\varphi} = L_z, \quad P_z = m\dot{z} = p_z. \tag{6.63}$$

7. Function of Hamilton

If, from (6.58) we determine the components $\dot{\rho}$, $\rho\dot{\varphi}$ and $\dot{z}$ of the velocity **v** through $P_\rho, P_\varphi, P_z, \rho$, and substitute them in (6.57), we will obtain the energy of the particle through its generalized momenta, which are canonical conjugates to the co-ordinates ρ, φ and z:

$$H(\rho,\varphi,z,P_\rho,P_\varphi,P_z) = \frac{1}{2m}\left(P_\rho^2 + \frac{P_\varphi^2}{\rho^2} + P_z^2\right), \tag{6.64}$$

or according to (6.63):

$$H\left(\rho,\varphi,z,P_\rho,P_\varphi,P_z\right)=\frac{1}{2m}\left(P_\rho^2+\frac{L_z^2}{\rho^2}+P_z^2\right) \tag{6.65}$$

8. Cyclic co-ordinates: φ and z.

The canonical conjugates corresponding to these co-ordinates, are constants of the motion, i.e. the *z*-components of the angular momentum L_z and the momentum p_z are constants:

$$P_\varphi = m\rho^2\dot{\varphi} = L_z = \text{const}, \quad P_z = m\dot{z} = p_z = \text{const}. \tag{6.66}$$

9. Hamilton's equations:

$$\begin{aligned} &\frac{\partial H}{\partial \rho}=-\dot{P}_\rho, && \frac{\partial H}{\partial \varphi}=-\dot{P}_\varphi, && \frac{\partial H}{\partial z}=-\dot{P}_z, \\ &\frac{\partial H}{\partial P_\rho}=\dot{\rho}, && \frac{\partial H}{\partial P_\varphi}=\dot{\varphi}, && \frac{\partial H}{\partial P_z}=\dot{z}. \end{aligned} \tag{6.67}$$

c) Spherical co-ordinate system

In spherical co-ordinates we shall consider the motion of a particle in a central field $U(r)$ (this is an example for the basic object of chemistry, the atom).

1. Co-ordinates: r,θ,φ.
2. Generalized velocities: $\dot{r},\dot{\theta},\dot{\varphi}$.
3. Components of the velocity $\mathbf{v}$ and the momenta $\mathbf{p}=m\mathbf{v}$:

Changing the co-ordinates by dr, $d\theta$ and $d\varphi$, the radius-vector of the particle changes by $dr, rd\theta$ and $r\sin\theta\, d\varphi$ (see Fig. 1-6 and formulae (1.70) and (1.71)). Dividing these displacement elements by dt we obtain the velocity components, and multiplying the last by m we get the momentum components:

$$\begin{aligned} &v_r=\dot{r}, && v_\theta=r\dot{\theta}, && v_\varphi=r\sin\theta\,\dot{\varphi}, \\ &p_r=m\dot{r}, && p_\theta=mr\dot{\theta}, && p_\varphi=mr\sin\theta\,\dot{\varphi}. \end{aligned} \tag{6.68}$$

4. Kinetic energy and Lagrangian

$$T=\frac{m}{2}v^2=\frac{m}{2}\left(\dot{r}^2+r^2\dot{\theta}^2+r^2\sin^2\theta\,\dot{\varphi}^2\right), \quad \mathscr{L}=T-U(r). \tag{6.69}$$

5. Generalized momenta

$$P_r = \frac{\partial \mathscr{L}}{\partial \dot{r}} = m\dot{r}, \quad P_\theta = \frac{\partial \mathscr{L}}{\partial \dot{\theta}} = mr^2\dot{\theta}, \quad P_\varphi = \frac{\partial \mathscr{L}}{\partial \dot{\theta}} = mr^2 \sin^2\theta\,\dot{\varphi}\,. \tag{6.70}$$

6. Physical significance of the generalized momenta.

The generalized momentum P_r is equal to the r-component of the mechanical momentum. We shall verify that the generalized momentum P_θ is equal to the L_φ-component of the angular momentum and the generalized momentum P_φ - to the component of angular momentum along Z-axis. For this purpose we determine the components of the angular momentum in a spherical co-ordinates. Taking into account the components of the momentum from (6.66) and that the radius-vector $\mathbf{r} = r\mathbf{r}^0$ of a particle has only one component (!) along $\mathbf{r}$ (see Fig 6-5), we readily determine the angular momentum

$$\mathbf{L} = \mathbf{r} \times m\mathbf{v} = m\begin{vmatrix} \mathbf{r}^0 & \boldsymbol{\theta}^0 & \boldsymbol{\varphi}^0 \\ r & 0 & 0 \\ \dot{r} & r\dot{\theta} & r\sin\theta\,\dot{\varphi} \end{vmatrix}, \tag{6.71}$$

and its components are

$$\begin{aligned} &L_r = 0, \\ &L_\theta = -mr^2\sin\theta\,\dot{\varphi}, \\ &L_\varphi = mr^2\dot{\theta}\,. \end{aligned} \tag{6.72}$$

L+et us determine the projection of **L** along the Z-axis. The unit vector $\boldsymbol{\varphi}^0$ is perpendicular to the Z-axis ($\boldsymbol{\varphi}^0 \perp \mathbf{z}^0$ in Fig. 6-5), and the projection of $\mathbf{L}_\varphi = L_\varphi \boldsymbol{\varphi}^0$ along the Z-axis is zero. Thus the projection of **L** along the Z-axis is determined only by $\left(\mathbf{L}_\theta\right)_z$. In Fig. 6-5 it is evident that

$$L_z = \left(\mathbf{L}_\theta\right)_z = \left|L_\theta\right|\cos\left(\frac{\pi}{2} - \theta\right) = mr^2\sin^2\theta\,\dot{\varphi} = P_\varphi\,. \tag{6.73}$$

Finally, we have for the three components of the generalized momentum the following:

$$P_r = m\dot{r} = p_r, \quad P_\theta = mr^2\dot{\theta} = L_\varphi, \quad P_\varphi = mr^2\sin\theta\,\dot{\varphi} = L_z\,. \tag{6.74}$$

The common feature in the three considered co-ordinate systems is that the generalized momenta, canonically conjugated to the linear co-ordinates, are components of the mechanical momentum and the ones canonically conjugated to the angular co-ordinates are components of the angular momentum.

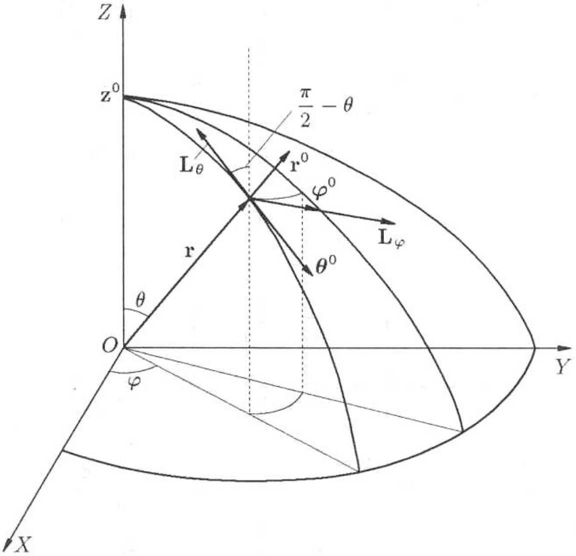


Figure 6-5. In a spherical co-ordinate system the angular momentum has only two components $\mathbf{L}=L_\theta\boldsymbol{\theta}^0+L_\varphi\boldsymbol{\varphi}^0$. The projection of **L** along the *Z*-axis is determined by $\mathbf{L}_\theta$, because $\boldsymbol{\varphi}^0 \perp \mathbf{z}^0$ and, consequently, $\mathbf{L}_\varphi \perp OZ$.

7. Function of Hamilton:

Here we proceed in a similar way to the determination of the Hamiltonian in the cylindrical system, adding the potential energy $U(r)$. According to (6.69) and (6.70), we have

$$H(r,\theta,\varphi,P_r,P_\theta,P_\varphi)=T+U(r)=\frac{P_r^2}{2m}+\frac{P_\theta^2}{2mr^2}+\frac{P_\varphi}{2mr^2\sin^2\theta}+U(r). \quad (6.75)$$

The expression of the kinetic energy, respectively the Hamiltonian, through the angular momentum in spherical co-ordinates is very useful, especially in quantum mechanics. To find this dependence we note that the vector of the momentum can be represented as a sum of two mutually perpendicular vectors: $\mathbf{p_r}$, along the radius-vector $(\mathbf{p_r} \parallel \mathbf{r})$, and $\mathbf{p}_\perp$, tangential to the sphere of the radius **r** $(\mathbf{p}_\perp \perp \mathbf{r})$:

$$\mathbf{p} = \mathbf{p}_\mathrm{r} + \mathbf{p}_\perp. \tag{6.76}$$

The kinetic energy, expressed through these two components, has the following form

$$T = \frac{p^2}{2m} = \frac{p_r^2}{2m} + \frac{p_\perp^2}{2m}. \tag{6.77}$$

At the same time, for the angular momentum we can write

$$\mathbf{L} = \mathbf{r}\times\mathbf{p} = \mathbf{r}\times(\mathbf{p}_\mathrm{r} + \mathbf{p}_\perp) = \mathbf{r}\times\mathbf{p}_\perp, \tag{6.78a}$$

$$\text{or } L = rp_\perp \Rightarrow p_\perp = \frac{L}{r}. \tag{6.78b}$$

As a result of substituting $p_\perp$ in the relationship for T (6.77), we get for the kinetic energy and the Hamiltonian, respectively,

$$\begin{aligned} T &= \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}, \\ H &= \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + U(r). \end{aligned} \tag{6.79}$$

8. Cyclic co-ordinate: φ.

A constant of the motion is the generalized momentum P_φ, i.e. angular-momentum component L_z, according to (6.73):

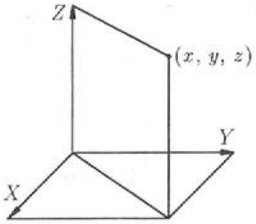
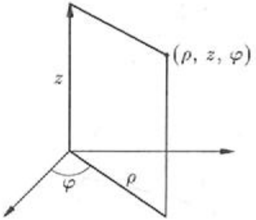
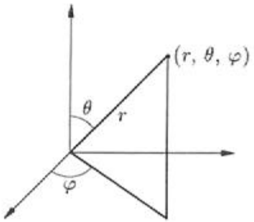
$$P_\varphi = mr^2 \sin^2\theta\, \dot{\varphi} = L_z = \text{const}. \tag{6.80}$$

9. Hamilton's equations

$$\begin{aligned} &\frac{\partial H}{\partial r} = -\dot{P}_r, \quad \frac{\partial H}{\partial \theta} = -\dot{P}_\theta, \quad \frac{\partial H}{\partial \varphi} = -\dot{P}_\varphi, \\ &\frac{\partial H}{\partial P_r} = \dot{r}, \quad \frac{\partial H}{\partial P_\theta} = \dot{\theta}, \quad \frac{\partial H}{\partial P_\varphi} = \dot{\varphi}. \end{aligned} \tag{6.81}$$

The main results for a free particle in Cartesian, cylindrical and spherical co-ordinate systems, are presented in Table 6-1.

Table 6.1. Hamiltonian of a free particle in three co-ordinate system

	Cartesian co-ordinates	Cylindrical co-ordinates	Spherical co-ordinates
Frames			
Momenta	$p_x = m\dot{x},\ p_y = m\dot{y},\ p_z = m\dot{z}$	$p_\rho = m\dot{\rho},\ p_\varphi = m\rho\dot{\varphi},\ p_z = m\dot{z}$	$p_r = m\dot{r},\ p_\theta = mr\dot{\theta},\ p_\varphi = mr\sin\theta\dot{\varphi}$
Generalized momenta	$P_x = m\dot{x},\ P_y = m\dot{y},\ P_z = m\dot{z}$	$P_\rho = m\dot{\rho},\ P_\varphi = m\rho^2\dot{\varphi},\ P_z = m\dot{z}$	$P_r = m\dot{r},\ P_\theta = mr^2\dot{\theta},\ P_\varphi = mr^2\sin^2\theta\dot{\varphi}$
Hamiltonian	$H(x, y, z, P_x, P_y, P_z) =$ $= \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2)$	$H(\rho, \varphi, z, P_\rho, P_\varphi, P_z) =$ $= \frac{1}{2m}(P_\rho^2 + \frac{P_\varphi^2}{\rho^2} + P_z^2)$	$H(r, \theta, \varphi, P_r, P_\theta, P_\varphi) =$ $= \frac{P_r^2}{2m} + \frac{P_\theta^2}{2mr^2} + \frac{P_\varphi^2}{2mr^2\sin^2\theta}$
Cyclic co-ordinates	x, y, z	φ, z	φ
Constants of motion	$P_x = p_x = \text{const}$ $P_y = p_y = \text{const}$ $P_z = p_z = \text{const}$	$P_\varphi = L_z = \text{const}$ $P_z = p_z = \text{const}$	$P_\varphi = L_z = \text{const}$

SUMMARY

The function of Hamilton plays a fundamental role in mechanics:

$$H\left(q_j,P_j,t\right)=\sum_i P_i\dot{q}_i-\mathscr{L}\left(q_j,\dot{q}_j,t\right).$$

To each generalized co-ordinate q_i corresponds a generalized momentum $P_i=\partial\mathscr{L}/\partial\dot{q}_i$. Such a pair, q_i and P_i, is called canonical conjugate. The Hamiltonian satisfies Hamilton's canonical equations

$$\frac{\partial H}{\partial P_i}=\dot{q}_i,\quad \frac{\partial H}{\partial q_i}=-\dot{P}_i,$$

which are the equations of motion. For a conservative system, the function of Hamilton is interpreted as the total energy of the mechanical system

$$H\left(q_j,P_j\right)=T\left(q_j,P_j\right)+U\left(q_j\right).$$

If the function of Hamilton does not depend explicitly on time it is a constant of the motion. The generalized momentum, canonically conjugate to a cyclic co-ordinate, is also a constant of the motion.

For a system of s degrees of freedom, it is convenient to use $2s$-dimensional space with mutually perpendicular axes q_j,P_j, called phase space. During the motion of a set of many conservative systems with one and the same Hamiltonian, occupying a given region, the form of this region changes, but its volume remains constant (Liouville's theorem).

The Hamilton function of a free particle is

$$H\left(x,y,z,P_x,P_y,P_z\right)=\frac{P^2}{2m}=\frac{1}{2m}\left(P_x^2+P_y^2+P_z^2\right).$$

The Hamiltonian of a charged particle in an electromagnetic field is expressed by a vector and a scalar potential:

$$H=\frac{1}{2m}\left(\mathbf{P}-e\mathbf{A}\right)^2+e\Phi.$$

The representation of a particle’s kinetic energy in spherical system is:

$$T = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}.$$

The Hamiltonian of a particle in central field $U(r)$ in spherical co-ordinate system plays an important role in quantum mechanics:

$$H\left(r,\theta,\varphi,P_r,P_\theta,P_\varphi\right) = T + U(r) = \frac{P_r^2}{2m} + \frac{P_\theta^2}{2mr^2} + \frac{P_\varphi}{2mr^2\sin^2\theta} + U(r).$$

In that case the generalized momentum P_φ is equal to the L_z-component of the angular momentum and is a constant of the motion.

The definition of Poisson's bracket for functions F and G is

$$\{F,G\} = \sum_i \left(\frac{\partial F}{\partial P_i}\frac{\partial G}{\partial q_i} - \frac{\partial F}{\partial q_i}\frac{\partial G}{\partial P_i} \right).$$

If a physical quantity, which does not depend explicitly on time, is a constant of the motion, then

$$\{H,F\} = 0,$$

i.e. its Poisson bracket with the Hamiltonian is equal to zero.

QUESTIONS

1. In its general form, the Hamiltonian depends on time explicitly and through the generalized co-ordinates and momenta, $H = H(q_j(t), P_j(t), t)$. How does H change with time when it does not depend explicitly on it?
2. Do the cyclic co-ordinates of the Lagrangian and the Hamiltonian for the same mechanical system differ?
3. Which quantity is a constant of the motion for a cyclic co-ordinate?
4. How is the state of a mechanical system determined in classical mechanics?
5. What is the condition for a quantity, which is independent of time, to be a constant of the motion?
6. What is the kind of the generalized momentum, canonically conjugate to the generalized co-ordinate q ?
7. What are the constants of motion of a free particle in Cartesian, cylindrical and spherical co-ordinates?

8. What components possess the radius-vector in cylindrical and spherical co-ordinate systems?
9. What is the physical meaning of the generalized momentum canonically conjugate to: a) the linear co-ordinate; b) the angular co-ordinate?
10. How is, in spherical co-ordinates, the kinetic energy of a particle in a central potential related to the angular momentum?

PROBLEMS

1. Using the vector relation $\mathbf{L}^2 = (\mathbf{r}\times\mathbf{p})^2 = r^2p^2\sin^2(\mathbf{r},\mathbf{p}) = r^2p^2 + (\mathbf{rp})^2$, verify that the energy of a free particle in spherical co-ordinates is:

$$E = H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}, \text{ where } p_r = (\mathbf{pr})/r.$$

2. Prove that the Poisson bracket for the x- and y-components of the angular momentum is equal to the value of its z-component with a negative sign: $\{L_x, L_y\} = -L_z$.
3. Find the Hamiltonian of a particle of mass m moving in one-dimensional constant homogeneous potential field $U(x)$.
4. Find the kinetic and potential energies and the Hamiltonian of the harmonic oscillator.
5. Find the Hamiltonian of a particle of mass m, moving on the surface of a sphere of radius r, the so-called space rotator.
6. Find the kinetic and potential energies and the Hamiltonian of an electron in the Coulomb field of a point charge $+Ze$.
7. Find the Hamiltonian of the hydrogen atom, reducing the two body problem to the one body problem.
8. Prove that the Hamiltonian $H = (\mathbf{P} - e\mathbf{A})^2/2m_e + e\Phi$ of a charged particle in an electromagnetic field $\mathscr{E}, \mathbf{B}$, where $\mathscr{E} = \text{grad}\Phi - \frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \text{curl}\mathbf{A}$, at non-relativistic velocity leads to the known equation of motion, i.e. to the canonical equation identical to the equation $m\frac{dv}{dt} = e(\mathscr{E} + (\mathbf{v}\times\mathbf{B}))$ (see [R15], Appendix 24).

Chapter7

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SUGGESTED READING

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7.1 EVIDENCE OF THE INADEQUACY OF CLASSICAL PHYSICS

At the end of the XIX century an opinion predominated among the physicist that their science was near competition - the basic laws were discovered and it remained only to apply them to the concrete problems. At the background of the big success a few hard nuts to crack remained - few experimental results were fully unexplained by classical physics. But from the motion of the astronomy bodies to the motion of the freely falling bodies, of rotating bodies on an inclined plane or of oscillating bodies around equilibrium, classical physics ensures the adequate picture. The dynamics of the charged particles in electromagnetic fields, the oscillations of coupled oscillators and of membranes, the deformation of solid states, the acoustic waves in gases, the fluids flow, the heat, the kinetic theory of the gases are only a part of the phenomena to which classical conception was applied successfully - a triumph for the scientists.

At the beginning of the last century some scientists found explanations one after another for the problems, unsolved by classical physics (the blackbody radiation, the photoelectric effect, the specific heat of solids, the structure of the atom, Compton effect). But these explanations were in striking contradiction with classical physics. Classical physics was in a condition of a tangle and dimness. Quantum mechanics was born with a lot of dramatism and rapture. It differed radically from classical mechanics and suggests fundamentally a new way for the knowledge of the nature. It is difficult with a few words to express the difference between the basics of the two manners - the classical and the quantum. Here we shall mention two important topics.

The famous Newton laws about the motion lay down in the basic of classical mechanics. These laws can be "derived", they can be confirmed experimentally as well as the predicted by them results. Quantum mechanics was developed on the basic of assumption, of the postulates. They arise out of the result of the intuition and of the analogy with the classical conception and could not be checked experimentally. But the experiment confirms the predicted results on the base of these postulates. The service belongs to the genius, to the founders of quantum mechanics, who were capable to suggest a method, a conception for prediction of the behaviour of physical system with microscopic dimensions. This quantum conception stands a test not only of the experimental results, explained by classical physics, but also of any others, showing the inadequacy of classical mechanics.

In classical mechanic the measurements in principle are *repeatable*. The disturbance of the system by the measurement may be made negligible value. In quantum mechanics the precise effect of the disturbance is unknown and unpredictab le. This lead to the *unrepeatable results* of the measurements and to uncertainty of the measurements value. For example, the measurement of the position of the microscopic object leads to uncertainty of the momentum. It is obvious that the concept of the trajectory, which is so important for classical mechanics, simply loses its meaning.

In this chapter we shall shortly consider the essence of the problems, whose explanation place the beginning of quantum mechanics.

7.1.1 Blackbody radiation

Blackbody fully absorbs incident on it electromagnetic radiation, independently on the wavelength; at the same time it reflects nothing. The absorbing and emitting properties are reversible. This means that the blackbody is the best emitter of energy with arbitrary frequency compared with any other body. A close approximation to a perfect blackbody is a cavity with a small hole. A negligible amount of the incident radiation will be reflected back through this small hole and the inner walls of the cavity will absorb almost the whole incident radiation. If the walls of the cavity are heated to a temperature T_0, they will emit the radiation and a small fraction of it will pass through the hole. The radiation emitted by the hole has blackbody spectrum. We note that the radiation is in thermal equilibrium with the walls of the cavity. The electromagnetic field inside is a superposition of standing electromagnetic waves. The amplitude of the standing waves obeys a sinusoidal law. From the view of the energy changing, these waves have the behaviour of harmonic oscillator analyzed in Chapter 5. Therefore we can apply the classical laws of usual mechanical oscillators. The average kinetic energy in thermal equilibrium according to these laws is $T = kT_0/2$ where $k = 1{,}38.10^{-23}$ J/K is Boltzmann's constant and T_0 is the absolute temperature. For the harmonic oscillator the average potential energy is equal to average kinetic energy (Chapter 5, the problem 3). Then the total average energy is

$$E = kT_0. \tag{7.1}$$

The number of the oscillators (of the standing waves) at a given frequency ν per unit volume is $8\pi\nu^2/c^3$ (for the derivation and for the details see [R15], Chapter 5 and Appendices 33, 34). Then the average total energy $I(\nu, T_0)$ of the radiation in the frequency interval $\nu, \nu + d\nu$ per unit volume and at the temperature T_0 is

$$I(\nu,T_0)=\frac{8\pi\nu^2}{c^3}kT_0. \tag{7.2}$$

This is the well-known Rayleigh-Jeans formula for the blackbody radiation. A few years before them, in 1832, Wien proved that the spectral distribution $I(\nu,T_0)$ of the radiation obeyed the following law:

$$I(\nu,T_0)=\nu^3 f\left(\frac{\nu}{T_0}\right). \tag{7.3}$$

As the consequence of Wien's formula we obtain, that in the maximum of the curves of the spectral distribution $I(\nu,T_0)$ as a function of the frequency, the dot λT_0 is constant, i. e. $\lambda T_0 = cT_0/\nu = \text{const}$. Really, with the increasing temperature the maximums of the experimental curves shift to higher frequencies (Fig. 7.1).

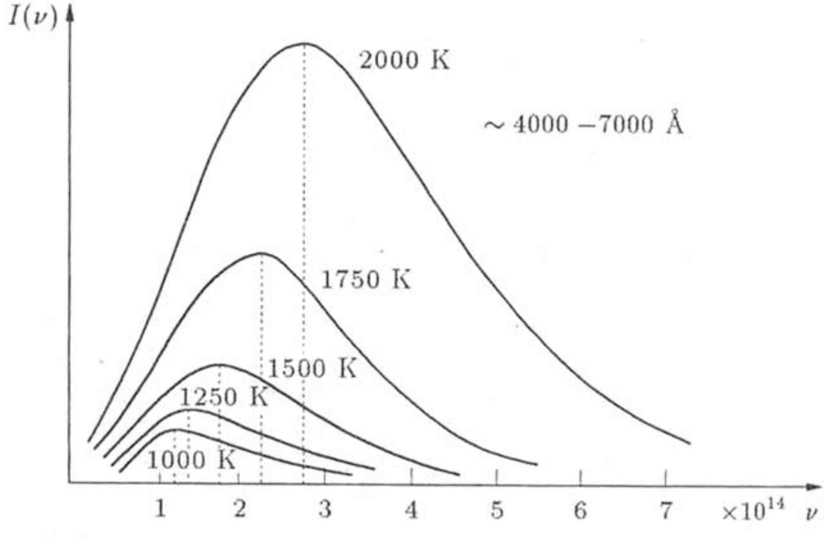

Figure 7-1. Spectral distribution of the blackbody radiation at different temperatures. The maximum of the each curve shifts to the higher frequency with increasing T_0.

Rayleigh-Jeans formula describes correctly only the initial interval of the spectral distribution - $I(\nu)\propto\nu^2$. At high frequency it is in total contradiction with the experiment. More than this, according to classical physics the energy $\int_0^\infty I(\nu)d\nu$ will be infinitely large, which obviously is nonsense. Ehrenfest calls the disagreement between the theory and the experiment at high frequency (ultraviolet band) an ultraviolet catastrophe for classical physics.

7.1.2 The photoelectric effect

The ejection of electrons from a surface by the action of light is called photoelectric effect. The phenomenon was discovered by Heinrich Hertz in 1887. It is well known by the course of general physics and therefore we shortly shall summarize its basic.

1. If the frequency ν of the incident light is kept constant, the photoelectric current i_p increases with increasing intensity I of the light.
2. Photoelectrons are emitted within less than 10^{-9} s after the surface is illuminated by light.
3. For a given element, the emission of the photoelectrons takes place only above a certain minimum frequency ν_0, called a threshold frequency.
4. The maximum kinetic energy $T_{\max}$ of photoelectrons is independent of the intensity of the incident light - the stopping potential V_0 (the potential at which the photocurrent becomes zero) is the same for the light of different intensities (Fig. 7-2a), i.e. $T_{\max} = \left|eV_0\right|$.
5. The maximum kinetic energy $T_{\max}$ of the photoelectrons depends of the frequency of the incident light. The stopping potential is different for different frequencies, even though the intensity of the light is the same (Fig. 7-2b).
6. The dependence of the kinetic energy is linear one on the frequency ν, as shown in Fig. 7-2c for different metals: cesium, potassium and tungsten. The analytical relation is following:

$$T_{\max} = a\nu + b. \tag{7.4}$$

7. Here a is the slope of the straight line and it is the same for all elements, while b is the intercept with the axis Y and it is different for different elements.

The classical theory explains point 1, contradicts points 2÷5 and can not explain point 6 at all.

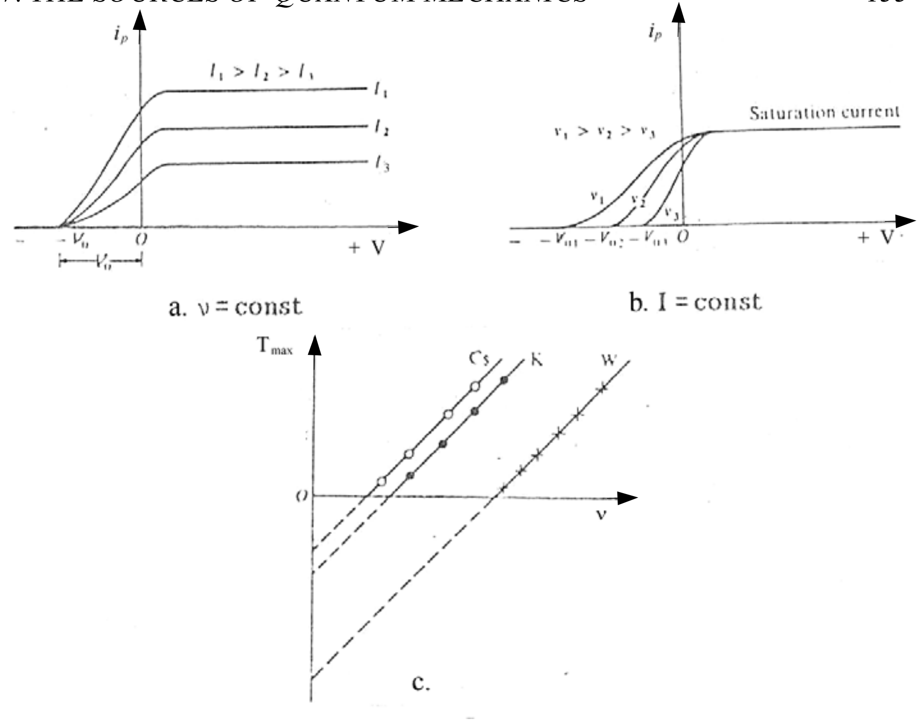

Figure 7-2. Photoelectric effect: a) at a fixed frequency ($\nu = \text{const}$) the stopping potential V_0 is the same for different intensities of the incident light; b) the stopping potential and, hence, the kinetic energy of photoelectrons are function of the frequency of light even though its intensity is fixed (I=const); c) a linear dependence of the maximum kinetic energy $T_{\max}$ of photoelectrons on the frequency ν for different metals ($T_{\max} = a\nu + b$).

7.1.3 The dependence of specific heat on temperature

Here we shall consider the specific heat of solids. As theirs atoms oscillate around the lattice points each atom has 3 vibrational degrees of freedom. A mole of a solid consists of N_A atoms and has $3N_A$ degrees of freedom. We saw in Chapter 5 that classically each degree has an average energy kT_0 ($kT_0/2$ kinetic energy and $kT_0/2$ potential energy). Thus the internal energy of a mole of a solid should be $E = 3N_A kT_0 = 3RT_0$, where N_A is Avogadros number, k is Boltzmann's constant and R is a gas constant ($R \approx 8,31$ J/mol.K). From here, the molar specific heat should be a constant $c = 3R \approx 25$ J/mol.K. This is the law of Dulong and Petit. The molar heat for many monatomic substances is approximately $3R$ at room temperature.

But *for many solids the law of Dulong and Petit is not satisfied. Moreover, it is found experimentally that for all solids the specific heat is function of temperature and* $c \propto T_0^3$ (Fig. 7-3).

7.1.4 Atomic spectrum and structure of an atom

At the end of XIX century it was known that the atom can absorb the electromagnetic radiation and pass into excited states. Atoms in an excited energy state do not remain there and emit excess energy in the form of electromagnetic radiation. At this *the spectrum of any material's atom consists of discrete lines.* In contrast to the continuous spectrum of electromagnetic radiation, for instance, of the surface of blackbody, the free atoms emit only a number of discrete wavelengths - generally they can be a lot. When the additional energy is large enough the atom ejects an electron - a particle with negative charge and small mass ($\sim 10^{-4}$ from the atom mass). It was naturally to suggest that in a neutral atom the electrons were tied with the positive-charge "atomic core". At excitation the electrons begin to oscillate, as a result of which one sees the emitted atomic spectrum. According to the classical theory the frequency of the radiation should be equal to the the

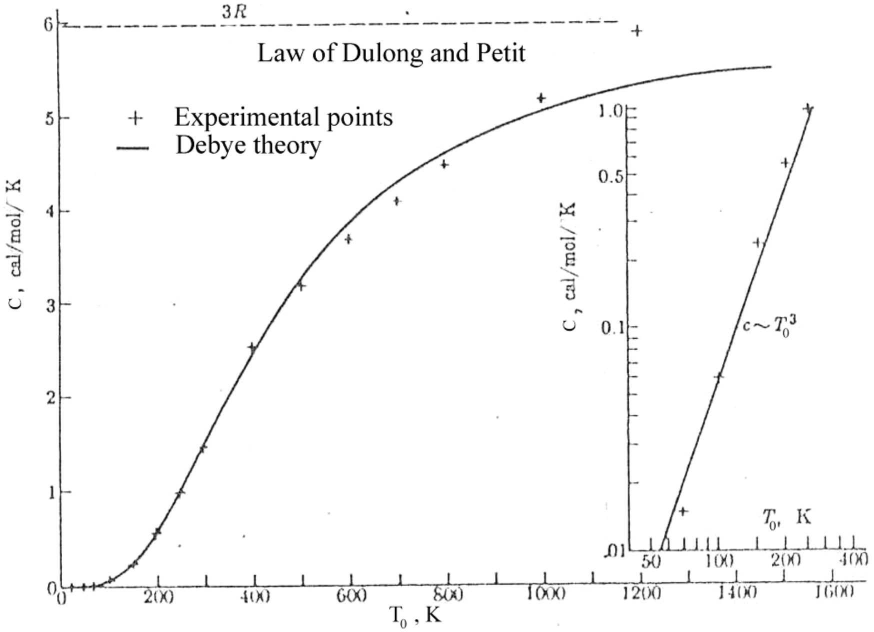

Figure 7-3. The specific heat of diamond as a function of temperature. It is obvious the inadequacy of classical physics (the dashed line) to the experimental results (the crosses). The solid lines are plotted according to the theory of Debye.

frequency of the electron oscillation or multiple value of it (let recall the string, which oscillates with frequencies $\nu_0, 2\nu_0, 3\nu_0, ...$). But experimentally one observed the frequencies, which are not multiple to one or to a few frequencies. This suggested assuming as many degrees of freedom, as the number of the spectral line emitted by the atom. But even for the simplest atom (hydrogen) a number of the degrees of freedom becomes innumerable.

Investigation of the spectra of each kind of atom shows that it has its own characteristic spectrum, i.e. its own combination of spectral lines. Thus the spectrum is a characteristic of the type of atom. Atomic spectra became a useful tool for identification of their characteristic lines. And this transforms spectroscopy in a very useful addition to the traditional techniques of chemical analysis. Chiefly for this reason in the last years of XIX century the scientists expended great efforts in measuring wavelength of line spectra of the elements. Experimental measurements were difficult, because the spectra consisted of hundreds of lines and were very complicated, especially for the multielectron atoms.

The spectrum of hydrogen atom is relatively simple because it consists of a single proton and a single electron. The visible part of the hydrogen spectrum is shown in Fig. 7-4. We see that the lines exhibit definite regularities. They group in the so-called spectral series. In the figure is shown the first series, which was discovered by J. J. Balmer in 1885. The space between the wavelength of the adjustment lines continuously decreases with decreasing wavelengths. Each series converges to the so-called series limit of the wavelengths. For the Balmer's series, shown in the figure, this is 3456,8 Å. The regularity of the H spectrum tempted Balmer to find an empirical formula for the wavelengths of the series:

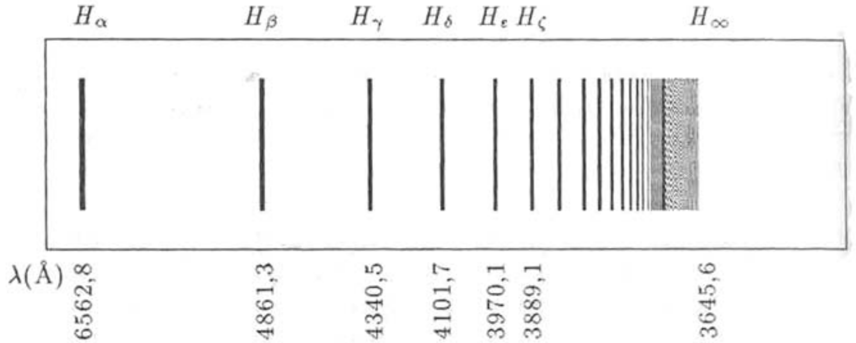

Figure 7-4. The visible part of the hydrogen spectrum.

$$\lambda = 3645{,}6\frac{n^2}{n^2-4}\ \text{Å}, \tag{7.5}$$

where $n = 3, 4, 5, \ldots$. For $n = 3$ we have H_α line, for $n = 4$ - H_β and so on. For $n = \infty$ one obtains the series limit $\lambda = 3645{,}5$ Å. A little later Rydberg expressed Balmer series in more convenient form:

$$\nu^* \equiv \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \tag{7.6}$$

where ν^* shows the number of wavelengths per unit length and is called spectroscopic frequency (the reciprocal wavelength) and R is the Rydberg constant, the most recent value of which is

$$R = 10967757 \pm 1{,}2\ \text{m}^{-1}. \tag{7.7}$$

Formulae of the type of (7.6) were found for a number of series for H spectrum. For instance, we show five series of lines in Table 7-1.

Table 7-1. Some of the spectrum series in the hydrogen atom

Series of	Wavelength ranges	Formulae	Value of the number n
Lyman	Ultraviolet	$\nu^* = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$	n=2, 3, 4, ...
Balmer	Near ultraviolet and visible	$\nu^* = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$	n=3, 4, 5, ...
Pashen	Infrared	$\nu^* = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$	n=4, 5, 6, ...
Brackett	Infrared	$\nu^* = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$	n= 5, 6, 7, ...
Pfund	Infrared	$\nu^* = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$	n=6, 7, 8, ...

All these formulae strongly suggest that the spectroscopic frequency (the reciprocal wavelength) can be written as a difference of two terms, each of the form

$$T(n) = \frac{R}{n^2}, \qquad n = 1,\ 2,\ 3, \ldots \tag{7.8}$$

This statement amounts to the Ritz combination principle. The two terms $T(m)$ and $T(n)$ combine to produce a spectral line at a spectroscopic frequency given by

$$\begin{gathered} v^* = T(m) - T(n) = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \\ m = 1, 2, 3\ldots, \quad n = 1, 2, 3\ldots, \quad n > m. \end{gathered} \tag{7.9}$$

The inadequacy of classical physics becomes quite obvious at the explanation of the atom structure. In 1912 Ernest Rutherford on the series of experiments with positively charged α-particles, which shot through thin metallic foils, made the following conclusion:

1. The a-particle are scattered by strong Coulomb repulsion;
2. "Atomic core" with almost the whole mass of the atom is positively charged and is concentrated in a small region in the centre with radius $10^{-12} - 10^{-11}$ cm; it is called the nucleus;
3. The structure of the atom is like the Solar system, the electrons being circling around the nucleus as the planets - around the Sun.

Classical physics is in contradiction to the results of the experiments and with the suggested in their basis planetary model of the atom. The electron circling around the "atomic core", i.e. around the nucleus, ought to collapse into the nucleus, because it radiates electromagnetic waves and loses energy. This is in contradiction with the observed stability of the atom.

Really, if the orbit of the electron in the atom around the nucleus is a circle of radius r then the atom has an electric dipole moment $\mathbf{d} = e\mathbf{r}$. Due to the dipole radiation the energy of the electron E does not remain constant, but decreases and consequently the orbit radius also decreases. As the relative estimate shows the electron should lose his energy only for 10^{-8} s. Then the radiation frequency which is reciprocal to the radius in the degree 3/2) (the third law of Kepler) should change continuously and no discrete lines in the atom spectrum would be observed.

Let us summarize the results of the Rutherford planetary model from the classical point of view:

- the atom can not be stable; more than this it ought to lose all its energy for very short time - 10^{-8} s;
- the frequency of the radiation which is reciprocal to orbit radius in the degree 3/2 (the third law of Kepler) must be continuous; this is in contrary to the observed discrete line spectrum.

7.1.5 Roentgen rays and the Compton effect

In 1895 the German scientist Wilhelm Roentgen discovered that *when the electron, accelerated by the potential V, strikes a metallic target, a highly penetrating radiation is emitted. The rays were called X-rays* because nobody knew what this radiation was. Experimentally were found outstanding features of X-rays spectrum:

1. At relatively not high energy of the electrons the spectrum was continuous up to a certain maximum frequency $\nu_{\max}$ which is proportional to the potential V - $\nu_{\max} = \text{const}|V|$.
2. When V increases at a given value of V discrete lines superimpose on the continuous X-ray spectrum. These lines are different for different atoms and do not depend of the potential V. But for this discrete spectrum the maximum limit frequency $\nu_{\max}$ retains.

In 1912 von Laue confirmed the wave character of the X-rays. But the existence of the high frequency limit and its dependence on V can not be explained by classical physics.

The classical theory shows helplessness and at the explanation of the X-rays scattering by free electrons. According to classical electrodynamics when an electromagnetic wave of frequency ν is incident on a free charged particle (in our case this is an electron) the last one begins to oscillate with the same frequency ν. In turn, the oscillating electron reradiates an electromagnetic wave of a frequency ν, i.e. of the frequency of the incident wave. So, from the point of view of the classical theory the scattered by the free-electron wave should have the frequency of the incident wave, but the experimental observations show that the frequency of scattered wave ν' is less than the one of the incident wave ν - $\nu' < \nu$ (or wavelength $\lambda' > \lambda$). This effect was explained by American physicist Arthur Compton and therefore is called Compton effect. The schematic sketch of the experiment is shown in Fig. 7-5a. A beam of monochromatic X-rays is obtained from the source *S.* After the collimator *C* (a slit system) it is made incident on the target *T* made of something (for instance of carbon) in which the outer electron are almost free, i.e. their binding energy is negligible to the energy of the incident wave. The results for the wavelength of the scattered wave at different angles are shown in Fig. 7.5b. The points are experimentally measured values and the lines are calculated by Compton on the base of quantum hypothesis of Plank (see the next section 7.2)

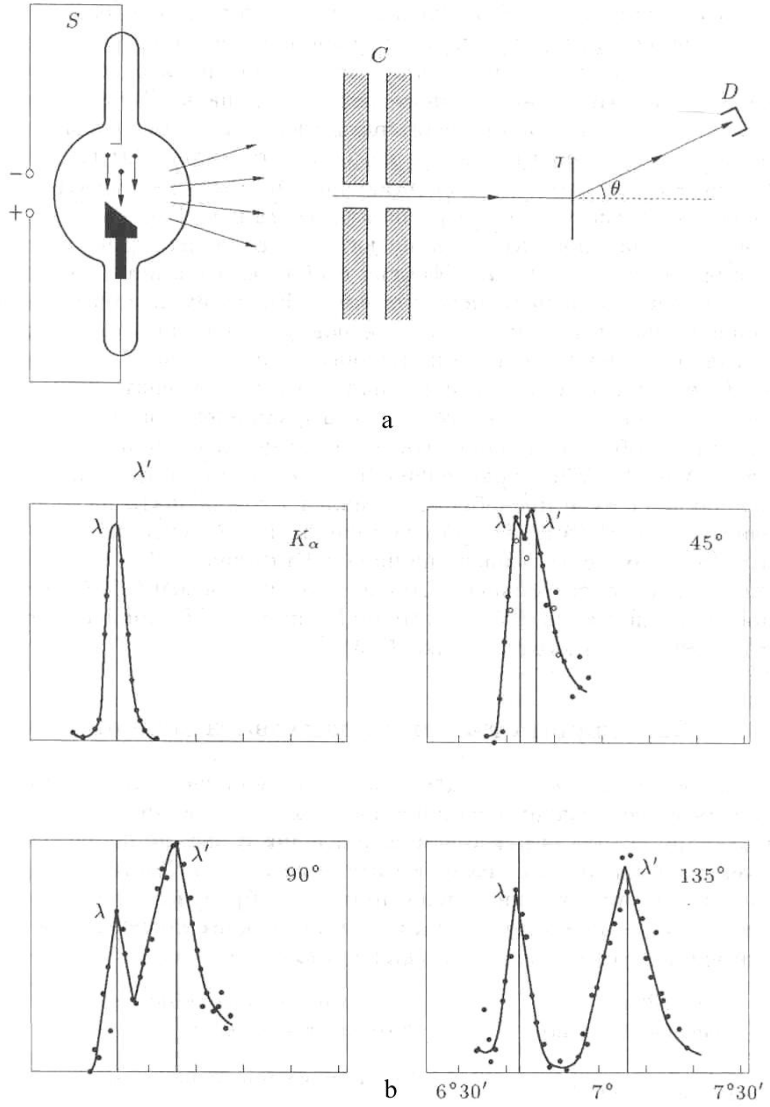

Figure 7-5. Compton effect: a) Compton's experimental arrangement: S - a X-rays tube, C - a collimator, T - a target, D - detector of scattering radiation; b) scattering of the K_α line of molybdenum (wavelength λ) on the carbon at angles 45°, 90° and 135°. Here λ' stands for the wavelength of the scattered wave.

7.2 THE FIRST STEPS IN QUANTUM MECHANICS

At the beginning of the XX century one by one the phenomena out of the scope of classical physics found explanations by new ideas. But for classical physics the ideas were strange even scandalous ones. With these ideas the "hard nuts", on which it stumbles, were explained. In a short time the separate ideas form the fundamental of new mechanics - quantum mechanics. Chronically, the basic moments of the quantum-mechanics creation are:

1901	Planck	Blackbody radiation
1905	Einstein	Photoelectric effect
1907 1912	$\left.\begin{array}{l}\text{Einstein}\\ \text{Debye}\end{array}\right\}1907$	Specific heat of solids
1913	Bohr	Quantum theory of an atom and spectra
1922	Compton	Photon scattering on electrons
1924	Pauli	Exclusion principle
1925	de Broglie	Matter waves
1926	Schroedinger	Wave equation
1927	Heisenberg	Uncertainty principle
1927	Davisson and Germer	Experimental verification of wave properties of electrons
1927	Born	Interpretation of the wave function

In this section we shall consider in details the new explanation of the phenomena, exposed in the previous section.

7.2.1 Planck's hypothesis and the blackbody radiation - quanta

For the explanation of blackbody radiation Max Planck has introduced absolutely incredible assumption that the energy of the emitted and absorbed radiation with frequency ν can not be arbitrary but only a discrete set of energy. The radiation with frequency ν exists only in multiples of $h\nu$ - $nh\nu$ or $\left(n\hbar\omega = n\left(h/2\pi\right)2\pi\nu\right)$. The constant h $\left(\hbar \equiv h/2\pi\right)$, which has the value $h = 6{,}626.10^{-34}$ J.s ($\hbar = 1{,}055.10^{-34}$ J.s), is called Planck's constant and the bundle of energy

$$E = h\nu = \hbar\omega \qquad (7.10)$$

is called an energy quantum or (later) a photon (in 1926 the chemist Gilbert Lewis suggested the name "photon"). The expression (7.10) is called the Planck radiation law. Postulating that the energy is quantized, Planck defined the spectrum of the blackbody, which coincide with the experimental one (Fig. 7-1). For a given frequency ν all the quanta have the same energies; the quanta of high frequencies have high energies and the quanta of low frequencies - low energies. When a blackbody is in thermal equilibrium, the atoms (molecules) within it will emit radiation with frequency ν only if they have energy equal or greater than $h\nu$. From the Maxwell-Boltzmann distribution it is clear, that for low frequency many atoms correspond to this condition, but as ν increases the number of atoms (molecules) having energy in excess of $h\nu$ decreases. Therefore $I(\nu)$ does not increase with increasing ν, but goes to zero asymptotically. Thus ultraviolet catastrophe predicted by classical physics is avoided.

According to the Maxwelll-Boltzmann distribution if there are N_0 particles in a system in equilibrium, the number of atoms N_n with energy E_n at temperature T_0 is as follows:

$$N_n = N_0 \exp\left(-\frac{E_n}{kT_0}\right). \tag{7.11}$$

Using for the energy his quantum hypothesis $E_n = h\nu$, Planck calculated the mean energy and arrived at the following formula for the spectral distribution of the blackbody radiation:

$$I(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp(h\nu / kT_0) - 1}. \tag{7.12}$$

This is the famous Plank radiation law. In Fig. 7-6 the theoretical formula

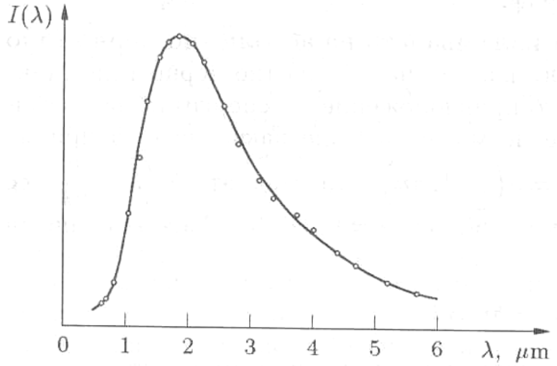

Figure 7-6. Comparison between the experimental blackbody spectrum (open dots) and the theoretical Plank's radiation expression (continuous curve). The agreements between them confirms the Planck quantum hypothesis.

and the experimental points are compared. It is obvious that the agreement is very good. Such agreement is observed at the value of Plank constant $h = 6{,}625.10^{-34}$ J.s.

7.2.2 Quanta and the photoelectric effect

Einstein did the next step. For the explanation of photoelectric effect he applied the Planck hypothesis as he went further. Namely, he suggested that *electromagnetic waves were not only emitted and absorbed in the form of bundles that existed as quanta, but also exist in the form of quanta.* These quantizied electromagnetic waves were later called *photons. When the light incidents on a metallic surface the electron absorbs a photon of energy* $h\nu$ *. For the escaping of the surface it uses up an amount of energy w, called the work function of the metal. The rest of energy of the absorbed photon appears as kinetic energy of the electron.* Its possible maximum is:

$$T_{\max} = \frac{mv^2_{\max}}{2} = h\nu - w. \tag{7.13}$$

We receive the linear dependence (7.4) of the kinetic energy of the photoelectrons on the frequency. Comparison shows that h is the slope *a* and *-w* is the intercept *b* of the straight line $T_{\max}(\nu)$ (see the text under Fig. 7-2c). On the other hand we can obtain the Planck's constant from the experimental results. This value agrees with the value of h obtained by fitting Planck radiation law (7.10) to the spectrum of the blackbody radiation. Thus the quantum hypothesis explains point (6) of section (7.1.2). The explanation of points (1) to (5) is simple and logical and therefore we leave it to the reader.

7.2.3 Quanta and the specific heat of solids

We see that according to classical physics the specific heat of solids should not depend on the temperature, which is in disagreement with the experimental results. In 1907 Albert Einstein proposed the solids to be treated as a set of harmonic oscillators with frequency *ν*, which energy was discrete, i.e. it was quantizied. The essence of the problem of the specific heat is the same as the radiation of blackbody. *According to the Planck's hypothesis the heating* (*the cooling*) *of bodies is accompanied with absorption* (*emission*) *of quanta by them. As soon as the solids consist of oscillators with energy hν, at low temperature the transmitted energy consists of low energetic quanta, which can not excite the oscillators. Therefore the specific heat decreases* (Fig. 7-3). Einstein assumed that the solids consist of oscillators with fixed frequency. The obtained theoretical results agree with the observed specific heat over a wide range of temperatures. However at low temperatures the theoretical specific heat was in disagreement with its observed variation. This was made more precise by Debye in 1912. Like the proposal of Planck for the blackbody he treated the solid as a set of oscillators with various frequencies. The comparison between the theory of Debye and the experimental results is shown in Fig. 7-3.

7.2.4 The Bohr's theory of the atom and the atomic spectrum

In 1913 Neils Bohr took a decisive step further, applying Planck's idea for the quantizying of the energy to other observable, namely to the angular momentum. On the base of his famous postulates, which were rather strange from the point of view of classical physics, he suggested a model of the atom, which was in a very good agreement with the known at that time spectroscopic data (in particular with these of H spectrum). These postulates are following:

1. An electron in an atom can move in certain circular orbits around the nucleus under the influence of Coulomb attraction between them. These orbits are called allowed stationary states (they are discrete) and the motion in them obeys the laws of classical mechanics.
2. Instead of the infinity of orbits which would be possible in classical mechanics, the allowed orbits are only those for which the orbital angular momentum is equal to an integral multiple of $\hbar$ $(\hbar = h/2\pi)$:

$$L = n\hbar, \quad n = 1, 2, 3, ... \tag{7.14}$$

3. An electron moving in such an allowed orbit does not radiate electromagnetic energy, despite of the fact that the motion is with constant acceleration. Thus in allowed stationary orbits (states) the total energy remains constant.
4. An electron moves on from the orbit (state) of initial higher energy E to the orbit (state) of final lower energy E' with a jump (not continuously) emitting only one photon (quantum) of energy $h\nu$ so that

$$h\nu = E - E'. \tag{7.15}$$

The first postulate confirms the existence of the atomic nucleus (it passed only one year from the famous experiment of Rutherford about the scattering of the α-particles). The second postulate introduces the quantization. It is important to note the difference between Bohr's quantization of the orbital angular momentum of an atomic electron moving under the influence of the Coulomb force ($\propto 1/r^2$) and Plank quantization of energy of the oscillator (this can be the motion of electron which moves under the influence of the harmonic force). The third postulate is needed to prevent the instability of an atom, predicted by classical electromagnetic theory. In the experiments atoms are observed to be stable. The fourth postulate is just Einstein's postulates combined with the law of conservation of energy - the energy of photon $h\nu$ is equal to the difference between the energy of the initial and the final electron states.

These postulates are a mixture of classical and non-classical physics. It is supposed that an electron moves in circular orbit obeying the laws of classical mechanics, but the idea for the discreteness (the quantization) of angular momentum is included. It is supposed that the electron obeys one of the laws of classical electromagnetic theory (the Coulomb law) but it does not obey the other law (namely the law for the emission of electromagnetic radiation of a moving with the acceleration charged body). But we should not be surprised that *the laws of classical physics, which were based on our experience with macroscopic system, are not entirely valid when we analyze the microscopic systems like the atoms.*

The Bohr's postulates give the possibility to receive clear expression for the spectral term (7.8) and to determine the known spectral lines of the hydrogen atom. We shall consider in details these questions in the next chapter.

7.2.5 Photons and Compton effect

The next who dares to use the unusual quanta of Planck was American physicist A. Compton. With them he successfully explained the scattering of X-rays on the free electrons and thus obtained a dramatic confirmation of the particle-like nature of radiation. The word "dares" is not random. Despite the success of the theory of the quanta the physicists considered them as a newcomers. In this sense the known exclamation of Schroedinger is very indicative: "If we are going to save these accursed quantum jumps I regret that in generally have had deal with the quantum theory".

Compton uses the suggestion of Einstein the light to be considered as a beam of photons of energy $h\nu$. Then according to theory of relativity the energy E and the momentum p of the photons can be written as follows:

$$E = h\nu, \qquad E = pc \quad \rightarrow \quad p = \frac{h\nu}{c}. \tag{7.16}$$

And here as at the photoeffect (despite there not so obviously) we consider the photons of electromagnetic waves as particles (corpuscles). *The idea of the wave and particle characteristics of one material object is the second basic idea of quantum mechanics* (after the idea of discreteness). At such an interpretation of the photons the scattering of the X-rays may be considered as an elastic collision between the photon and the electron (Fig. 7-7). Then the momentum conservation law in *x*- and *y*-direction and the energy conservation law require following:

$$\begin{aligned}
&\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + p_e\cos\alpha,\\
&0 = \frac{h\nu'}{c}\sin\theta - p_e\sin\alpha,\\
&h\nu = h\nu' + T_e.
\end{aligned} \tag{7.17}$$

From these three equations we can express the scattering wave through the incident one. First, we eliminate the angle α and rewrite the first two equations in the form:

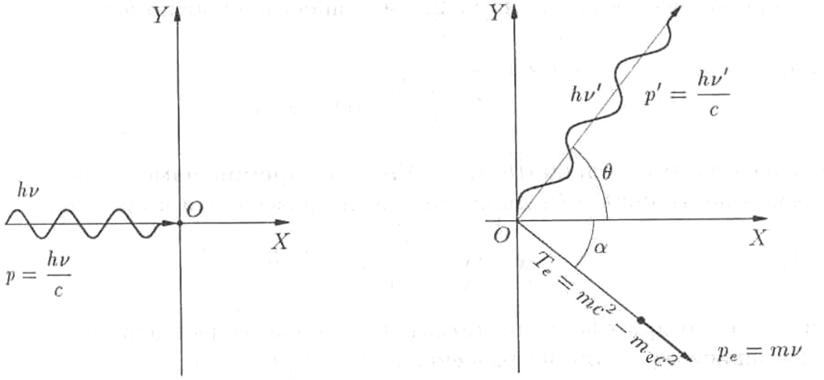

Figure 7-7. Scattering of X-rays can be considered as a collision between a photon and an electron. Here the sign "'" stands for the values after the collision and p_e, T_e, m and m_e are the momentum, the kinetic energy, mass and rest mass of the electron, respectively.

$$\begin{aligned}
&p_e c\cos\alpha = h\nu - h\nu'\cos\theta,\\
&p_e c\sin\alpha = h\nu'\sin\theta.
\end{aligned} \tag{7.18}$$

Squaring and adding these equations, we find

$$p_e^2c^2 = (h\nu)^2 + (h\nu')^2 - 2(h\nu)(h\nu')\cos\theta. \tag{7.19}$$

By using the third equation we obtain the total relativistic energy of the recoiling electron

$$E = E_{ke} + m_e c^2 = (h\nu - h\nu') + m_e c^2, \tag{7.20}$$

which from the theory of relativity is equal to

$$E = \sqrt{p_e^2 c^2 + m_e^2 c^4}. \tag{7.21}$$

We equate Eqs. (7.20) and (7.21) and square:

$$p_e^2 c^2 = (h\nu - h\nu')^2 - 2(h\nu - h\nu')m_e c^2. \tag{7.22}$$

Now we equate Eqs. (7.19) and (7.22) and solve for $h\nu'$:

$$h\nu' = \frac{h\nu}{1 + (\frac{h\nu}{m_e c^2})(1 - \cos\theta)}. \tag{7.23}$$

By using relation $\lambda\nu = \lambda'\nu' = c$ we may turn on from the frequency to the wavelength and to obtain for the change in the wavelength:

$$\lambda' = \lambda + \frac{h}{m_e c}(1 - \cos\theta). \tag{7.24}$$

Thus Compton confirms theoretically the experimental fact that the scattering wavelength λ' is longer than the incident wavelength λ ($\lambda' > \lambda$) *and it depends on scattering angle θ* - ($\lambda(\theta)$).

7.3 WAVES VERSUS PARTICLES - DUAL NATURE OF THE RADIATION

The old dispute in classical physics for the essentiality of the light (weather it is a beam of particles (corpuscles) or represents a wave) terminated with the victory of the supporters of the wave character of the light. It formed an opinion that the light was electromagnetic wave and the theory of radiation of Maxwell-Lorentz appeared. The experiment of diffraction and the interference of the light were decisive. We shall remind them shortly (the details may be seen in H. J. Pain, The Physics of Vibrations and Waves, 2nd Edition, John Wiley&Sons, 1976, Chapter 10).

All waves display the phenomena of interference and diffraction. *These phenomena arise from the superposition of waves from separate sources*. The difference between interference and diffraction is merely of scale. In the interference from *N* narrow slits of separation $d >> \lambda$, each slit may be seen as the source of single waves (a point source) and the interference picture is a result of the superposition of the waves from these sources. In diffraction from a slit (source), the aperture α is of the order of the wavelength λ and according to Huygens' principle every point of the wave front in the slit represents a source of secondary waves and the resultant diffraction picture is a superposition of these secondary waves. (*We shall note that at these cases the sources at the interference are separated and at the diffraction are continuously placed*). For the interference from *N* equal sources (slits) of separation *d* (Fig. 7-8) and each of intensity I_s (the square of the amplitude) the intensity at the distant point *P* in a direction θ from the slits is:

$$I = I_s \frac{\sin^2\left(\frac{N\pi d \sin\theta}{\lambda}\right)}{\sin^2\left(\frac{\pi d \sin\theta}{\lambda}\right)} = I_s \frac{\sin^2 N\beta}{\sin^2\beta}, \quad \beta \equiv \left(\frac{\pi d}{\lambda}\right)\sin\theta. \tag{7.25}$$

When one have two slits (Young slit's experiment) the intensity is as follows

$$I == I_s \frac{\sin^2 2\beta}{\sin^2\beta} = 4I_s \cos^2\beta. \tag{7.26}$$

At the diffraction from a slit with a finite width *a* picture is obtained as at the interference from *N* ($N \to \infty$) point sources continuously placed in the slit. We would like to underline that the phenomenon of interference lays in the basis of an every diffraction picture. The intensity of radiation is:

$$I_d = I_0 \frac{\sin^2\alpha}{\alpha^2}, \qquad a \equiv \frac{\pi a}{\lambda}\sin\theta\ , \tag{7.27}$$

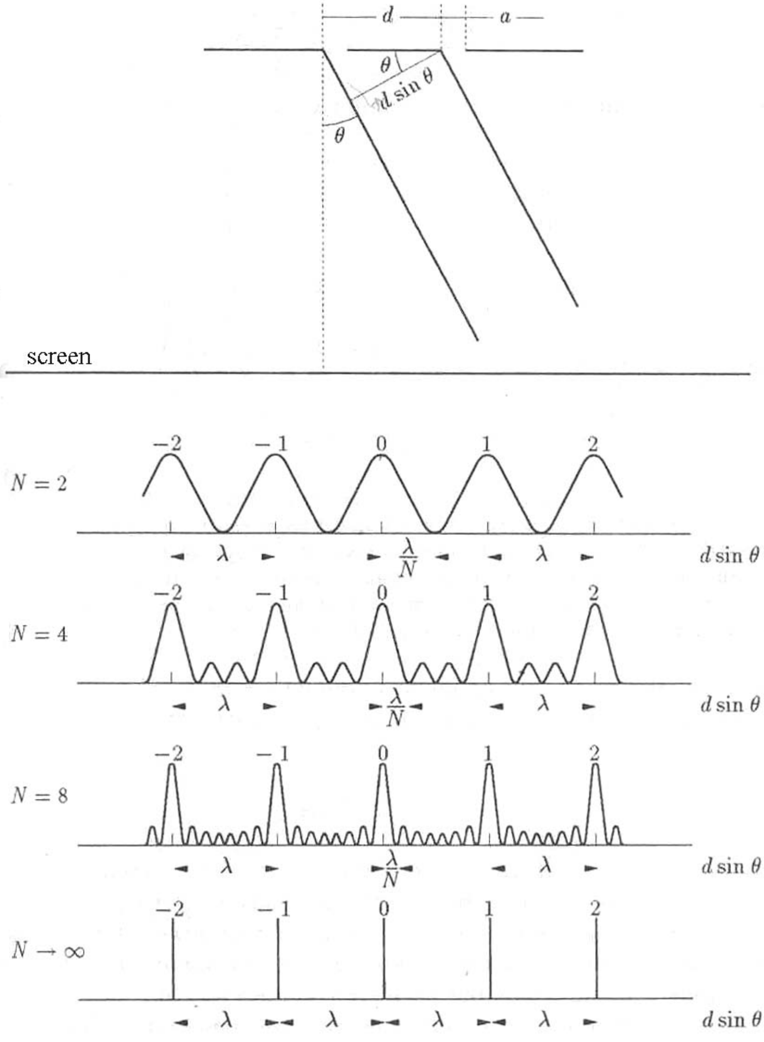

Figure 7-8. Interference from N equal sources of separation d. The separation between principal maxima is $d\sin\theta = n\lambda$ $(n = 0, \pm1, \pm2, ...)$ and their intensity is $I = N^2 I_s$. With increase of the number N of the sources the principal maxima increase $(I \propto N^2)$ and their width decrease ($\propto 1/N$).

where I_0 is the intensity of the central maximum (Fig. 7-9a).

The intensity of the diffraction pattern from two equal slits ($N = 2$) of width a and separation d is as follows:

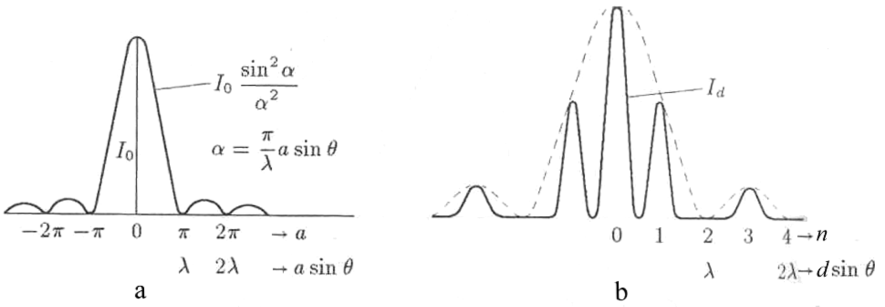

Figure 7-9. Diffraction pattern: a) from a single slit of width a - the diffraction maxima are at $a\sin\theta = m\lambda$; b) from two equal slits of the same width at the distance d - the interference fringes, defined by the condition $d\sin\theta = n\lambda$, are modified by the envelope of a single slit diffraction pattern.

$$I_d = 4I_0 \frac{\sin^2\alpha}{\alpha^2}\cos^2\beta. \tag{7.28}$$

The presence of the interference is obviously - $I_d \propto \cos^2\beta$ (compare with (7.26)). Together with this we have diffraction from a slit of width a - $I_d \propto \sin^2\alpha/\alpha^2$. As a result we see the interference picture from two slits in which interference fringes are modified by the envelope of a single slit diffraction pattern (Fig. 7-9b). We shall note that when the slit is circle one the considered diffraction patterns present concentric light and dark rings.

After a short return to the classical wave theory let deal again with the difficult phenomena of Section 7.1. The consideration of the light as an electromagnetic wave could not explain the blackbody radiation, the photoelectric effect and the Compton effect. Only the introduction of the energy bundles (quanta or photons) gives the possibility to explain it. At the analysis of Compton effect besides energy of these photons we prescribe them momentum. As the energy, the mass and the momentum are characteristics of the particles, the photons should be considered as particles (corpuscles). But then will they (the particles) be able to explain diffraction and interference? In fact what are the photons - particles or waves? There arises quite strange situation in which the optical phenomena split on the two groups, the one of them can be explained only by particles and the other - only by waves. In classical physics these points of view are mutually exclusive. This confrontation was called *wave-particle duality*. Classical physics considers two types of motion - of particles and waves. Consequently it defines two categories of objects - matter and radiation. The matter consists of particles, which are localized in space, and their motion with the defined trajectory obeys Newton's laws. The wave motion is nonlocalized. The wave is without restriction and it has not a trajectory. On contrary of the matter the radiation can not be divided on separate particles, which save its space localization in time. The radiation obeys the electromagnetic theory of Maxwell and the phenomena diffraction and interference shows that it has wave character.

Namely these two phenomena we may use in classical physics as a criterion to differ particles and waves. Such criterion significantly will ease us to understand the strangeness and dual character of the microscopic world.

Fig. 7-10 shows a thought experiment on the transition of a beam of classical particles from the source S through the slits A_1 and A_2. Shutting consecutively the slits A_1 and A_2 we obtain the intensities I_1 and I_2 of the particles (the number of particles through the unity surface for time 1 s) on the screen E. When the both slits are open the beams from A_1 and A_2 superimpose themselves and the measured intensity is a sum of the both intensities:

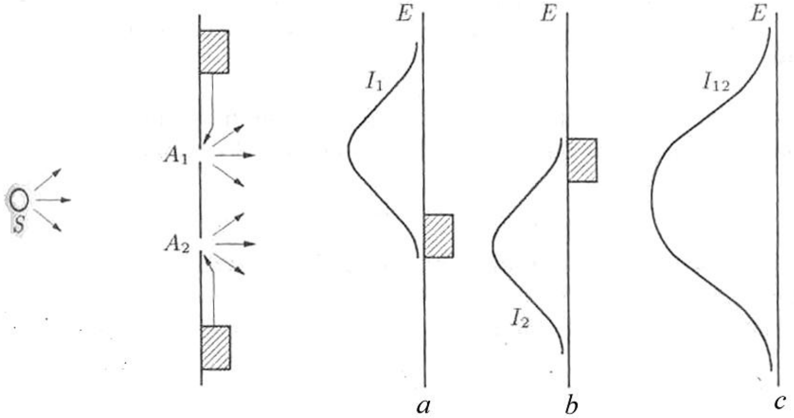

Figure 7-10. Transition of a beam of classical particles trough two slits A_1 and A_2 (S - source, E - screen, I - intensity): a) the slit A_2 is closed; b) the slit A_1 is closed; c) the both slits are opened - their intensities add, i.e. the total intensity is $I_{12} = I_1 + I_2$.

$$I_{12} = I_1 + I_2 . \qquad (7.29)$$

Let consider the same experiment, but instead of a source of particles to have a source of waves (Fig 7-11). The wave is characterized by the wave function $\psi(\mathbf{r},t)$ (for example, $\psi(\mathbf{r},t)=\mathrm{const}\exp[i(\mathbf{kr}-\omega t)$ for a plane wave.

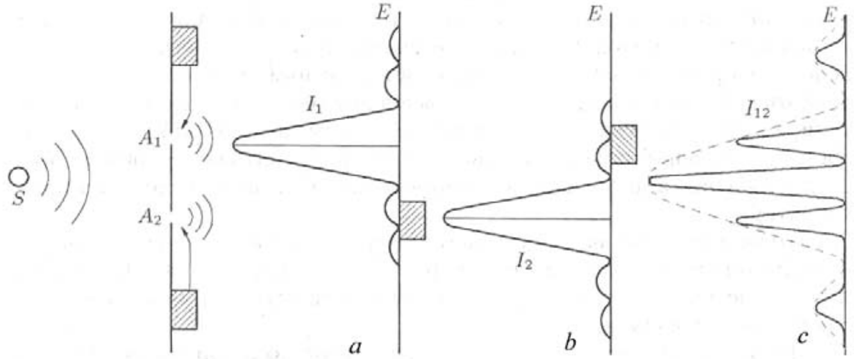

Figure 7-11. Transition of a wave trough two slits A_1 and A_2: a) the slit A_2 is closed; b) the slit A_1 is closed; c) the both slits are opened the interference-diffraction picture is not the sum of the both diffraction picture, i. e. the total intensity is not a sum of the separate intensities $I_{12} = I_1 + I_2$.

The intensity of the wave (the wave energy through the unity surface normally to the propagation for time 1 s) is defined by the square of the module of the wave function:

$$I \propto |\psi|^2 . \tag{7.30}$$

If the photons are particles, then the luminosity upon the screen should be determined by their number $I \propto n$, but if they are waves - by the square of amplitude $I \propto |\psi|^2$. In our experiment we have

$$I_{12} \neq I_1 + I_2 , \tag{7.31}$$

i.e. the total intensity is not the sum of the both intensities - we observe well known diffraction-interference picture. Here we shall note that the same values of the wave are added:

$$\psi_{12} = \psi_1 + \psi_2 . \tag{7.32}$$

For example, when one has an electromagnetic wave, the intensities of the electrical field are added (not the intensities of the waves).

So we have very important criterion: *when the beams of classical particles are superimposed their intensities add and when the waves are superimposed the meanings of the oscillating values are added but their intensities do not are added.*

Let us now apply the criterion to the photons, i.e. to conduct the double slits experiments with the photons. In the real experiment one uses for the slits the distance between the atoms in a single crystal (this ensures the identity of the slits). The first experiment was conducted by Laue in 1912 with Roentgen quanta. He obtained the result of Fig. 7-11. Consequently the photons are waves. Nevertheless the photoeffect and the effect of Compton exist?! Then we may arrange the additional test for the photon. We shall launch the photons in our experiment one by one. Let one of the slits to be covered up. When the photons strike the screen one by one we observe a separate flashes and there is no diffraction picture. This means that the photons are particles (even when the intensity of the wave is very weak, the last exhibits diffraction properties). Instead of clearing the matters, our test makes them more strange and incomprehensible. One photon has the behaviour of a particle, but the beam of photons - of a wave. More than this, if we launch the photons one by one a long time so theirs numbers is equal to the photons number at short exposition we shall obtain the same diffraction pattern as at this short exposition (Fig. 7-12).

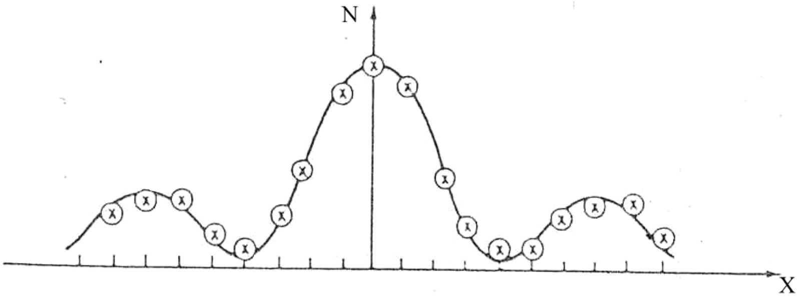

Figure 7-12. Experiment with photons in which the individual electrons are only emitted one at a time. The distribution of the photons coincides with the intensity of the diffraction pattern.

If the both slits are opened we also observe flashes of the separate photons on the screen. But when we increase the number of photons these flashes form the typical diffraction-interference picture of the double slits (Fig. 7-13).

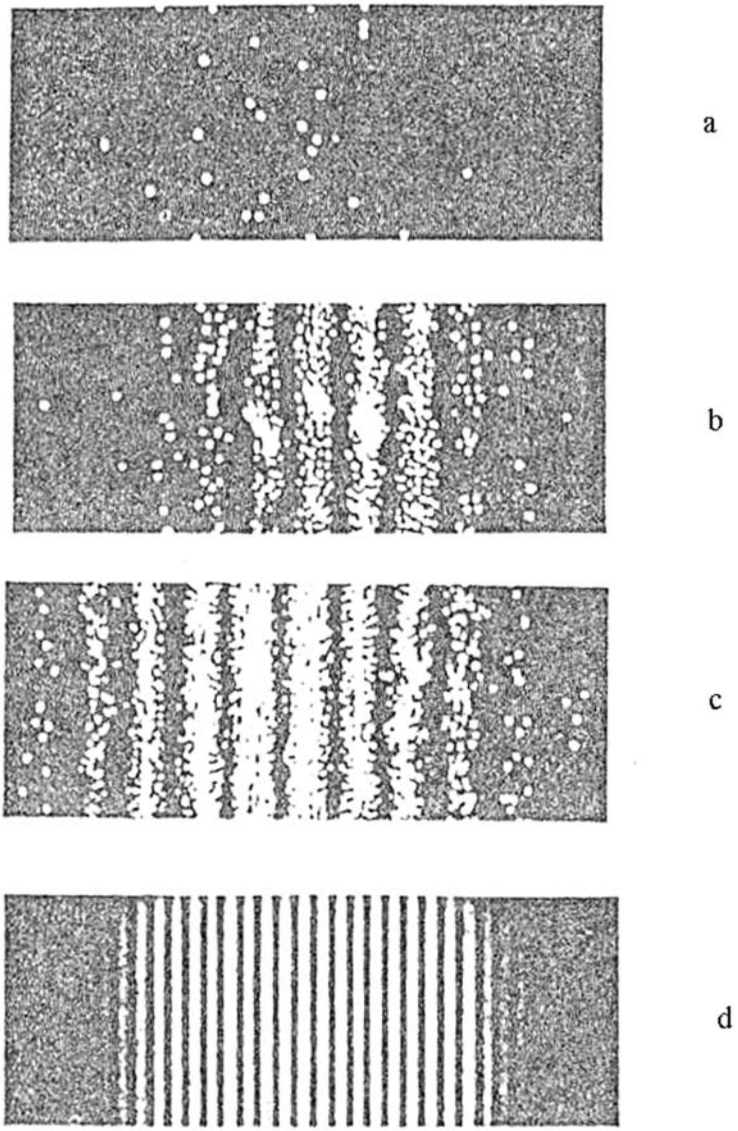

Figure 7-13. Growth of the interference-diffraction picture (only the central maximum is shown) when a beam of photons is incident on a double-slit system. The photographic plate is struck by: a) 28 photons: b) 1000 photons; c) 10 000 photons; d) 10^6 photons. (Note that the width of the slits and the separation between them in the case d) is different than in the other cases.)

The photons have clearly expressed dual character. In one case they have the behaviour of the particles, but in other - of the waves. The idea for particle-wave duality of the photons was raised firstly by Einstein in 1917 when he suggested the introduced by Plank quanta to be considered as peculiar particles with the energy $E = \hbar\omega$ and momentum $p = \hbar\omega / c$ (the photons one call them after 1923).

7.4 DE BROGLIE'S WAVES. WAVE-PARTICLE DUALITY

Let summarize the principal problems considered up to now. The Maxwell's theory for the electromagnetic waves and the experiments of Hertz prove the wave nature of the radiation. However this wave theory can not explain some experimental facts as the spectrum of blackbody radiation, photoelectric effect, the specific heat of solids and the Compton effect. For their explanation one suggests the hypothesis of the quanta (the photons), according to which the radiation has discrete character and exhibit particles-like properties. To every electromagnetic wave with frequency ν and wavelength λ can be associated energy E and momentum p so that:

$$E = \hbar\omega = h\nu, \qquad p = \hbar k = \frac{h}{\lambda}. \tag{7.33}$$

Discreteness and wave-particle dualism are two basic ideas, which have not an analogue in classical physics and which development leads up to quantum mechanics.

In 1924 Louis de Broglie did the next step. He suggested that *if the radiation had a particle-like nature, then it should follow from basic concepts of symmetry that particles ought to posses a wave-like nature.* Moreover he went out to suggest that the same basic relationships about the energy and the momentum should exist in the both case. Thus *the frequency and the wavelength of the waves in order to be associated with particles ought to be related to their energy and momentum by the same relation* as Eqs. (7.33):

$$\begin{aligned} &\nu = E / h, \qquad \lambda = h / p, \qquad \text{or} \\ &\omega = E / \hbar, \qquad k = p / \hbar. \end{aligned} \tag{7.34}$$

Thus for particles the equalities (7.33) have a real physical sense if they are read from right to the left. So we get to the fundamental connection between particles and waves. The waves associated with particles are called de Broglie's waves. Then, taking into account the relativistic character of the energy, de Broglie maintains the connection between the phase v_{ph} and the group v_g velocities of these waves with the velocity v of the particles.

Substituting the wave characteristics ν and λ and taking into account that $E = mc^2$ we obtain

$$v_{ph} = \lambda\nu = \frac{E}{p} = \frac{mc^2}{mv} = \frac{c^2}{v}. \tag{7.35}$$

As always $v < c$, *the phase velocities of the de Broglie's waves is greater than the velocity of light.*

According to the definition, the group velocity is $v_g = \partial\omega / \partial k$. Passing from wave to particles characteristic and finding the derivation $\partial E / \partial p$, we obtain following:

$$E^2 = p^2c^2 + m_0^2c^4, \quad \frac{\partial E}{\partial p} = \frac{pc^2}{E}, \quad v_g = \frac{\partial\omega}{\partial k} = \frac{\partial E}{\partial p} = \frac{mvc^2}{mc^2} = v. \tag{7.36}$$

The group velocity of the de Broglie's wave is equal to the particle velocity.

If de Broglie's suggestion is correct, the wavelength of the associated wave with a microscopic particle is $\lambda = h/p$. For example, for an electron after it has been accelerated through say 150 volts it is $\lambda = 1$ Å and for some atoms at room temperature it is as follows: for H it is $\lambda = 1{,}2$ Å (for the molecule H_2 it is $\lambda = 0{,}84$ Å), for He it is $\lambda = 0{,}7$ Å, for Ag - $\lambda = 0{,}06$ Å. For an observation of the diffraction of the wave with such small wavelength one needs slits of the same order. Therefore the crystal lattice of some element (the atoms have a spacing of several angstroms between them) appears to be suitable.

The first experimental proof of the existence of matter wave was being undertaken by Davisson and Germer in 1927. Their brilliant experiment is shown on Fig. 7-14. A beam of electrons is directed onto the surface of nickel crystal. The electrons have been elastically scattered from the crystal surface. Angular distribution of the scattered electrons has been measured. The electron scattering was found to have very pronounced maxima and minima. For the distribution they received a diffraction picture of dark and light rings which intensity decreased out of the centre. The explanation of this is trivial if accept the hypothesis of de Broglie, that with the electron can be associated a wave with wavelength λ. A study of Fig. 7-14 indicates that the path-length difference for rays, which have been scattered from successive layers of nickel, is given by $2d\sin\theta$. At the condition (Bragg relations)

$$\begin{gathered} 2d\sin\theta = n\lambda, \\ 2d\sin\theta = (n+\frac{1}{2})\lambda \end{gathered} \tag{7.37}$$

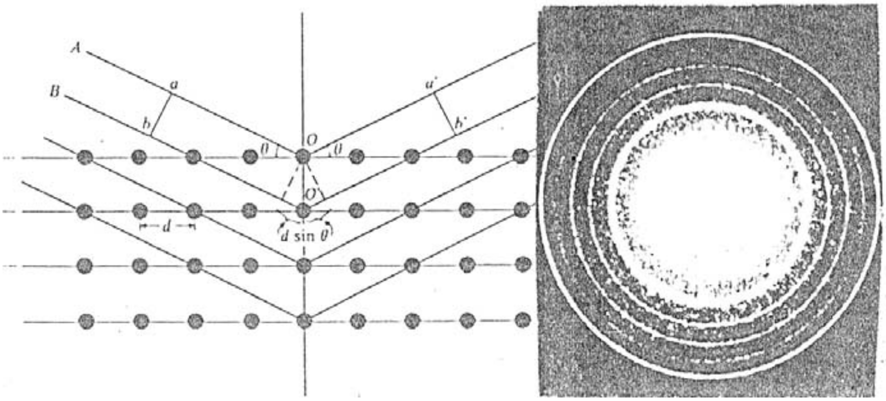

Figure 7-14. The experiment of Davisson and Germer: a beam of electrons incidents on at monocrystal (a); The electrons reflected from successive atomic layers with a path-length $\Delta = 2d\sin\theta$ interfere according to the de Broglie hypothesis and as a result one get the diffraction picture (b).

one obtains correspondingly bright and dark rings.

The experiment of Davisson and Germer is a realization of the considered experiment criterion and proves that the particles, such as electrons, exhibit wave-like properties. More than this, in 1949 Russian physicist Fabricant passed weak electron beam through the diffraction apparatus, which corresponded, to our criterion. The time interval between two electrons was larger than the pass time (the time from source to the screen) 10^4 time. In fact the electrons pass individually. The registration was made by the fluorescent screen. The result was analogous to the corresponding experiment with photons and the view was analogous to the Fig 7-12 and Fig. 7-13 (the difference was only in wavelength). Like the photons the electrons were registered as particles. But after a long exposition (many electrons) their distribution on the screen forms a diffraction pattern and fall into their bands (rings).

A lot of experiments prove dual character of the microscopic objects. (To the last ones we relate the photons, the molecules, the atoms and the elementary particles.) *It is remarkable that one and the same* *object once exhibit wave properties* (*the photons and the electrons diffract when they pass through the slits of enough small dimensions - the diffraction grating or the crystal lattices*), *but the other time - particle properties* (*the photons - the photoelectric effect and the effect of Compton, the electrons - for example in the cathode-ray tube*). *Sometimes a microscopic object exhibits itself as a wave* (*for example at the propagation*), *but some times - as particles* (*for example at the registration*). But this does not mean "it behaves as it wants". Quantum mechanics allows defining in which experiments it will appear as a particle and in which - as a wave. *In modern physics the wave-particle dualism is understood as potential possibility of the microscopic object to exhibit these or those properties in the dependence of the outer conditions* (in particular plus the measurement and the observe conditions). Clearly and shortly the essence of the dualism is expressed by V. A. Fock in the article "For Interpretation of Quantum Mechanics" (V. A. Fock, Philosophy Question of the Modern Physics, Moscow, AS of SU (in Russian)) so: "*One may say that the potential possibility exists for atomic objects to appear or as a particle, or as a wave on dependence of the outer condition. The wave-particle dualism consists namely, in this potential possibility of different appearing of the property inhered of the microscopic object.* Every other, literal understanding of this dualism as some model is not correct".

The microscopic object is neither a particle nor a wave. It is a peculiar object, which can appear wave-like and particle-like properties depending on the conditions.

Let us summarize some important properties of the dualism. The phenomenon of interference is inhered to all microscopic objects. It cannot be explained by the interaction of the microscopic objects between them, i.e. neither by their collective properties, but by the properties of the separate, individual microscopic object. From the experiment-criterion it is clear that it is impossible to predict in which point of the screen the single microscopic object will fall. But one can predict the behaviour of the great number of the microscopic objects, i.e. how they will be distributed on the screen.

The interference-diffraction picture is obtained and when the microscopic objects are launched one by one to the double slits (see I_{12} on Fig. 7-11). This picture is not a sum of the pictures when one of the slits is covered up, i.e. $I_{12} \neq I_1 + I_2$. Therefore we are forced to recognize that the photon passes some how through both slits at the same time. If we suppose that it passes through only one of the slits we must admit that it "knows" about the existence of the other slit and it is influenced by this knowledge. Of course from such concept the phenomena do not become clearer and more obvious. It is impossible to imagine how this happens, but the experimental fact remains.

At the end, when we have a notation for the basic ideas - a discreteness and a wave-particle dualism - we shall underline *the fundamental role of the Planck's constant. First it serves as a measure of the discreteness of the microscopic systems. It defines the bundle* $h\nu$ *of the radiation energy and the step* $h/2\pi$ *of changing of the orbital angular momentum. It serves and as a measure of the limit of the microscopic phenomena* (*the quantum phenomena*) *and the macroscopic phenomena* (*the classical phenomena*). For example, if the orbital angular momentum is much greater that $\hbar$ the quantization may be neglected and the angular momentum may be considered as classical one. In this aspect it is interesting to note that the intrinsic angular momentum S can not be essentially large. Therefore the quantization can not be neglected and the spin has not a classical analogue!

Second it plays the role of a connection between the wave $(\omega, \mathbf{k})$ *and particles'* $(E, \mathbf{p})$ *properties of the microscopic objects:* $E = \hbar\omega$, $\mathbf{p} = \hbar\mathbf{k}$. *We would like to underline that one and the same constantplays the both roles. This fundamental fact results from the intrinsic unity of the both basic ideas of quantum mechanics.*

SUMMARY

The principal difficulties of classical physics when it tries to explain the properties of the microworld are in the following phenomena: the blackbody radiation, the photoelectric effect, the specific heat of solid state, the atomic spectra and the atom structure, the X-rays and the Compton effect. In all these phenomena the difficulties arise from the mechanism of interaction of the mater with radiation.

The main particularity of the phenomena of the microscopic world consists of character discreteness, appearing in the existence of an indivisible quantum of action h. This discreteness of the action is one of the most fundamental properties of the Nature. In macroscopic scale h is infinitesimal value and neglecting it we can consider dynamical values classically as exactly defined and changing continuously. In atomic and subatomic physics h can not be neglected and the phenomena are purely quantum ones. The discreteness, i.e. the quantization is observed as at the radiation (quanta $h\nu$) as at the matter (the qauntization of the energetic levels and the orientation of the angular momentum of the electrons in the atoms and etc.).

In some experiments the photons exhibit as wave (interference and diffraction), but in others - as particles (a photoelectric effect, a Compton effect). The same appears for microscopic particles as well. They may interfere and diffract (a diffraction of electrons and neutrons) or register as particles on the screen, on the photographic plate or in Wilson camera. Microscopic objects can exhibit as waves or as particles depending of the conditions. The compatibility of these properties is not possible in classical physics. The wave-particle dualism is the second basic idea in quantum mechanics.

Planck, Einstein, Bohr and de Broglie did the first suggestions and hypothesis, which led to the development of these ideas.

Planck - the energy emission and the absorption of electromagnetic radiation are discrete with quanta $\hbar\omega$

$$E = \hbar\omega.$$

Eistein - the light is a beam of Planck quanta (photons); later: the photons (the quanta) with an angular frequency ω and a wavelength λ can be considered as particles of energy E and a momentum p

$$E = \hbar\omega, \qquad p = \hbar k.$$

Bohr - the quantization (the discreteness) is character for the atom - the energies between the energetic levels are equal to the Planck quanta; the space quantization is multiple to the Planck constant.

De Broglie - as the photons with a frequency ν and a wavelength λ can appear as particles with energy E and momentum p so the microscopic particles with energy E and a momentum p can appear as waves with a frequency ν and a wavelength λ ($\nu = E/h, \lambda = 2\pi/k = h/p$) - wave-particle dualism.

QUESTIONS

1. What could not explain classical physics in the blackbody radiation?
2. Which is the experimental and theoretical (classical) dependence of the specific heat of solid state on the temperature?
3. Why is not the Rutherford's model realistic one according to classical physics?
4. What is the relation between the wavelength of the incident and scattering wave, when Roentgen wave are scattered by free electrons?
5. What is the idea of Planck for explanation of blackbody radiation?
6. What is new in comparing the suggestion for the explanation of photoelectric effect with the idea of Planck?
7. How do you explain physically the increase of the wavelength of the scattered wave of the Compton effect using the Planck's quanta?

8. What do you understand when it is said that the phenomenon interference is presented in every diffraction?
9. How do the diffraction patterns from one and two slits (apertures) differ?
10. What is the income of the diffraction and of the interference of photons, passing trough two slits?
11. What are the basic categories of classical objects and how do they differ from one another?
12. What is the principal difference in passing of particles and wave through two slits?
13. In what does the dualism consist of the electrons, passing one by one through two slits? Through which slit does a single electron pass?
14. What is the connection of the group velocity of de Broglie waves with the particle properties of the microscopic objects?
15. What does the experiment of Davisson and Germer prove?
16. How does modern quantum mechanics interpret the dual character of the microscopic objects?
17. Which are the both basic ideas of quantum mechanics?
18. What is the role of the Planck constant in the both basic ideas of quantum mechanics?

PROBLEMS

1. In a photoelectric-effect experiment, it is found that when the surface of sodium metal is illuminated with light of wavelength $\lambda = 4200$ Å, the stopping potential is $V_0 = 0{,}65$ V. When a metal is illuminated with light of wavelength $\lambda = 3100$ Å, the stopping potential is $V_0 = 1{,}69$ V. Calculate Planck constant for these data.
2. Calculate the de Broglie wavelength associated with an electron with a kinetic energy of 150 eV.
3. Obtain the dependencies $\omega(k)$, $v_{ph}(k)$ and $v_g(k)$ for the de Broglie plane wave, which describes the free motion of a particle of rest mass m_0.
4. Find out the wavelength of the de Broglie wave for a nonrelativistic particle of mass m_0 and temperature T_0.
5. The photons with a wavelength $\lambda = 0{,}024$ Å impinge on free electrons. Calculate the wavelength of the photon that scattered at the angle 30° and kinetic energy of the electron. Which will be these values at the scattering angle 120°?
6. How many infrared light quanta with the wavelength $\lambda = 10$ μm (the frequency $\nu = 3.10^{13}\ \mathrm{s}^{-1}$) are necessary to heat 1 mol water from temperature of 0 °C to 100 °C?

Chapter 8

OLD QUANTUM MECHANICS

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8.4 Success and Failures of the Old Quantum Theory
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8.1 BOHR'S MODEL

As it has been mentioned the difficult problem of the stability of the atom has been solved by the Bohr's postulates. The verification of these postulates as of any set of postulates can be found only by comparing the predictions that can be done from the postulates with the results of the experiment. In this section we consider some of these predictions and compare them with the data from Section 7.2.

Let us consider an atom, consisted of a nucleus of charge $+Ze$ and mass M and a single electron of charge $-e$ and mass m_e. Such atoms are, for instance, hydrogen atom with $Z=1$, a singly ionized helium atom with $Z=2$, a doubly ionized lithium atom with $Z=3$, etc. (The ionized atoms having only single electrons are called *hydrogen-like ions*.) According to Bohr the electron revolves in a circular orbit around the nucleus. Initially we shall suppose that the mass of electron is completely negligible compared to the mass of nucleus, i.e. the nucleus remains fixed in space. The second Netown's law for the circular motion of the electron gives

$$k_0 \frac{Ze^2}{r^2} = m_e \frac{v^2}{r}, \tag{8.1}$$

where v is the speed of the electron and r is the radius of its orbit. This is merely the equation $F = m_e a$. The Coulomb force acts on the electron and keeps it in its orbits by the normal acceleration. As the acting force is central one (see (3.18)) the orbital angular momentum of the electron must be a constant. Applying the second Bohr's postulate to the $L = m_e vr$ we have

$$m_e vr = n\hbar, \qquad n = 1, 2, 3, \ldots \tag{8.2}$$

Finding v and substituting it into (8.1), we obtain

$$r = \frac{n^2\hbar^2}{k_0 m_e Z e^2} = \frac{n^2 a_0}{Z}, \qquad \frac{\hbar^2}{k_0 m_e e^2} \equiv a_0, \qquad n = 1, 2, 3, \ldots \tag{8.3}$$

Now from the Eq. (8.2) it is easy to define the speed v of the electron

$$v = \frac{n\hbar}{m_e r} = \frac{k_0 Z e^2}{n\hbar}, \qquad n = 1, 2, 3, \ldots \tag{8.4}$$

The application of the Bohr's rules of the angular-momentum quantization is restricted to allowed ones of the radii $r \propto n^2$ (8.3). Replacing the known values of the constants we obtain for the radius of the smallest orbit (n=1) of the hydrogen atom (Z=1) as follow

$$r_1 = a_0 \equiv \frac{\hbar^2}{k_0 m_e e^2} = 0{,}53.10^{-10}\,\mathrm{m} \approx 0{,}5\ \text{Å}. \tag{8.5}$$

A little further on we shall show that the electron has minimal total energy on the orbit with n=1. Therefore we may interpret this radius as a radius of a hydrogen atom in its normal state. The other methods gives an estimate of the order of magnitude 1 Å. So the Bohr's postulates predict a reasonable size for the H atom. For the orbital speed v in the normal state we obtain from (8.4) $2{,}2.10^6$ m/s. It is apparent from the Eq. (8.4) that this is the maximal possible velocity for the electron of the hydrogen atom. This velocity is much smaller than the velocity of light (~1%) and this fact allows to use classical mechanics for the H atom in Bohr's model. At the same time Eq. (8.4) shows that for large values of Z the electron velocity becomes relativistic. And an other interesting conclusion from this equation - the quantum number n cannot take the value n=0.

Knowing the velocity of the electron and the force between it and the nucleus, we can find the total energy of the electron. The potential energy at a given distance from the nucleus is

$$U = -\frac{k_0 Z e^2}{r}. \tag{8.6}$$

The potential energy of the electron is zero when it is in the infinitely distance from the nucleus and the sign is negative because the Coulomb force is attractive. From (8.1) we obtain for the kinetic energy the following:

$$T = \frac{1}{2} m_e v^2 = \frac{k_0 Z e^2}{2r}. \tag{8.7}$$

Then the total energy E of the electron is

$$E = U + T = -\frac{k_0 Ze^2}{2r} = -T. \tag{8.8}$$

Substituting in this formula r from (8.3), we have

$$E_n = -\frac{k_0^2 m_e Z^2 e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{Z^2\mathfrak{R}}{n^2}, \qquad n = 1,2,3,\ldots \tag{8.9}$$

Substituting the value of m_e, k_0, e and $\hbar$ we receive for the constant $\mathfrak{R}$ approximately

$$\mathfrak{R} = \frac{m_e e^4 k_0^2}{2h^2} = 2{,}17.10^{-18}\ \text{J} = 13{,}6\ \text{eV}. \tag{8.10}$$

From the expression (8.9) we can do an important conclusion: *the quantization of the orbital angular momentum leads to the quantization of the total energy of the electron.* The energy-level diagram is shown in Fig. 8-1. With the increasing quantum number n the total energy becomes less negative.

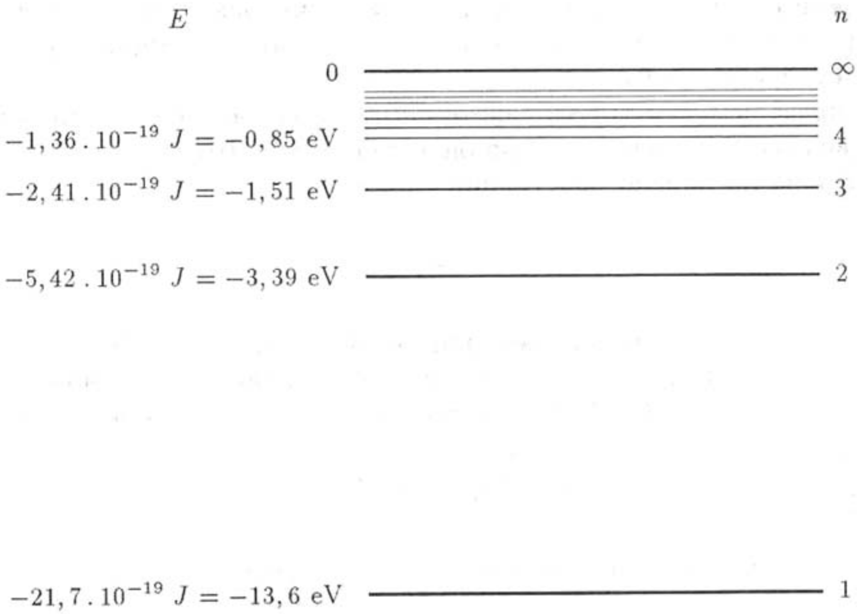

Figure 8-1. An energy-level diagram for the hydrogen atom.

And it approaches zero as n approaches infinity. The normal state of any system is the state with lowest energy. From the diagram we see that this is the state with n=1. From Eqs. (8.9) and (8.10) for the H atom (Z=1) we obtain

$$E = -\Re = -13{,}6 \text{ eV}, \tag{8.11}$$

which very well fits the experimentally obtained binding energy for H atom.

Let us consider the next situation. Initially an electron moves in an orbit with quantum number n_i; then it changes its state to one with number n_f ($n_i > n_f$). When the electron makes such transition it emits the electromagnetic radiation of frequency ν. Using the Bohr's model, namely the fourth postulate, and (8.11) we obtain

$$\nu \equiv \frac{E_i - E_f}{h} = \frac{Z^2\Re}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = Z^2\mathscr{R}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{8.12}$$

where $\mathscr{R}$ stands for

$$\mathscr{R} \equiv \frac{\Re}{h} = \frac{k_0^2 m_e e^4}{4\pi\hbar^3} \approx 3{,}27.10^{15} \text{ s}^{-1}. \tag{8.13}$$

Going to spectroscopic frequency (see (7.6)) we can write (8.12) in the following form:

$$\nu^* = \frac{\nu}{c} = \frac{Z^2\mathscr{R}}{c}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right). \tag{8.14}$$

The expressions (8.9) and (8.12) allow concluding:

1. The state with the lowest energy, which is called *ground state* (sometimes it is called *normal state*) is the state with $n = 1$.
2. The states, in which $n > 1$ have higher energy and they are called *exited states*. In some physical processes the electron receives additional energy and it makes transition to these states.
3. Any physical system tends to the lowest energy. Thus, an electron in an excited state makes the series of transitions to the states of lower energy. At every transition the difference of energy ΔE between levels is emitted as a photon with the frequency $\nu = \Delta E / h$ under the form of the electromagnetic radiation. For example, the electron is exited into state $n = 6$ and transits successively to the states $n = 4$, $n = 3$, $n = 2$ and

$n=1$. Four lines of the hydrogen spectrum are emitted with frequency given by (8.12) ($Z=1$) for $n_i=6$ and $n_f=4$, $n_i=4$ and $n_f=3$, $n_i=3$ and $n_f=2$, and $n_i=2$ and $n_f=1$.

4. During the measurement of the atom's spectrum a very large number of atoms are excited and then successively deexcited. So all possible transitions occur and the complete spectrum is emitted. The frequencies of the spectral lines are defined by (8.12). For emission spectrum $n_i > n_f$.

When Bohr suggested his hypothesis the Balmer series had been well known. Therefore let us consider the series of spectral lines of hydrogen with $n_f=2$ and any $n_i>2$. According to (8.14) the spectroscopic frequencies of these lines are following:

$$\nu^* = \frac{\mathscr{R}}{c}\left(\frac{1}{2^2}-\frac{1}{n_i^2}\right), \qquad n_i = 3, 4, 5, ... \tag{8.15}$$

This coincides with the phenomenological formula (7.6) for the Balmer series if the relation

$$\frac{\mathscr{R}}{c} = \frac{k_0^2 m_e e^4}{4\pi\hbar^3 c} \tag{8.16}$$

is equal to the experimentally found Rydberg constant R (7.7). Substituting the constants in (8.16) we found that $\mathscr{R}/c$ very good agrees with the experimental value of R. Thus the Bohr's model does not only explains the spectral lines but also gives the explicit view of the Rydberg constant through well known physical constants:

$$R = \frac{\mathscr{R}}{c} = \frac{\mathfrak{R}}{ch} = \frac{k_0^2 m_e e^4}{4\pi\hbar^3 c}. \tag{8.17}$$

Here we would like to note that the introduced constants $\mathfrak{R}$ (8.10) and $\mathscr{R}$ (8.13) are received by multiplying Rydberg constant with other constants - respectively by ch and c. Customarily the three constant values are called Rydberg constants, being expressed R in m^{-1}, $\mathscr{R}$ in s^{-1} and $\mathfrak{R}$ in J or eV.

According to Bohr each of the known series for the H atom (Table 7-1) arises as the transitions of an electron to the fixed final state n_f. The first five series are shown in Fig. 8-2. Only the lines of the Balmer series are in

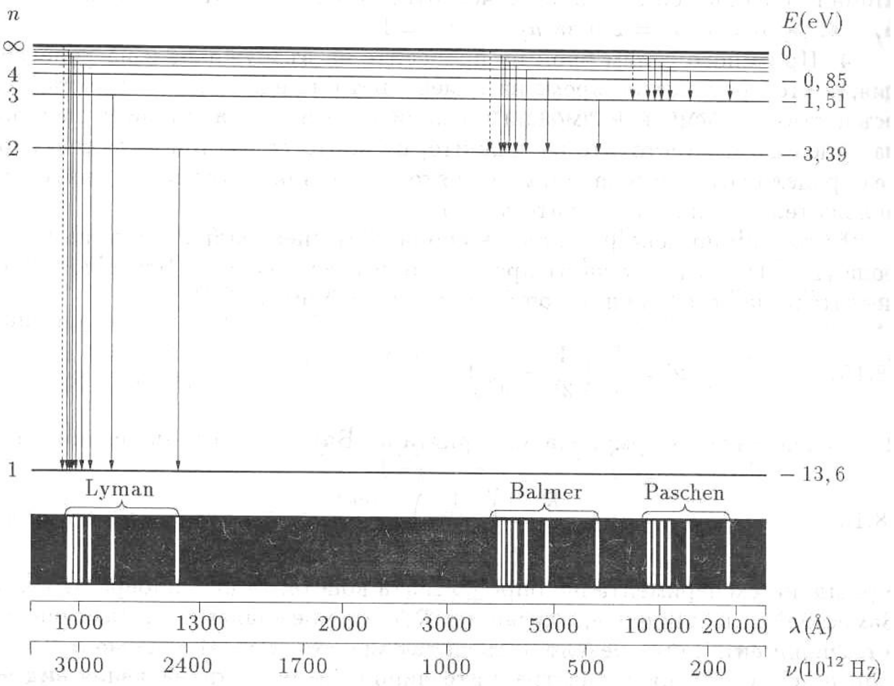

Figure 8-2. Energy-level diagram for hydrogen with some of the possible transitions (top) and the corresponding spectral lines for the shown three series.

the visible region. This is the reason why the other series were discovered only after they had been predicted by Bohr theory (these series were named after the scientists who experimentally discovered them). This was a great triumph for Bohr's model.

We have obtained for one-electron atom the spectrum (8.14) for arbitrary *Z*. If we take singly ionized helium atom for which $Z = 2$, we obtain the spectrum that agrees very well with the experimentally obtained one. The spectrum of He^+ is analogous to the spectrum of the hydrogen, but frequencies of the lines are four ($Z^2 = 4$) times as great.

Above we assumed the mass of the nucleus to be infinitely larger than the mass of an electron. Now we shall evaluate this approximation, taking into account that the nucleus mass is in fact finite. In such a case the electron and the nucleus move around the their common centre of the mass. According to the analysis performed in Chapter 3, we can use the results, obtained for the fixed nucleus replacing in them the mass of the electron m_e with the reduced mass $\widetilde{m}$ of the system:

$$\widetilde{m} = \frac{m_e M}{m_e + M}. \tag{8.18}$$

Here M is the mass of the nucleus. Because of this fact the Rydberg constant is actually less than that evaluated by (8.17) by a factor $1/\left(1 + m/M\right)$. For the hydrogen atom it is only with 1/2000 fraction less than $\Re$:

$$\Re_{\widetilde{m}} = \frac{\widetilde{m}}{m_e}\Re. \tag{8.19}$$

Here $\Re_{\widetilde{m}}$ stands for the Rydberg constant of a single-electron atom with reduced mass $\widetilde{m}$.

8.2 INTERPRETATION OF THE QUANTIZATION RULES

The Sections 7.2 and 8.1 have given evidence, that the energy of an electron in an atom is quantizied. If E is to be quantized, some restriction has to place on fixed series of values, such as r, v or some functions of them. Bohr had chosen to restrict the angular momentum. But no indication has been given of why this should be so or how the values, which the energy may have, can be calculated. The Bohr'r postulates are in the base of the so-called old quantum mechanic which is a mix of classical mechanic and rules of quantization. Now it has been replaced by new quantum mechanics, which is described in the following chapters. But the old quantum mechanics is of great historical interest and is extremely useful in giving a qualitative description of the behavior of the atoms. So we think that it is well worth understanding it and their qualitative picture would be very helpful to the chemists. The old quantum mechanics is exposed in details in the book of Sommerfeld [R33].

In 1916 Wilson and Sommerfeld, trying to solve the mystery of the Bohr's postulates, suggested a rule for quantization:

For a given physical system any co-ordinates, which is a periodic function of time, satisfied the quantum condition

$$\oint P_q dq = n_q h, \tag{8.20}$$

where q is one of the generalized co-ordinate, P_q is a generalized momentum canonically conjugated with it, n_q is an integer quantum number and the integration is taken over one period of the co-ordinate q.

Planck has considered the blackbody radiation as the set of the sinusoidal waves and therefore let illustrate the quantization rules by an example of one-dimensional harmonic oscillator with mass m. According to Section 5.2 its total energy as a function of the co-ordinate x and the momentum p_x (for the oscillator the canonically conjugated momentum p_x of the co-ordinate x is equal to the mechanical momentum (see Section 6.5)) is:

$$E = T + U = \frac{p_x^2}{2m} + \frac{\kappa x^2}{2}. \tag{8.21}$$

In phase space (x, p_x-plane) this is the equation of the ellipse (Fig. 6-2c) with the semiaxes $a = \sqrt{2E/\kappa}$ and $b = \sqrt{2mE}$ - $x^2/a^2 + p_x^2/b^2 = 1$. The value of the integral $\oint p_x dx$ is equal to the area of this ellipse πab:

$$\oint p_x dx = \pi\, ab\,. \tag{8.22}$$

Substituting in this equation the semiaxes a and b we obtain:

$$\oint p_x dx = 2\pi E/\omega_0\,, \tag{8.23}$$

where $\omega_0 = \sqrt{\kappa/m}$ is a natural angular frequency of the oscillator. If now we apply the Wilson-Sommerfeld quantization rule (the co-ordinate x is a periodical function of time) we have:

$$\oint p_x dx = 2\pi E/\omega_0 = n_x h \equiv nh \qquad \Rightarrow \qquad E = nh\nu\,. \tag{8.24}$$

Thus using the Wilson-Sommerfeld quantization rule we obtain Planck's quantization law.

As a second example we shall consider the Bohr's rule of the angular-momentum qauntization. We shall show that it can be deduced from the Wilson-Sommerfeld rule. According to the Bohr's model the electron of hydrogen is revolving around the proton in a circular orbit with the constant angular momentum L. The angular co-ordinate φ is a periodic function of time. As the function of time it increases linearly from zero to 2π in one period and this is repeated in each succeeding period. The generalized momentum for the co-ordinate φ is angular momentum L (see Table 6-2). The Wilson-Sommerfeld quantization rule (8.20) for the considered case becomes

$$\oint L d\varphi = nh\,. \tag{8.25}$$

But as the angular momentum is constant (see for details Section 3.3) the simple integral on the left side is equal to $2\pi L$. Hence from (8.25) we have

$$2\pi L = nh, \qquad \Rightarrow \qquad L = \frac{nh}{2\pi} \equiv n\hbar. \tag{8.26}$$

But this is a Bohr's quantization rule and in the old quantum mechanics it can be deduced by the Wilson-Sommerfeld quantization rule. The physical meaning of the Bohr's quantization rule was given in 1924 by de Broglie. According to his hypothesis a wave is associated to every particle. But an electron in atom is shut up in a confined space, and the associated wave is therefore a standing wave. According to Bohr's model the electron in an atom moves in a circle. This does not correspond to the reality, since the electron in atom, as the new quantum mechanics shows, is not constrained to move in a circle. But this gives an elegant and simple connection between the quantization ant the wave properties of the electron. Consider the electron at point P in the Fig. 8-3a, at a distance x from some fixed point O on the circle, measured along the circumference. The wave, which describes it moving around the circle with velocity v, is

$$\psi = \cos(\omega t \pm kx) \qquad k = m_e v / \hbar.. \tag{8.27}$$

The plus or minus represents that the wave can propagate in either direction, i.e. the electron can traverse the orbit in either direction. The both waves superimpose and form the standing wave. This wave is fully analogous to the standing wave of a string secured at both ends. But if the wave function is to come back to the same value on going round the circle, so that it is single valued, an integral number of wavelengths must fit into the

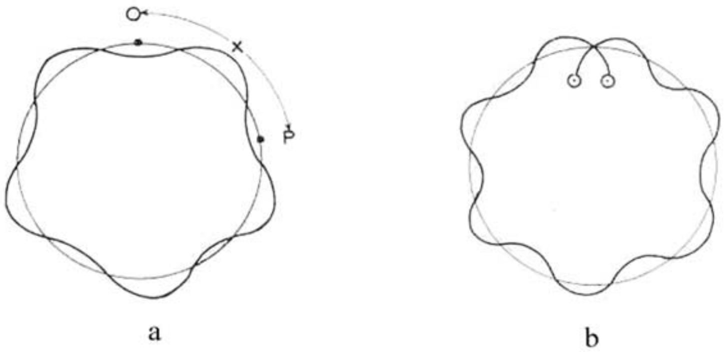

Figure 8-3. Wave function of a particle on a circle. a) A continuous single-valued solution of the equation, which does describe a physical state - this is an *n* (*n*=5) *equivalent* of a standing de Broglie wave. b) A solution which does not describe a physical state.

circumference. Otherwise there will be a misfit (Fig. 8-3b). So, it follows that

$$n\lambda = 2\pi r\ . \tag{8.28}$$

Here r is the radius of the circle and n is an integer. Using (7.34) for the electron ($\lambda = h / m_e v$), this gives

$$m_e v r = n\hbar\ , \tag{8.29}$$

which is the Bohr's condition for the quantization of the angular momentum.

There is however one important difference between this condition and the Bohr's postulates (7.14). There is no reason why n should not have the value zero in Eq. (8.29). Actually, the new quantum mechanics shows the angular momentum in the state with minimal energy is zero.

We shall consider one more example, from which one can see, that the Wilson-Sommerfeld rule is connected with the requirement that the de Broglie waves form a standing wave. Consider a particle of mass *m*, which moves freely along the *X*-axis from $x = 0$ to $x = a$. We can imagine that the free electron moves in one-dimensional piece of metal. The particle bounces back and forth between the ends of the region with constant magnitude of the momentum $p_x = p$, which only changes its sign. As the co-ordinate *x* is a periodical function, we can apply the Wilson-Sommerfeld quantization rule:

$$\oint p_x dx = \oint p dx = p\oint dx = p2a = nh \qquad \Rightarrow \qquad n\frac{h}{p} = 2a\,. \tag{8.30}$$

But according to (7.34) *h/p* is just the de Broglie wavelength of the particle:

$$n\frac{\lambda}{2} = a\,. \tag{8.31}$$

Thus an integral number of de Broglie half wave fits the trajectory of the particle in one traversal of the region, giving the possibility the waves with successive traversals to be in phase and hence to set up a standing wave.

The considered example has an interesting result. For the energy of the particles we easy obtain:

$$E = \frac{p^2}{2m} = \frac{n^2h^2}{8ma^2} = \frac{\pi^2\hbar^2}{2ma^2}n^2\,. \tag{8.32}$$

The discussed example is identical to the problem of particle in the infinite square well potential. In quantum mechanics this problem can be solved exactly (Section 12.2). The obtained here result coincides with the precise result within the coefficient. It is important to underline that the energy of the particle is quantizied.

8.3 SOMMERFELD'S MODEL

We know from classical mechanics that electron in hydrogen atom can move in elliptic orbits (Section 3.4). Assuming the elliptical motion in polar co-ordinate r and φ, which are periodical functions of time, we can apply the Wilson-Sommerfeld's rule. At this, a generalized momentum for the co-ordinate φ is angular momentum L and for co-ordinate r - the r-component p_r of the momentum p, and we can write the following:

$$\oint L d\varphi = n_\varphi h, \qquad \oint p_r dr = n_r h. \tag{8.33}$$

The first quantum condition is the same as about the circular motion and we know the restriction on the angular momentum:

$$L = n_\varphi \hbar, \qquad n_\varphi = 1, 2, 3, ... \tag{8.34}$$

The second relation gives the relationship between angular momentum and semiaxes of the ellipse (see Fig. 4-3):

$$L(a/b-1)=n_r\hbar, \qquad n_r=0,1,2,3,... \tag{8.35}$$

Here *a* and *b* are the semimajor and semiminor axes of the ellipse. In the Bohr-Sommerfeld model the Bohr quantization (7.14) for angular momentum for a circular orbit is replaced by two quantum conditions: one for radial momentum p_r with radial quantum number n_r and one for angular momentum L_φ with azimutal quantum number n_φ.

Sommerfeld has used third equation (the details can be seen in [R35]), which gives him possibility to find the three unknown quantities - semimajor and semiminor axes *a* and *b* and also the energy of the electron. The complete analysis shows that the energy depends only on the sum of the two quantum numbers:

$$n=n_\varphi+n_r, \qquad n=1,2,3,... \tag{8.36}$$

The quantum number *n* is called principal quantum number. For our short exposition it is enough to give only the energy:

$$E=-\frac{k_0^2\widetilde{m}Z^2e^4}{2n^2\hbar^2}. \tag{8.37}$$

Here $\widetilde{m}$ is the reduced mass (8.18) of the electron and the nucleus. The energy depends on principal quantum number *n,* but not on numbers n_r and n_φ. To each value of *n* there are *n* different allowed orbits, which have the same energy. Thus, when $n=1$, $n_\varphi=1$ and $n_r=0$ the orbit is circular; when $n=2$, either $n_\varphi=2$ and $n_r=0$ or $n_\varphi=1$ and $n_r=1$ (two orbits); when $n=3$ there are three possible orbits, corresponding to the azimuthal numbers $n_\varphi=1,2,3$. For this values of *n* the orbits are shown in Fig. 8-4. The similar phenomenon is observed in planetary and satellite motion, which is governed by the gravitational force. It is the inverse square force, i.e. it is change analogous to the acting in the atom Coulomb force as $1/r^2$.

Here we shall note that, as we shall see later, quantum mechanics proves that an electron in an atom can have angular momentum $L=0$, i.e. $n_\varphi=0$. The visualization of the Bohr-Sommerfeld model is very useful. In order to use it for qualitative illustrations we are forced to imagine the case with $L=0$ as "the motion" along a line segment forward and backward in relation to the nucleus (see Fig. 14-7). This interpretation is present in Fig. 8.4. We underline that this is an imagination, not reality.

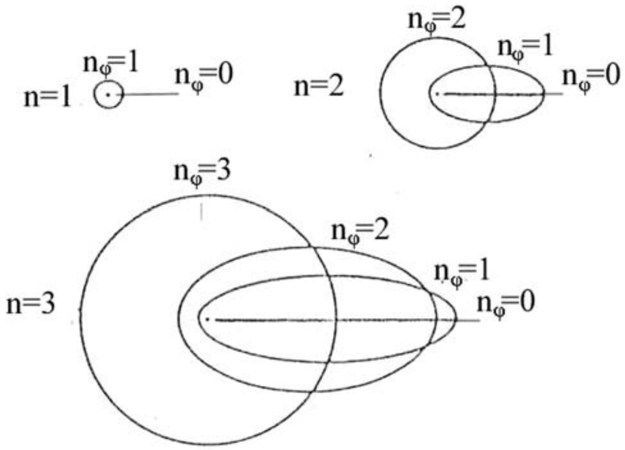

Figure 8-4. The elliptical Bohr-Sommerfeld orbits for *n*=1, 2, 3. The indicated by the dot nucleus is located at the focus of the ellipses. To illustrate the motion with *L*=0 which is proved both by new quantum mechanics and experimentally we are forced to imagine the elctron motion as a "motion" along a line segment forward and backward.

The analysis above in the frame of the Bohr-Sommerfeld model shows that the energy of the electron does not depend on the angular momentum, i.e. it is defined only by the quantum number *n* and the state with fixed *n* and consequently with energy E_n in reality consists of *n* state with this energy but with different angular momenta. The introduction of elliptical orbits does not introduce any new energy levels. The problem of the splitting of the spectral lines, which has been experimentally proven, remains. Sommerfeld showed that it could be solved if relativistic effects are taken into account. The electron in a circular orbit has constant velocity, but the electron in an elliptical orbit has different velocities in different positions, accelerating up when the electron is near the nucleus and slowing down when it is far away. This will lead to the relativistic variation of the mass of the order $(v/c)^2$. Due to this the elliptical path actually becomes a precessing ellipse, i.e. a rosette, analogous to that in Fig. 4-4. The precession rate depends on *L,* i.e. it depends on n_φ. Hence energy of the electron depends except on quantum number *n*, also and on n_φ. Sommerfeld showed that the energy is equal to

$$E = -\frac{k_0^2 \tilde{m} Z^2 e^4}{2n^2\hbar^2}\left[1+\frac{\alpha^2 Z^2}{n}\left(\frac{1}{n_\varphi}-\frac{3}{4n}\right)\right]. \tag{8.38}$$

The quantity α is a number, which is expressed by fundamental physical constants and is called *the fine structure constant*:

$$\alpha \equiv \frac{k_0 e^2}{\hbar c} = 7{,}297.10^{-3} \approx \frac{1}{137}. \tag{8.39}$$

Fig. 8-5 shows the energy-level diagram for the first three level of the hydrogen atom in which the relativistic effects are taken into account. Lines corresponding to the transitions represented by the solid lines are in very good agreements with the experimentally observed ones. The lines corresponding to the transitions represented by the dashed lines are not found experimentally in the spectrum. Only those transitions are observed for which n_φ changes by unity - $\Delta n_\varphi = \pm 1$.

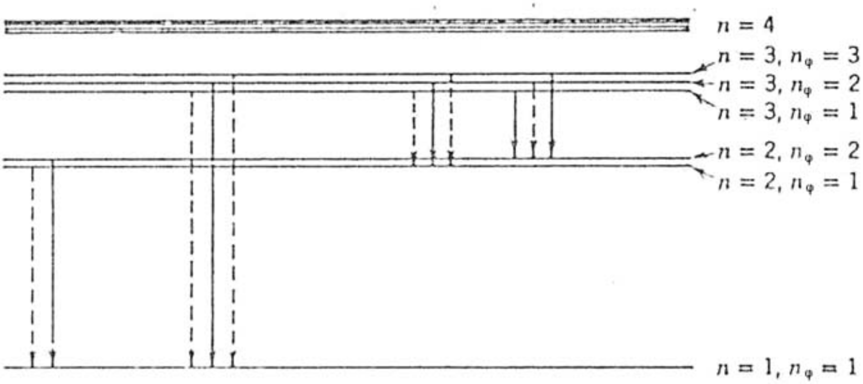

Figure 8-5. Energy-level diagram with relativistic correction that leads to the fine structure - the transitions with dashed lines are not allowed and with solid lines are allowed.

8.4 SUCCESS AND FAILURES OF THE OLD QUANTUM THEORY

The ideas in the first steps of quantum mechanics, briefly presented in the Chapter 7 as well the exposition in this chapter are the foundations of the old quantum mechanics. Most generally it could be said that this is the classical consideration combined with different rules of quantization of Plank, of Bohr, of Wilson-Sommerfeld. In many aspects this theory was very successful. It was more successful than may be apparent to the readers, because we have not mentioned here many good applications of the old quantum mechanics, which were confirmed by the experiment.

One of the most impressive achievements of the old quantum mechanics was the quantized energy of the atomic electron, which had been observed in the experiment. The expression (8.9) gives the allowed energy value for the electron in an one-electron atom, not for the electrons in a multielectron atom or in atoms combined in molecules or solids. But the quantization is true for all atoms and for this matter for the molecules and the solids. The quantization is by no means restricted to hydrogen. It has survived the introduction of the new quantum mechanics and as we shall see in Chapter 14 has been confirmed by it though the orbital theory which Bohr used to calculate E_n for the simplest atom of H. This was amply confirmed by experiment and now we shall describe some of the experimental evidence.

The experiment of Franck and Hertz has confirmed the discrete character of the energy of an atom. The apparatus which they have used is shown schematically in Fig. 8-6a. The electrons are emitted by the heated cathode *C*. Then they are accelerated by a potential V_0 towards the anode *A,* made as a grid. Some electrons pass through this grid and if they have enough energy to overcome the small retarding potential V_r between *A* and the plate *P* reach *P*. The tube *T* is filled at low pressure with the vapors of the element under investigation. The resulting current is indicated by the ammeter *I*.

The experiment is carried out by the mercury vapor. The result is shown in Fig. 8-6b. At low voltage the current increases with increasing voltage V_0. But when V_0 reaches 4,9 V there is a sudden decrease in the current. This shows that in this case the electrons have enough energy to cause inelastic collisions with atoms of Hg. In this case the electron gives up the greater part of its energy to the atom, causing the excitation of the latest. When such electrons reach anode *A* they have not enough energy to overcome the small retarding potential V_r. At further increase of V_0 the electrons gain enough

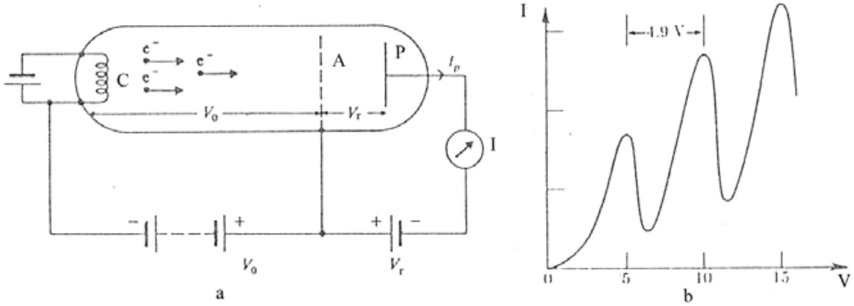

Figure 8-6. The experiment of Franck and Hertz, proving that the atomic energy is quantizied: a) schematic of the apparatus; b) the dependence of the current on the accelerating voltage.

kinetic energy to reach the plate *P* and the current I_p increases once again. If the electrons have enough energy they can cause more than one inelastic collision. Thus we can expect peaks in the current at 4,9 V, 2.4,9=9,8 V, 3.4,9=14,7 V, etc. We can see in Fig.8-6b the abrupt droppings of the current just beyond these voltages.

This interpretation is in accordance with the existence of the discrete energy level of the Hg atom. Let us suppose that first excitation state is with the energy level 4,9 eV larger than that of the ground state. Then the atom simply can not accept the energy of the striking electron, if the last has the energy smaller than 4,9 eV. If the changing of energy between the ground state and the first excitation level is really 4,9 eV there should be a line in the Hg spectrum with the photon with energy 4,9 eV. Frank and Hertz found in the experiment that when the energy of the electron is slightly above 4,9 eV only a single line is seen in the spectrum, namely the line with 2536 Å, corresponding exactly to the photon with such energy.

The old quantum theory explains many elementary aspects of the atomic spectra of hydrogen and hydrogen-like ions. But many aspects of physics of atoms, mainly of many electron atoms, remained unexplained, which did not permit it to develop as consecutive and self-consistent theory. Some of unexplained aspects are following:

1. The behavior of the systems, which are not periodic (the theory tell us how to treat systems which are periodic by using the Wilson-Sommerfeld quantization rules).
2. The spectra of atom, having more than one valence electron (the theory is only successful for one-electron atom and it treats approximately the alkali elements (Li, Ka, Rb, Cs), which have one valence electron, but it fails badly for other multielectron atoms).
3. The intensities of different transitions (the theory does not tell us how to calculate the rate of these transitions and it can not always tell us which transitions are observed and which are not).
4. All of the effects of the magnetic field on atomic spectra (the theory explains only the simplest cases, but not all).
5. The logical reason for using the different quantum numbers.

The entire theory is intellectually unsatisfying - it is not consecutive and consistent. These difficulties have been overcome by the development of quantum mechanics. But in many cases the old quantum mechanics is frequently employed as the first approximation, because its mathematical procedures are considerably less complicated than those in quantum mechanics and it is helpful the visualizing many processes in atomic world.

SUMMARY

The old quantum mechanics is in essence a classical theory to which are added the quantization rules and the dual character of the macroscopic object. Dispite of its classical character it has remarkable achievements. This is due to the using of the two basic ideas for discreteness and duality of the matter object. Many phenomena irresistible for classical physics find their explanation through the quantization rules of Planck, Bohr and Wilson-Sommerfeld and through the de Broglie waves.

The Bohr postulates give the possibility to determine the radius, the velocity and the energy of the electron at its motion in the allowed orbit. The energy is defined by the quantum number *n:*

$$E_n = -\frac{k_0^2 m_e Z^2 e^4}{2\hbar^2}\frac{1}{n^2}, \qquad n = 1,2,3,...$$

The Bohr's model explains all spectral lines of the hydrogen atom and expresses the Rydberg constant through the known constant physical values:

$$\nu^* = \frac{\nu}{c} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \qquad n_f < n_i, \qquad R = \frac{\mathscr{R}}{c} = \frac{\Re}{ch} = \frac{k_0^2 m_e e^4}{4\pi\hbar^3 c}.$$

The Wilson-Sommerfeld quantization rule generalizes the Bohr's quantization rule for every generalized co-ordinate *q*, which is the periodical function of time:

$$\oint P_q dq = n_q h,$$

where P_q is a generalized momentum associated with q, n_q is an integer quantum number. This rule allows Sommmerfeld to widen the Bohr's model, to which besides the circular orbits he adds and elliptic ones. The widen model very often is called Bohr-Sommerfeld model. With taking into account the relativistic correction of the mass in the motion along the elliptic orbits the new model allows to determine the fine structure of the atomic spectrum. It depends on so-called constant of the fine structure

$$\alpha = \frac{k_0 e^2}{\hbar c} = 7,297.19^{-3} \approx \frac{1}{137}.$$

The old quantum mechanics have had the decisive role in the creation of the modern concept of the microscopic words. With its accessible mathematics and the visualize ability today it takes an important place in the education at the understanding of the complicated categories and objects of quantum mechanics.

QUESTIONS

1. How do the radius, the velocity and the energy of the electron depend on the quantum number *n* in the Bohr's model?
2. What is the physical meaning of the radius of Bohr?
3. Why the quantum number *n* can not be zero?
4. Which are the basic conclusions that can be done about the physics of hydrogen in the Bohr's model?
5. How can the hydrogen spectrum be explained by the Bohr's model?
6. How do the finite mass of nucleus influence the Rydberg constant and the hydrogen spectrum?
7. To the quantization of which variable does lead the Wilson-Sommerfeld rule, if we apply it to harmonic oscillator?
8. How can you explain the rule of Bohr's quantization by the de Broglie waves?
9. What is new in Sommerfeld's model compared to the Bohr's model?
10. How does the atomic spectrum change when Sommerfeld made the relativistic correction of the electron mass?
11. How does Sommerfeld explain the splitting of spectral lines?
12. What is the interpretation of the results of the Franck-Hertz experiment?
13. What is new in the old quantum mechanics compared with classical mechanics?

PROBLEMS

1. Determine the Rydberg constant for deuterium. What is the relationship between its spectrum and the hydrogen spectrum?
2. Compare the gravitational force and the Coulomb force between the electron and the proton in the ground state in the hydrogen atom. Is it correct to neglect the gravitational force?
3. Determine the energy, the momentum and the wavelength of the photon, which is emitted from the hydrogen atom at the transition from a state with $n = 10$ to the ground state.
4. Using the Bohr'h model, find for the electron in the ground state of the hydrogen atom: a) the force, acting on it: b) the quantum number and the

orbital radius; c) the linear velocity and the angular one; d) the momentum and the angular momentum; e) the potential and the kinetic energies; f) the total energy.

5. Applying Bohr's model to a singly ionized helium atom, find its spectrum and determine the relationship between this spectrum and the hydrogen spectrum.
6. In the Franck-Hertz experiment the Hg atom after the collision with a 4,9 eV electron emits a photon with the wavelength 2536 Å. Calculate the value of *h* from this experimental result and compare with Planck's values.

Chapter 9

THE WAVE FUNCTION

SUGGESTED READING

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9.1 STATISTICAL INTERPRETATION OF THE DE BROGLIE'S WAVES

The experiments with double slits have been persuaded ourselves that the electron is connected with a wave process. The wave properties of the electron appear in the fact that the both slits influence its motion. As the result of this we observe the diffraction picture. But it is not correct to equalize the electron with some wave. If this would be true, the single electron would form the whole diffraction picture. Nevertheless that it would be weak.

At the experiment the single electron incidents in one point of the plate as a particle. The place of the falling up of an electron and a particle obeys totally different laws (for particles (7.29) and Fig. 7-11 and for electrons (7.31) and (7.32) and Fig. 7-12). The behaviour of the particle exhibits itself both when there is a single particle and when there are many of them. When there is a single electron it fixes as a particle and its wave properties exhibit only when there are many of them (including many times singles).

The wave properties of the electron are completely explained with the de Broglie wave. But this wave does not appear in the experiment with one single electron. Then the question arises how to interpret the wave.

One of the first interpretations belongs to Schroedinger: microscopic particle consists by a wave packet, localized in space. If we take waves of the quantity A with different wavenumbers from k-Δk to $k+\Delta k$ and add them we obtain a wave packet R_k, the centre of which moves like a particle with the group velocity of the wave (Fig. 9-1):

$$A = A_0 \cos[\omega(k) - kx],$$
$$R_k = \int_{k-\Delta k}^{k+\Delta k} A_0 \cos[\omega(k) - kx]dk. \qquad (9.1)$$

But the de Broglie waves are waves with dispersion, i.e. their phase velocity v_{ph} depends on the wave number *k*. Actually using the expression (7.36) for the energy of the microscopic particle and the expression $k = p/\hbar$ we can determine $v_{ph}(k)$:

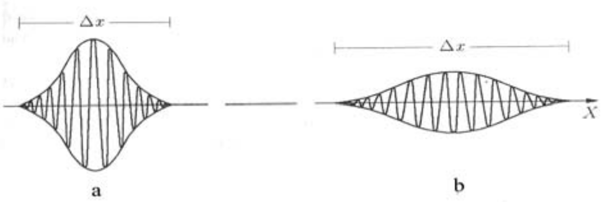


Figure 9-1. The wave packet is lokalized in space (a), but because of the dispersion it spreads (b).

$$\omega = \frac{E}{\hbar} = \sqrt{\frac{m_0^2 c^4}{\hbar^2} + \frac{p^2 c^2}{\hbar^2}} = \sqrt{\frac{m_0^2 c^4}{\hbar^2} + k^2 c^2},$$
$$v_{ph} = \frac{\omega}{k} = \sqrt{\frac{m_0^2 c^4}{\hbar^2 k^2} + c^2} = v_{ph}(k). \qquad (9.2)$$

As the result of the dispersion, the wave packet spreads (*at the end it disappears*).

Classical physics suggests a different interpretation - are not the de Broglie waves an analogue of the acoustic waves in the air? But then the diffraction picture would depend on the intensity of the incident beam of the particles. We saw in the Chapter 7 that this did not happen - the experiment shows that at final intensity and at small intensity but with increase exposition the picture is the same. The number of passing particles is important. The hydrogen atom has only one electron but it exhibits wave properties. It is obvious that the wave is not connected with particles, forming the medium (by analogy with the wave in a lake).

The analysis of the experiments of the diffraction of the microscopic particles leads Max Born to *a probability interpretation of the de Broglie waves*. Let us remember the experiment about the interference of the electrons. We can not say where a single electron will fall on. But if we pass into double slit many times by one electron, the distribution of the electrons will correspond to the distribution of the intensity of the interfered by double slit de Broglie waves. There, where the interference picture has a maximum, the most particles fall on and vice versa. On one hand we have the probability for finding the particles, and on other hand - the intensity of the wave. At this, the probability of finding the particle increases, achieves its maximum, decreases and achieves its minimum there, where the intensity of the wave has the same behaviour. Max Born makes a conclusion that the intensity of the de Broglie wave which is determined by the square of the amplitude, in every place is proportional to the probability to find a particle in this place.

The experiments with two slits prove that the falling on the screen of the single electron has accidental character - it can absolutely accidentally fall on into this or that point of the diffraction patterns. It is obvious that the behavior of the electron have to be characterized by some probability function. *But as the blackening of the plate on one hand is proportional to the incident particles, and on other hand - to the intensity of the de Broglie wave, it is clear that this probability may be expressed by the properties of the wave*. To do this we have to be able *to describe the wave, i.e. to associate with it some function, called wave function.*

9.2 THE WAVE FUNCTION

We need a function to describe both the probability and the wave character of the quantum object. To this object we correspond some wave. As the square of the amplitude of this wave, which defines its intensity, is proportional to the probability of finding the quantum object to the position near the point x, y, z in given moment of time it is clear that this is a function of the co-ordinates and time:

$$\psi(x,y,z,t) \equiv \psi(\mathbf{r},t)\,. \tag{9.3}$$

This function is called a wave function or ψ-function (psi-function). The simplest case is that of a free particle, which is described by a plane wave with a wave function

$$\psi(\mathbf{r},t) = A\exp[-i(\omega t - \mathbf{kr})] = A\exp\left[-\frac{i}{\hbar}(Et - \mathbf{pr})\right]. \tag{9.4}$$

In general case $\psi(\mathbf{r}, t)$ is a complicate function of the co-ordinates and time and it has nothing in common with the functions, describing the classical waves. The physical meaning of the square of the ψ-function according to the Max Born is following: *the value* $|\psi(x,y,z,t)|^2 dV$ *is proportional to the probability to find the microscopic particle at moment t in element of volume dV near the point x, y, z.*

Let us denote this probability with dW. Then

$$dW \propto |\psi(\mathbf{r},t)|^2 dV. \tag{9.5}$$

This physical interpretation clearly indicates that the wave described by the ψ-function differs essentially from the waves known in classical physics. This peculiarity exhibits in the fact, that the physical meaning has $|\psi|^2$, but not the ψ-function itself. In most general case the wave function is complex and therefore

$$|\psi(\mathbf{r},t)|^2 dV = \psi(\mathbf{r},t)\psi^*(\mathbf{r},t)dV. \tag{9.6}$$

As according to (9.5) it determines the space-time distribution, it is obvious that the functions

$$\psi(\mathbf{r},t) \quad \text{and} \quad A\psi(\mathbf{r},t) \tag{9.7}$$

describe one and the same distribution. If we integrate $|\psi(\mathbf{r},t)|^2$ over all possible co-ordinates within the total volume V we obtain some number N

$$\int_V |\psi(\mathbf{r},t)|^2 dV = N. \tag{9.8}$$

Taking into account (9.7) we can find new wave function

$$\psi'(\mathbf{r},t) = N^{-1/2}\psi(\mathbf{r},t), \tag{9.9}$$

which will describe the same probability distribution and then

$$\int_V |\psi'|^2 dV = 1. \tag{9.10}$$

Such a function is called normalized and (9.10) *is the condition for normalization.*

Example: We consider a normalized wave function of particles with an energy *E* and a momentum *p,* which has one degree of freedom and moves in direction *x* from 0 to *a.* The wave function has the view of (9.4)

$$\psi(x,t) = A\exp\left[-\frac{i}{\hbar}(Et - px)\right]. \tag{9.11}$$

According to the normalization condition

$$1 = \int_0^a |\psi(x,t)|^2 dx = \int_0^a \left| A\exp\left[-\frac{i}{\hbar}(Et - px)\right]\right|^2 dx = \int_0^a |A|^2\, dx = |A|^2 a \tag{9.12a)}$$

$$\text{or} \qquad A = 1/\sqrt{a}. \tag{9.12b)}$$

The wave function for the considered example is the next

$$\psi(x,t) = \frac{1}{\sqrt{a}}\exp\left[-\frac{i}{\hbar}(Et - px)\right]. \tag{9.13}$$

For the normalized wave function (9.5) is written as equality:

$$dW = |\psi(\mathbf{r},t)|^2\, dV = \psi(\mathbf{r},t)\psi^*(\mathbf{r},t)dV \quad \text{or} \tag{9.14a)}$$

$$dW = \rho(\mathbf{r},t)dV. \tag{9.14b)}$$

Here $\rho(\mathbf{r},t) = dW/dV = |\psi(\mathbf{r},t)|^2$ is the probability density. The probability to find the particle in the volume *V'* is

$$W(V',t)=\int_{V'}dW=\int_{V'}\psi(\mathbf{r},t)\psi^*(\mathbf{r},t)dV. \tag{9.15}$$

We note the normalized wave function (9.10) is determined within the phase factor $\exp(i\alpha)$, where α is any real function of the coordinates and of time $\alpha=\alpha(\mathbf{r},t)$. This is so, because $|\exp(i\alpha)|=1$.

The wave function possesses significant properties in space and time:

a) *finiteness* - ψ takes finite values in all points of space (completely rigorously said ψ must be quadratically integrable function, as according to its physical interpretation the integral $\int|\psi|^2dV$ should to be finite);
b) *single valuedness* - in every point of space ψ has a single value;
c) *continuity* - ψ is differentiable in every point of space.

9.3 THE WAVE FUNCTION OF A PARTICLE SYSTEM

Let us have two particles with positions $\mathbf{r}_1(x_1,y_1,z_1)$ and $\mathbf{r}_2(x_2,y_2,z_2)$. The both particles are described by the following wave function:

$$\psi(x_1,y_1,z_1,x_2,y_2,z_2,t)\equiv\psi(\mathbf{r}_1,\mathbf{r}_2,t). \tag{9.16}$$

The probability to have at the same time the first particle in the element of volume dV_1 near the point x_1,y_1,z_1 and the second - in the element dV_2 near the point x_2,y_2,z_2 is

$$dW(\mathbf{r}_1,\mathbf{r}_2,t)=|\psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2\,dV_1dV_2. \tag{9.17}$$

The corresponding density of probability is

$$\rho(\mathbf{r}_1,\mathbf{r}_2,t)\equiv\frac{dW(\mathbf{r}_1,\mathbf{r}_2,t)}{dV_1dV}=|\psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2. \tag{9.18}$$

The condition for the normalization of the ψ-function of the both particles, moving correspondingly in the volumes V_1 and V_2 is

$$\int\limits_{V_1}\int\limits_{V_2}|\psi(\mathbf{r}_1,\mathbf{r}_2,t)|^2\,dV_1dV_2=1. \tag{9.19}$$

It is not difficult to generalize the expressions (9.16÷9.19) for the system of N particles with radius-vectors $\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N$. To such a system we shall correspond the wave function

$$\psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N,t)\equiv\psi(\mathbf{r}_j,t). \tag{9.20}$$

As in the first part of this book the subscript j stands here for all radius-vectors. For one, two or many particles it should not be any principal difference. Then the interpretation of $\psi(\mathbf{r},t)$ and of $\psi(\mathbf{r}_j,t)$ should be the same, i.e. for the normalized $\psi(\mathbf{r}_j,t)$ -function the value

$$|\psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N,t)|^2\,dV_1dV_2...\,dV_N \tag{9.21}$$

defines the probability in the moment t of time the first particle to be in a element of the volume dV_1 near the point $\mathbf{r}_1$, the second - in dV_2 near the point $\mathbf{r}_2$ and so on or:

$$dW=\psi(\mathbf{r}_j,t)\psi^*(\mathbf{r}_j,t)dV_1,dV_2...\,dV_N. \tag{9.22}$$

The condition for normalization is

$$\int\limits_{V_1}\int\limits_{V_2}...\int\limits_{V_N}|\psi(\mathbf{r}_j,t)|^2\,dV_1dV_2...\,dV_N=1. \tag{9.23}$$

If we integrate on the volume of the allowed regions of motion of all particles with the exception of one of them, e.g. of the first, we obtain:

$$dW_1=dV_1\int\limits_{V_2}...\int\limits_{V_N}|\psi(\mathbf{r}_j,t)|^2\,dV_2...\,dV_N. \tag{9.24}$$

This is the probability of the first particle to be in the element dV_1 while the others particles are in arbitrary positions.

Now let us consider a system of N noninteracting particles, each of which is described correspondingly by the wave function $\psi_1(\mathbf{r}_1,t)$, $\psi_2(\mathbf{r}_1,t),...,\psi_N(\mathbf{r}_N,t)$ and the system - by the function (9.20). The probability of the first particle to be in element of the volume dV_1 is $dW_1 = |\psi_1(\mathbf{r}_1,t)|^2 dV_1$, of the second particle to be in dV_2 - $dW_2 = |\psi_2(\mathbf{r}_{12},t)|^2 dV_2$ etc. According to the rule for the multiplying the probabilities, the probability dW to observe these N events is

$$\begin{aligned} dW &= dW_1 dW_2 ... dW_N \\ &= |\psi_1(\mathbf{r}_1,t)|^2 dV_1 |\psi_2(\mathbf{r}_2,t)|^2 dV_2 ..., |\psi_N(\mathbf{r}_N,t)|^2 dV_N . \end{aligned} \tag{9.25}$$

Expressing dW through the $\psi(\mathbf{r}_j,t)$ we get

$$\psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N,t) = \psi_1(\mathbf{r}_1,t), \psi_2(\mathbf{r}_1,t), ..., \psi_N(\mathbf{r}_N,t), \tag{9.26}$$

i.e. *the wave function of the noninteracting particles is equal to the product of the wave functions of the separate particles.*

9.4 MEASUREMENT, EIGENSTATES AND EIGENVALUES OF THE OBSERVABLES

Mechanically, describing a system means first, describing the state in a given fixed time and second, describing the change of the state in time, i.e. the motion. It has been mentioned in Section 6.2, that the state is completely defined by the values of the generalized co-ordinates and momenta in given time, particularly by the Cartesian co-ordinates and momenta. In such a case classically the state is described by the 2s-dimensional vector $\mathbf{\Lambda}$ in the phase space. The knowing of the state $\mathbf{\Lambda}(t_0)$ in some initial moment t_0 allow us to calculate all physical quantities, characterizing the system, and with the laws of the mechanics to define its state $\mathbf{\Lambda}(t)$ in any moment of time t.

In Sections 9.2 and 9.3 we have seen that the behaviour of the quantum objects is described by the wave function $\psi(\mathbf{r}_j,t)$. Further it will become clear, that this function implies an information not only about the character of the motion of the system, but as well as for the values of physical quantities (usually in quantum mechanics they are called *observables*) which defines it. Therefore, the state of a quantum mechanical system in any time t is described by *the wave function* $\psi(\mathbf{r}_j,t)$, which *is* called also *the state function.*

In classical mechanics for the description of the initial state is necessary to measure the co-ordinates and momenta of the particles. They principally can be measured simultaneously with desired high accuracy and their values can be obtained independently of the order of the measurement. The determination of the state in classical mechanics is trivial in some sense.

This is not the way in quantum mechanics. The determination of the state different to classical mechanics is a principal question, which goes on the importance out of the dynamical problems. The measurement of a quantum mechanical system essentially differs from that of classical one. *In quantum mechanics under the measurement one realizes every interaction of the quantum objects with a classical apparatus.* As every apparatus consists of the quantum objects, in which their specific properties can appear, the classical is that apparatus which quantum properties can be neglected.

In classical physics every measurement is repeatable, that is the results by the subsequent repeated measurement coincide. For example, let us measure the position of the classical particle, which starts at point $A(x_0, y)$ with a momentum **p** (Fig. 9-2a), by the slit in point $B(x_1, y)$ and by the ruled screen E at $x = x_2$ (the particle makes a track on it).

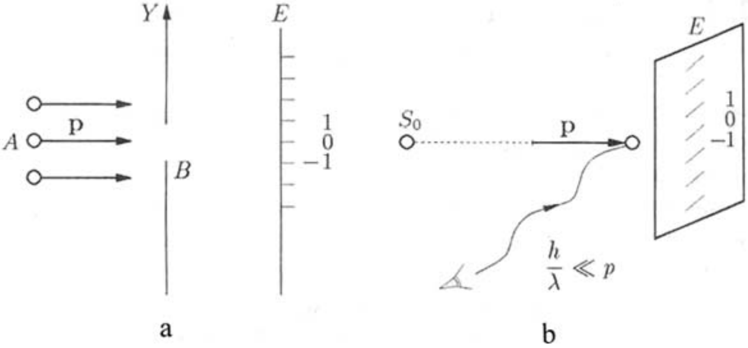


Figure 9-2. Measurement of the co-ordinates of the classical particle, moving horizontally of the axis *X* with a momentum p. The measurements are repeatable: a) a measurement by a slit; b) measurement by a "look" - the momentum of the photon is much smaller than the particle momentum.

The measurement of the observables of quantum objects is not always repeatable. As when in the experiment on the passing of electrons through the one slit (*aperture*) *the defining of the y co-ordinate by this slit is repeatable. The measurement of the position of passing electrons by the screen is not repeatable - it gives different results* (see the described in the Section 7.4 experiment of Fabricant and Fig. 7-13). Every measurement changes the state of the electron and this changing principally can not be made negligibly small, as the energy of the interaction is $E = \hbar\omega$. Before the slit the electron is in the state with fixed momentum p_x ($p_y = 0$), but behind the slit it can have different values of the transverse component p_y, as a result of which it fall on the different places of the diffraction picture. The interaction between the electron and the classical apparatus, the slit, changes the momentum with $c \sim h/\lambda$. In the classical scale h/λ is negligibly small, but in the small-scale system (microscopic system) this changing is compared with the particle momentum. But can one, instead by the slit to determine the electron position, without doing anything with it, but simply to "look" at it? So, we can determine the position of the classical particle as well (Fig. 9-2b). It is enough to look at the scale behind the trajectory (Fig 9-3).

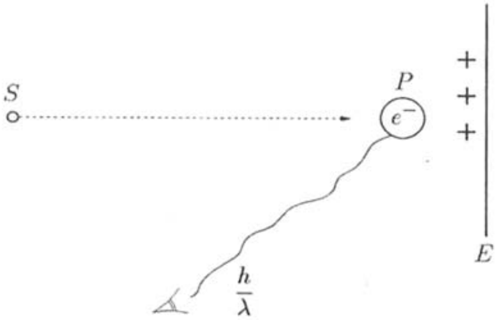


Figure 9-3. The determination of the position of the electron in the point *P* by a "look". In order to "see" the electron, it has to be "illuminated". The scattered by such illumination photon of the momentum *p=h/λ* changes unpredictably the electron momentum - the measurement is not repeatable and the electron falls on different places of the screen *E*.

In order to "see" the electron, it has to be "illuminated", i.e. at least one photon has to fall on it. But the photon has momentum *h/λ*, which is compared with the momentum of the electron. As the result of its scattering, the electron will obtain an additional momentum (see the Compton effect in the Section 7.2). In the subsequent experiments the electron falls on different positions on the screen *E*. The position on the screen *E* is unpredictable (but the probability is predictable). The measurement of the momentum p_y is not repeatable. By doing measurement we disturb the electron. *The essence of the problem is that we have not enough "delicate and tender" agents for observation of the small-scale object. It is impossible, in principle, to have such agents, i.e. it is impossible to make measurements, which do not at the same time disturb the system in a generally unpredictable way.* When we measure the position of a large-scale body (Fig. 9-2), the momentum of the photon is negligibly small compared with the momentum of the body $h/\lambda << p$.

The character of the measurement in quantum mechanics depends on the state of the system. In one state it can be repeatable, but in another - unrepeatable (for example, the measurement of the position before and behind the slit (Fig. 7-2a)). *The measurement of the values of some observables may be simultaneously repeatable. But there are such observables which in no possible state are simultaneously repeatable* (*for example,* x *and* p_x). Such observables are called, respectively, *compatible and incompatible.*

For a given quantum system a restriction exists on the number of independence observables, which are compatibles. The maximal number depends on the same system. *All independent observables, for which is possible repeatable measurement form a complete set of observable*s. The number of observables in this complete set is equal to the degrees of freedom of the given quantum system. For example, for one particle the next complete sets are possible (without spin): a) x, y, z; b) p_x, p_y, p_z; c) E, p_z, L_z. Every state of a quantum mechanical system is characterized by that complete set of independent observables, which are simultaneously measured in this state.

When the measurement of the given observable is repeatable, such observable is defined or certain; when the measurement is not repeatable it is undefined or uncertain. If we add to the complete set of observables: a) a independent observable, it will be uncertain: b) a dependent observable, it will be certain.

The state, in which the observable f is certain, i.e. its measurement is repeatable, is called eigenstate. The value f_i, *which f obtains - eigenvalue and wave function* ψ_i, *which describes this state - eighenfunction*:

state	1^{st}	2^{nd}	3^{rd}	... N^{th}	eigenstates;
value of *f*	f_1	f_2	f_3	... f_N	eigenvalues;
wave function	ψ_1	ψ_2	ψ_3	... ψ_N	eigenfunctions.

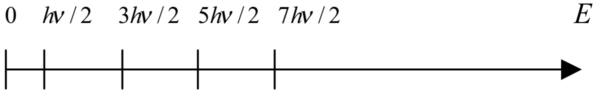
In the state, in which the measurement of the observable is not repeatable we obtain different values, but always one of the eigenvalues. The experiment shows that an observable could not have another values.

The problems in quantum mechanics essentially differ from classical ones. Here are some examples:

1. To define the possible complete set of observeables for a given system.
2. To find the wave function for a given complete set of observeables.
3. What are the expectation values of given observable?

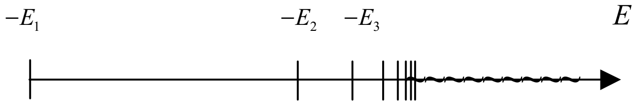
The set of eigenstates of the observable is called spectrum. The spectra can be as follows:

a) Descrete: for instance the energy of quantum oscillator $E=(n+1/2)h\nu, \quad n=0,1,2,3,...$).



b): Continuous: for instance, the momentum of free electron - in the fixed range all values of momentum are possible.

c) Compounds: for instance, the energy of the electron in the atom - in a bound state it is discrete, but in an ionized state it is continuos.



Usually at the measurement of the observable f in different eigenstates, described by the eigenfunctions ψ_{f_i}, we obtain different eigenvalues:

$$\psi_{f_1} \neq \psi_{f_2} \quad \rightarrow \quad f_1 \neq f_2. \tag{9.27}$$

Such states are called *nondegenerate states* and respectively *eigenvalues - nondegenerates*. If at the measurement of the observable f in different eigenstates we obtain equal eigenvalues, for instance f_0, i.e.

$$\psi_{f_1}^{(1)} \neq \psi_{f_2}^{(2)}, \quad \text{but} \quad f_0^{(1)} = f_0^{(2)}, \tag{9.28}$$

they are called *degenerate states and degenerate eigenvalues. If to one eigenvalue* f_i *correspond N different eigenfunctions* $\psi_{f_i}^{(1)}, \psi_{f_i}^{(2)}, ..., \psi_{f_i}^{(N)}$*, this eigenvalues is N-fold degenerate.*

9.5 THE SUPERPOSITION PRINCIPLE

A superposition of the waves means simply a superimposition of them. The phenomena is well known in classical physics (in particularly it leads to the considered in Chapter 7 interference). Let us recall the vibrations of coupled oscillators (Figs. 5-1 ÷ 5-3). We saw in Section 5.4, that two normal modes are possible: antisymmetric modes with the angular frequency ω_a

$$\xi_1 = 2a\cos\omega_a t \tag{9.29}$$

and symmetric modes with the angular frequency ω_s

$$\xi_2 = 2a\cos\omega_s t\,. \tag{9.30}$$

As the result of superposition (superimposition) of these two normal modes the other kind of vibrations is possible, which is the linear combination of the asymmetric and the symmetric vibrations. For example:

$$\frac{1}{2}\xi_1 + \frac{1}{2}\xi_2 \equiv x_1 = \frac{1}{2}2a\cos\omega_a t + \frac{1}{2}2a\cos\omega_s t\,. \tag{9.31}$$

The vibration of the both oscillators for such superposition is shown in Fig. 5-5.

Two kinds vibrations of linear symmetric molecule - symmetric x_s and antisymmetric x_a - are shown in Fig. 5-8:

$$\begin{aligned} x_s &= A_s\cos\omega_s t, \\ x_a &= A_a\cos\omega_a t. \end{aligned} \tag{9.32}$$

Here x_a is the sum and x_s is a difference of the displacements of the atoms from the equilibrium positions and scripts *a* and *s* are related to the asymmetric and the symmetric vibrations. It is also possible to have an oscillation of the molecule, which is a superposition of these two oscillations:

$$x = x_a + x_s\,. \tag{9.33}$$

And now let us return to the diffraction of quantum object from two slits (Fig. 7-12). Before the slits the particles (photons or electrons) can be in different states, which differ by the value and the direction of the momentum. The state with momentum **p**, which corresponds to the fixed de Broglie wave, is described with wave function $\psi_p(\mathbf{r},t)$.

After passing trough the one of the two slits the beam of particles can be considered as conical beams of the different momenta. In every narrow cone, where the momentum of the particles is fixed, they obtain additional transverse momentum - different for different cones. Due to this addition we obtain the set of conical beams with momenta $\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_n$ (only one of them cannot be obtained). The state of the particles in the conical beams, in which the particles have equal momenta, is described by the de Broglie wave of fixed wavelength, i.e. by the functions $\psi_{p_1}(\mathbf{r},t),\psi_{p_2}(\mathbf{r},t),...,\psi_{p_n}(\mathbf{r},t)$. In this we can persuade ourselves as with a slit separate the one of the conical beams with the momentum p_i and direct it to two slits - as the result we obtain again the same diffraction picture. On the other hand this whole set is an unified wave field and it is expressed with one wave function $\psi(\mathbf{r},t)$. The conclusion is obvious: *the state of the diffraction from two slits is a superposition of the states of free particles described by the de Broglie waves*:

$$\psi(\mathbf{r},t)=\sum_i C(p_i)\psi_{p_i}(\mathbf{r}). \tag{9.34}$$

The new state (the diffraction picture) is a superposition of the states with rigorously certain momenta. The superposition appears also when the particles pass through the both slits (Fig. 7-12b). When the second slit is closed, the state is described by the wave function $\psi_1(\mathbf{r},t)$ and the probability density to find the particle in the point **r** of the screen is as follows:

$$\rho_1(\mathbf{r},t)=\left|\psi_1(\mathbf{r},t)\right|^2. \tag{9.35}$$

When the first slit is closed, the state is described by $\psi_2(\mathbf{r},t)$ and the probability density is analogue to the (9.35):

$$\rho_2(\mathbf{r},t)=\left|\psi_2(\mathbf{r},t)\right|^2. \tag{9.36}$$

Despite of the fact that small scale systems obey probability laws, the densities ρ_1 and ρ_2 are not summarized, but the amplitude of the states are or according to Dirac the amplitude of the probabilities:

$$\begin{aligned}&\psi_{1,2}(\mathbf{r},t)=C_1\psi_1(\mathbf{r},t)+C_2\psi_2(\mathbf{r},t), \qquad (C_1=C_2=1),\\&\rho_{1,2}(\mathbf{r},t)=\left|\psi_{1,2}(\mathbf{r},t)\right|^2\neq\rho_1(\mathbf{r},t)+\rho_2(\mathbf{r},t).\end{aligned} \tag{9.37}$$

The considered examples of the diffraction are partial cases of the principle of the superposition. According to it, *if the systems could be found in the states with wave functions* $\psi_1(\mathbf{r},t),\psi_2(\mathbf{r},t),...,\psi_n(\mathbf{r},t)$, *it can be found and in the state with the wave function* $\psi(\mathbf{r},t)$, *which is the linear combination of the functions* $\psi_i(\mathbf{r},t)$*:*

$$\psi(\mathbf{r},t)=\sum_i C_i\psi_i(\mathbf{r},t). \tag{9.38}$$

The coefficients C_i can be arbitrary, but they have to obey the condition of normalization of the wave function:

$$\int |\psi(\mathbf{r},t)|^2 dV = \int \left| \sum_i C_i \psi_i \right|^2 dV = 1. \tag{9.39}$$

In classical physics the superposition is a consequence of the linearity of the system. The linear oscillations of such a system are described by the system of linear differential equation and its general solution is a linear combination of partial solutions. This is the mathematical formulation for the principle of superposition. Because of these reasons we can expect that the wave function will obey a linear differential equation.

Let look wider to the superposition principle from the linear-algebra point of view. We are interested in the physical quantity f (very often one speaks about a dynamical variable or about an observable). From the experiment we know the eigenvalues $f_1, f_2, ..., f_n$, measured in the corresponding eigenstates $\psi_{f1}, \psi_{f2}, ..., \psi_{fn}$. We can consider the set of wave functions, describing all possible eigenstates, as a linear vector space on the axes of which we plot the functions themselves. The wave functions are bases of this space. The analogue with the configuration space is very sue - there we plot the generalized co-ordinates, but here - the wave functions of the eigenstates. In the linear space, like the scalar product **ab** of two vectors, we shall introduce the scalar product of two functions φ and ψ:

$$(\varphi,\psi) = \int \varphi^* \psi dV. \tag{9.40}$$

We are going further with the analogy. As far as two orthogonal vectors in the real space have zero scalar product $\mathbf{x}_i \mathbf{x}_k = 0$ $\left(\mathbf{x}_i \perp \mathbf{x}_k,\ i \neq k\right)$, the scalar product of the two different basis functions from the linear space is zero:

$$(\psi_{f_i}, \psi_{f_k}) = 0, \quad i \neq k. \tag{9.41}$$

When $i = k$, the scalar product according to the normalization is equal to the unity:

$$(\psi_{f_i}, \psi_{f_k}) = \int \psi^*_{f_i}, \psi_{f_k} dV = \int \left|\psi_{f_k}\right|^2 dV = 1. \tag{9.42}$$

The equalities (9.41) and (9.42) can be united as follows:

$$(\psi_{f_i},\psi_{f_k})=\delta_{ik}, \qquad \delta_{ik}=\begin{cases}1, & i=k,\\ 0, & i\neq k.\end{cases} \tag{9.43}$$

Here δ_{ik} is Kronecker's symbol. The eigenfunctions of certain physical quantity form an orthonormal system of functions.

In general the set of quadratic integrated functions ψ forms Hilbert space ([4], Section 3.3) - it is infinitely dimension linear vector space, in which the scalar product is defined (9.40).

Very often the scalar product (9.40) is written in "bra" and "ket" notation, which had been introduced by Dirac:

$$\langle\varphi|\psi\rangle\equiv\int\varphi^*\psi dV. \tag{9.44}$$

This is a product of two elements $\langle\varphi|$ ("bra" element) and $|\psi\rangle$ ("ket" element). The names of these elements form the "bra-ket" (bracket). Every expression in integral representation can be written in Dirac notation. For instance, the orthonormality relation is written as:

$$\int\psi_i{}^*\psi_k dV\equiv\langle\psi_i|\psi_k\rangle=\delta_{ik}. \tag{9.45}$$

Every possible wave function ψ can be expanded in terms of orthogonal complete set of functions ψ_n, which are bases of the linear space:

$$\psi=\sum_i C_i\psi_{f_i}. \tag{9.46}$$

From the normalization condition and using (9.43), we obtain

$$\begin{aligned}\int\psi^*\psi dV&=\int\left(\sum_k C_k^*\psi_{f_k}^*\sum_l C_l\psi_{f_l}\right)dV=\sum_{k,l}C_k^*C_l\int\psi_{f_k}^*\psi_{f_l}dV\\&=\sum_{k,l}C_k^*C_l\delta_{kl}=\sum_k|C_k|^2=1.\end{aligned} \tag{9.47}$$

We have already underlined that *the coefficients C_k* are arbitrary, but they *satisfy the normalisation condition*. For them the normalisation is

$$\sum_k|C_k|^2=1. \tag{9.48}$$

It is obvious that $|C_k| \leq 1$. The mathematical condition $\int \psi^* \psi dV = \sum_k |C_k|^2 = 1$ is a condition for the completeness of the basis (the studious reader will find details, for instance in [R34], Chapter 3).

To understand the physical meaning of the coefficients C_k let us consider a state with wave function $\psi(\mathbf{r})$, in which we measure the observable *f*. If this state does not coincide with the one of eigenstate ($\psi(\mathbf{r}) \neq \psi_{f_i}(\mathbf{r}),\quad i = 1, 2, ..., n$), we shall measure the eigenvalues f_i with the respective probabilities W_i:

measured value	f_1,	f_2,	f_3,	...,	f_n,
probability	W_1,	W_2,	W_3,	...,	W_n.

If $\psi(\mathbf{r}) = \psi_{f_k}(\mathbf{r})$, i.e. the measurement is in one of the eigenstate ψ_{f_k}, then $W_k = 1$ and $W_i = 0\,(i \neq k)$.

According to the superposition principle in this case we can write

$$\begin{aligned} &\psi(\mathbf{r}) = 0.\psi_{f_1} + 0.\psi_{f_2} + ... + 1.\psi_{f_k} + ... + 0.\psi_{f_n}, \\ &C_k = 1, \qquad C_i = 0, \qquad i \neq k. \end{aligned} \tag{9.49}$$

Consider the non-eigenstate $\psi(\mathbf{r})$, which is a superposition of two states ψ_{f_1} and ψ_{f_2}:

$$\psi(\mathbf{r}) = C_1\psi_{f_1} + C_2\psi_{f_2}. \tag{9.50}$$

From the condition for the normalization of the coefficients we have:

$$|C_1|^2 + |C_2|^2 = 1. \tag{9.51}$$

Measuring the observable *f* in this state, we obtain for the values f_1 and f_2 respectively the probabilities W_1 and W_2. The probability to obtain $f_n \quad (n \neq 1, 2)$ is zero, i. e. $W_n = 0$, and therefore

$$W_1 + W_2 = 1. \tag{9.52}$$

The comparison between (9.51) and (9.52) hints the assumption $W_k = |C_k|^2$, which is confirmed in the experiment.

Let us generalize for the non-eigenstate, which is a superposition of *n* eigenstates:

$$\psi(\mathbf{r}) = \sum_i C_i \psi_{f_i}(\mathbf{r}). \tag{9.53}$$

From the measurements we obtain one of the eigenvalues $f_1, f_2, ..., f_n$ with a probability $W_1, W_2, ..., W_n$. These probabilities are determined by the square of the module of corresponding superposition coefficient:

$$W_k \equiv W(f = f_k) = |C_k|^2, \qquad \sum_k W_k = \sum_k |C_k^2| = 1. \tag{9.54}$$

Namely, this equality expresses the physical meaning of the coefficients C_k - *the square* $|C_i|^2$ $(i = 1, 2, ..., n)$ *determines the probability of measurement in the non-eigenstate ith eigenvalue.*

9.6* SUPERPOSITION OF STATES WITH A CONTINUOUS SPECTRUM

As an example of a continuous variable we shall take the momentum of a free particle, which can accept any value on the interval $-\infty, +\infty$. In one-dimensional case this free particle is described by the wave function ψ_p (9.11). Let try to normalize this function:

$$\int_{-\infty}^{\infty} |\psi_p|^2 dx = \int_{-\infty}^{\infty} |A|^2 dx = |A|^2 \int_{-\infty}^{\infty} dx \to \infty. \qquad (!) \tag{9.55}$$

From all our discussions up to here, based on the experiments we reach the conclusion, that this integral is the probability W of finding the particle in the given range ($-\infty, +\infty$). But here $W \to \infty$ which is physical absurdity. The way out was found by Dirac. The normalization of the wave function of continuous variable has to be done in a way to escape this divergence. The problem is not to change the wave function and the probability distribution, but to find such a condition that enables us to obtain suitable constant before the wave function: $\text{const}\,\psi_p(\mathbf{r}, t)$. In the connection with the physical meaning of the wave function we want to choose much suitable constant. For the discrete variables the wave functions are orthonormal (for simplicity we consider one-dimensional case):

$$\int \psi_m^* \psi_n dV = \delta_{mn} = \begin{cases} 1, & m = n, \\ 0, & m \neq n. \end{cases} \tag{9.56}$$

By analogy with the expression (9.56) Dirac introduces the normalization condition for the wave function of a state with a continuous variable. The wave functions $\psi_p(x,t)$ and $\psi_{p'}(x,t)$ correspond to the states with two fixed values of the momentum p and p'. Then, by analogy we have

$$\int \psi_{p'}^* \psi_p dx = \delta(p - p'), \tag{9.57}$$

where $\delta(p-p')$ is called *Dirac delta function*. The function has the properties as follows:

1. $\delta(p-p') = \begin{cases} 0, & x \neq a, \\ \infty, & x = a; \end{cases}$
2. $\int\limits_{x_1}^{x_2} \delta(x-a)dx = \begin{cases} 1, & x_1 \leqq a \leqq x_2, \\ 0, & a < x_1 \text{ or } a > x_2; \end{cases}$
3. $\int\limits_{x_1}^{x_2} F(x)\delta(x-a)dx = F(a);$
4. $\delta(k) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} e^{ikx}dx;$
5. $x\delta(x) = 0.$

Using the normalization (9.57) and the property 4. we determine the coefficient A of the ψ_p-function (9.11):

$$\begin{gathered} \delta(p-p') = \int\limits_{-\infty}^{\infty} A^* A \exp\left[-i\left(\frac{Et}{\hbar} - \frac{px}{\hbar}\right)\right]\exp\left[i\left(\frac{Et}{\hbar} - \frac{p'x}{\hbar}\right)\right]dx \\ = \hbar\int\limits_{-\infty}^{\infty} |A|^2 \exp\left[i(p-p')\frac{x}{\hbar}\right]d\left(\frac{x}{\hbar}\right) = \hbar|A|^2 2\pi\delta(p-p') \;\Rightarrow \\ A = \frac{1}{\sqrt{2\pi\hbar}}. \end{gathered} \tag{9.58}$$

Finally, for the normalized wave function of the de Broglie wave of a free particle we have:

$$\psi_p(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\exp\left[-\frac{i}{\hbar}(Et-px)\right]. \tag{9.59}$$

For the three-dimensional motion the wave function becomes:

$$\psi_{\mathbf{p}}(\mathbf{r},t)=\frac{1}{(2\pi\hbar)^{3/2}}\exp\left[-\frac{i}{\hbar}(Et-\mathbf{pr})\right]. \tag{9.60}$$

The superposition of the states with the continuous momentum we present by analogy with the superposition of discrete states, replacing the summation with integration:

$$\begin{aligned}\psi(x,t)&=\int_{-\infty}^{\infty}C(p)\psi_p(x,t)\,dp=A\int_{-\infty}^{\infty}C(p)\exp\left[-\frac{i}{\hbar}(Et-px)\right]dp\\&=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\varphi(p,t)\exp\left(\frac{i}{\hbar}px\right)dp,\end{aligned} \tag{9.61}$$

where $\varphi(p,t)\equiv C(p)\exp\left(-\frac{i}{\hbar}Et\right)$. *When we know the function* $\varphi(p,t)$*, i.e.* $C(p)$*, we can determine* $\psi(x,t)$*. If we know* $\psi(x,t)$*, we can determine* $\varphi(p,t)$. For this it is enough to recall the Fourier transformation for functions $U(k)$ and $V(x)$:

$$\begin{aligned}U(k)&=\left(\frac{\alpha}{2\pi}\right)^{1/2}\int_{-\infty}^{\infty}V(x)\exp(-i\alpha kx)\,dx,\\V(x)&=\left(\frac{\alpha}{2\pi}\right)^{1/2}\int_{-\infty}^{\infty}U(k)\exp(i\alpha kx)\,dk.\end{aligned} \tag{9.62}$$

According to this transformation we obtain from (9.61) the following:

$$\varphi(p,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x,t)\exp\left(-\frac{i}{\hbar}px\right)dx. \tag{9.63}$$

As the knowing of the function $\varphi(p,t)$ allows the determining $\psi(x,t)$, this function determines the state of the system. In other words it is a wave function of the system. But it depends on the momentum and is determined in "momentum space" unlike of $\psi(x,t)$, which is determined in the real space (the co-ordinate space). So the wave function $\varphi(p,t)$ determines the probability distribution of the particle momentum.

On the one hand the blacking of the plate in the point M is proportional to the number of particles with co-ordinate x_M, i.e. $\propto\left|\psi(x_M,t)\right|^2 dx$ $\equiv\left|\psi_M\right|^2 dx$. On the other hand, the blacking is proportional to the probability the particles to have momentum p_M, i. e. $\propto\left|\varphi(p_M,t)\right|^2 dp$ (Fig. 9-4). So, *with the same success we can use the wave function* $\psi\,(x,\ t)$ *in the co-ordinate representation or the wave function* $\varphi(p,t)$ *in the momentum representation. It is logically to suppose that the co-ordinates and the momenta are not privileged dynamical variables and the wave function can be expressed in the space of other variables, for instance of the energy, of the angular momentum and* etc. This topic is considered in Section 15.1.

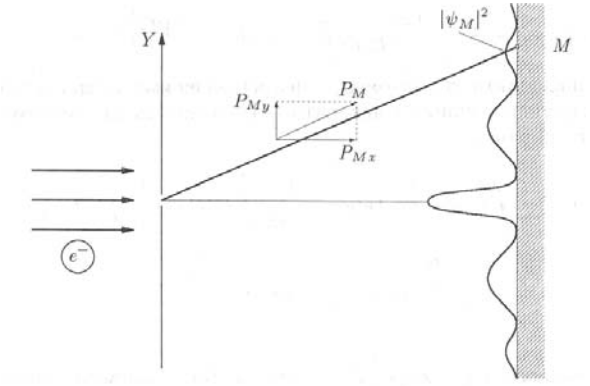


Figure 9-4. The blacking in point M is proportional to the number of the particles with co-ordinates x_M - $\propto\left|\psi(x_M,t)\right|^2 dx$. But in the same time it can be determined by the number of the particles with the momentum p_M, which is proportional to $\left|\varphi(p_M,t)\right|^2 dp$.

SUMMARY

The de Broglie waves are "particular waves". In these waves nothing oscillates. The wave function of these waves has not physical meaning, it is not itself a physical quantity. The waves have a statistical, a probabilistic character - the square of the module of the wave function in a given place determines the probability to find the particle in this position. The de Broglie waves are the waves of the probability. In quantum mechanics normalized ψ-functions are used in the connection of the physical meaning of the wave function:

$$\int_V \left|\psi(\mathbf{r},t)\right|^2 dV = 1.$$

The motion of a free particle is described by the wave function of the plane wave:

$$\psi(\mathbf{r},t) = \text{const}\,\exp\left[-i(\omega t - \mathbf{kr})\right] = \text{const}\,\exp\left[-\frac{i}{\hbar}(Et - \mathbf{pr})\right].$$

The wave function is a single-valued function of the co-ordinates of the particle and time and it is finite and differentiable.

The measurement in quantum mechanics can be repeatable and unrepeatable. In the first case the system is in eigenstate and for a certain quantity at the measurement we obtain only one value - the eigenvalue. The eigenstate is characterized by the complete set of observables and is described by the eigenfunction ψ.

One of the fundamental principle governing the quantum states is called the superposition principle. It states that quantum mechanical system, which can take on the discrete states ψ_i, is also able to occupy the state

$$\psi = \sum_i C_i \psi_i .$$

The square of the module of the coefficients $\left|C_i\right|^2$ determines the probability to measure the value f_i of the observable f in this non-eigenstate. All eigenfunctions of the physical system are orthonormal:

$$(\psi_i, \psi_k) = \delta_{ik}.$$

When the observable has continuous spectrum the normalization is made by the δ-function

$$\int_{-\infty}^{\infty} \psi_{p'}^{*}(x)\psi_{p}(x) = \delta(p-p')$$

and for the superposition instead of the sum we have the integration of the eigenfunctions.

QUESTIONS

1. Why the Schroedinger's interpretation is not correct?
2. Why the de Broglie wave is not interpreted as the wave of particles like the acoustic wave?
3. Physically to what is proportional the intensity of the wave of quantum particles, passing through double slit?
4. Does the wave function have physical meaning?
5. Why is the wave function normalized?
6. Which are the properties of the wave function?
7. What is the connection between the wave function of the system of noninteracting particles and the functions of the separate particles?
8. What is the principal difference between the measurements in classical and quantum mechanics?
9. What do you understand under the eigenstates and eigenvalues of the observable?
10. What are the values of the observable in measurement in the non-eigenstate?
11. How does appear the superposition principle in the oscillations of tree atomic linear symmetric molecule?
12. How does appear the superposition principle at the diffraction of the electrons from one or two slits?
13. What do you understand under the orthonormal wave functions?
14. What is the physical meaning of the coefficients C_i in the expression

    $$\psi(\mathbf{r},t) = \sum_i C_i \psi_i(\mathbf{r},t)\ ?$$

15. How is the wave function of the free particle normalized?
16. What does mean the wave function in the momentum space?

PROBLEMS

1. Prove that $\psi^*(x,t)\psi(x,t)$ is always real number - positive or zero.
2. The state of the particle is described by the ψ-function $\psi = Ae^{i\omega t}e^{-\left(x^2/2a\right)}$, where angular frequency ω and the "length" a are known constant. Find the normalized wave function.
3. Normalize the wave function $\psi(x) = A\sin(2\pi x/L)$ in the interval $0 < x < L$.
4. The eigenstates of the particle of mass m in one-dimensional potential well are described with the wave functions
$$\psi_n\psi(x) = \sqrt{\frac{2}{L}\sin\frac{2\pi x}{L}}, \qquad n = 1, 2, ...,$$
to which correspond energy E_n ($n = 1, 2, ...$). The particle is in the state with wave function $\psi(x,0) = (3\psi_2 + \psi_9)/5$. Is that function normalized? What kind of energy values will be measured in this state? With what probability will be measured those values?
5. Can the functions $\sin\varphi$ and $\tan\varphi$ be wave functions?
6. What restriction has to be imposing on the function $\exp(im\varphi)$ to be it a wave function?
7. We are interested in the observable F and in a single measurement we have obtained $F = F_k$. Can we conclude that before the measurement the particle has been found in the state $F = F_k$?

Chapter 10

OPERATORS

10.1 Mean Values and Operators

Mean values in quantum mechanics; a presentation by coefficients C_k*; operator; mean value of an observable by an operator; operators and observables; operators of the co-ordinate and of the momentum.* 230

10.2 Operators in Quantum Mechanics

Definition; linear and Hermitian operators in quantum mechanics; sum; product; commutator. 234

10.3 Eigenvalues and Eigenfunctions of Operators

Eigenvalues and eigenfunctions; operators; orthonormal functions of a Hermitian operator; compatible observables. 236

10.4 Operators of the Co-ordinates and the Momentum and Their Eigenfunctions and Eigenvalues

Operators $\hat{x}, \hat{y}, \hat{z}$ and $\hat{f}(r)$*; eigenfunction of* $\hat{x}$*; operators* $\hat{p}_x, \hat{p}_y, \hat{p}_z, \hat{\mathbf{p}}$ *and* $\hat{p}^2$*; eigenfunction of the operator* $\hat{p}^2$*; the commutator of the position and the momentum operators.* 240

10.5^+ Angular-Momentum Operator

Operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$ and $\hat{L}^2$*; commutators of the angular-momentum components; commutators of the Cartesian components of* $\hat{\mathbf{L}}$ *with* $\hat{L}^2$*;*

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10.1 MEAN VALUES AND OPERATORS

In the experiments on a diffraction of the electrons we persuaded ourselves that their momenta after the slit (the slits) are different. The momentum of the separate electron is unpredictable. But can we find the mean momentum of the electrons? This is the particular case of more general question. If the system is in non-eigenstate $\psi(\mathbf{r})$ and we measure the eigenvalues $f_1, f_2, ..., f_n$ of the observable f with the corresponding probability $W_1, W_2, ..., W_n$, the question is how to find the mean value $\overline{f}$. By the definition it is:

$$\overline{f} = \sum_k W_k f_k, \tag{10.1}$$

which according to (9.54) can be written as:

$$\overline{f} = \sum_k |C_k|^2 f_k = \sum_k C_k C_k^* f_k. \tag{10.2}$$

The coefficient C_k describes "the specific gravity" of the eigenstate ψ_k in the considered non-eigenstate ψ. Let define C_k through the wave functions ψ_k and ψ. For this purpose let find their scalar product:

$$(\psi_k, \psi) = \int \psi_k^* \psi dV = \int \psi_k^* \sum_i C_i \psi_i dV = \int \psi_k^* C_k \psi_k dV = C_k. \tag{10.3}$$

Taking the complex conjugated of this relation, we obtain for the conjugate coefficient C_k^* following:

$$C_k^* = \int (\psi_k^* \psi)^* dV = \int \psi_k \psi^* dV = (\psi, \psi_k). \tag{10.4}$$

We substitute C_k^* into (10.2)

$$\overline{f} = \sum_k C_k f_k \int \psi_k \psi^* dV = \int \psi^* \sum_k C_k f_k \psi_k dV. \tag{10.5}$$

We are interested in the state $\psi = \sum C_k \psi_k$. Let suppose, that the function $\sum C_k f_k \psi_k$ in the integral of (10.5) is obtained as a result of the mathematical operation over ψ, i. e.

$$\hat{f}\psi \equiv \sum_k C_k f_k \psi_k. \tag{10.6}$$

Here we denote with $\hat{f}$ an operator, which is related to f. From the relation (10.5) we obtain for the mean value $\bar{f}$ of the observable f:

$$\bar{f} = \int \psi^*(\mathbf{r}) \hat{f} \psi(\mathbf{r}) d\mathbf{r}. \tag{10.7}$$

To define the mean value of the observable f in the non-eigenstate, it is enough to know the wave function $\psi(r)$ and the operator $\hat{f}$.

When the considered system is in the *i*th eigenstate, it is described by the wave function ψ_i:

$$\psi = \psi_i, \qquad C_i = 1, \qquad C_k = 0, \qquad k \neq i \tag{10.8}$$

and then according to (10.6) we have

$$\hat{f}\psi_i = f_i \psi_i. \tag{10.9}$$

The observables are described by operators. *To each quantum-mechanical variable corresponds an operator. The operators of the dynamical quantities satisfy the same relations and equalities as the corresponding classical quantities do.* These statements represent *the second postulate in quantum mechanics*; let us remember *the first one - the state of every quantum mechanical object is described by the wave function.*

The question for the correspondence between the experimental measured dynamical variables and the known mathematical categories is fundamental for every physical theory. But the same physics can not define which mathematical categories correspond to the dynamical variables. In classical mechanics these are scalars, vectors and tensors in the real space. The "visualizability" and the "tangibility" of the classical phenomena naturally, almost intuitively have led to this correspondence. In quantum mechanics, where the visualizability is lacked, for the realization of the fact, that to the *quantum-mechanical variable corresponds an operator* the physicists have passed a long and difficult way.

Let us consider two examples of operators. To take the co-ordinate *x*, which is continuous value. For the mean value of the *x* in the state $\psi(x)$ according to (10.1) we obtain

$$\bar{x} = \int_{x_1}^{x_2} x dW(x) = \int_{x_1}^{x_2} x |\psi(x)|^2 dx = \int_{x_1}^{x_2} \psi^*(x) x \psi(x) dx. \tag{10.10}$$

On the other hand, according to the (10.7) we have

$$\bar{x} = \int_{x_1}^{x_2} \psi^*(x)\hat{x}\psi(x)dx. \tag{10.11}$$

From the comparison of (10.10) and (10.11) it is clear, that *the operator* $\hat{x}$ *of the co-ordinate x is equal to its value*:

$$\hat{x}\psi = x\psi, \qquad \hat{x} = x. \tag{10.12}$$

Let find the operator of the component of the momentum over *X,* i.e. $\hat{p}_x$. In the state of free movement a microparticle is described by the plane wave of de Broglie (for example, before the slit in the diffraction experiment):

$$\psi(x) \equiv \psi_{p_x} = \frac{1}{\sqrt{2\pi\hbar}} \exp\left[-\frac{i}{\hbar}(Et - p_x x)\right]. \tag{10.13}$$

As the particle is in an eigenstate, the probability to have momentum p_x is $|C_p| = 1$ and according to the definition of the operator (10.6)

$$\hat{p}_x\psi(x) = p_x\psi(x) \equiv p_x\psi_{p_x}. \tag{10.14}$$

Differentiating (10.13) over *x* we obtain:

$$\frac{\partial}{\partial x}\psi_{p_x} = \frac{ip_x}{\hbar}\psi_{p_x}, \tag{10.15a}$$

or

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_{p_x} = p_x\psi_{p_x}. \tag{10.15b}$$

By the comparison of (10.15b) with (10.14) *for the operator of the x-component of the momentum* we obtain

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}. \tag{10.16}$$

The other two components of the momentum are written by analogy with $\hat{p}_x$ (see Section 10.5).

10.2 OPERATORS IN QUANTUM MECHANICS

In the most general sense *the operator is the rule through which we correspond to the function* ψ *other function* φ, i.e.

$$\psi = \hat{A}\varphi, \qquad \hat{A} - \text{an operator.} \tag{10.17}$$

Not all of the operators are suitable for quantum mechanics. To indicate adequately the property of the microscopic objects, they have to respond to some conditions. *Firstly, the operators in quantum mechanics should satisfy the superposition principle. Secondly, as it can be seen from the example of the momentum* (10.15b)*, at the action of the operator on the wave function one obtains a real number. The linear operator responds to the first requirement and the Hermitian operators - to the second one.*

Let have operator $\hat{A}$ and two arbitrary functions $u(x)$ and $v(x)$. *Operator* $\hat{A}$ *is a linear operator if the next condition is fulfilled*:

$$\hat{A}\left[C_1u(x)+C_2v(x)\right]=C_1\hat{A}u(x)+C_2\hat{A}v(x), \tag{10.18}$$

where C_1 and C_2 are arbitrary constant. The result of the action of the operator on the linear combination of the both functions is equal to the linear combination of the action of the operator on each of the functions.

We would like to underline, that the operator $\hat{f}$, which we have introduced in (10.6) to define the mean value $\overline{f}$, is a linear one. Actually, for non-eigenstate with a wave function $\psi = \sum C_k\psi_k$ according to the definition (10.6) and the expression (10.9) we have

$$\hat{f}\psi = \sum_k C_k f_k \psi_k = \sum_k C_k \hat{f}\psi_k . \tag{10.19}$$

If two operators satisfy the condition

$$\int u^*(x)\hat{A}v(x)dx) = \int v(x)\hat{B}^*u^*(x)dx), \tag{10.20}$$

they are called adjoint. When $\hat{A}=\hat{B}$ *then (10.20) becomes*

$$\int u^*(x)\hat{A}v(x)dx) = \int v(x)\hat{A}^* u^*(x)dx), \tag{10.21}$$

and the operator $\hat{A}$ *is called self-adjoint or Hermitian.*

The operator $\hat{C}$ is *a sum of the operators* $\hat{A}$ *and* $\hat{B}$ if

$$\hat{C}\psi = \hat{A}\psi + \hat{B}\psi \tag{10.22a}$$

or symbolically

$$\hat{C} = \hat{A} + \hat{B}. \tag{10.22b}$$

The operator $\hat{C}$ is *a product of two operators* $\hat{A}$ *and* $\hat{B}$, if

$$\hat{C}\psi = \hat{A}\hat{B}\psi, \qquad \hat{C} = \hat{A}\hat{B}. \tag{10.23}$$

The product of two operators depends on the order of the multipliers. For example, if $\hat{A} = i\frac{\partial}{\partial x}$ and $\hat{B} = x$, then

$$\begin{aligned} \hat{C}\psi &= \hat{A}(\hat{B}\psi) = i\frac{\partial}{\partial x}(x\psi) = i\psi + ix\frac{\partial\psi}{\partial x} = \left(i + ix\frac{\partial}{\partial x}\right)\psi, \\ \hat{C}'\psi &= \hat{B}(\hat{A}\psi) = ix\frac{\partial\psi}{\partial x} = \left(ix\frac{\partial}{\partial x}\right)\psi. \end{aligned} \tag{10.24}$$

Obviously, $\hat{C} \neq \hat{C}'$, i.e. $\hat{A}\hat{B} \neq \hat{B}\hat{A}.$ It is important to realize that the product of two operator in general does not commute. The algebra of the linear operators in quantum mechanics is algebra of noncommutative quantities. The term commutator takes a very important place in it. *The commutator* $[\hat{A}\hat{B}]$ *of two operators* $\hat{A}$ *and* $\hat{B}$ *is defines by the difference of the products* $\hat{A}\hat{B}$ *and* $\hat{B}\hat{A}$:

$$[\hat{A}\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{10.25}$$

If the operator $[\hat{A}\hat{B}]$ is equal to zero - $[\hat{A}\hat{B}]=0$, i.e. *if the commutator is zero, $\hat{A}$ and $\hat{B}$ are commutative operators, but if $[\hat{A}\hat{B}]\neq 0$ they are non commutative operators*. An arbitrary operator always commutes with a constant and with itself.

Finally we shall note that *when $\hat{A}$ and $\hat{B}$ are Hermitian operators, their product in the general case is not a Hermitian operator*. It can always be represented in the following way:

$$\begin{gathered}\hat{C}=\hat{A}\hat{B}=\frac{1}{2}\left(\hat{A}\hat{B}+\hat{B}\hat{A}\right)+\frac{1}{2}\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right) \quad \text{or} \\ \hat{C}=\hat{F}+\hat{G}, \quad \hat{F}=\frac{1}{2}\left(\hat{A}\hat{B}+\hat{B}\hat{A}\right), \quad \hat{G}=\frac{1}{2}\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right).\end{gathered} \tag{10.26}$$

The operator $\hat{F}$ is a Hermitian one, and the operator $\hat{G}$ is not a Hermitian one, but the operator $i\hat{G}$ is a Hermitian operator:

$$i\hat{G}=\frac{i}{2}\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right). \tag{10.27}$$

The product of a Hermitian operator $\hat{A}$ with a constant, as well its square - const$\hat{A}$ and $\hat{A}^2$ - are Hermitian operators.

10.3 EIGENVALUES AND EIGENFUNCTIONS OF THE OPERATORS

In Section 10.1 we have shown (see (10.9)), that as a result of acting of the operator $\hat{f}$ of the observable f on its eigenfunction ψ_i the last is multiplied by the eigenvalue f_i of this observable:

$$\hat{f}\psi_i=f_i\psi_i. \tag{10.28}$$

Mathematically the expression (10.28) is an equation of the unknown function ψ_i. We can obtain its solution if we add the boundary conditions. *The functions, which are a solution of the Eq.* (10.28*), are called eigenfunctions of the operator $\hat{f}$ and numbers f_i at which the equation has a solution - eigenvalues of the operator $\hat{f}$* .

Example: We look for the eigenfunction and the eigenvalues of the operator $-\frac{d^2}{dx^2}$. To determine them we have to solve the equation of the string:

$$\frac{d^2}{dx^2}u_i + k_i^2 u_i = 0. \tag{10.29}$$

If *a* stands for the string length ($0 \le x \le a$) the boundary conditions have the following form:

$$u_i(0) = 0, \qquad u_i(a) = 0. \tag{10.30}$$

The solution of the Eq. (10.29) is well known:

$$u_i = A\sin k_i x + B\cos k_i x. \tag{10.31}$$

From the boundary conditions we obtain:

$$B = 0, \qquad A\sin k_i a = 0 \tag{10.32}$$

i.e. $k_i a = i\pi,\ k = i\pi / a,\ i = 1, 2, \ldots$

Taking into account this, the solution (10.31) deduces to the following:

$$u = A\sin\frac{i\pi}{a}x, \qquad i = 1, 2, \ldots \tag{10.33}$$

So for the operator $-\frac{d^2}{dx^2}$ we have obtained the following eigenfunctions and eigenvalues:

$$\begin{aligned} &u_1 = A\sin\frac{1.\pi}{a}x, \quad u_2 = A\sin\frac{2.\pi}{a}x, \quad \ldots, \quad u_i = A\sin\frac{i.\pi}{a}x, \quad \ldots, \\ &k_1^2 = 1^2\frac{\pi^2}{a^2}, \qquad k_2^2 = 2^2\frac{\pi^2}{a^2}, \qquad \ldots, \quad k_i^2 = i^2\frac{\pi^2}{a^2}, \qquad \ldots \end{aligned} \tag{10.34}$$

Let us summarise briefly the results of the Section 9.2 and the results of this chapter up to now. *To every physical quantity we attach an operator and to the state of the system - a wave function. The states in which the measurement of the physical quantity f is reproducible one, are defined by us* *as eigenstates. They are described by the wave functions* ψ_i *and in the measurement of the observable f, one obtains the values* f_i*. The last ones satisfy the Eq.* (10.28)*. In this equation the functions* ψ_i *and the values* f_i *are the eigenfunctions and eigenvalues of the operator* $\hat{f}$ *.*

The set of the eigenvalues of the operator are called a spectrum of the operator. If to the n different eigenfunctions of one operator correspond one and the same eigenvalue the spectrum is n-fold degenerate.

Now it is clear why the operators in quantum mechanics are Hermitian ones. In Eq. (10.28) the values f_i, i.e. the measured ones in the experiment eigenvalues of the observable *f*, are real numbers, but always real eigenvalues have namely the Hermitian operator.

The eigenfunctions of the Hermitian operator are orthogonal. We shall prove this. Let ψ_i and ψ_k are two eigenvalues of the operator $\hat{f}$ and f_i, f_k are its corresponding eigenvalues. Then we can write the equation (10.28) for ψ_κ and the complex conjugate equation for ψ_i:

$$\begin{aligned} \hat{f}\psi_k &= f_k\psi_k, \\ \hat{f}^*\psi_i^* &= f_i\psi_i^*. \end{aligned} \qquad (10.35)$$

We multiply the first equation to ψ_i^*, the second to ψ_k, substrate two obtained equations and integrate to the variables *x*:

$$\int \psi_i^* \hat{f}\psi_k dx - \int \psi_k \hat{f}^* \psi_i^* dx = \int (f_k - f_i)\psi_i^*\psi_k dx. \qquad (10.36)$$

Because of the Hermicity of the operator the left part of this equation is equal to zero and therefore:

$$\int (f_k - f_i)\psi_i^*\psi_k dx = 0. \qquad (10.37)$$

As $f_i \neq f_k$, the condition of the orthogonality is as follows:

$$\int \psi_i^*\psi_k dx = 0 \qquad i \neq k. \qquad (10.38)$$

If we add the normalization condition, we obtain that *the eigenfunctions of one operator form the orthonormal system* (9.43):

$$\int \psi_i^*\psi_k dx = \delta_{ik}. \qquad (10.39)$$

For a continuous observable, the orthogonal condition has the form (9.55).

The system of the eigenfnctions of a Hermitian operator creates a complete system. This means that every function $\psi(x)$ can be represented as a linear combination of the eigenfunctions:

$$\psi(x)=\sum_i C_i\psi_i(x). \tag{10.40}$$

Earlier, in Section 9.5, we proposed the possibility of such expansion, taking into account the superposition principle. Now on the basis of the properties of the linear operators we can state that such expansion is always possible.

If the function of the state $\psi(x)$ and the eigenfunction of the operator $\hat{f}$ of the observable *f* are known, it is possible to be found the coefficients C_k of the relative gravity of the eigenstate ψ_k. The knowing of the C_k give us the possibility to define the probability $W_k=|C_k|^2$ (9.51). In fact when we multiply (10.40) to ψ_i^* and then integrate to dx, we obtain C_k (see (10.3)):

$$\int\psi_k^*\psi dx=\sum_i C_k\delta_{ik}=C_k. \tag{10.41}$$

Having the mathematical apparatus of the operators and their eigenfunctions and eigenvalues, we are able to answer the question whether two observables *M* and *N* can be measured simultaneously. Let the wave function of the state to be ψ_i and it to be eigenfunction of the operators *M* and *N,* i.e.

$$\hat{M}\psi_i=M_i\psi_i, \qquad \hat{N}\psi_i=N_i\psi_i. \tag{10.42}$$

We act on the second equation with the operator $\hat{M}$ and on the first - with the operator $\hat{N}$ and the second result is subtracted from the first result:

$$\begin{aligned}&\hat{M}\hat{N}\psi_i-\hat{N}\hat{M}\psi_i=N_i\hat{M}\psi-M_i\hat{N}\psi_i=N_iM_i\psi_i-M_iN_i\psi_i\\&=(N_iM_i-M_iN)_i\psi_i=0 \qquad \text{or} \qquad (\hat{M}\hat{N}-\hat{N}\hat{M})\psi_i=0.\end{aligned} \tag{10.43}$$

The condition is fulfilled for the arbitrary wave function and therefore

$$\hat{M}\hat{N}-\hat{N}\hat{M}=[\hat{M}\hat{N}]=0. \tag{10.44}$$

Two observables are simultaneously measurable if their operators commute.

Finally we shall notice that as a matter of fact the first three sections of this Chapter are an introduction to the mathematical basics of quantum mechanics. The reader can find a complete exposition of this question in the Chapter 4 of the book of W. Greiner [1].

10.4 OPERATORS OF THE CO-ORDINATES AND THE MOMENTUM AND THEIR EIGENFUNCTIONS AND EIGENVALUES

In the considered example in Section 10.1 we have proved that the operator of the co-ordinate x is the same co-ordinate x (10.12). Following this, we can choose any of the co-ordinates x, y, z for a relative operator and can write

$$\hat{x} = x, \qquad \hat{y} = y, \qquad \hat{z} = z. \tag{10.45}$$

Transmitting from the projections x, y, z to the vector **r** we obtain

$$\hat{\mathbf{r}} = \mathbf{r}. \tag{10.46}$$

In general, using the proof for $\hat{x} = x$, we can proof that the operator of every physical quantity f, which depends only on the co-ordinates, i.e. $f = f(x,y,z)$ is the same function:

$$\hat{f} = f(x,y,z). \tag{10.47}$$

To define the eigenfunction of the operator $\hat{x}$ we write the equation for its eigenfunction

$$\hat{x}\psi_{x'}(x) = x'\psi_{x'}(x). \tag{10.48}$$

And now let remember the introduced in Section 9.6 Dirac's function. According to the relation for the variable $x - x'$ (property 5.) we can write

$$(x - x')\delta(x - x') = 0. \tag{10.49}$$

This equation can be written in another way:

$$x\delta(x-x')=x'\delta(x-x'). \qquad (10.50)$$

After replacing x with $\hat{x}$ we obtain

$$\hat{x}\delta(x-x')=x'\delta(x-x'). \qquad (10.51)$$

From the comparison of this equation with the Eq. (10.48) it is clear that *the eigenfunction of the operator* $\hat{x}=x$ *is δ-function**

$$\psi(x)=\delta(x-x'), \qquad 10.52)$$

where x' is the value of the co-ordinate x.

For the operators of the momentum components according to the (10.16) we have

$$\hat{p}_x=-i\hbar\frac{\partial}{\partial x}, \qquad \hat{p}_y=-i\hbar\frac{\partial}{\partial y}, \qquad \hat{p}_z=-i\hbar\frac{\partial}{\partial z}. \qquad (10.53)$$

Let us multiply the equalities (10.53) by the relative orts $\mathbf{x}^0,\mathbf{y}^0,\mathbf{z}^0$ and then to sum them up. As a result we obtain the operator of the momentum

$$\hat{\mathbf{p}}=-i\hbar\left(\mathbf{x}^0\frac{\partial}{\partial x}+\mathbf{y}^0\frac{\partial}{\partial y}+\mathbf{z}^0\frac{\partial}{\partial z}\right)=-i\hbar\nabla. \qquad (10.54)$$

Squaring the equalities in (10.53) and summing them up, we obtain the operator $\hat{p}^2$:

$$\hat{p}^2=\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2=-\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=-\hbar^2\nabla^2=-\hbar^2\Delta. \qquad (10.55)$$

Here $\Delta=\nabla^2$ is the operator of Laplace.

Let write the equation of the eigenfunction $\psi_{p_x}(x)$ for the operator $\hat{p}_x$:

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*This eigenfunction of the operator $\hat{x}$ is in a co-ordinate representation, i.e. in an eigenrepresentation (see Section 15.1). *The eigenfunction of the operator in an eigenrepresentation is always δ-function.*

$$\begin{gathered}\hat{p}_x\psi_{p_x}(x)=p_x\psi_{p_x}(x),\\ -i\hbar\frac{\partial}{\partial x}\psi_{p_x}(x)=p_x\psi_{p_x}(x).\end{gathered}\tag{10.56}$$

Here we shall note that in quantum mechanics the operators of the momentum and its components - (10.54) and (10.53) - are customary denoted respectively with $\hat{\mathbf{p}}$ and $\hat{p}_x, \hat{p}_y, \hat{p}_z$. Strictly speaking, we have to write the operators $\hat{\mathbf{P}}$ and $\hat{P}_x, \hat{P}_y, \hat{P}_z$, i.e. the operators of the general momentum, canonically conjugated to the co-ordinates $\mathbf{r}$ and x, y, z. This is possible as far as in Cartesian co-ordinates the general momentum **P** is equal to the mechanical momentum **p**. This will help the curious readers not to be misled by the form of the operator of Hamilton for the charged particle in electromagnetic field (see (10.104)).

The wave function of the free particle with momentum p_x

$$\psi=\psi_{p_x}(x)=\frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{i}{\hbar}p_x x\right)\tag{10.57}$$

satisfies Eq. (10.56). This can be checked readily, if we substitute (10.57) in (10.56). Consequently, it is the eigenfunction of the operator $\hat{p}_x=-i\hbar\frac{\partial}{\partial x}$. In this p_x can take arbitrary value in the interval

$$-\infty<p_x<+\infty.\tag{10.58}$$

These values are eigenvalues of the operator $\hat{p}_x$. On the analogy of this we can prove that *the eigenfunction of the operator* $\hat{\mathbf{p}}=-i\hbar\nabla$ is

$$\psi_{\mathbf{p}}(\mathbf{r})=\frac{1}{\sqrt{(2\pi\hbar)^3}}\exp\left(\frac{i}{\hbar}\mathbf{pr}\right).\tag{10.59}$$

Let find the commutators of the considered so far operators. Two arbitrary co-ordinates, for example *x* and *y*, commute, i.e. their commutator $[\hat{x},\hat{y}]$ is equal to zero. Really

$$\begin{gathered}[\hat{x},\hat{y}]\psi=\hat{x}\hat{y}\psi-\hat{y}\hat{x}\psi=\hat{x}(\hat{y}\psi)-(\hat{y}\hat{x})\psi=xy\psi-yx\psi=0,\\ [\hat{x},\hat{y}]=\hat{x}\hat{y}-\hat{y}\hat{x}=0.\end{gathered}\tag{10.60}$$

The operators of every two components of the momentum commute, because they are independent one from other, and the order of the differentiation can be changed:

$$[\hat{p}_x, \hat{p}_y] = \hat{p}_x \hat{p}_y - \hat{p}_y \hat{p}_x = 0. \tag{10.61}$$

Do the operators of the co-ordinate and the momentum commute? First, let consider the commutator of the momentum component with the unlike co-ordinate:

$$\begin{aligned} &[\hat{y}, \hat{p}_x]\psi = \hat{y}(\hat{p}_x\psi) - \hat{p}_x(\hat{y}\psi) = y\left(-i\hbar\frac{\partial\psi}{\partial x}\right) + i\hbar\frac{\partial}{\partial x}(y\psi) = 0\,, \\ &[\hat{y}, \hat{p}_x] = \hat{y}\hat{p}_x - \hat{p}_x\hat{y} = 0. \end{aligned} \tag{10.62}$$

The momentum components commute with unlike co-ordinates.

Secondly, let consider the momentum component p_x and its relative co-ordinate x. Operating with the operator of the commutator $[\hat{x}, \hat{p}_x]$ for the function ψ, we obtain

$$\begin{aligned} &[\hat{x}, \hat{p}_x]\psi = \hat{x}(\hat{p}_x\psi) - \hat{p}_x(\hat{x}\psi) = -i\hbar x\frac{\partial}{\partial x}\psi + i\hbar\frac{\partial}{\partial x}(x\psi) = i\hbar\psi, \\ &[\hat{x}, \hat{p}_x] = i\hbar. \end{aligned} \tag{10.63a}$$

The relation between every two similar co-ordinate and momentum component is the same:

$$\begin{aligned} &[\hat{y}, \hat{p}_y] = i\hbar, \\ &[\hat{z}, \hat{p}_z] = i\hbar\ . \end{aligned} \tag{10.63b}$$

The momentum components do not commute with their relative co-ordinate.

10.5$^+$ ANGULAR-MOMENTUM OPERATOR

The knowledge of the operators of the co-ordinate and the momentum is of essential significance for the determination of the operators of an arbitrary physical quantity. It is enough this quantity to be represented as a function of the co-ordinates and the momentum components, and the last ones to be replaced with their operators. Then for *the angular-momentum operator* $\hat{\mathbf{L}}$

and its components according to the definition (2.34) and the relations (2.36) we obtain the following operator:

$$\begin{aligned}
&\hat{\mathbf{L}} = \mathbf{r}\times\hat{\mathbf{p}} = -i\hbar\mathbf{r}\times\nabla\\
&\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),\\
&\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),\\
&\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).
\end{aligned} \tag{10.64}$$

For the square of the angular momentum we get:

$$\begin{aligned}
&\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\\
&= -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) - \hbar^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)^2 - \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)^2.
\end{aligned} \tag{10.65}$$

Let see what are the commutating properties of the obtained operators. We shall take the operators of two of the components, for example $\hat{L}_y$ and $\hat{L}_x$. For their commutator according to (10.64) we have:

$$\begin{aligned}
&[\hat{L}_y, \hat{L}_z] = (z\hat{p}_x - x\hat{p}_z)(x\hat{p}_y - y\hat{p}_x) - (x\hat{p}_y - y\hat{p}_x)(z\hat{p}_x - x\hat{p}_z)\\
&= z\hat{p}_y(\hat{p}_x x - x\hat{p}_x) + y\hat{p}_z(x\hat{p}_x - \hat{p}_x x)\\
&= z\hat{p}_y(-i\hbar) + y\hat{p}_z(-i\hbar) = i\hbar(-z\hat{p}_y + y\hat{p}_z) = i\hbar\hat{L}_x.
\end{aligned} \tag{10.66}$$

We use the commutator (10.63a) $\left[\hat{x}, \hat{p}_x\right] = i\hbar.$ By analogy we obtain also the other commutators of the components of the angular momentum:

$$\begin{aligned}
&[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x,\\
&[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y,\\
&[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z.
\end{aligned} \tag{10.67}$$

The operators of the angular-momentum components do not commute.

The three commutation relations can be represented in a vector form

$$i\hbar\hat{\mathbf{L}} = \hat{\mathbf{L}}\times\hat{\mathbf{L}}, \tag{10.68a}$$

or in a matrix form

$$i\hbar\left(\mathbf{x}^0\hat{L}_x+\mathbf{y}^0\hat{L}_y+\mathbf{z}^0\hat{L}_z\right)=\begin{vmatrix}\mathbf{x}^0 & \mathbf{y}^0 & \mathbf{z}^0\\ \hat{L}_x & \hat{L}_y & \hat{L}_z\\ \hat{L}_x & \hat{L}_y & \hat{L}_z\end{vmatrix}. \tag{10.68b}$$

To define the commutators $[\hat{L}_i,\hat{L}^2]$ $\left(i=x,y,z\right)$ we shall use (10.67). We multiply its last equality on the right and on left by the operator $\hat{L}_y$:

$$\begin{aligned}\hat{L}_x\hat{L}_y^2&=\hat{L}_y\hat{L}_x\hat{L}_y+i\hbar\hat{L}_z\hat{L}_y,\\ \hat{L}_y^2\hat{L}_x&=\hat{L}_y\hat{L}_x\hat{L}_y-i\hbar\hat{L}_y\hat{L}_z.\end{aligned} \tag{10.69}$$

After subtracting these equations we obtain:

$$\hat{L}_x\hat{L}_y^2-\hat{L}_y^2\hat{L}_x=i\hbar(\hat{L}_z\hat{L}_y+\hat{L}_y\hat{L}_z). \tag{10.70}$$

By analogy from the second commutator of (10.67) after multiplying by $\hat{L}_z$ we obtain:

$$\hat{L}_x\hat{L}_z^2-\hat{L}_z^2\hat{L}_x=-i\hbar(\hat{L}_z\hat{L}_y+\hat{L}_y\hat{L}_z). \tag{10.71}$$

We add the relation (10.70) to (10.71) and take into account that $\hat{L}_x\hat{L}_x^2-\hat{L}_x^2\hat{L}_x=0$:

$$\hat{L}_x\hat{L}^2-\hat{L}^2\hat{L}_x=0\,. \tag{10.72}$$

Choosing other two commutators from (10.67) we obtain similar expression for $\hat{L}_y$ and $\hat{L}_z$:

$$[\hat{L}_x,\hat{L}^2]=0,\qquad [\hat{L}_y,\hat{L}^2]=0,\qquad [\hat{L}_z,\hat{L}^2]=0. \tag{10.73}$$

The operators of the angular-momentum components commute with the operator of the square of the angular momentum.

The angular momentum as an integral of the motion takes a very important place in the problems with central forces (see Chapter 3). From here it is clear its significance in the analysis of the atoms and atomic systems, in which namely such forces act. In connection with this we should add that very often both of the operators of the component $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ and the operator $\hat{L}^2$ are necessary in the spherical co-ordinates.

To obtain these operators we have to express the connections both of the Cartesian co-ordinates with spherical ones (see (1.69) and Fig. 1.5) and of the spherical co-ordinates upon the Cartesian ones:

$$\begin{aligned} &x = r\sin\theta\cos\varphi, \qquad y = r\sin\theta\sin\varphi, \qquad z = r\cos\theta, \\ &r^2 = x^2 + y^2 + z^2, \qquad \cos\theta = \frac{z}{r}, \qquad \tan\varphi = \frac{y}{x}. \end{aligned} \tag{10.74}$$

Using these relations we easy may express the derivative of the spherical co-ordinate upon the Cartesian:

$$\begin{aligned} &\frac{\partial r}{\partial x} = \sin\theta\cos\varphi, \qquad \frac{\partial r}{\partial y} = \sin\theta\sin\varphi, \qquad \frac{\partial r}{\partial z} = \cos\theta, \\ &\frac{\partial \theta}{\partial x} = \frac{\cos\varphi\cos\theta}{r}, \qquad \frac{\partial \theta}{\partial y} = \frac{\sin\varphi\cos\theta}{r}, \qquad \frac{\partial \theta}{\partial z} = -\frac{\sin\theta}{r}, \\ &\frac{\partial \varphi}{\partial x} = -\frac{\sin\varphi}{r\sin\theta}, \qquad \frac{\partial \varphi}{\partial y} = -\frac{\cos\varphi}{r\sin\theta}, \qquad \frac{\partial \varphi}{\partial y} = 0. \end{aligned} \tag{10.75}$$

Now we can easy obtain the operator $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$:

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi} \\ &= \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{\cos\varphi\cos\theta}{r}\frac{\partial}{\partial \theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}, \\ \frac{\partial}{\partial y} &= \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\sin\varphi\cos\theta}{r}\frac{\partial}{\partial \theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}, \\ \frac{\partial}{\partial z} &= \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}. \end{aligned} \tag{10.76}$$

We substitute the derivative $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ into the expressions of the operators for angular-momentum components (10.64) and obtain them in the spherical co-ordinates form:

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right),$$

$$\hat{L}_y = -i\hbar\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right), \tag{10.77}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}.$$

By analogy substituting (10.76) into (10.65) we might obtain also the operator $\hat{L}^2$. We shall obtain it by another way using two *ladder operators* $\hat{L}_+$ *and* $\hat{L}_-$:

$$\begin{aligned}\hat{L}_+ &= \hat{L}_x + i\hat{L}_y = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right),\\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y = \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right).\end{aligned} \tag{10.78}$$

The product of these operators is:

$$\hat{L}_+\hat{L}_- = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) = \hat{L}_x^2 + \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y]\,. \tag{10.79}$$

Expressing the square of the angular-momentum operator $\hat{L}^2$ through the operator $\hat{L}_+\hat{L}_-$ (and also through the $\hat{L}_z$) we get

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}_+\hat{L}_- + \hat{L}_z^2 - \hbar\hat{L}_z. \tag{10.80}$$

And now we shall obtain the product of the ladder operators $\hat{L}_+\hat{L}_-$. We use (10.80) and carefully differentiate strictly keeping the order of operators in the products:

$$\begin{aligned}\hat{L}_+\hat{L}_- &= -\hbar^2 e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\left(-e^{-i\varphi}\frac{\partial}{\partial\theta} + ie^{-i\varphi}\cot\theta\frac{\partial}{\partial\varphi}\right)\\ &= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right).\end{aligned} \tag{10.81}$$

We substitute $\hat{L}_z$ from (10.77) and $\hat{L}_+\hat{L}_-$ from (10.81) into (10.80) and obtain the square of the angular-momentum operator $\hat{L}^2$ in spherical co-ordinates:

$$\begin{aligned}\hat{L}^2 &= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\ &= -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.\end{aligned} \tag{10.82}$$

The operator

$$\hat{\Lambda} = -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \tag{10.83}$$

is called the operator of Legendre. Often instead of $\hat{\Lambda}$ we uses the operator $\Delta_{\theta,\varphi} \equiv \nabla^2_{\theta,\varphi} = -\hat{\Lambda}$, called Laplacian upon the sphere or an angular Laplacian:

$$\hat{L}^2 = \hbar^2\hat{\Lambda} = -\hbar^2\Delta_{\theta,\varphi}. \tag{10.84}$$

The operator $\Delta_{\theta,\varphi}$ is the angular part of the operator of Laplace Δ in the spherical co-ordinate system:

$$\begin{aligned}\Delta &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\Delta_{\theta,\varphi} = \Delta_r + \frac{\Delta_{\theta,\varphi}}{r^2}.\end{aligned} \tag{10.85}$$

The operator Δ_r is the radial Laplacian.

10.6 EIGENVALUES AND EIGENFUNCTIONS OF THE OPERATORS $\hat{L}_z$ AND $\hat{L}^2$

We shall start with the component L_z of the angular momentum. The equation for the eigenfunctions of the operator $\hat{L}_z$ appears as

$$i\hbar\frac{\partial\psi}{\partial\varphi}=L_z\psi. \qquad (10.86)$$

The solution of this equation is:

$$\psi(\varphi)=A\exp\left(\frac{iL_z}{\hbar}\varphi\right). \qquad (10.87)$$

From the condition of single-valued function (Section 9.2) - $\psi(\varphi)=\psi(\varphi+2\pi)$ - we obtain:

$$A\exp\left(\frac{iL_z}{\hbar}\varphi\right)=A\exp\left[\frac{iL_z}{\hbar}(\varphi+2\pi)\right], \qquad (10.88a)$$

or

$$\exp\left(\frac{iL_z}{\hbar}2\pi\right)=1. \qquad (10.88b)$$

The values of the component L_z at which this condition is satisfied, are *the eigenvalues of the operator* $\hat{L}_z$*:*

$$L_z=m\hbar, \qquad m=0,\pm 1,\pm 2,.... \qquad (10.89)$$

The z-component of the angular momentum quantizied and it can have only discrete values, equal to the integral $\hbar$. Taking into account these values in (10.87), the eigenfunction becomes:

$$\psi(\varphi)=A\exp(im\varphi). \qquad (10.90)$$

With the determination of the constant *A* from the condition of normalization we get the final solution of the problem:

$$\int_0^{2\pi}|\psi(\varphi)|^2 d\varphi=\int_0^{2\pi}A^2\left|e^{im\varphi}\right|^2 d\varphi=A^2\int_0^{2\pi}d\varphi=2\pi A^2=1\Rightarrow A=\frac{1}{\sqrt{2\pi}}.(10.91)$$

The normalized eigenfunctions of the operator $\hat{L}_z$ have the following form

$$\psi(\varphi) = \frac{1}{\sqrt{2\pi}} \exp(im\varphi). \tag{10.92}$$

The equation for the eigenfunction of the operator $\hat{L}^2$ of the square of the angular momentum after taking into account (10.84), becomes:

$$\hat{\Lambda}\psi = \frac{L^2}{\hbar^2}\psi. \tag{10.93}$$

The explicit view of this equation is

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{L^2}{\hbar^2}\psi = 0. \tag{10.94}$$

This equation has a solution satisfying the finiteness of the wave function (Section 9.2) only for determined values of $L/\hbar$, namely:

$$\frac{L^2}{\hbar^2} = l(l+1), \qquad l = 0, 1, 2, \ldots \tag{10.95}$$

and its solutions are spherical functions $Y_{lm}(\theta,\varphi)$ (they are called also spherical harmonics; see, for example [2], Appendix V):

$$\psi_{lm}(\theta,\varphi) = Y_{lm}(\theta,\varphi), \qquad m = 0, 1, 2, \ldots \tag{10.96}$$

Spherical functions are eigenfunctions of the operators $\hat{L}^2$ and the condition (10.96) determines its eigenvalues:

$$L^2 = l(l+1)\hbar^2, \qquad l = 0, 1, 2, \ldots \tag{10.97}$$

The number l is called an orbital quantum number. Both the spectrum of the square of the angular momentum L^2 and that of the *z*-component L_z are discrete ones. The operators $\hat{L}^2$ and $\hat{L}_z$ commute (10.74) and have common eigenfunctions, i.e.

$$\hat{L}_z Y_{lm}(\theta,\varphi) = \hbar m Y_{lm}(\theta,\varphi), \qquad m = 0, 1, 2, \ldots \tag{10.98}$$

If we fix the square of the angular momentum $L^2 = l(l+1)\hbar^2$, i.e. the number *l,* the component L_z may have $2l+1$ values:

$$L_z = m\hbar, \qquad m = 0, \pm 1, \pm 2, ..., \pm l. \tag{10.99}$$

In other words, $2l+1$ z-components values of **L** and relspectively $2l+1$ wave functions, which differ on *m*, correspond to the state with fixed angular momentum. The spectrum of the operator $\hat{L}^2$ is ($2l+1$)-fold degenerate. *Physically this means, that the angular momentum vector with a fixed value, i.e. with a fixed number l, can have* $2l+1$ *orientations in space*.

10.7 VECTOR INTERPRETATION OF THE ANGULAR MOMENTUM

The angular momentum is a vector. The value of this vector is determined by L^2. Taking into account the experimentally measured values of L^2 we can measure anyone of the Cartesian component of $\mathbf{L}$. Let assume, that we consider the state with fixed values of L^2 and L_z (the corresponding operators of these quantities commute (10.73)). However the values of the two other components of the angular momentum L_x and L_y are indefinites. Their corresponding operators do not commute (10.67). In other words, *at simultaneous experimental measuring we obtain fixed values of* L^2 *and* L_z *and different values of* L_x *and* L_y. The situation, of course is, totally different in classical mechanics - for example, the angular momentum of the rotating wheel in one plane around fixed centre has determined values of both the vector and of its three components. Can the classical model be used in the presentation of the quantum mechanical moment with fixed L^2 and L_z and undefined L_x and L_y? If both the wheel and together with it the vector $\mathbf{L}$ precesses around the *Z*-axis, the values of L^2 and L_z will be fixed but not these of L_x and L_y. *The model of the vector of the angular momentum with fixed value, precessing around Z-axis and having fixed* L_z*-component and indefinite* L_x*- and* L_y*-components* (*Fig.10-1b*) *is a good visual representation of the quantum mechanical angular momentum.* We, however, shall underline that this is only one presentation, but not the real precessing of the vector $\mathbf{L}$. In fact it lies on the cone of the precession and another useful presentation shows it is spread over it.

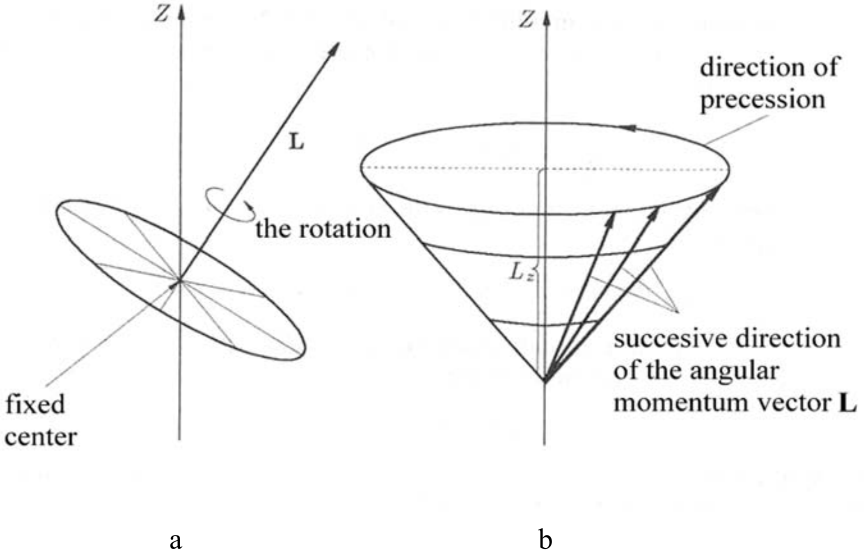

Figure 10-1. The vector representation of the angular momentum: a) angular momentum of the rotating wheel in one plane around fixed centre; b) classical vector representation of the quantum mechanical angular momentum - vector **L** precesses around the *Z*-axis.

The vector representation of the state with l=2 is shown in Fig. 10-2. We note that we are forced to accept the precession of the vector with zero *Z*-component for the same reason as for the other orientations.

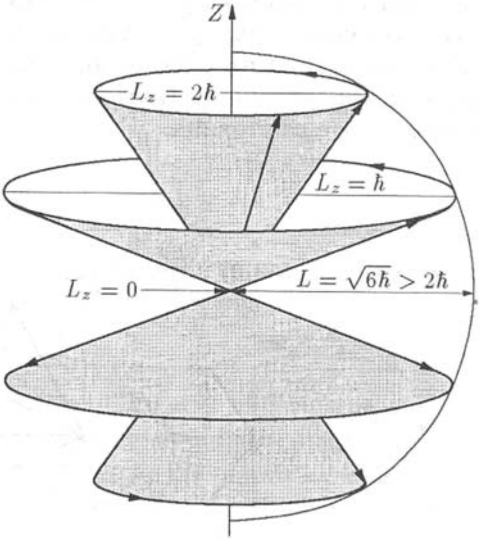

Figure 10-2. Vector representation of angular momentum in the state with l=2. In all possible orientations, including this with zero L_z-component, the vector **L** precesses around *Z*-axis.

In Section 10.6 we have established that the value of L is determined by the number l. It is referred as *the orbital quantum nu*mber. The number m, which determines the value of the component L_z of the moment **L,** is referred as *the azimuthal or magnetic quantum number.* In quantum mechanics the state of a particle with a fixed angular momentum, i.e. with fixed l is denoted except numerically and literately. The states with different angular momentum, theirs literal denotes and the possible components are given in the Table 10-1.

Table 10-1. Quantum numbers and the observables, which they determines, and theirs values

The value of the orbital number l	0	1	2	3	4
Literal symbol	s	p	*d*	*f*	*g*
The value of $L=\hbar\sqrt{l(l+1)})$	0	$\hbar\sqrt{2}$	$\hbar\sqrt{6}$	$\hbar\sqrt{12}$	$\hbar\sqrt{20}$
The value of the magnetic number m	0	$0,\pm 1$	$0,\pm 1,\pm 2$	$0,\pm 1,\pm 2,\pm 3$	$0,\pm 1,\pm 2,\pm 3,\pm 4$
The value of $L_z = m\hbar$	0	$0,\pm\hbar$	$0,\pm\hbar,\pm 2\hbar$	$0,\pm\hbar,\pm 2\hbar,\pm 3\hbar$	$0,\pm\hbar,\pm 2\hbar,\pm 3\hbar,\pm 4\hbar$
Multiplicity of the degeneration	0	3	5	7	9

So, at fixed orbital quantum number l, i.e. at fixed value of the vector of the orbital moment, it can have only $2l+1$ orientations in the space. In this case one speaks about *space quantization*. Conveniently and obviously these orientations are represented by vector diagrams. For *s*-, *p*-, *d*- and *f*- states of a particle these diagrams are shown in Fig. 10.3. To construct the diagram, for example of the *p*-state, from the beginning O of the Z-axis we draw the half circle with the radius equal to $L=\hbar\sqrt{l(l+1)}=\hbar\sqrt{2}$ and then construct three orientations of the vector **L,** so that its components to the Z-axis to be respectively $-\hbar$, 0 and $\hbar$. Similarly we construct the diagrams of the rest states as well.

The angle, which the vector **L** makes with the Z-axis, is determined by the quantum numbers l and m:

$$\cos\theta = \frac{L_z}{L} = \frac{m\hbar}{\hbar\sqrt{l(l+1)}} = \frac{m}{\sqrt{l(l+1)}}. \qquad (10.100)$$

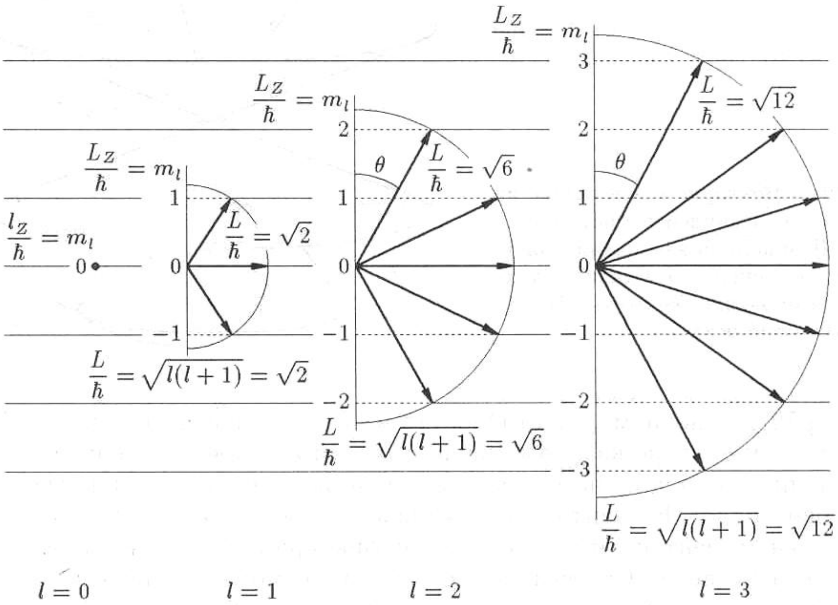

Figure 10-3. Vector diagrams of the angular momentum for different states: *s*-, *p*-, *d*- and *f*-states.

For given value of *L,* i.e. for *l*, the maximum value of *m* is *l*. But $m = l < \sqrt{l(l+1)}$. Therefore the vector of the angular moment **L** never align itself completely in the direction of *Z*-axis.

10.8 ENERGY OPERATORS

Firstly we shall determine the operator of the kinetic energy of a particle with mass m_0. Substituting momentum components into classical expression for the kinetic energy *T* (e.g. in (6.53)) with theirs operators, we obtain:

$$\hat{T} = \frac{1}{2m_0}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = -\frac{\hbar^2}{2m_0}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m_0}\nabla^2. \quad (10.101a)$$

*The kinetic-energy operator is expressed by the operator of Laplac*e:

$$\hat{T} = -\frac{\hbar^2}{2m_0}\nabla^2 = -\frac{\hbar^2}{2m_0}\Delta. \quad (10.101b)$$

In spherical co-ordinates using (10.85) we can write the operator of the kinetic energy as follows:

$$\hat{T}=-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\Delta_{\theta,\varphi}=\hat{T}_r+\frac{\hat{L}^2}{2m_0r^2}, \qquad (10.102)$$

i.e. the operator $\hat{T}$ represents by the operator of the radial kinetic energy and the operator of the square of the angular momentum. The separation of the kinetic energy in quantum mechanics to radial energy $\hat{T}_r$ and centrifugal energy $\hat{L}^2/2m_0r^2$ fully corresponds to both parts of the kinetic energy in classical mechanics (6.79). We shall note that in quantum mechanics the centrifugal energy $\hat{L}^2/2m_0r^2$ customary is called *rotational en*ergy.

The operator of the total energy is a sum of the operator $\hat{T}$ and the operator of the potential energy U. As U depends only on the co-ordinates its operator is the same function U. Consequently the operator of Hamilton in Cartesian and spherical co-ordinates can be written as follows:

$$\begin{gathered}\hat{H}==\hat{T}+U(x,y,z)=-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\Delta+U(x,y,z),\\ \hat{H}==\hat{T}_r+\frac{\hat{L}^2}{2m_0r^2}=-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\Delta_{\theta,\varphi}+U(r).\end{gathered} \qquad (10.103)$$

Very important in quantum mechanics is the operator of the total energy of charged particle in electromagnetic field. We shall obtain it substituting physical quantities in the classical Hamiltonian (6.33) $H=(\mathbf{P}-e\mathbf{A})^2/2m_0+e\Phi$ by theirs operators. Remembering the comments for $\hat{\mathbf{p}}$ and $\hat{\mathbf{P}}$ in Section 10.4, for the operator $\hat{\mathbf{P}}$ we can write $\hat{\mathbf{P}}=-i\hbar\nabla$. The vector potential $\mathbf{A}$ is a function of the co-ordinates and therefore $\hat{\mathbf{A}}=\mathbf{A}$. Then for the operator of Hamilton we can write

$$\hat{H}=\frac{1}{2m_0}\left(\hat{\mathbf{P}}-e\mathbf{A}\right)^2+e\Phi=\frac{1}{2m_0}\left(-i\hbar\nabla-e\mathbf{A}\right)^2+e\Phi. \qquad (10.104)$$

Now we shall define the eigenfunctions and the eigenvalues of the operator of the kinetic energy in one-dimensional motion:

$$\hat{T}\psi = T\phi \;\rightarrow\; -\frac{\hbar^2}{2m_0}\frac{\partial^2\psi}{\partial x^2} = \frac{p_x^2}{2m_0}\psi. \tag{10.105}$$

The solution of this equation is the function $\psi_{p_x}(x)$ (10.57) and the eigenvalues of the energy forms the continuos spectrum from $-\infty$ to $+\infty$.

For three-dimensional motion the operator $\hat{T}$ has the form (10.101) and the equation for its eigenfunction

$$-\frac{\hbar^2}{2m_0}\Delta\psi = \frac{p^2}{2m_0}\psi. \tag{10.106}$$

has the solution $\psi_{\mathbf{p}}(\mathbf{r})$ (10.59), which describes the plane wave of de Broglie. The momentum p of a free particle has an arbitrary value from $-\infty$ to $+\infty$ and the energy spectrum is continuous.

10.9 THE HEISENBERG UNCERTAINTY PRINCIPLE

We know that the state of a system is described by a wave function and the physical quantities - by operators. *When the measurement of one quantity is repeatble, in the experiment we get the eigenvalues of its operator*, and the wave function of the state is the eigenfunciton of the operator. In this case the physical quantity is defined. *When the measurement is not repeatble, we obtain different values, but always one of the eigenvalues of quantity's operator*. The same quantity is undefined. The two quantities are compatible, i.e. they are simultaneously measured, when their operators commute. The set of the eigenfunctions of these quantities forms a complete set of functions.

When the operators of two observables A and B do not commute they are undefined. Let the commutator of the corresponding Hermitian operators $\hat{A}$ and $\hat{B}$ obeys the relation

$$\hat{A}\hat{B} - \hat{B}\hat{A} = i\hat{C}, \tag{10.107}$$

where $\hat{C} = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)/i$ is a Hermitian operator (problem 3). Does the connection exist in the uncertainties of both observables A and B in the state $\psi(x)$?

We shall characterize the uncertainties of both observables with the minimal possible product of their fluctuations. As a measure for the deviation of measured values of A and B from the mean value we shall use the root-mean-square deviations (the dispersions) $\Delta A = \sqrt{\overline{\delta A^2}}$ and $\Delta B = \sqrt{\overline{\delta B^2}}$. Here δA and δB stand for the deviations from the mean value:

$$\begin{aligned} &\delta A = A - \bar{A}, \quad \overline{\delta \mathrm{A}^2} = \overline{A^2} - 2\bar{A}\bar{A} + \bar{A}^2 = \overline{A^2} - \bar{A}^2, \\ &\delta B = B - \bar{B}, \quad \overline{\delta B^2} = \overline{A^2} - 2\bar{B}\bar{B} + \bar{B}^2 = \overline{B^2} - \bar{B}^2. \end{aligned} \tag{10.108}$$

Without loosing the generality we can set

$$\bar{A} = 0, \qquad \bar{B} = 0. \tag{10.109}$$

This is a question of choice of the co-ordinate system and of the initial point of reading. In this case the values of quantities A and B are equal to their deviations:

$$A = \delta A, \qquad B = \delta B. \tag{10.110}$$

In order to find the connection between the uncertainties δA and δB we consider the integral

$$I(\alpha) = \int \left| \left(\alpha \hat{A} - i\hat{B} \right) \psi \right|^2 dx, \tag{10.111}$$

where α is an arbitrary real number and the $I(a) \geq 0$.

We represent the integral as a product of complex conjugate factors and use the fact that operators $\hat{A}$ and $\hat{B}$ are Hermitian ones:

$$\begin{aligned} I(\alpha) &= \int \left(\alpha\hat{A} - i\hat{B} \right) \psi \left(\alpha \hat{A}^* + i\hat{B}^* \right) \psi^* dx \\ &= \int \left(\alpha\hat{A} - i\hat{B} \right) \psi \alpha \hat{A}^* \psi^* dx + i \int \left(\alpha\hat{A} - i\hat{B} \right) \psi \hat{B}^* \psi^* dx \\ &= \int \psi^* \alpha \hat{A} \left(\alpha\hat{A} - i\hat{B} \right) \psi dx + \int \psi^* i\hat{B}^* \left(\alpha\hat{A} - i\hat{B} \right) \psi dx \\ &= \int \psi^* \left[\alpha^2 \hat{A}^2 - i\alpha \left(\hat{A}\hat{B} - \hat{B}\hat{A} \right) + \hat{B}^2 \right] \psi dx \\ &= \int \psi^* \left[\alpha^2 \hat{A}^2 + \alpha \hat{C} + \hat{B}^2 \right] \psi dx = \alpha^2 \overline{A^2} + \alpha \bar{C} + \overline{B^2}. \end{aligned} \tag{10.112}$$

In this derivation we use the expression (10.107).

A necessary and sufficient condition the integral

$$I(\alpha) = \alpha^2 \overline{A^2} + \alpha \bar{C} + \overline{B^2}, \tag{10.113}$$

which is a square trinomial in respect to α, to be positive, is the discriminant of the trinomial to be negative

$$4\overline{\delta A^2}\,\overline{\delta B^2} \ge \bar{C}^2 \quad \rightarrow \quad \overline{\delta A^2}\,\overline{\delta B^2} \ge \frac{1}{2}\bar{C}^2 \quad \rightarrow \quad \Delta A \Delta B \ge \frac{1}{2}\left|\bar{C}\right|. \qquad (10.114)$$

The condition (10.114) *is known as the uncertainty relation of Heisenberg for two incompatible quantities. It is also called uncertainty principle.* It states that *if measurement of A is uncertain by the amount* ΔA*, then the measurement of B is uncertain by the amount* ΔB*, such that* $\Delta A \Delta B \ge \left|\bar{C}\right|/2$. The more precisely we measure *A,* the more we give up ability to determine *B* accurately. If *A* is exactly known, we know nothing at all about *B*, i.e. if $\Delta A = 0$, $\Delta B = \infty$, and vice versa. *The uncertainty relation is a consequence of the basic principles of quantum mechanics and is related to any two physical quantities which operators do not commute.*

Let us consider one concrete example with the co-ordinate y and momentum component p_y. According to (10.63b) the operator $\hat{C}$ in this case is

$$\hat{C} = \frac{y\hat{p}_y - y\hat{p}_y}{i} = \hbar \qquad (10.115)$$

and the Heisenberg relation can be written as

$$\Delta y \Delta p_y \ge \frac{\hbar}{2}. \qquad (10.116)$$

The product of the root-mean-square deviations (*the dispersions*) *of the co-ordinate and the corresponding component of the momentum in the same direction are larger or equal to* $\hbar/2$. Obviously it is not possible to make an experiment, in which simultaneously $\Delta p_y \equiv \sqrt{\overline{\delta p_y^2}} = 0$ and $\Delta y \equiv \sqrt{\overline{\delta y^2}} = 0$. *The localization of the particle give the uncertainty of the momentum and the particle with the precise momentum is spread in the space. This makes impossible the use of the term trajectory in quantum mechanics.*

We shall illustrate the Heisenberg relation with the experiment on the diffraction of the electron by a slit (Fig. 10-4). Before the slit the electron is in the state with certain momentum $p_x = p,\ p_y = 0,\ p_z = 0,$ which is described by the plane de Broglie wave $\psi = A\exp\left[i(\mathbf{pr} - Et)/\hbar\right]$. The probability to find the particle in the volume element dV is

$$dW = |\psi|^2\, dV = |A|^2\, dV \tag{10.117}$$

It does not depend on the co-ordinates and it is the same in all the space. *The particles with the precise determined momentum have totally uncertain co-ordinates*, which is in conformity with the uncertainty relation (10.116).

Let try to fix the co-ordinate y by the slit of the width a. Then we shall see the well-known diffraction pattern. As it is symmetrical we can write that $\overline{p_y} = 0$ and $p_y = \Delta p_y$. We shall do the estimation by the first diffraction maximum. Its limit is defined by the angle θ, i.e. by the first diffraction minimum. At this angle the rays from the both halves of the slit (two by two) interfere destructively as their path difference is $\lambda/2$, i.e.

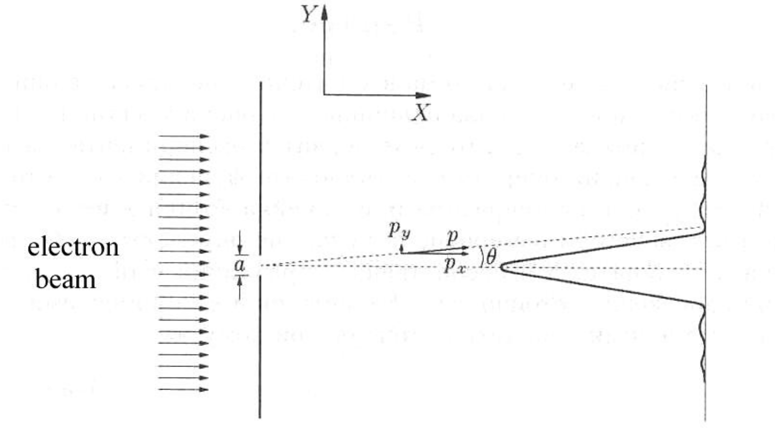

Figure 10-4. The measurement of the co-ordinate y of a beam of electrons by the slit leads to its decay on conical beams with different p_y momentum. The limit momentum of the first diffraction maximum is defined by the electron, which fall in the first minimum, i.e. by the ∠θ.

$$\frac{a}{2}\sin\theta = \frac{\lambda}{2}. \tag{10.118}$$

As the y-component of the momentum in the minimum is $p\sin\theta$, it changes from the $-p\sin\theta$ to $p\sin\theta$. Hence, from (10.118) we obtain for the deviation from the averaged value $\overline{p} = 0$ the following

$$\Delta p_y = p\sin\theta = \frac{h}{\lambda}\sin\theta = \frac{h}{\lambda}\frac{\lambda}{a} = \frac{h}{a}. \tag{10.119}$$

As the deviation of the co-ordinate y is $\Delta y = a/2$, we can write

$$\Delta p_y \Delta y = \frac{h}{a}\frac{a}{2} = \frac{h}{2}, \tag{10.120}$$

i.e. our estimation is very close to the calculated value (10.116).

It is clear, that with the decreasing the slit width and so the precise fixing of the co-ordinate y the uncertainty of p_y increases. Because of the diffraction the precise measurement of the co-ordinate y leads to a bigger uncertainty of the momentum p_y. The wave particle duality places the limit of the simultaneous measurement of the position and the momentum of the particle.

The uncertainty relation is a consequence from the specific character of the microscopic object, namely from its dual character.

SUMMARY

The state of a system in quantum mechanics is described by a wave function and the physical quantity (the observable) - by an operator (Table 10-2). The values of the quantity, which are measured in the experiment, are

Table 10-2. Basic operators and theirs eigenfunctions and eigenvalues

Physical quantity	Operator	Eigenfunctions	Eigenvalues
Co-ordinate x	x	$\psi(x) = \delta(x - x')$	$-\infty < x < \infty$
Radius-vector **r**	$\mathbf{r}$	$\psi(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$	$0 < \lvert\mathbf{r}\rvert < \infty$
Momentum x-component, p_x	$-i\hbar\frac{\partial}{\partial x}$	$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{i}{\hbar}p_x x\right)$	$-\infty < \lvert p_x\rvert < \infty$
Momentum **p**	$-i\hbar\nabla$	$\psi(\mathbf{r}) = \frac{1}{\sqrt{(2\pi\hbar)^3}}\exp\left(\frac{i}{\hbar}\mathbf{pr}\right)$	$0 < \lvert\mathbf{p}\rvert < \infty$
Angular momentum z-component, L_z	$-i\hbar\frac{\partial}{\partial\varphi}$	$\psi(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im\varphi)$	$L_z = m\hbar$
Square of the angular momentum	$\hbar^2\hat{\Lambda} = -\hbar^2\Delta_{\theta,\varphi}$	$\psi(\theta,\varphi) = Y_{l,m}(\theta,\varphi)$	$L^2 = \hbar^2 l(l+1)$
Kinetic energy, T	$-\frac{\hbar^2}{2m_0}\Delta$	$\psi(\mathbf{r}) = \frac{1}{\sqrt{(2\pi\hbar)^3}}\exp\left(\frac{i}{\hbar}\mathbf{pr}\right)$	$0 < \frac{p^2}{2m_0} < \infty$
Total energy, $E = H$	$-\frac{\hbar^2}{2m_0}\Delta + U(r)$	ψ and E depend on the view of $U(r)$	

eigenvalues of its operator, and the wave functions of the state are eigenfunctions of the operator or a linear combination of them. From the measurement in the eigenstate we obtain certain eigenvalues of the quantity (of its operator) and in the non-eigenstate - different values, but always one of the eigenvalues. Two physical quantities (observables) are compatible, i.e. simultaneously measured, if their operators commute.

Linear Hermitian operators are used in quantum mechanics. They obey the superposition principle and their eigenvalues are real numbers.

The operator $\hat{A}$ is Hermitian if it satisfies the condition

$$\int u^*(x)\hat{A}v(x)dx = \int v(x)\hat{A}^*u^*(x)dx.$$

The average value of the physical quantity *f* is defined by its operator and the wave function of the state

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

The eigenfunctions of an operator form a complete orthonormal set of functions.

The dispersions (root-mean-square deviation) ΔA and ΔB of two incompatible quantities A and B satisfy the Heisenberg uncertainty principle $\Delta A\Delta B \geq |\bar{C}|/2$, where C is defined by the operator $\hat{C} = [\hat{A}\hat{B}]/i$. Applied for the co-ordinate x and the momentum p_x, the uncertainty principle

$$\Delta x\Delta p_x \geq \frac{\hbar}{2}$$

leads to an inapplicability of the term trajectory in quantum mechanics.

QUESTIONS

1. How is average value of the observable expressed by:
   a) superposition coefficients C_k; b) its operator?
2. What kind of operators are used in quantum mechanics and why?
3. Which operators are Hermitian?
4. If two operators are Hermitian, are the operators of their:
   a) sum Hermitian; b) product Hermitian?
5. What is the commutator of two operators?
6. Do the following operators commute:

a) x and $\hat{p}_x$; b) z and $\hat{p}_y$; c) x and y; d) $\hat{p}_x$ and $\hat{p}_y$?

7. How are the operators of the angular-momentum components obtained?
8. Do the next operators commute:
   a) operators of the angular-momentum components;
   b) operators of the angular-momentum components with the operator of the square of angular momentum?
9. How are the operators of the energy obtained for:
   a) a free particle; b) a charged particle in electromagnetic field?
10. What are the eigenfunctions and the eigenvalues of an operator?
11. What is the complete set of functions?
12. What is the necessary and sufficient condition two quantities to be compatible?
13. What is the kind of spectrum of: a) the momentum components; b) the momentum: c) the components and the square of the angular moment; d) the energy of the free particle?
14. What is the degeneracy?
15. At the fixed value of the square of angular momentum L^2 (fixed l) the component L_z has $2l+1$ values. What does this mean physically?
16. What is the connection between the uncertainties of two incompatible quantities?
17. How can you explain physically the Heisenberg uncertainty relation for the momentum and the co-ordinate of a particle?

PROBLEMS

1. Prove that the operator $\hat{p}_x$ of the x-component of the momentum is Hermitian.
2. Prove that the commutator of the operator $\hat{p}_x$ and of the operator of the arbitrary physical quantity $f(x,y,z)$, which depends only on the co-ordinates, satisfies the condition $\hat{p}_x\hat{f}(x,y,z)-\hat{f}(x,y,z)\hat{p}_x=-\hbar\frac{\partial f}{\partial x}$.
3. Prove that if the operators $\hat{A}$ and $\hat{B}$ are Hermitian, the operator $\hat{C}=\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)/i$ is also Hermitian.
4. Taking into account that the product of two Hermitian operators can be present as $\hat{A}\hat{B}=\left(\hat{A}\hat{B}+\hat{B}\hat{A}\right)/2+\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)/2\equiv\hat{F}+\hat{G}$, prove that the operators $\hat{F}$ and $\mathrm{i}\hat{G}$ are Hermitian.

5. Prove that the component L_y of the angular momentum commutes with the operator of the square of angular momentum L^2: $\hat{L}_y\hat{L}^2 - \hat{L}^2\hat{L}_y = 0$.
6. Knowing the connection between the Cartesian and the spherical polar co-ordinates $x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$, $z = r\cos\theta$, prove that $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$.
7. Knowing the connection between the Cartesian and the spherical polar co-ordinates (problem 6.) prove that:

$$\hat{L}_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right),$$

$$\hat{L}_y = -i\hbar\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right).$$

8. Knowing the operators $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ in the spherical co-ordinates (problems 6. and 7.) prove, without using the ladder operators $\hat{L}_+$ and $\hat{L}_-$,

that $\hat{L}^2 == -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$.

9. Prove that the operator of Hamilton $\hat{H} = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2} + U(x)$ is Hermitian.
10. Obtain the Hamiltonian for the H-atom.
11. Obtain the Hamiltonian for the harmonic oscillator.

Chapter 11

THE SCRHOEDINGER EQUATION AND TIME DEPENDENCE OF THE OBSERVABLES

SUGGESTED READING

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3. Gasiorowicz S., Quantum Physics, John-Wiley & Sons, 3rd ed., 2003, Chapter 3.
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11.1 THE SCHROEDINGER WAVE EQUATION

The knowledge of the wave function of a quantum-mechanical system allows us to describe its state. The operator $\hat{f}$ of the observables gives us the possibility to define what values can accept this observable and what is their probability distribution. But knowing the state of given quantity in certain instant is not enough. It is necessary to know the behaviour, i.e. the changes of state in time as well. Then we can determine how the observables change in time. So, the question, which we put on, is how the wave function ψ changes in time. Said in other words, if in an instant $t=0$ it is $\psi(\mathbf{r},0)$ what will be $\psi(\mathbf{r},t)$?

In classical mechanics the equations of motion allow us, if we know the state in a given instant, to define it in every subsequent instant of time. In Newton mechanics the basic equation of motion (the second Newton's law) allows, if we know the co-ordinates and the velocities of the particles in a given instant of time, to define them in an arbitrary subsequent instant. In Hamilton mechanics, if we know the canonical conjugate general co-ordinates and momenta in the instant t we can define them in the arbitrary instant of time by Hamilton's equations.

By analogy, in quantum mechanics, in order to know the change of the state, it is necessary to know the equation, which is satisfied by the wave function ψ. For this we shall pay attention to the causality in quantum mechanics. In classical mechanics if we know the values of a quantity in an instant $t=0$, we can precisely determine its values in the instant t. *In quantum mechanics if we know the probability distribution of a given quantity in the instant $t=0$, we can determine its probability distribution in every instant t.* In other words, in quantum mechanics the causality has statistical, probabilistic character unlike its deterministic character in classical mechanics.

The wave function satisfies the Schroedinger equation. This is a basic statement in quantum mechanics. The Schroedinger equation can not be derived - it is postulated (as the second Newton's law is postulated). Some properties of Schroedinger equation can be established form the peculiarity of the quantum-mechanical systems.

Acording to the superposition principle, if the system can be in the states with the wave functions $\psi_1, \psi_2, \psi_3, ..., \psi_n$ it can be found and in the state with wave function $\psi = \sum_i C_i \psi_i$. All these functions obey the Schroedinger equation. This is possible if the equation is linear.

The state in the given instant $t = 0$, i.e. the wave function $\psi(\mathbf{r}, 0)$ in this instant (one constant with respect to time) determines the casual state in the instant *t*, i.e. the wave function $\psi(\mathbf{r}, t)$. This is possible only if the Schroedinger equation is of the first order in respect to time, i.e. it contains a derivative $\partial\psi / \partial t$. If, e.g. it were of the second order the two constants would be obtained. Then in order to know the state in the instant *t*, the wave function at $t = 0$, i.e. $\psi(\mathbf{r}, 0)$, would be insufficient - one more quantity is necessary.

We shall obtained the Schroedinger equation using of the wave function of the free particle with the momentum **p**:

$$\begin{aligned} \psi(\mathbf{r}, t) &= \frac{1}{\sqrt{(2\pi\hbar)^3}} \exp\left[-\frac{i}{\hbar}(Et - \mathbf{pr}) \right] \\ &= \frac{1}{\sqrt{(2\pi\hbar)^3}} \exp\left[-\frac{i}{\hbar}\left(Et - p_x x - p_y y - p_x z\right) \right]. \end{aligned} \tag{11.1}$$

We emphasize this is not a way that represents a proof but the illustration of the Schroedinger equation. We can subsequently determine as follows:

$$\begin{aligned} & i\hbar \frac{\partial\psi}{\partial t} = i\hbar\left(-\frac{i}{\hbar} E\psi \right) = E\psi, \\ & -\frac{\hbar^2}{2m}\Delta\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)\psi \\ & = -\frac{\hbar^2}{2m}\left(-\frac{p_x^2}{\hbar^2} - \frac{p_y^2}{\hbar^2} - \frac{p_z^2}{\hbar^2} \right)\psi = \frac{p^2}{2m}\psi = E\psi. \end{aligned} \tag{11.2}$$

We equalize the left-hand parts of these equations and obtain that the wave function (11.1) obeys the equation:

$$i\hbar \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi. \tag{11.3}$$

As $\hat{H}$ for a free particle has a form $\hat{H} = -\hbar^2/2m\Delta$, the Eq. (11.3) becomes

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi(\mathbf{r},t). \tag{11.4a}$$

This is the equation of Schroedinger. It is satisfied not only by the wave function of a free particle but by any wave function $\psi(\mathbf{r},t)$ of arbitrary quantum system.

If the system has the potential energy $U(r)$ and hence the Hamiltonian becomes $\hat{H} = -(\hbar^2/2m)\Delta + U(r)$, the Schroedinger equation take a form:

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\Delta + U(r)\right]\psi(\mathbf{r},t). \tag{11.4b}$$

If ψ -function has harmonic time dependence on time, i.e.

$$\psi(\mathbf{r},t) = \psi(\mathbf{r})\exp\left(-\frac{i}{\hbar}Et\right), \tag{11.5}$$

the Eq. (11.4b) reduces to

$$\Delta\psi(\mathbf{r}) + \frac{2m}{h^2}\left[E - U(r)\right]\psi(\mathbf{r}) = 0, \tag{11.6a}$$

or written by the Hamiltonian $\hat{H}$, we get

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{11.6b}$$

The Eq. (11.6) *is called a time-independent equation of Schroedinger, while the Eq.* (11.4) - *time-dependent equation.* Sometimes they are called correspondingly *stationary and general equation of Schroedinger.*

We have underlined that the Schroedinger equation is postulated. Accurate exposition of quantum mechanics begins with the postulates, which we have reached following our way of exposition. Let us sum up the basic statements in quantum mechanics:

1. The state of the quantum-mechanical objects is described by a wave function (I *postulate*).
2. The obseravbles are described by operators (II *postulate*).

3. The operators of the observables are Hermitian (III *postulate*).
4. The eignfunctions of a Hermitian operator $\hat{f}$, which are the solutions to the equation $\hat{f}\psi_i = f\psi_i$, form the complete set (in the general case infinite) of linear independent functions (IV *postulate*).
   The arbitrary function ψ can be represented as a linear combination of these functions $\psi = \sum_i C_i\psi_i$.
   The eigenfunctions are orthonormal $(\psi_i, \psi_k) = \int \psi_i^* \psi_k d\mathbf{r} = \delta_{ik}$.
5. In states, in which the measurement of the observable *f* is repeatable, for it we obtain one of the values $f_1, f_2, f_3, ..., f_n$, which are eigenvalues of the operator $\hat{f}$; these states are described by the wave functions $\psi_1, \psi_2, \psi_3, ..., \psi_n$, which are eigenfunctions of the operator $\hat{f}$: $\hat{f}\psi_i = f\psi_i$.
6. In a state, in which the measurement of the observable is unrepeatable, for it we obtain different values $f_1, f_2, f_3, ..., f_n$, but always one of the eigenvalues f_i of the operator $\hat{f}$; such state is a superposition of the eigenstates $\psi = \sum_i C_i\psi_i$ and the probability to measure the value f_i is $W_{f_i} = |C_i|^2$.
7. In a state, which is described by a wave function ψ, the mean value (the expectation value) of the observable *f* is $\overline{f} = \int \psi^* \hat{f} \psi dV$ (V *postulate*).
8. If two observables are compatible, their operators commute and have the common set of eigenfunctions; if they are incompatible - their operators do not commute and their dispersion are connected by the Heisenberg uncertainty principle.
9. The wave function satisfies the Schroedinger equation (VI *postulate*).

11.2 STATIONARY STATE

By the definition, *the stationary state is such a state, for which the Hamiltonian $\hat{H}$ does not depend on time.*

Considering for simplicity one-dimensional motion, we can write the Schroedinger equation with the operator $\hat{H}$, which is time-independent on time as follows:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\psi(xt). \tag{11.7}$$

This equation can be solved by the method of the separation of the variables. The solution is found as a product of two functions: $\psi(x)$, depending only on *x* and $\varphi(t)$ depending only on *t*:

$$\psi(x,t)=\psi(x)\varphi(t). \tag{11.8}$$

Substituting it in (11.7), we get:

$$i\hbar\psi(x)\frac{\partial\varphi(t)}{\partial t}=\varphi(t)\hat{H}\psi(x). \tag{11.9}$$

We divide both sides of this equation to $\psi(x)\varphi(t)$ and obtain:

$$i\hbar\frac{\frac{\partial\varphi(t)}{\partial t}}{\varphi(t)}=\frac{\hat{H}\psi(x)}{\psi(x)}. \tag{11.10}$$

On the left-hand side we have a function of time, and on the right-hand side - the function of the co-ordinate, i.e.

$$i\hbar\frac{\partial\varphi(t)}{\partial t}=\mathrm{const}\,\varphi(t), \tag{11.11a}$$

$$\hat{H}\psi(x)=\mathrm{const}\,\psi(x). \tag{11.11b}$$

The Eq. (11.11b) is an equation for the eigenfunctions of the operator $\hat{H}$. Let they be $\psi_1(x),\psi_2(x),\psi_3(x),...,\psi_n(x)$. For each of them the number constants determine the eigenvalues of the operator $\hat{H}$, i.e. of the energy operator: $\mathrm{const}=E_1, E_2, E_3, ..., E_n$; respectively the functions $\psi_k(x)$ are partial solutions of the Eq. (11.11b). For each of these solutions $\psi_k(x)$, the Eq. (11.11a)

$$i\hbar\frac{\partial\varphi_k(t)}{\partial t}=E_k\varphi_k(t) \tag{11.12}$$

has correspondingly a partial solution

$$\varphi(t)=A_k\exp\left(-\frac{i}{\hbar}E_k t\right). \tag{11.13}$$

Hence the partial solution of the origin Eq. (11.7), according to (11.8) is

$$\psi_k(x,t) = \psi_k(x)\exp\left(-\frac{i}{\hbar}E_k t\right). \tag{11.14}$$

As the Eq. (11.7) is linear, its general solution is a superposition of the partial solutions:

$$\psi(x,t) = \sum_k C_k \psi_k(x,t) = \sum_k C_k \psi_k(x)\exp\left(-\frac{i}{\hbar}E_k t\right). \tag{11.15}$$

Coefficients C_k do not depend on time t and the co-ordinate x and according to (10.3) are determined as follows:

$$C_k = \int \psi_k^*(x,t)\psi(x,t)\,dx. \tag{11.16}$$

From the solution of the equation of the stationary state we can make the following conclusion about general properties of such a state, independently of the concrete quantum system:

1. The energy of the system determines the time dependence. For eigenstate, i.e. for the state with determined energy (for example E_k), this dependence is harmonic:

$$\varphi(t) = A_k \exp\left(-\frac{i}{\hbar}E_k t\right) = A_k \exp(-i\omega_k t), \qquad \omega_k \equiv \frac{E_k}{\hbar}. \tag{11.17}$$

   Here ω_k stands for the angular frequency.
2. The probability density does not depend on time

$$\rho_k = \frac{dW_k}{dx} = \psi_k^*(x,t)\psi_k(x) = \rho_k(x). \tag{11.18}$$

3. The mean value of the observable. i.e. the expectation value, which not depends on time ($f \neq f(t)$; $\hat{f} \neq \hat{f}(t)$), does not change with time:

$$\begin{aligned}\overline{f} &= \int_{-\infty}^{+\infty}\psi^*(x,t)\hat{f}\psi(x,t)\,dx \\ &= \int_{-\infty}^{+\infty}\sum_k C_k^*\psi_k^*(x)\exp\left(\frac{i}{\hbar}E_k t\right)\sum_l C_l f_l\psi_l(x)\exp\left(-\frac{i}{\hbar}E_l t\right)dx \\ &= \sum_k C_k^*\exp\left(\frac{i}{\hbar}E_k t\right)\sum_l C_l f_l\exp\left(-\frac{i}{\hbar}E_l t\right)\int_{-\infty}^{+\infty}\psi_k^*(x)\psi_l(x)\,dx \\ &= \sum_k C_k^*\exp\left(\frac{i}{\hbar}E_k t\right)\sum_l C_l f_l\exp\left(-\frac{i}{\hbar}E_l t\right)\delta_{kl} = \sum_k |C_k|^2 f_k \neq \overline{f}(t).\end{aligned} \tag{11.19}$$

4. In a stationary state with the wave function $\psi(x,t)$ (11.15) the probability W_{f_i} to measure the value f_i of the observable *f* does not depend on time. In fact, according to (9.52) this probability is constant:

$$W_{f_i} = |C_i|^2. \tag{11.20}$$

5. The spectrum of the energy of the stationary state in central symmetrical field depends on the sign of the energy (e.g., see [R14], Section 49). When the total energy of the system is negative $E < 0$, it has a discrete spectrum, the eigenfunctions $\psi_k(x)$ of the operator $\hat{H}$ not being zero only in the limited region. Such state is called bound. When the total energy is positive $E > 0$, then $\psi(x) \propto \exp\left(\frac{i}{\hbar}p_x x\right)$, i.e. $\psi(x)$ represents a plane wave. The probability density does not depend on *x*: then $\rho(x) = |\psi(x)|^2 = \text{const}$ and the energy has a continuous spectrum. The state is called free.

11.3* DERIVATIVE OF AN OPERATOR WITH RESPECT TO TIME

The direct application of the term derivative to the precise values of a quantum-mechanical quantity is impossible. But it can be applied to the mean values of the observable (see, for example [3], Section 26). The mean value $\overline{f}$ of the quantity *f* can be expressed through the function $\psi(x,t)$ and the operator $\hat{f}$ (10.7) and it is defined in every instant: more than this as ψ^*, ψ and $\hat{f}$ are continuous function of time, it is also continuous. This mean value varies with time. This is strange as then we make one wonder how quickly it varies, i.e. what is the rate of its change. This means to determine the time derivative of the mean value $\overline{f}$:

$$\begin{gathered}\frac{d\overline{f}}{dt}=\frac{d}{dt}\int_{-\infty}^{+\infty}\psi^*(x,t)\hat{f}\psi(x,t)dx=\int_{-\infty}^{+\infty}\frac{\partial\psi^*(x,t)}{\partial t}\hat{f}\psi(x,t)dx\\+\int_{-\infty}^{+\infty}\psi^*(x,t)\frac{\partial\hat{f}}{\partial t}\psi(x,t)dx+\int_{-\infty}^{+\infty}\psi^*(x,t)\hat{f}\frac{\partial\psi(x,t)}{\partial t}dx.\end{gathered}\tag{11.21}$$

The function $\psi(x,t)$ satisfies the Schroedinger equation and $\psi^*(x,t)$ - its complex conjugate form:

$$\hat{H}\psi=i\hbar\frac{\partial\psi}{\partial t},\qquad \hat{H}^*\psi^*=-i\hbar\frac{\partial\psi^*}{\partial t}.\tag{11.22}$$

We determine $\partial\psi/\partial t$ and $\partial\psi^*/\partial t$ and after substituting them in (11.21) we obtain:

$$\frac{d\overline{f}}{dt}=-\frac{1}{i\hbar}\int_{-\infty}^{+\infty}\hat{H}^*\psi^*\hat{f}\psi dx+\int_{-\infty}^{+\infty}\psi*\frac{\partial\hat{f}}{\partial t}\psi dx+\frac{1}{i\hbar}\int_{-\infty}^{+\infty}\psi*\hat{f}\hat{H}\psi dx.\tag{11.23}$$

In the first integral we change the places of $\hat{H}^*\psi^*$ and $\hat{f}\psi$ and apply the rule for a hermiticivity to the operator $\hat{H}$

$$\begin{gathered}\int_{-\infty}^{+\infty}\hat{H}^*\psi*(x,t)\hat{f}\psi(x,t)dx=\int_{-\infty}^{+\infty}\hat{f}\psi(x,t)\hat{H}^*\psi*(x,t)dx\\=\int_{-\infty}^{+\infty}\psi*(x,t)\hat{H}\hat{f}\psi(x,t)dx.\end{gathered}\tag{11.24}$$

Substituting into (11.23), we get

$$\begin{gathered}\frac{d\overline{f}}{dt}=\int_{-\infty}^{+\infty}\psi^*(x,t)\frac{\partial\hat{f}}{\partial t}\psi(x,t)dx+\int_{-\infty}^{+\infty}\psi^*(x,t)\frac{\hat{f}\hat{H}-\hat{H}\hat{f}}{i\hbar}\psi(x,t)dx\\=\int_{-\infty}^{+\infty}\psi^*(x,t)\left(\frac{\partial\hat{f}}{\partial t}+\frac{\hat{f}\hat{H}-\hat{H}\hat{f}}{i\hbar}\psi(x,t)dx\right).\end{gathered}\tag{11.25}$$

We introduce the designation

$$\frac{\hat{f}\hat{H}-\hat{H}\hat{f}}{i\hbar}=\frac{[\hat{f},\hat{H}]}{i\hbar}=\left\{\hat{f},\hat{H}\right\}. \tag{11.26}$$

As we can see further, *in quantum mechanics the operator* $\left\{\hat{f},\hat{H}\right\}$ *performs the same role as the Poisson bracket in classical mechanics. Therefore the operator* $\left\{\hat{f},\hat{H}\right\}$ *is called quantum-mechanical bracket of Poisson* and the relation (11.26) is considered as the definition. Finally for the time derivative of the mean value of f we obtain

$$\frac{d\overline{f}}{dt}=\int_{-\infty}^{+\infty}\psi*(x,t)\left(\frac{\partial\hat{f}}{\partial t}+\left\{\hat{f},\hat{H}\right\}\right)\psi(x,t)dx. \tag{11.27}$$

The operator $\partial\hat{f}/\partial t+\left\{\hat{f},\hat{H}\right\}$ of a quantity is written in the brackets. In classical mechanics the total time derivative from f (see Chapter 6) is

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+\{f,H\}. \tag{11.28}$$

The operator of this quantity is $d\hat{f}/dt$ and it is equal to the operator $\partial\hat{f}/\partial t+\left\{\hat{f},\hat{H}\right\}$. In such way, on the basis of the analogy with classical mechanics, we introduce the time derivative of an operator:

$$\frac{d\hat{f}}{dt}=\frac{\partial\hat{f}}{\partial t}+\left\{\hat{f},\hat{H}\right\}. \tag{11.29}$$

Taking into account this we can write (11.27) as

$$\frac{d\overline{f}}{dt}=\int_{-\infty}^{+\infty}\psi*(x,t)\frac{d\hat{f}}{dt}\psi(x,t)dx=\overline{\frac{df}{dt}}. \tag{11.30}$$

The last equality we have written on the basis of the definition of the mean value of the quantity df/dt (10.7).

So, looking for the reply of the question to what is equal the derivative of the $\overline{f}$, we suddenly have reached an interesting result: *the time derivative of* *the mean value of an observable is equal to the mean value of time derivative of this value.*

Finally we shall note, that when the operator $\hat{f}$ does not depend explicitly on time, its total derivative is

$$\frac{d\hat{f}}{dt} = \left\{\hat{f}, \hat{H}\right\}, \tag{11.31}$$

i.e. it is equal to the Poisson quantum-mechanical bracket of $\hat{f}$ and Hamilton's operator $\hat{H}$.

11.4 CONSTANTS OF THE MOTION

In classical mechanics the quantity f is a constant of the motion if the total derivative of f in respect to time is equal to zero: $df/dt = 0$. By analogy, in quantum mechanics f is a constant of the motion if $d\hat{f}/dt = 0$:

$$\frac{d\hat{f}}{dt} = \frac{\partial\hat{f}}{dt} + \left\{\hat{f}, \hat{H}\right\} = 0. \tag{11.32}$$

When $\hat{f}$ does not depend explicitly on time, the condition (11.32) reduces to

$$\left\{\hat{f}, \hat{H}\right\} = 0, \tag{11.33}$$

i.e. *f is a constant of the motion, if the Poisson's bracket of the operator $\hat{f}$ and Hamilton's operator $\hat{H}$ is equal to zero.*

When f is a constant of the motion, i.e. when (11.32) is satisfied we obtain for the derivative of mean value $\overline{f}$, according to (11.30), as follows:

$$\frac{d\overline{f}}{dt} = 0, \qquad \overline{f} = \text{const}. \tag{11.34}$$

The mean value of a given quantity, which is a constant of the motion, does not change with time. We shall underline the difference between the constants of the motion in classical mechanics and quantum mechanics: In *the first case the same quantity remains constant in time, but in the second - its mean value.*

We shall note one more peculiarity in the case when f does not depend explicitly on time. In this case $\{\hat{f},\hat{H}\}=0$ and according to (11.26) the commutator $[\hat{f},\hat{H}]$ is also equal to zero - $[\hat{f},\hat{H}]=0$. The last one means that the operators $\hat{f}$ and $\hat{H}$ have common eigenfunctions $\psi_k(x)$:

$$\begin{aligned} \hat{f}\psi_k(x) &= f_k\psi_k(x), \\ \hat{H}\psi_k(x) &= E_k\psi_k(x). \end{aligned} \tag{11.35}$$

Let in this case (f does not explicitly depend on time) consider the state with a function $\psi(x,t)$. Let expand these functions in eigenfunctions $\psi_k(x)$:

$$\psi(x,t)=\sum_k C_k(t)\psi_k(x). \tag{11.36}$$

Every function $C_k(t)\psi_k(x)$ satisfies the Schroedinger equation. Substituting into this equation (for example, in (11.7) and taking into account (11.35), we obtain for $C_k(t)$ an equation, which is fully analogous to (11.12) and its solutions - to (11.13):

$$C_k(t)=C_k\exp\left(-\frac{i}{\hbar}E_kt\right). \tag{11.37}$$

In essence we have a stationary state, for which according to (11.36) and (11.37) we can write

$$\psi(x,t)=\sum_k C_k(t)\psi_k(x)=\sum_k C_k\exp\left(-\frac{i}{\hbar}E_kt\right)\psi_k(x). \tag{11.38}$$

From this equation it follows that C_k is equal to $C_k(t)$ at $t=0$:

$$C_k=C_k(0). \tag{11.39}$$

The probability to find the value f_k of the observable f is

$$W_{f_k}=\left|C_k(t)\right|^2=\left|C_k\right|^2=\left|C_k(0)\right|^2. \tag{11.40}$$

A conclusion: if the observable f is a constant of the motion and does not depend explicitly on time, in the non-eigenstate $\psi(x,t)$ *the probability* W_{f_k} *to measure the eigenvalue* f_k *does not depend on time.*

We shall consider some concrete constants of the motion of quantities, which do not depend explicitly on time.

Example 1: The total energy of a system, which does not depend on time. For Hamiltonian, which does not depend explicitly on time, we get:

$$\frac{d\hat{H}}{dt}=\left\{\hat{H},\hat{H}\right\}=\frac{[\hat{H},\hat{H}]}{i\hbar}=0, \tag{11.41}$$

i.e. *the energy is a constant of the motio*n. The equality $d\hat{H}/dt=0$ expresses the law of the energy conservation.

Example 2: The momentum of a particle in a constant potential field $U(x,y,z)=\text{const}$. As the potential energy is determined correct to the constant, we can put $U(x,y,z)=0$ and then

$$\hat{H}=\frac{\hat{p}^2}{2m}+U(x,y,z)=\frac{\hat{p}^2}{2m}. \tag{11.42}$$

The operators $\hat{p}_x$, $\hat{p}_y$, $\hat{p}_z$ and $\hat{p}^2$ commute with the operator $\hat{H}$. Hence, for their Poisson's brackets with the operator $\hat{H}$ (11.33) we have

$$\left\{\hat{p}_x,\hat{H}\right\}=0,\quad \left\{\hat{p}_y,\hat{H}\right\}=0,\quad \left\{\hat{p}_z,\hat{H}\right\}=0,\quad \left\{\hat{p}^2,\hat{H}\right\}=0. \tag{11.43}$$

The momentum $\mathbf{p}$ *and its components* p_x, p_y, p_z *are constants of the motion.*

Example 3. The component L_z *of the angular momentum and its value L (or* L^2*) in a spherically symmetrical field with the potential* $U(r)$. In such a field the Hamiltonian can be written as (see (10.101)÷(10.103)):

$$\hat{H}=\hat{T}(r,\theta,\varphi)+U(r)=\hat{T}_r(r)+\frac{\hat{L}^2(\theta,\varphi)}{2mr^2}+U(r). \tag{11.44}$$

The operators $\hat{L}_z$ and $\hat{L}^2$ do not depend on *r*. Besides this $\hat{L}_z$ commutes with $\hat{L}^2$ and hence

$$\left[\hat{L}_z,\hat{H}\right]=i\hbar\left\{\hat{L}_z,\hat{H}\right\}=0,$$
$$\left[\hat{L}^2,\hat{H}\right]=i\hbar\left\{\hat{L}^2,\hat{H}\right\}=0. \tag{11.45}$$

In a spherically symmetrical field L_z and L^2 *are constants of the motion.*

SUMMARY

It is postulated in quantum mechanics that the wave function satisfies the time dependent Schroedinger equation:

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

where $\hat{H}$ is the Hamiltonian of the system. When the system has a potential energy $U(r)$ the operator $\hat{H}$ has the form $\hat{H}=-(\hbar^2/2m)\Delta+U(r)$. It is a linear differential equation, which is of the first order in respect to time.

The states, in which the Hamiltonian does not depend explicitly on time, are called stationary states. In these states the wave function has harmonic dependence on time:

$$\psi(\mathbf{r},t)=\psi(\mathbf{r})\exp\left(-\frac{i}{\hbar}Et\right).$$

The equation, which is satisfied by the space part of the wave function, is called time-independent Schroedinger equation or stationary equation.

$$\hat{H}\psi(\mathbf{r})=E\psi(\mathbf{r}) \quad \text{or} \quad \Delta\psi(\mathbf{r})+\frac{2m}{h^2}\left[E-U(r)\right]\psi(\mathbf{r})=0.$$

In stationary states:

- the energy of the system determines single-dependence on time;
- the probability density does not depend on time;
- the mean value $\overline{f}$ of a observable, which does not depends on time $(f\neq f(t))$, is a constant;
- the probability W_{f_i} to measure the value f_i of the observable f does not depend on time;

– the energy spectrum in central symmetrical field is discrete, when the total energy of the system is negative (bound state), and continuous, when the total energy of is positive (free state).

The time derivative from the mean value of the observable is equal to the mean value of the time derivative of this quantity:

$$\frac{d\overline{f}}{dt} = \int_{-\infty}^{+\infty} \psi^*(x,t)\frac{d\hat{f}}{dt}\psi(x,t)\,dx = \overline{\frac{df}{dt}}.$$

The total time derivative of an operator is:

$$\frac{d\hat{f}}{dt} = \frac{\partial\hat{f}}{\partial t} + \left\{\hat{f},\hat{H}\right\},$$

where

$$\left\{\hat{f},\hat{H}\right\} = \frac{\hat{f}\hat{H} - \hat{H}\hat{f}}{i\hbar} = \frac{[\hat{f},\hat{H}]}{i\hbar}.$$

is the Poisson quantum-mechanical bracket of the operators $\hat{f}$ and $\hat{H}$. In quantum mechanics they perform the role analogous to this of the Poisson bracket in classical mechanics.

The physical quantity f is a constant of the motion if the total time-derivative of the operator $\hat{f}$ is equal to zero: $d\hat{f}/dt = 0$. When its operator $\hat{f}$ does not depend on time, i.e. $\partial\hat{f}/\partial t = 0$ and the Poisson bracket of the operator $\hat{f}$ and the Hamiltonian is equal to zero, it is a constant of the motion.

The mean value of an observable, which is a constant of the motion, does not vary in time $\left(f \neq f(t)\right)$.

QUESTIONS

1. Why is the Schroedinger equation necessary?
2. Why the Schroedinger equation is from the first order in respect to time?
3. Why is the Schroedinger equation linear?
4. Which is the form of: a) the time-dependent (the general) Schroedinger equation; b) the time-independent (the stationary) Schroedinger equation?

5. Which is the dependence on time of the wave function, satisfying the stationary Schroedinger equation?
6. What are the properties of the stationary state?
7. What is determined the character of the energy spectrum in the stationary state from?
8. To what is equal the time-derivative of the mean value of a quantum-mechanical value?
9. What is the Poisson bracket in quantum mechanics?
10. What is the condition for the constant of the motion in quantum mechanics?
11. Which is the physical significance of the constant of the motion?
12. Explain which physical quantity are constants of the motion and which of them are constants of the motion in the next case: a) a system with Hamiltonian, independent on time; b) the particle in the constant field; c) the particle in spherically symmetric field?

11. PROBLEMS

1. Show through the direct substitution, that the Schroedinger equation is satisfied by the wave function $\psi(x,t)=\psi(x)\exp(-iEt/\hbar)$, if $\psi(x)$ satisfies the stationary Schroedinger equation with the potential $U(x)$.
2. Prove that the state, formed by the superposition of two stationary states $\psi(x,t)=\psi_1(x)\exp(-iE_1t/\hbar)+\psi_2(x)\exp(-iE_2t/\hbar)$, is not stationary. Does the probability density $\psi^*(x,t)\psi(x,t)$ depends on time?
3. What is the Poisson bracket for the operators $\hat{p}_x$ and $\hat{x}$, $\hat{p}_y$ and $\hat{y}$?
4. Show that, if the functions $\psi_1(x,t)$, $\psi_2(x,t)$ and $\psi_3(x,t)$ are solutions of the Schroedinger equation with the potential $U(x)$, then every linear combination $\psi_1(x,t)=c_1\psi_1(x,t)+c_2\psi_2(x,t)+c_3\psi_3(x,t)$ is also a solution of this equation.
5. The quantum-mechanical system consists by two independent parts, whose stationary states are described by $\psi_1(x,t)$ and $\psi_2(x,t)$. The Hamitonian of the system can be represented as $\hat{H}(x_1,x_2)=\hat{H}_1(x_1)+\hat{H}_2(x_2)$, where $\hat{H}_1(x_1)$ and $\hat{H}_2(x_2)$ are the Hamiltonians of the independent subsystems (1) and (2). Prove that the stationary state of the system is described by the wave function $\psi(x,t)=\psi_1(x,t)\psi_2(x,t)$.

Chapter 12

MOTION IN ONE-DIMENTIONAL POTENTIAL

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12.3 The Step Potential

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12.6 The Tunnel Effect and Alpha-Decay

Passage trough barrier; tunnel effect - definition; real barrier; cold electron emission; ammonia molecule inversion; α *-decay rate and*

SUGGESTED READING

1. Liboff R. L., Introductory Quantum Mechanics, Holden-Day Inc., 4th ed., 2003, Sections 7.3-7.7, 8.1.
2. Wichmann E. H., Quantum Physics, Berkeley Physics Course, Vol. IV, McGraw-Hill Book Co., 2nd. ed., 1973, Chapter 7.
3. Spolsky, E. V., Atomic Physics, Vol. 1, Mir Publishing House, 1963, Sections 153-157.
4. Arya A., Elementary modern physics, Addison-Wesley Publishing Co., 1976, Sections 3.6 and 12.4.

12.1 MOTION IN A CONSTANT POTENTIAL FIELD

Let us consider the one-dimensional motion of the particle of mass m in the potential field, which is constant in respect to the co-ordinate x and independent in time:

$$U(x) = \text{const} = U. \tag{12.1}$$

The Hamiltonian of the system can be written as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\ . \tag{12.2}$$

It does not depend on time. Hence, the Schroedinger equation (11.4a) has a stationary solution:

$$\psi(x,t) = \psi(x)\exp\left(-\frac{i}{\hbar}Et\right) = \psi(x)\exp(-i\omega t), \qquad \omega \equiv \frac{E}{\hbar}. \tag{12.3}$$

We substitute the solution in Eq. (11.4a) and after eliminating the exponential multiplier $\exp(-iEt/\hbar)$ we have received the equation for $\psi(x)$:

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m}{\hbar^2}(E-U)\psi(x) = 0, \tag{12.4}$$

i.e. in a constant potential field the equation has the form:

$$\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0, \qquad k^2 \equiv \frac{2m}{\hbar^2}(E-U). \tag{12.5}$$

The solution of this equation depends on the sign of k^2:
a) at $k^2 > 0$, i.e. $E > U$, the solution of the Eq. (12.5) is harmonic

$$\psi_1(x) = A\exp(ikx) + B\exp(-ikx). \tag{12.6}$$

b) at $k^2 < 0$, i.e. $E < U$, we put $-k^2 = \kappa^2$ (in this chapter κ is not a force constant) and

$$\kappa^2 = \frac{2m}{\hbar^2}(U - E) > 0. \tag{12.7}$$

The solution of the equation is a linear combination of exponential functions:

$$\psi(x) = A\exp(\kappa x) + B\exp(-\kappa x). \tag{12.8}$$

In (12.6) and (12.8) *A* and *B* are arbitrary constants, which are defined by the boundary conditions.

Using the solutions (12.6) and (12.8) let's try to analyze the motion of a free particle. The potential energy of such a particle is zero, $U = 0$.

a) $k^2 = \frac{2m}{\hbar^2}E = \frac{p_x^2}{\hbar^2} > 0$, or $\mathrm{E} > 0$.

The solution (12.6) can be expressed through the energy E or through the momentum p_x:

$$\psi(x) = A\exp\left(\frac{i}{\hbar}\sqrt{2mE}x\right) + B\exp\left(-\frac{i}{\hbar}\sqrt{2mE}x\right), \tag{12.9a}$$

$$\psi(x) = A\exp\left(\frac{i}{\hbar}p_x x\right) + B\exp\left(-\frac{i}{\hbar}p_x x\right). \tag{12.9b}$$

In the three cases (12.6), (12.9a) and (12.9b) the solution is represented as a superposition of the partial solution $\psi_1(x)$ and $\psi_2(x)$, i.e. $\psi(x) = \psi_1(x) + \psi_2(x)$, where $\psi_1(x)$ and $\psi_2(x)$ are, respectively

$$\begin{aligned} \psi_1(x) &= A\exp(ikx) = A\exp\left(\frac{i}{\hbar}\sqrt{2mE}x\right) = A\exp\left(\frac{i}{\hbar}p_x x\right), \\ \psi_2(x) &= B\exp(-ikx) = B\exp\left(-\frac{i}{\hbar}\sqrt{2mE}x\right) = B\exp\left(-\frac{i}{\hbar}p_x x\right). \end{aligned} \tag{12.10}$$

The general solution is not an eigenfunction of the operator $\hat{p}_x$:

$$\hat{p}_x\psi(x)=\hat{p}_x\psi_1(x)+\hat{p}_x\psi_2(x)=p_x\psi_1(x)-p_x\psi_2(x)\neq p_x\psi(x). \qquad (12.11)$$

The partial solution $\psi_1(x)$ is an eigenfunction of the operator $\hat{p}_x$ with the eigenvalue $\hbar k$ of the momentum:

$$\hat{p}_x\psi_1(x)=\hbar k\psi_1(x) \quad \rightarrow \quad p_x=\hbar k. \qquad (12.12)$$

The solution $\psi_2(x)$ is also an eigenfunction of the operator $\hat{p}_x$, but with another eigenvalue of the momentum - $-\hbar k$:

$$\hat{p}_x\psi_2(x)=-\hbar k\psi_2(x) \quad \rightarrow \quad p_x=-\hbar k. \qquad (12.13)$$

The solutions $\psi_1(x)$ and $\psi_2(x)$ are correspondingly only the space parts of the wave functions $\psi_1(x,t)$ and $\psi_2(x,t)$. Adding the time-dependent function (12.3), we obtain the de Broglie plane waves:

$$\begin{aligned}\psi_1(x,t)&=\psi_1(x)\exp\left(-\frac{iEt}{\hbar}\right)=A\exp\left[-i(\omega t-kx)\right],\\ \psi_2(x,t)&=\psi_2(x)\exp\left(-\frac{iEt}{\hbar}\right)=B\exp\left[-i(\omega t+kx)\right].\end{aligned} \qquad (12.14)$$

The first solution $\psi_1(x)$ corresponds to the de Broglie wave, travelling in the direction of the positive x, ant the second $\psi_2(x)$ - to the de Broglie wave, travelling in the negative direction of the axıs X. In the corpuscle language this means, that $\psi_1(x)$ describes the particle with a positive momentum $\hbar k$ (12.12) and $\psi_2(x)$ - the particle with a negative momentum $-\hbar k$ (12.13).

We shall add that the functions $\psi_1(x)$ and $\psi_2(x)$ are the eigenfunctions of the Hamilton's operator $\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The operators $\hat{p}_x$ and $\hat{H}$ commute with $\hat{H}$ and hence the momentum p_x and the energy E are the constants of the motion.

b) $k^2<0,\ E<0$.

In this case, according to (12.7) we can write:

$$\kappa^2=-k^2=\frac{2m|E|}{\hbar^2}, \qquad (12.15)$$

and for the solution of the equation (12.5) -

$$\psi(x) = A\exp\left(\frac{\sqrt{2m|E|}}{\hbar}x\right)B\exp\left(-\frac{\sqrt{2m|E|}}{\hbar}x\right). \tag{12.16}$$

This function according to the properties of the wave function is limited, including at $x \to \pm\infty$. From the condition of the limitedness at $x \to +\infty$ it follows that $A = 0$, and at $x \to -\infty$ - $B = 0$. So, at the negative energy ($E < 0$) the wave function of a free particle is $\psi(x) = 0$. But physically $|\psi(x)|^2$ represents the probability density $\rho(x)$ in the point of the co-ordinate x (see Chapter 8). It is clear that this density is zero for all possible values of x. *Conclusion: a free particle with negative energy does not exist.*

12.2 THE INFINITE SQUARE WELL POTENTIAL

We shall analyze the motion of the quantum particle of mass m in an infinite square potential well, i.e. in the region $0 < x < a$, where $U(x) = 0$. At $x \leqq 0$ and $x \geqq 0$ the potential $U(x) \to \infty$. As in the both regions the potential field is constant, the Hamiltonian of the system does not depend explicitly on time. Hence the wave function satisfies the time-independent equation of Schroedinger (12.4).

At $x \leq 0$ and $x \geq 0$ it can be written in the next form:

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m}{\hbar^2}\left(E\psi(x) - \infty\psi(x)\right) = 0. \tag{12.17}$$

The only one way to satisfy this equation is to put $\psi(x) = 0$ in the given region. This yields:

$$\psi(0) = 0, \quad \psi(a) = 0, \tag{12.18}$$

which are the boundary conditions of the wave equation

$$\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0, \quad k^2 \equiv \frac{2m}{\hbar^2}E. \tag{12.19}$$

in the region $x \in (0, a)$. The solution of this equation is:

$$\psi_1(x) = A\exp(ikx) + B\exp(-ikx). \tag{12.20}$$

From the boundary condition at $x = 0$ we obtain:

$$B = -A\,. \tag{12.21}$$

The substitution of (12.21) into (12.20) yields:

$$\psi(x) = A\left[\exp(ikx) - \exp(-ikx)\right]\,. \tag{12.22}$$

We multiply and divide by $2i$ and then use the Euler's formula. As the result we obtain:

$$\psi(x) = A'\sin kx, \qquad A' \equiv 2iA, \tag{12.23}$$

From the boundary condition at $x = a$ we have:

$$A'\sin ka = 0, \tag{12.24a}$$

or

$$k_n a = n\pi, \qquad n = 1, 2, 3, ... \tag{12.24b}$$

We shall note that $n = 0$ is a solution of the Eq. (12.19) and this leads to $\psi(x) = 0$ which physically means that there is not a particle in the well. This solution does not correspond to the physical condition of the problem and therefore is rejected in (12.24b).

Finally for the solution of the Eq. (12.19) we obtain:

$$\psi_n(x) = A'\sin\frac{n\pi}{a}x. \tag{12.25}$$

The constant A' is determined by the condition of normalization:

$$\begin{aligned} 1 &= \int_0^a |\psi|^2 dx = \int_0^a |A'|^2 \sin^2\frac{n\pi}{a}x dx = |A'|^2 \int_0^a \frac{1-\cos 2k_n x}{2} dx \\ &= |A'|^2 \frac{a}{2} \;\Rightarrow\; A' = \sqrt{\frac{2}{a}}\,. \end{aligned} \tag{12.26}$$

Thus the normalized wave functions of the particle inside the infinite potential well are:

$$\psi(x)=\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x. \tag{12.27}$$

Substituting the values of k_n from (12.24b) into $k^2=2mE/\hbar^2$ we obtain:

$$E_n=\frac{\pi^2\hbar^2}{2ma^2}n^2,\quad n=1,2,3... \tag{12.28}$$

The energy of the quantum particle in an infinite potential well is quantizied. The number n is called a quantum number.

The spectrum of the quantum particle in an infinite potential well is discrete, while that of classical particle is continuous. *The energy levels are nonequidistant* - the space between them grows with the increasing the energy, i.e. with the increasing the quantum number *n*:

$$\Delta E_n=E_{n+1}-E_n=\frac{\pi^2\hbar^2}{2ma^2}(2n+1). \tag{12.29}$$

The energy values relate as the square of the integer:

$$E_1:E_2:E_3:...E_n=1:4:9:...:n^2. \tag{12.30}$$

Here we shall note that as the energy values (12.28) and the space between the energy levels (12.29) are significant if the mass of the particle and/or the well width *a* are small enough quantities. For example, for an electron ($m_e=9{,}1.10^{-31}\,\text{kg}$) in a well of width $a=10^{-10}$ m (here $a=2a_0$, where a_0 is the radius of Bohr) one gets $E_n=n^2.0{,}34\,\text{eV}$ and $\Delta E_n=(2n+1).0{,}34\ \text{eV}\sim 1\text{eV}$. At such small values of mass m_e and the width *a* the discrete character of the energy is clearly expressed. But if this electron is in the well of the width $a=10^{-2}$ m (a macroscopic size), then $E_n=n^2.0{,}34.10^{-16}$ eV and $E_n=(2n+1).0{,}34.10^{-16}$ eV. The values of the energy and of the space between the energy levels are so insignificant, that practically we can consider the energy as a continuous quantity. The physical significance of the solution (12.27) becomes obvious after expressing the function $\psi(x)$ through the exponential functions according to the Euler's formula:

$$\psi(x)=\frac{1}{2i}\sqrt{\frac{2}{a}}\left[\exp\left(\frac{\sqrt{2m|E|}}{\hbar}x\right)B\exp\left(-\frac{\sqrt{2m|E|}}{\hbar}x\right)\right]. \tag{12.31}$$

The general solution is a superposition from two de Broglie waves with the wavelength $\lambda = 2\pi / k = 2\pi a / n\pi = 2a / n$: the one with the wave function $\psi^{+}(x) = \text{const}\exp(in\pi x / a)$, travelling along the axis X and the other with the wave function $\psi^{-}(x) = \text{const}\exp(-in\pi x / a)$, travelling in the reverse direction. As a result of the superposition the standing de Broglie wave (12.22) is produced.

Let us consider in detail the first three states. The state with the minimal particle energy is called a ground state. The ground state has quantum number $n = 1$ and a wave function and energy as follow:

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\frac{\pi}{a}x, \quad E_{\min} = E_1 = \frac{\pi^2\hbar^2}{2ma^2}. \tag{12.32}$$

For a comparison we recall, that in classical mechanics the minimal particle energy in the well is zero $E_{\min}^{cl} = 0$, i.e. the particle can be at rest.

The probability density in the ground state is:

$$\rho_1 = \frac{dW_1(x)}{dx} = |\psi(x)|^2 = \frac{2}{a}\sin^2\frac{\pi}{a}x. \tag{12.33}$$

Let us determine the classical probability density. The probability $dW^{cl}(x)$ to find the particle in the interval dx is proportional to the time interval dt, during which it is found there: $W^{cl} \propto dt.$ Passing to the equality and substituting $dt = dx / v$, we get:

$$dW^{cl}(x) = \frac{c}{v}dx = \text{const}\, dx, \tag{12.34}$$

where c is constant and v is the velocity of the classical particle. For $\rho^{cl}(x)$:

$$\rho^{cl}(x) = \frac{dW^{cl}(x)}{dx} = \frac{c}{v} = \text{const}. \tag{12.35}$$

The probability of the classical particle is one and the same in every point of the well $0 < x < a$ and does not depend on the energy when $E \neq 0.$ When

$E=0$ and the particle is at rest in the point x_0 (an initial position) the probability density is $\rho(x)=\delta(x-x_0)$.

The wave function $\psi_1(x)$ (12.32) and $\rho_1(x)$ (12.33) are shown in Fig. 12-1. For comparison in the same figure the standing wave of a string, secured at both ends is shown.

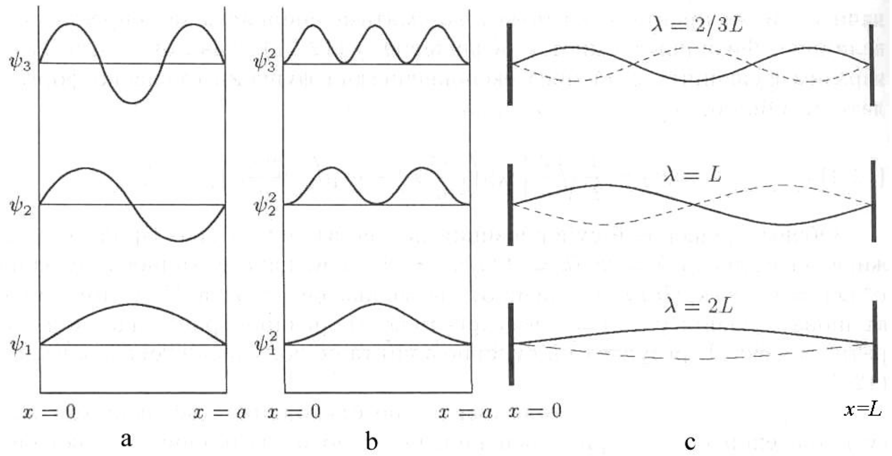


Figure 12-1. The wave functions $\psi_n(x)$ (a) and the probability densities $\rho_n(x)$ of the first three state of the particle in infinite potential well with the width *a* (b) and the standing waves in a string, secured at the both ends (c).

By analogy for the state with $n=2$ and $n=3$ we can write:

$$\begin{aligned}
&n{=}2:\quad E_2=\frac{2^2\pi^2\hbar^2}{2ma^2}=4E_1,\ \psi_2(x)=\sqrt{\frac{2}{a}}\sin\frac{2\pi}{a}x,\ \ \rho_2=\frac{2}{a}\sin^2\frac{2\pi}{a}x,\\
&n{=}3:\quad E_2=\frac{3^2\pi^2\hbar^2}{2ma^2}=9E_1,\ \psi_3(x)=\sqrt{\frac{2}{a}}\sin\frac{3\pi}{a}x,\ \ \rho_3=\frac{2}{a}\sin^2\frac{3\pi}{a}x.
\end{aligned}\tag{12.36}$$

These states are also shown in Fig 12-1.

The points, in which $\psi_n(x)=0$, are called nodes of the wave function. In the region $0<x<a$ the function $\psi_1(x)$ has no nodes, $\psi_2(x)$ has 1 node, $\psi_3(x)$ has 2 nodes and so on, $\psi_n(x)$ has $(n-1)$ nodes. We note that with the increasing the number of the nodes the state energy also increases.

Let sum up the results for the particle motion in an infinite potential well:

1. The energy of the particle has discrete character.
2. The energy $E_n=\left(\pi^2\hbar^2/2ma^2\right)n^2$ is determined by the quantum number *n*, which has the values $n=1,2,3\,...$

3. The energy levels are nonequidistant, $\Delta E_n = \left(\pi^2\hbar^2/2ma^2\right)(2n+1)$.
4. The minimal possible energy is different from zero, $E_{\min} = E_1 \neq 0$.
5. In the ground state ($E = E_{\min} = E_1$) the probability to find the particle in every point of the well is different from zero.
6. The quantization of the energy shows its worth at sufficiently small mass of the particle and/or width of the well.

12.3 THE STEP POTENTIAL

In this section we shall solve another simple problem with one-dimensional potential. Like the problem of an infinite potential well, it is interesting with the illustration of a new quantum effect, which has no analogy in classical mechanics. In this case this is the penetration of the particle in the region of the potential greater than its energy.

We shall consider the potential with the form shown in Fig. 12-2:

$$\begin{aligned} &U(x) = 0, \quad x < 0, \\ &U(x) = U, \quad x \geq 0. \end{aligned} \tag{12.37}$$

We designate the region $x < 0$ with 1 and the region $x > 0$ with 2.

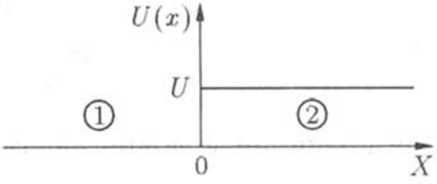


Figure 12-2. The potential step.

The Hamiltonian of the system

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \tag{12.38}$$

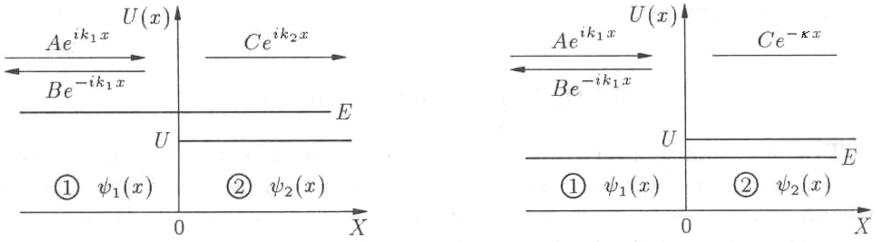
does not depend on time and the wave function $\psi(x)$ satisfies the time-independent Schroedinger equation (see Eq. (12.4)):

$$\frac{\partial^2}{\partial x^2}\psi(x)+\frac{2m}{\hbar^2}(E-U(x))\psi(x)=0, \tag{12.39}$$

Firstly we shall consider the case $E > U$. Then the solution of the Eq. (12.39) in the two regions is, respectively:

$$\begin{aligned} &\psi_1(x)=A\exp(ik_1x)+B\exp(-ik_1x),\ k_1=\sqrt{\frac{2mE}{\hbar^2}}, && x<0,\\ &\psi_2(x)=C\exp(ik_2x)+D\exp(-ik_2x),\ k_2=\sqrt{\frac{2m(E-U)}{\hbar^2}}, && x<0. \end{aligned} \tag{12.40}$$

The term $D\exp(-ik_2x)$ together with the time-dependent factor $\exp(-ikEt/\hbar)$, i.e. $D\exp[-i(k_2x+\omega_2t)]$, represents the wave travelling in the direction of decreasing x in the region $x>0$. As there is not such a wave in this region we set $D=0$. The interpretation of the other terms with the amplitudes A, B and C are shown in Fig 12-3a.



a) $E > U$ b) $E < U$

Figure 12-3. The interpretation of the solutions of the problem with a potential step: $A\exp(ik_1x)$ - the incident de Broglie wave, $B\exp(ik_1x)$ - the reflected wave, $C\exp(ik_2x)$ - the refracted (transmitted) wave, $C\exp(-\kappa x)$ - the attenuated wave.

The solutions $\psi_1(x)$ and $\psi_2(x)$ are the wave functions of the system in region 1 and 2, respectively. The requirement of the continuity gives:

$$\begin{aligned} &\psi_1(0)=\psi_2(0),\\ &\frac{\partial}{\partial x}\psi_1(0)=\frac{\partial}{\partial x}\psi_2(0). \end{aligned} \tag{12.41}$$

From these equations we find two algebraic equations:

$$\begin{aligned} &A+B=C,\\ &A-B=\frac{k_2}{k_1}C, \end{aligned} \tag{12.42}$$

by which we determine B and C through A:

$$B=\frac{k_1-k_2}{k_1+k_2}A, \quad C=\frac{2k_1}{k_1+k_2}A. \tag{12.43}$$

The quantity

$$j=v|\psi(x)|^2=\frac{p}{m}|\psi(x)|^2=\frac{\hbar k}{m}|\psi(x)|^2 \tag{12.44}$$

determines the probability flux, which is the probability per second that a particle will be found crossing some reference point travelling in a particular direction. The incident, reflected and transmitted probability fluxes are, respectively:

$$j_{in}=\frac{\hbar k_1}{m}|A|^2, \quad j_r=\frac{\hbar k_1}{m}|B|^2, \quad j_{tr}=\frac{\hbar k_2}{m}|C|^2. \tag{12.45}$$

The ratio $j_r / j_{in}=R$ represents the reflection coefficient and the ratio $j_{tr} / j_{in}=T$ - transmission coefficient or transparency of the step (here T is not energy as in Eq. (1.36)). For these coefficients from (12.43)÷(12.45) we find:

$$\begin{aligned} &R=\frac{j_r}{j_{in}}=\left|\frac{B}{A}\right|^2=\frac{(k_1-k_2)^2}{(k_1+k_2)^2},\\ &T=\frac{j_{tr}}{j_{in}}=\frac{k_2}{k_1}\left|\frac{C}{A}\right|^2=\frac{k_2}{k_1}\frac{4k_1^2}{(k_1+k_2)^2}=\frac{4k_1k_2}{(k_1+k_2)^2}. \end{aligned} \tag{12.46}$$

The result shows that $R>0$ - there is a probability the particle to reflect even though the total energy of the particle is greater than the height of the potential step. It is surprising, because a classical particle would not be reflected if it had enough energy to pass the step height. We would like to underline that the reflection is connected with the potential discontinuity, but not with the fact that $U(x)$ becomes larger. At a corresponding discontinuity a classical wave will reflect, too. So the effect of the reflection of microscopic particle is the manifestation of its wavelike properties.

It is clear that $R+T=1$, which expresses the physical condition for the conservation of the particle number - the sum of the reflected and transmitted fluxes is equal to the incident flux:

$$j_{in}=\frac{\hbar k_1}{m}|A|^2=\frac{\hbar k_1}{m}|B|^2+\frac{\hbar k_2}{m}|C|^2. \tag{12.47}$$

Now let us consider the case when the particle energy is smaller than step height $E<U$. The solution of the Schroedinger equation (12.39) is

$$\begin{aligned} &\psi_1(x)=A\exp(ik_1x)+B\exp(-ik_1x), \qquad x<0,\\ &\psi_2(x)=C\exp(-\kappa x),\ \ \kappa=\sqrt{\frac{2m(U-E)}{\hbar^2}},\ \ x<0. \end{aligned} \tag{12.48}$$

For $\psi_2(x)$ we use (12.8), in which the constant before $\exp(\kappa x)$ is equal to zero ($D=0$), as at $x\to\infty$ the wave function $\psi_2(x)$ must be finite. The interpretation of the solution (12.48) is shown in Fig. 12-3b.

The boundary conditions allow to determine *B* and *C* through *A:*

$$B=\frac{k_1-i\kappa}{k_1+i\kappa}A, \quad C=\frac{2k_1}{k_1+i\kappa}A. \tag{12.49}$$

The probability density of the particles in the region 2 is

$$\rho(x)=|\psi_2(x)|^2=\frac{4k_1^2}{k_1^2+\kappa^2}|A|^2\exp(-2\kappa x). \tag{12.50}$$

In classical physics the region 2 is forbidden (see Chapter 3). However, in quantum mechanics the particles can penetrate in classically forbidden region. The effect is purely quantum and there is not classical analogous.

The values of *B* and *C* (12.49) allow using (12.46) to determine the coefficient of reflection and transmission:

$$R=\left|\frac{B}{A}\right|=1, \quad T=0. \tag{12.51}$$

The wave is fully reflected and therefore the transmission coefficient is equal to zero. *The particles penetrate to the certain destination and then are* *reflected. The probability to find them in the region 2 differs from zero, but theirs flux is zero.*

12.4* THE FINITE SQUARE WELL POTENTIAL

We shall consider the problem of motion of a particle with energy E in a square well with the width a and depth $U < E$ (Fig. 12-4). Inside the well the potential is zero:

$$U(x) = \begin{cases} U, & x \leq -a/2, \text{ or } x \geq +a/2, \\ 0, & -a/2 < x < +a/2. \end{cases} \tag{12.52}$$

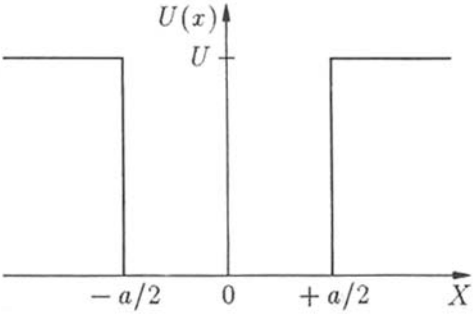


Figure 12-4. The finite square well.

Here the choice of origin of the co-ordinate axes, different from the case of the infinite potential well (in the middle of the well), is determined only by the reason of mathematically easier and more clearly visualized solution. As we shall see further that the equation of the finite well can be solved only graphically or numerically.

This type of well is very often used in quantum mechanic as a model of potential forces with a finite radius of action and without any influence over the region out of this radius. Out of the region of force action the potential can be considered as constant. Although with such simple potential some details of the motion are lost, the essential features of binding the particle by a certain force in a certain region remain. For example, the motion of a neutron in a nucleus can be successfully approximated by assuming the neutron motion in a square well potential with depth 50 MeV and width $\sim 10^{-14}$ m. On the ground of the discussion of an infinite well and a potential step we can assume that the wave function will describe the de Broglie standing waves with integer half waves inside the well and exponential attenuated wave out of it.

The solution of the Schroedinger equation can be written as follows:

$$\psi(x) = A\sin kx + B\cos kx, \quad -a/2 < x < a/2, \tag{12.53a}$$

$$\psi(x) = C\exp(\kappa x) + D\exp(-\kappa x), \quad x < -a/2, \tag{12.53b}$$

$$\psi(x) = F\exp(\kappa x) + G\exp(-\kappa x), \quad x > a/2. \tag{12.53c}$$

Here $k = \sqrt{2mE/\hbar^2}$ and $\kappa = \sqrt{2m(U-E)/\hbar^2}$.

For the determination of the unknown constants firstly we shall use the finiteness of the wave function. Obviously, at $x \to \mp\infty$ this requirement gives

$$D = 0, \qquad F = 0. \tag{12.54}$$

From the requirement of the continuity of the wave function and its derivative at $x = -a/2$ and $x = a/2$ one obtains the boundary conditions of the form (12.41). They give four equations for the constant A, B, C and G:

$$-A\sin(ka/2) + B\cos(ka/2) = C\exp(-\kappa a/2), \tag{12.55a}$$

$$Ak\cos(ka/2) + Bk\sin(ka/2) = C\kappa\exp(-\kappa a/2), \tag{12.55b}$$

$$A\sin(ka/2) + B\cos(ka/2) = G\exp(-\kappa a/2), \tag{12.55c}$$

$$Ak\cos(ka/2) - Bk\sin(ka/2) = -G\kappa\exp(-\kappa a/2). \tag{12.55d}$$

Subtracting from the Eq. (12.55c) the Eq. (12.55a) and adding these two equations we obtain

$$2A\sin(ka/2) = (G-C)\exp(-\kappa a/2), \tag{12.56a}$$

$$2B\cos(ka/2) = (G+C)\exp(-\kappa a/2). \tag{12.56b}$$

Performing similar procedure with the Eqs. (12.55d) and (12.55b), we get

$$2Bk\sin(ka/2) = (G+C)\exp(-\kappa a/2), \tag{12.57a}$$

$$2Ak\cos(ka/2) = -(G-C)k\exp(-\kappa a/2). \tag{12.57b}$$

We divide (12.57a) by (12.56b) and (12.57b) by (12.56a):

$$k\tan(ka/2) = \kappa\,, \tag{12.58a}$$

$$k\cot(ka/2) = -\kappa\,. \tag{12.58b}$$

It is easy to see that two equations (12.58) can not be satisfied simultaneously. If they could, then the equation, obtained by adding them

$$k\tan\frac{ka}{2}+k\cot\frac{ka}{2}=0\,, \qquad (12.59)$$

would be valid. Let multiply the last equation by $\tan(ka/2)$:

$$k\tan^2\frac{ka}{2}+k=0 \Rightarrow \quad \tan^2\frac{ka}{2}=-1. \qquad (12.60)$$

This cannot be like this, because according to the conditions of the problem k and a are real numbers. This way, only two possibilities remain: the Eq. (12.58b) has a solution, but Eq. (12.58a) has not or the Eq. (12.58a) has a solution, then Eq. (12.58b) has not. So, the eigenfunctions of the finite well form two classes of functions. For the first class (we take the first equation of (12.58))

$$k\tan\frac{ka}{2}=\kappa, \quad A=0, \quad G-C=0. \qquad (12.61)$$

With these results the Eq. (12.55c) is reduced to

$$B\cos\frac{ka}{2}=G\exp\left(-\frac{\kappa a}{2}\right)\Rightarrow \quad G=B\cos\frac{ka}{2}\exp\left(\frac{\kappa a}{2}\right)=C, \qquad (12.62)$$

and finally for the wave function we get:

$$\begin{aligned}
&\psi_1(x)=B\cos(kx), \quad -a/2<x<a/2,\\
&\psi_1(x)=\left[B\cos(ka/2)\exp(\kappa a/2)\right]\exp(\kappa x), \quad x<-a/2,\\
&\psi_1(x)=\left[B\cos(ka/2)\exp(\kappa a/2)\right]\exp(-\kappa x), \quad x>a/2.
\end{aligned} \qquad (12.63)$$

Inside the well the wave function is an even function ($\cos(kx)=\cos(-kx)$).

For the second class

$$k\cot\frac{ka}{2}=-\kappa, \qquad B=0, \qquad G+C=0. \qquad (12.64)$$

In this case the Eq. (12.55c) is reduced to:

$$A\sin\frac{ka}{2} = G\exp\left(-\frac{\kappa a}{2}\right) \Rightarrow \quad G = A\sin\frac{ka}{2}\exp\left(\frac{\kappa a}{2}\right) = -C, \tag{12.65}$$

and the wave functions are

$$\begin{aligned} &\psi_2(x) = A\sin(kx), \quad -a/2 < x < a/2, \\ &\psi_2(x) = \left[-A\sin(ka/)\exp(\kappa a/2)\right]\exp(\kappa x), \quad x < -a/2, \\ &\psi_2(x) = \left[A\sin(ka/)\exp(\kappa a/2)\right]\exp(-\kappa x), \quad x > a/2. \end{aligned} \tag{12.66}$$

Inside the well the wave function is an odd function* ($\sin(kx) = -\sin(-kx)$).

To determine the eigenvalues of the energy, we shall consider firstly the Eq. (12.61). Writing *k* and κ in an explicit form and multiplying by *a/2*, we obtain

$$\sqrt{\frac{mEa^2}{2\hbar^2}}\tan\sqrt{\frac{mEa^2}{2\hbar^2}} = \sqrt{\frac{m(U-E)a^2}{2\hbar^2}}. \tag{12.67}$$

After setting

$$\mathcal{E} = \sqrt{\frac{mEa^2}{2\hbar^2}}, \qquad p(\mathcal{E}) = \mathcal{E}\, tg\mathcal{E}, \qquad q(\mathcal{E}) = \sqrt{\frac{mUa^2}{2\hbar^2} - \mathcal{E}^2} \tag{12.68}$$

the Eq. (12.67) becomes:

---

*By solving the problem of an infinite potential well we obtained two classes of solutions and there the question of the parity of the waves functions did not arise. This is due to the choice of the beginning of the *X*-axis - there it coincides with the well wall, but here it is in the middle of the well. So in the last case the well potential *U*(*x*) is an odd function of the co-ordinate *x* (the reader can find details in [R19, Section 6.8 and in [3], Section 48). Of course the problem of the finite well potential can be solved similarly to the problem of the infinite well setting *x*=0 to coincide with the well wall (see for example Pain H. J., The Physics of Vibrations and Waves, 2nd ed., John Wiley & Sons, 1976, Chapter 12).

$$p(\mathcal{E})=\sqrt{\frac{mUa^2}{2\hbar^2}-\mathcal{E}^2},\quad \text{or}\quad p(\mathcal{E})=q(\mathcal{E}). \tag{12.69}$$

The points of intersection of the functions $p(\mathcal{E})$ and $q(\mathcal{E})$ define the values of $\mathcal{E}$ which are the solutions of (12.69). Such graphical solution is illustrated in Fig. 12-5a. The function $p(\mathcal{E})$ has zeros at $\mathcal{E}=0,\pi,2\pi,...$ and the asymptotes at $\mathcal{E}=\pi/2,3\pi/2,5\pi/2,...$ If we write the third equation of (12.68) in the form $q^2(\mathcal{E})+\mathcal{E}^2=mUa^2/2\hbar^2$ it becomes clear that $q(\mathcal{E})$ is a quarter-circle of a radius $\sqrt{mUa^2/2\hbar^2}$. We can see from Fig. 12-5a that the number of solutions depends of this radius. In Fig. 12-5a is shown the case when $\sqrt{mUa\ /2\hbar^2}=4$. Then we have two solutions: $\mathcal{E}\approx 1{,}25$ and $\mathcal{E}\approx 3{,}60$. For these values we get from the first equation of (12.68) the eigenvalues of the of the energy:

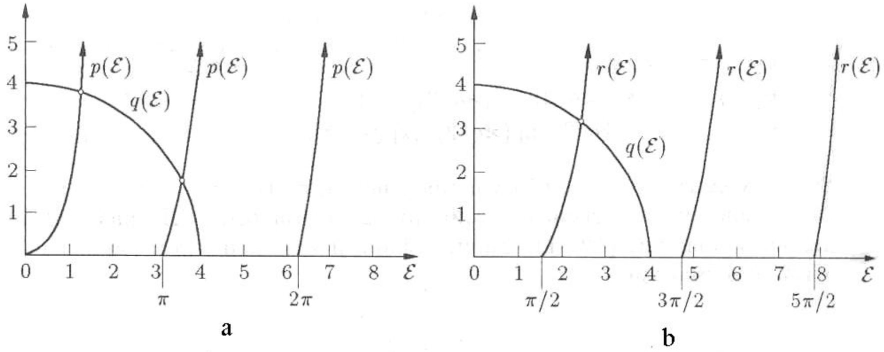


Figure 12-5. A graphical solution of the equation for eigenvalues of the energy of the particle in the square potential well with a finite depth: a) $p(\mathcal{E})=q(\mathcal{E})$ (even wave function $\psi_1(x)$and$\psi_3(x)$); b) $-\mathcal{E}\cot g\mathcal{E}=q(\mathcal{E})$ (odd wave function $\psi_2(x)$).

$$\begin{aligned} E&=\mathcal{E}^2\frac{2\hbar^2}{ma^2}=\mathcal{E}^2\frac{2\hbar^2}{mUa^2}U\approx\left(\frac{1{,}25}{4}\right)^2\approx 0{,}098U,\\ E&=\mathcal{E}^2\frac{2\hbar^2}{mUa^2}U\approx\left(\frac{3{,}60}{4}\right)^2\approx 0{,}808U. \end{aligned} \tag{12.70}$$

For the second class solutions, corresponding to odd functions, we shall obtain the eigenvalues as the solution of the first equation of (12.64). Evaluating k and κ (12.53) and multiplying it by $a/2$, this equation becomes:

$$\mathcal{E}\cot g\mathcal{E} = \sqrt{\frac{mEa^2}{2\hbar^2} - \mathcal{E}^2} \quad \text{or} \quad \mathrm{r}(\mathcal{E}) = q(\mathcal{E}). \tag{12.71}$$

The solution is similar to that of the Eq. (12.69). Graphical solution of Eq. (12.69) is illustrated in Fig. 12-5b. It is clear from the figure that for $E<U$ if $\sqrt{mUa^2/2\hbar^2} < \pi/2$ there is no eigenvalues corresponding to the odd eigenfunctions. However, if $\pi/2 \leqq \sqrt{mUa^2/2\hbar^2} < 3\pi/2$ there is one eigenvalue; if $3\pi/2 \leqq \sqrt{mUa^2/2\hbar^2} < 5\pi/2$ - two and so on. In the figure the case, when the radius of the circle is equal to 4 $\left(\sqrt{mUa^2/2\hbar^2} = 4\right)$is illustrated. It is seen that in this case the single solution is $\mathcal{E} \approx 2{,}47$ and the odd wave function ψ_2 has eigenvalues

$$E = E_2 = \mathcal{E}^2 \frac{2\hbar^2}{mUa^2} U \approx \left(\frac{2{,}47}{4}\right)^2 \approx 0{,}383U. \tag{12.72}$$

The eigenvalues and the eigenfunction of the considered case with three allowed bound states are shown in Fig. 12-6.

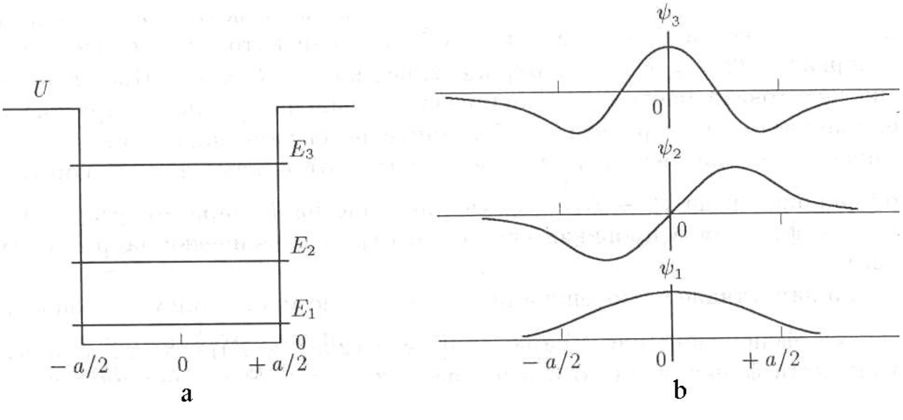


Figure 12-6. The eigenvalues (a) and the eigenfunctions (b) of three allowed bound states of the particle in the potential well with finite depth at $\sqrt{mUa^2/2\hbar^2} = 4$ and $E<U$.

We see that *in the potential well with a finite depth the number of the allowed bound state is restricted. These bound states have discrete eigenvalues* of energy $E<U$. When the potential wave is very shallow

or/and very narrow only a single eigenvalue of energy is allowed, which corresponds to the state with even wave function. With increasing values $\sqrt{mUa^2/2\hbar^2}$, i.e. *with increasing values of the well depth and/or well width, the number of the bound states increases*, as firstly the state with odd wave function appears, then the one with even etc. (there are excellent illustrations in Brandt, S., H. D. Dahmen, The Picture Book of Quantum Mechanics, John Wiley & Sons, 1985, Section 6.5).

As we can see from the analytical expressions (12.63) and (12.66) and from Fig. 12-6b, the solutions of the Schroedinger equation are de Broglie standing waves. But in this case the analogy with a string is not so much complete as in the case of the infinite potential well (Fig. 12-a, c). Firstly, let consider the particulars of the standing waves within the well. As higher is the eigenvalue of the energy, more numerous are the oscillations of the corresponding wave function and higher is its wave number *k*. This is so, because inside the well the wave number *k* is proportional to $E^{1/2}$. The particle in the case, shown in Fig. 12-6 does not have a fourth bound state, because the necessary value of wave number and hence of $E^{1/2}$, would be too large to satisfy the condition $E < U$. At the lowest energy state the wave function $\psi_1(x)$ does not have nodes, at the second energy level the wave function $\psi_2(x)$ has one node, and at the third - two nodes etc. The nodes however have not the same position along *X*-axis as the nodes in an infinite well. Now let consider those parts of the wave function, which are in the regions outside the well. In classical mechanics at $E < U$ these are forbidden domains and the particles cannot penetrate in them, because their kinetic energy becomes negative - $p^2/2m = E - U < 0$. With the increasing *E* the parameter $\kappa = \sqrt{2m(U-E)/\hbar^2}$ decreases and the wave functions penetrate more and more inside the classically forbidden domain.

Finally let sum up the results for the particle in the square potential well with a finite depth:

1. The energy of the particle at $E < U$ has a discrete character.
2. The energy levels are nonequidistant.
3. The number of the bound states depends on the depth U and the width of the well - at $\sqrt{mUa^2/2\hbar^2} < \pi/2$ there is only one bound state and with increasing the parameter $\sqrt{mUa^2/2\hbar^2}$ this number becomes larger.
4. The minimal possible energy is different from zero, $E_{\min} = E_1 \neq 0$.
5. In the ground state ($E = E_{\min} = E_1$) the probability to find the particle in every point of the well is different from zero.
6. The probability to find the particle in a classically forbidden domain is different from zero.

12.5$^+$ THE POTENTIAL BARRIER

In this section we shall consider a rectangular potential barrier (Fig.12-7), which potential can be written as follows:

$$\begin{aligned} &U(x)=0, \quad x<0, \\ &U(x)=0 \quad 0\leqq x\leqq a, \\ &U(x)=0 \quad x>a. \end{aligned} \tag{12.73}$$

The particle with mass m and energy $E<U$ moves from $-\infty$ along the X-axis. In corresponding regions the time independent Schroedinger equation at $E<U$ has the following solutions:

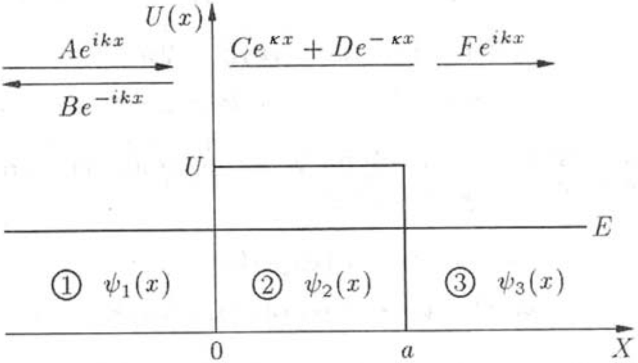


Figure 12-7. A potential barrier with height U and width a: in region 1 $U(x)=0$, $x<0$; in region 2 $U(x)=U$, $x\leq 0\leq a$; in region 3 $U(x)=0$, $x>a$.

$$\begin{aligned} &\psi_1(x)=A\exp(ikx)+B\exp(-ikx), \quad k=\sqrt{\frac{2mE}{\hbar^2}}, \qquad x<0, \\ &\psi_2(x)=C\exp(\kappa x)+D\exp(-\kappa x), \ \kappa=\sqrt{\frac{2m(U-E)}{\hbar^2}}, \ 0\leq x\leq 0, \\ &\psi_2(x)=F\exp(ikx), \qquad x>a. \end{aligned} \tag{12.74}$$

The interpretation of the solutions (Fig.12-7) is similar to that one of the problem with a potential step. The part of the incident de Broglie wave $A\exp(ikx)$, reaching the barrier reflects - $B\exp(-ikx)$, and the other part transmits in the region 3 - $F\exp(ikx)$. The wave function $\psi_2(x)$ describes the penetration of the quantum particle in the classically forbidden domain. We already know that there is some probability to find quantum particle in region 2, nevertheless that for a classical particle region 2 is an excluded region.

The requirement for continuity of the wave function at $x = a$ and $x = 0$ leads to the next boundary condition:

$$\begin{gathered} \psi_1(0) = \psi_2(0), \quad \psi_2(a) = \psi_3(a), \\ \frac{\partial}{\partial x}\psi_1(0) = \frac{\partial}{\partial x}\psi_2(0), \quad \frac{\partial}{\partial x}\psi_2(a) = \frac{\partial}{\partial x}\psi_3(a). \end{gathered} \tag{12.75}$$

These conditions together with the solutions (12.7) give the following system of the algebraic equations for the coefficients A, B, C, D and F :

$$A + B = C + D, \tag{12.76a}$$

$$ikA - ikB = \kappa C - \kappa D, \tag{12.76b}$$

$$\exp(\kappa a)C + \exp(-\kappa a)D = \exp(ika)F, \tag{12.76c}$$

$$\kappa \exp(\kappa a)C - \exp(-\kappa a)D = ik \exp(ika)F. \tag{12.76d}$$

We shall solve the system in the next way. Multiplying (12.7a) by κ and successively summing up and subtracting with (12.7b) we obtain

$$(\kappa + ik)A + (\kappa - ik)B = 2\kappa C\,, \tag{12.77a}$$

$$(\kappa - ik)A + (\kappa + ik)B = 2\kappa D. \tag{12.77b}$$

Now multiplying (12.7c) by κ and successively summing up and subtracting with (12.7d) we obtain

$$2\kappa C = (\kappa + ik)\exp(ika - \kappa a)F, \tag{12.78a}$$

$$2\kappa D = (\kappa - ik)\exp(ika + \kappa a)F. \tag{12.78b}$$

Replacing $2\kappa C$ and $2\kappa D$ from (12.78) into (12.77), we find the connection between A, B, F :

$$(\kappa + ik)A + (\kappa - ik)B = (\kappa + ik)\exp(ika - \kappa a)F, \tag{12.79a}$$

$$(\kappa - ik)A + (\kappa + ik)B = (\kappa - ik)\exp(ika + \kappa a)F. \tag{12.79b}$$

From term by term summing up and subtracting of these equation we get:

$$i\kappa(2A + 2B) = \left[(\kappa + ik)\exp(-\kappa a) + (\kappa - ik)\exp(\kappa a)\right]\exp(i\kappa a)F, \tag{12.80a}$$

$$i\kappa(2A - 2B) = \left[(\kappa + ik)\exp(-\kappa a) - (\kappa - ik)\exp(\kappa a)\right]\exp(i\kappa a)F. \tag{12.80b}$$

Let find the dependence of the transmitted-wave amplitude on the amplitude of the incident on the barrier wave. We multiply (12.80a) by ik and (12.80b) by κ and sum up the obtained equations. As the result we get:

$$F = \frac{4i\kappa k \exp(-ika)}{(\kappa + ik)^2 \exp(-\kappa a) - (\kappa - i\kappa)^2 \exp(\kappa a)} A. \tag{12.81}$$

In the most physical problems, which must be interpreted with the potential in the form (12.73), it appears that $\kappa a >> 1$. At this condition (12.81) reduces to:

$$F \approx -\frac{4i\kappa k \exp(-ika)}{(\kappa - ik)^2 \exp(\kappa a)} A, \qquad \kappa a > 1. \tag{12.82}$$

The coefficient T of the transmission, called a barrier penetration, is following:

$$T = \frac{j_{tr}}{j_{in}} = \frac{|F|^2}{|A|^2} = \frac{16k^2\kappa^2}{(k^2 + \kappa^2)^2} \exp(-2\kappa a) = T_0 \exp(-2\kappa a). \tag{12.83}$$

Note that here T_0 is not temperature as in Eq. (7.1). We shall give the physical interpretation in the next section. Here we shall only note that quantum particle penetrates in the region 2 and transmits through it in the region 3, which is impossible for the classical particle.

Here we shall pay attention to an important phenomenon in quantum mechanics - the scattering. In classical mechanics if the energy of particle E is less than the energy U of the inhomogeneity, it will reflect; if $E > U$, it will transmit. In sections 12.2÷12.5 we have persuaded ourselves that the quantum particle because of its wave properties is reflected by every inhomogeneity and transmits through it even if $E < U$. In other words it scatters from such inhomogeneity. Transmitting from the square well and barrier to the spherical geometry, quantum mechanics creates the model of the scattering of the real particle by another particle.

12.6 THE TUNNEL EFFECT AND ALPHA-DECAY

In the problem with the potential barrier of a height U and a width a at the energy of the quantum particle $E < U$ we observe the effect which is unknown in classical physics, namely the penetration of the particles through the barrier (Fig. 12-8). Because of the wave character of the quantum particle, the probability to find it behind the potential step at $x=0$ is different from zero (see Section 12.3). The probability decreases exponentially and if the width of the barrier is not too large, than behind it, i.e. in the region $x>a$, this probability is a finite value.

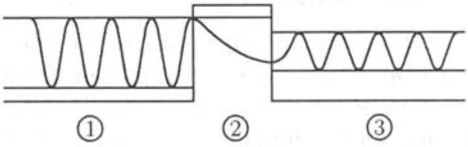


Figure 12-8. Tunnel effect - the penetration of a quantum particle of energy *E* through the barrier *U* (*U*>*E*) in the region 3, which is inaccessible for the classical particle.

It appears that in the most practical cases the coefficient of the transmission $T=\left|\psi_3\right|^2/\left|\psi_1\right|^2$ has the form (12.83):

$$T=T_0\exp\left(-2\kappa a\right)=T_0\exp\left(-\frac{2}{\hbar}\sqrt{2m\left(U-E\right)}\,a\right), \tag{12.84}$$

where T_0 is a value of the order of unity.

The region $0<x<a$ in Fig. 12-8 is a forbidden domain for a classical particle. According to (12.84) the quantum particle of mass *m* and energy *E*, which impinge on the potential barrier of the height *U* and width *a*, has a certain probability to penetrate through the barrier and to appear on its other side. The particle can leak through the barrier if as there were a hole in it. *The transition of the quantum particle through the potential barrier of a height greater than its total energy, i.e. through the classically forbidden domain, is called tunnelling or a tunnel effect* (in Fig. 12-8 the real part of the wave function is drawn).

The rectangular well is an idealization. When we have a real barrier, e.g. as in Fig. 12-9, we deal in the next way. We approximate the real barrier

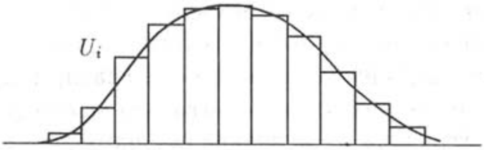


Figure 12-9. Approximation of real potential barrier by series of the square potential barriers.

with rectangular barriers of a depth dx and a height $U(x)$. The barrier penetration of the rectangular barriers of a depth dx and a height U is

$$T_i = T_{oi}\exp\left(-\frac{2}{\hbar}\sqrt{2m(U_i - E)}\,dx\right). \tag{12.85}$$

The coefficient of the transmission of the whole barrier is obtained by multiplying the expressions of such form for all elements dx of the real barrier. The exponents are summed up and we get:

$$T = T_o\exp\left(-\frac{2}{\hbar}\int_{x_1}^{x_2}\sqrt{2m[U(x) - E]}\right)dx. \tag{12.86}$$

We shall consider a few examples of tunnel phenomena.

Example 1. A cold (autoelectronic) emission of the electron. In the absence of outer electrical field the electrons are confined within the metal by an energy barrier formed by the work function (see the discussion of the photoelectric effect in Chapter 7). In other words their potential energy on the metal boundary changes with a jump from 0 to U_0. When the electric field with intensity $\mathcal{E}$ is applied, the electron potential energy is changed and it becomes $U = U_0 - \mathcal{E}x$ (Fig. 12-10). The triangle barrier with a finite width is formed, so that at a short distance from the surface of the metal the potential energy is less than the energy of the electrons inside the metal. Now although the electrons cannot classically penetrate the barrier of the metal surface they can pass through by quantum-mechanical tunnelling and

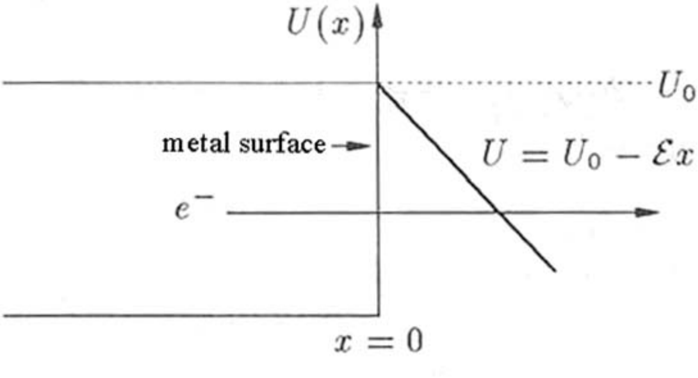


Figure 12-10. At the present of the external electrical field $\mathcal{E}$ the potential at the metal surface becomes $U = U_0 - \mathcal{E}x$ - the triangle potential barrier is formed. The electron penetrates through it due to the tunnel effect.

as a result we observe a cold electron emission. With the increasing the field intensity the barrier width decreases and the barrier penetration increases - autoelectronic current increases.

Example 2. The transitions of N *atom in the ammonia molecule,* NH_3. Fig 12-11 illustrates schematically the structure of this molecule. It consists by three-H atoms arranged in a plane on equal distances from N atom. There are two completely equivalent equilibrium positions arranged on the both sides of the plane of H atoms. The potential energy of N atom has two minima, corresponding to two equilibriums. These minima are symmetrically disposed with respect to the maximum at $x = 0$. This maximum, creating the barrier between these two regions, is due to Coulomb's forces of repulsion acting on N atom, when it penetrates in the plane of H atoms. In the frame of classical physics these forces do not allow to N atom to cross the barrier. But due to the tunnelling this atom can penetrate through the barrier in the classically forbidden domain. If it is initially on one side, it will appear on the other side and vice versa. In fact the N atom oscillates back and forth through the H-atom plane with a frequency $\nu = 2{,}3786.10^6$ Hz. The high accuracy at the determination of this frequency, which is based on the small width of the corresponding spectral line, allows using the frequency as a standard in the first atomic clock.

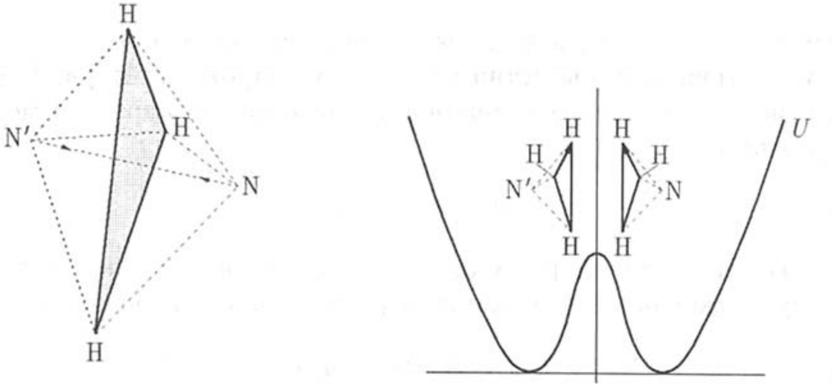


Figure 12-11. The both possible situations N and N' of the nitrogen atom and its potential energy in the ammonia molecule.

Example 3. Radioactive $\alpha-$decay. In 1928 the Russian physicist George Gamow gave the most famous example of quantum mechanical tunnelling in the explanation of the decay of the radioactive nuclei, which emit α-particles. If we suppose that an $\alpha-$particle exists in the parent nucleus (in reality it forms at the decay of the nucleus) its potential energy can (Fig. 12-12) be written as follows:

$$U(r)=\begin{cases} U_o=\text{const}, & r\leqq r_o, \\ \dfrac{2(Z-2)e^2k_o}{r}, & r\geqq r_o, \end{cases} \tag{12.87}$$

where Z and r_0 are respectively the number of neutrons and the radius of the parent nucleus and $k_0=1/4\pi\varepsilon_0$. The potential $U(r)$ at $r<r_0$ is due to nucleus forces and at $r>r_0$ - to the Coulomb repulsive forces.

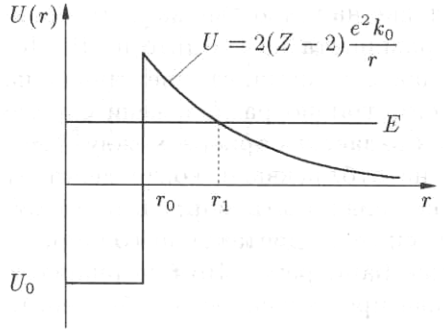


Figure 12-12. Model of the potential of α-particles in the process of α-decay - the particle in the parent nucleus is in the potential well due to the nucleus forces and at the decay it must overcome the potential barrier formed by the act of the electrostatic repulsive forces between α-particle and the daughter nucleus.

The experimental investigation of the decay shows, that this phenomena is conditioned by the internal forces of the nucleus and the number of the nuclei which decay in time dt is proportional to the number of the nuclei in the moment t and to the interval dt:

$$dN=-\lambda_o N dt. \tag{12.88}$$

Here λ_0 is the constant of the radioactive decay. After the integration we readily obtain the Curie law on the radioactive decay:

$$N=N_o\exp(-\lambda_o t). \tag{12.89}$$

The constant λ_0 can be connected with the period of half-life $\tau_{1/2}$ of the decay. Under the half-life $\tau_{1/2}$ we understand time for which the number of the nuclei decreases two times, i.e.

$$N_o \exp\left(-\lambda_o \tau_{1/2}\right) = \frac{1}{2} N_o = N_o \exp\left(-\ln 2\right). \tag{12.90}$$

The connection between λ_0 and $\tau_{1/2}$ is clear:

$$\tau_{1/2} = \frac{\ln 2}{\lambda_o} = \frac{0,693}{\lambda_o}. \tag{12.91}$$

Now we shall connect λ_0 and $\tau_{1/2}$ with the barrier penetration. If we assume that for 1 s *n*th part of α-particles reach the barrier (the point r_0 in Fig. 12-12), the nucleus should emit nT-part of the number of its α-particle. The barrier penetration is defined by the expression (12.86), where the integration is from r_0 to r_1 (see Fig. 12-12). From *N* nuclei dN will be decayed for the interval dt:

$$dN = -nTNdt. \tag{12.92}$$

By the comparison of (12.88) and (12.92) we can write

$$\lambda_o = nT, \tag{12.93}$$

or according to (12.86)

$$\lambda_o = n \exp\left(-\frac{2}{\hbar} \int_{r_o}^{r_1} \sqrt{2m\left(U - E\right) dr} \right). \tag{12.94}$$

For the final determination of λ_0 we have to know *n*. Finding *n* is a difficult problem. But this value can be estimated using the classical consideration. For 1 s the part $\sim v / r_0$ of the α-particle will reach the beginning of the barrier. According to the Heisenberg's uncertainty relation $mvr_0 \approx \hbar$ and for n we get

$$n \equiv \frac{v}{r_o} = \frac{\hbar}{mr_o^2}. \tag{12.95}$$

Finally for the constant of the radioactive α-decay we obtain:

$$\lambda_o = \frac{\hbar}{mr_o^2}\exp\left(-\frac{2}{\hbar}\int_{r_o}^{r_1}\sqrt{2m\left(U-E\right)}\,dr\right). \tag{12.96}$$

The α-decay of Uranium

$${}^{238}_{92}\mathrm{U}\rightarrow{}^{234}_{90}\mathrm{Th}+{}^{4}_{2}\mathrm{He}+4{,}2\ \mathrm{MeV} \tag{12.97}$$

has half-life $\tau_{1/2} = 0{,}45.10^{10}$ years. The estimation with the formula (12.92) for $r_0 = 10^{-14}$ m and barrier height $2\left(Z-2\right)e^2k_0/r_0 = 26$ Mev gives $\tau_{1/2} = 2{,}9.10^{10}$ years, which illustrates very well the possibilities of the theory if we take into account the estimation character of (12.91).

SUMMARY

The wave function of the state of the quantum particle of mass *m* in a constant one-dimensional potential field $U\left(x\right) = \mathrm{const} = U$ satisfies the stationary Schroedinger equation

$$\frac{\partial^2}{\partial x^2}\psi\left(x\right)+\frac{2m}{\hbar^2}\left(E-U\right)\psi\left(x\right)=0.$$

The form of the solution depends on the relation between the energy *E* of the particle and the potential *U* of the field. When $E > U$ the solution is a linear combination of two harmonic functions:

$$\psi_1\left(x\right)=A\exp\left(ikx\right)+B\exp-\left(ikx\right),\quad k^2=\frac{2m}{\hbar^2}\left(E-U\right)>0.$$

When $E < U$ the solution is a linear combination of two exponential functions:

$$\psi\left(x\right)=A\exp\left(\kappa x\right)+B\exp\left(-\kappa x\right),\qquad \kappa^2=\frac{2m}{\hbar^2}\left(U-E\right)>0.$$

The energy of the particle in the free state can be only positive.

The solutions of the Schroedinger equation for the infinite potential well

$$\psi_n\left(x\right)=\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x$$

are standing de Broglie waves.

In comparison with the classical particle the quantum particle manifests principally new properties - its energy is quantizied and its minimal energy is different from zero. The quantization of the energy shows its worth at sufficiently small mass of the particle and/or width of the well. The energy levels are defined by the quantum number *n*:

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2, \qquad n = 1, 2, 3, \ldots$$

When the quantum particle impinges on the potential step of the height *U* and its energy *E* is smaller than *U*, it penetrates in the classically forbidden domain $E < U$. The effect is completely quantum and has not a classical analogue.

When the particle is in the potential well with a finite depth to the character for the infinite well properties are added new quantum characters:

- the number of its bounded states depends on the depth *U* and on the width *a* of the well - with increasing *U* and/or of *a* their number increases;
- the particle penetrates in the classically forbidden domain - the probability to find it in this region is different from zero.

When the quantum particle of the energy *E* incident on the potential barrier of the height *U* and width *a* and $E < U$ we observe the effect unknown in classical physics - the penetration of the particle through the barrier. The penetration of the quantum particle through the potential barrier of the larger height than particle total energy, i.e. through the classically forbidden domain, is called the tunnel effect. With the tunnel effect are explained many phenomena for which classical physics is helpless - the autoelectronic emission, the transitions of N atoms in the molecule of NH_3 molecule, the radioactive α-decay etc.

The systems with one-dimensional constant (in the given region) are the simplest model of the real physical systems, in which the quantum properties of the microscopic word appear.

QUESTIONS

1. How does the solution depend of the stationary Schroedinger equation for the particle in the constant uniform field on its energy?
2. What are the solutions at $E < U$ and at $E > U$?
3. Why cannot the free particle have negative energy?
4. What is the energy spectrum in the infinite potential well?

5. How do the probabilities of the quantum and the classical particles in the potential well differ?
6. How does the space between the energy levels depend on the quantum number *n*?
7. Does the energy discrete character of the particle depend on its mass and on the well width?
8. What is the behaviour of the quantum and of classical particles, when they incident on the potential step (at $E < U$ and at $E > 0$)?
9. Compare the behaviour of classical and quantum particles, when they pass through the potential barrier?
10. What is the tunnel effect?

PROBLEMS

1. The states of the particle of mass *m* in an infinite potential well are described by standing de Broglie waves, which have integer half waves along the width of the well. Taking into account this fact and the connection between the wavelength and the particle momentum *p*, prove the quantization of its energy.
2. Two of the allowed states of the particle, which motion is free, but strictly limited in the region of the width *a*, are described with the wave eigenfunctions ψ_2 and ψ_3, which are shown in Fig. 12-1a. When the particle is in the state with ψ_2 its energy is 4 eV. What is its energy in the state with ψ_3? What is the minimal allowed energy of the particle in this system?
3. Find the energy E_1 of the ground state, the difference between the energies $E_2 - E_1$ and the wavelength of the photon with energy $E_2 - E_1$ of an electron in one-dimensional infinite potential well of the width 1 Å.
4. For the particle of mass *m* in the one-dimensional infinite potential well of width *a* find the average values of its co-ordinates *x*, of x^2, of its momentum *p* and of p^2.
5. The electron beam of a linear density 10^{15} electrons/ m^2, after its acceleration by the potential difference 100 V, incidents on the potential step of the height $U = 50$ V. Find the incident, reflected and transient current.
6. The electron beam of an energy 2 eV incidents on the potential step of the height 20 eV. To what distance from the beginning of the step will the beam density decrease *e* times?

Chapter 13

THE HARMONIC QUANTUM OSCILLATOR

SUGGESTED READING

1. Eisberg, R. and R. Resnic, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, John Wiley & Sons, 1974 $n = 1$, Section 6-9, Appendix H.

2. Greiner, W., Quantum Mechanics - An Introduction, Vol. 1, Springer-Verlag, 1989, Chapter 7.
3. Blokhintsev, D. I., Principles of Quantum Mechanics, Allyn and Bacon, 1964, §47, Appendix IX.
4. Spolsky, E. V., Atomic Physics, Vol. 1, Mir Publishing House, 1963, §158-§160.

13.1* THE SOLUTION OF THE OSCILLATOR EQUATION

In Chapter 5 we have considered the motion of the classical harmonic oscillator. Let remember briefly its results. The motion of the particle of the mass *m*, whose potential energy is near the position of the stable equilibrium, has the form

$$U(x)=\frac{\kappa x^2}{2}. \tag{13.1}$$

For a small deviation from an equilibrium it is valid the equation

$$\ddot{x}+\omega_0^2 x=0, \quad \omega_0^2=\frac{\kappa}{m}. \tag{13.2}$$

This equation has a harmonic solution

$$x=a\cos(\omega_o t+\delta). \tag{13.3}$$

The energy of the oscillator is defined as follows:

$$E=T+U=\frac{m\dot{x}}{2}+\frac{\kappa x^2}{2}=\frac{p_x^2}{2m}+\frac{m\omega_o^2 x^2}{2}. \tag{13.4}$$

The function of Hamilton is:

$$H=\frac{p_x^2}{2m}+\frac{m\omega_o^2 x^2}{2}. \tag{13.5}$$

In the turning points $x=\pm a$ the total energy is a potential one:

$$E=U=\frac{m\omega_o^2 x^2}{2}. \tag{13.6}$$

The region

$$x^2 > a^2 \tag{13.7}$$

is a forbidden domain for the classical oscillator.

Let now consider the quantum mechanical form of the problem of the harmonic oscillator. According to (13.5) the operator of Hamilton has the following form:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{m\omega_o^2 x^2}{2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega_o^2 x^2}{2}. \tag{13.8}$$

The theory of the quantum oscillator is very important in quantum physics as the Hamiltonian of the form (13.8) is used in all problems, in which the oscillations are quantizied. For example, we find it in the oscillations of molecules and crystals, in quantum electrodynamics and in the quantum field theory. The problem of the quantum oscillator is a beautiful illustration of the formalism and the basic principles of quantum mechanics. Therefore we shall expose this problem in details.

The Hamiltonian (13.8) is not the explicit function of time and hence the oscillator wave function satisfies the time-independent Schroedinger equation $\hat{H}\psi(x) = E\psi(x)$, i.e.

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}E\psi(x) - \frac{m^2\omega_o{}^2 x^2}{\hbar^2}\psi(x) = 0. \tag{13.9}$$

The multiplying this equation by $\hbar / m\omega_0$ gives:

$$\frac{\hbar}{m\omega_o}\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2}{\hbar\omega_o}E\psi(x) - \frac{m\omega_o x^2}{\hbar}\psi(x) = 0. \tag{13.10}$$

The ratio $\hbar / m\omega_0$ has the dimension of the square length $[\hbar / m\omega_0] = \mathrm{ML^2T^{-2}T/\left(MT^{-1}\right) = L^2}$. We set:

$$\frac{\hbar}{m\omega_0} \equiv x_0^2, \quad \frac{x}{x_0} \equiv \xi \quad \frac{2E}{\hbar\omega_0} \equiv \mathcal{E}. \tag{13.11}$$

With the new dimensionless quantities, dimensionless co-ordinate ξ and dimensionless energy $\mathcal{E}$, the Eq. (13.9) is reduced to:

$$\frac{\partial^2\psi(\xi)}{\partial\xi^2}+\left(\varepsilon-\xi^2\right)\psi(\xi)=0. \tag{13.12}$$

We first discuss the asymptotic form of the solution when ξ is very large so the equation is approximately:

$$\frac{\partial^2\psi_\infty}{\partial\xi^2}-\xi^2\psi_\infty=0. \tag{13.13}$$

The solution of this equation is:

$$\psi_\infty=e^{\pm\frac{\xi^2}{2}}, \tag{13.14}$$

Actually, after finding the second derivation

$$\begin{aligned}&\frac{\partial\psi_\infty}{\partial\xi}=\pm\xi e^{\pm\frac{\xi^2}{2}},\\&\frac{\partial^2\psi_\infty}{\partial\xi^2}=\xi^2e^{\pm\frac{\xi^2}{2}}\pm e^{\pm\frac{\xi^2}{2}}\approx\xi^2\psi_\infty\end{aligned} \tag{13.15}$$

and taking into account $\xi\to\pm\infty$, we are readily persuaded that (13.14) satisfies the Eq. (13.13).

The solution with the "+" at $\xi\to\pm\infty$ increases indefinitely. Such a wave function does not satisfy the condition of the finiteness (Section 9.2). Hence asymptotically ($\xi\to\pm\infty$) the wave function has the form $\psi_\infty=e^{-\frac{\xi^2}{2}}$. We seek the solution of (13.12) in the following form:

$$\psi(\xi)=\eta(\xi)e^{-\frac{\xi^2}{2}}, \tag{13.16}$$

where $\eta(\xi)$ is an unknown function. Finding the second derivative of (13.16)

$$\begin{aligned}\frac{\partial\psi(\xi)}{\partial(\xi)} &= \frac{\partial\eta}{\partial\xi}e^{-\frac{\xi^2}{2}} + \eta e^{-\frac{\xi^2}{2}}(-\xi),\\ \frac{\partial^2\psi(\xi)}{\partial\xi^2} &= \frac{\partial^2\eta}{\partial\xi^2}e^{-\frac{\xi^2}{2}} - 2\xi\frac{\partial\eta}{\partial\xi}e^{-\frac{\xi^2}{2}} - \eta e^{-\frac{\xi^2}{2}} + \xi^2\eta e^{-\frac{\xi^2}{2}}\end{aligned} \tag{13.17}$$

and substituting it in (13.12) we get for the unknown function $\eta(\xi)$:

$$\frac{\partial^2\eta}{\partial\xi^2} - 2\xi\frac{\partial\eta}{\partial\xi} + (\mathcal{E}-1)\eta = 0\,. \tag{13.18}$$

We seek for the solution in the form:

$$\eta(\xi) = \sum_{k=o}^{\infty} a_k\xi^k. \tag{13.19}$$

Finding the first and the second derivatives of the power series $\eta(\xi)$:

$$\begin{aligned}\frac{\partial\eta}{\partial\xi} &= \sum_{k=0}^{\infty} a_k k\xi^{k-1},\\ \frac{\partial^2\eta}{\partial\xi^2} &= \sum_{k=0}^{\infty} a_k k(k-1)\xi^{k-2}\end{aligned} \tag{13.20}$$

and replacing them in (13.18) we have:

$$\sum_{k=0}^{\infty} a_k k(k-1)\xi^{k-2} - 2\sum_{k=0}^{\infty} a_k k\xi_k + (\xi-k)\sum_{k=0}^{\infty} a_k\xi^k = 0. \tag{13.21}$$

For every value of ξ the relation (13.12) can be only satisfied if all powers of ξ are equal to zero. For the coefficients before ξ^m this means:

$$a_{m+2}(m+2)(m+1) - 2a_m m + (\mathcal{E}-1)\,a_m = 0\,, \tag{13.22a}$$

or

$$a_{m+2} = \frac{2m - (\mathcal{E} - 1)}{(m+2)(m+2)} a_m . \tag{13.22b}$$

If we know a_m we can determine a_{m+2} and then a_{m+4} etc. All even coefficients $a_2, a_4, a_6, ..., a_{2m}$ can be determined, if we know a_0, and $a_3, a_5, a_7, ..., a_{2m+1}$ - if we know a_1. Two constants are necessary as the Eq. (13.18) is one of the second order.

Two power series of the even and odd powers correspond to two partial solutions of the differential equation (13.18). For clarification of the character peculiarities of the oscillator is enough to consider one of these solutions. Let assume that $a_1 = 0,\ a_0 \neq 0$. Then the partial solution

$$\psi(\zeta) = \eta(\xi) e^{-\frac{\xi^2}{2}} = \sum_{k=0}^{\infty} a_{2k} \xi^{2k} e^{-\frac{\xi^2}{2}} . \tag{13.23}$$

is expressed by the even powers.

At great ξ the sum $\sum_0^{\infty} a^{2k} \xi^{2k}$ increases indefinitely as $\exp(\xi^2)$ (for the proof see [2]). Hence the asymptotic solution $\psi(\xi \to \infty) \propto e^{\xi^2/2}$ appears to be infinite. The function does not satisfy the condition of the finiteness of the wave function (Section 9.2). The problem is that the series $a_{2k}\xi^{2k}$ is too long. We note, however, that if $a_{n+2} = 0$, then all next terms $a_{n+4}, a_{n+6}, ...$ etc. will be equal to zero. Hence the series may be restricted to the *n*th term ($a_n \neq 0$) if

$$a_{n+2} = \frac{2n - (\mathcal{E} - 1)}{(n+2)(n+1)} a_n = 0 . \tag{13.24}$$

This is equivalent to the condition

$$\mathcal{E} = 2n + 1, \quad n = 0, 1, 2, 3 \ldots \tag{13.25}$$

The Eq. (13.18) at the condition (13.25) for the parameter $\mathcal{E}$ has as a solution the polynomial $\eta(\xi)$ with the coefficients, determined by (13.22).

The polynomials $\eta(\xi)$ are called Hermite polynomials:

$$\eta_n(\xi) = A_n \mathscr{H}(\xi) \; . \tag{13.26}$$

The constants A_n are determined by the normalization condition of the wave function $\psi(\xi)$ (13.16):

$$A_n = \sqrt{\frac{x_0}{2^n n!\sqrt{\pi}}} = \sqrt{\frac{1}{2^n !n\sqrt{\pi}}\sqrt{\frac{\hbar}{m\omega_0}}} \tag{13.27a}$$

and the Hermite polynomials - by the formula

$$\mathscr{H}_n(\xi) = (-1)^n e^{\varepsilon^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \; . \tag{13.27b}$$

We shall once again underline, that the Hermite polynomials (13.26) are the solution of the Eq. (13.18) only at the condition (13.25):

$$\mathscr{E} = \frac{2E}{\hbar\omega_0} = 2n+1, \quad n = 0, 1, 2, 3\ldots, \tag{13.28a}$$

i.e. at

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 = \left(n + \frac{1}{2}\right)h\nu_0 \; . \tag{13.28b}$$

The number $n = 0, 1, 2, 3, \ldots$ is called the quantum number of the oscillator. The *n*th state is described with the wave function $\psi_n(\xi)$:

$$\psi_n(\xi) = A_n e^{-\frac{\xi^2}{2}} \mathscr{H}_n(\xi) = \sqrt{\frac{1}{2^n !n\sqrt{\pi}}\sqrt{\frac{\hbar}{m\omega_0}}} (-1)^n e^{\frac{\xi^2}{2}} \frac{d^n e^{-\frac{\xi^2}{x}}}{d\xi^n} \; . \tag{13.29}$$

The energy of the quantum oscillator is quantizied. It has discrete character. The energy levels are equidistant

$$\Delta E_n = E_{n+1} - E_n = \hbar\omega_0 = h\nu_0 \; . \tag{13.30}$$

and at the transition between every two adjacent levels (from the higher to the lower) the photon of energy $h\nu_0$ is emitted, where ν_0 is the oscillator frequency.

13.2 GROUND STATE AND ZERO-POINT ENERGY

The state with minimum energy is called a ground state. The quantum oscillator has minimal energy in the state with $n = 0$:

$$E_{\min} = E_0 = \frac{\hbar\omega_0}{2} . \tag{13.31}$$

At $n = 0$ from (13.27) we easy obtain $\mathscr{H}_0 = 1$ and hence the wave function in the ground state is following:

$$\psi_o(\xi) = A_0 e^{-\frac{\xi^2}{2}} . \tag{13.32}$$

The probability density of this state is:

$$\rho_0 = (\zeta) = \left|\psi(\zeta)\right|^2 = A_0^2 e^{-\zeta^2} . \tag{13.33}$$

The functions $\psi_0(\xi)$ and $\rho_0(\xi)$ are shown in Fig. 13-1. The wave function and the probability density are different from zero in a classically forbidden domain (the shaded regions). The probability density of the classical oscillator with the minimal energy ($E_{\min}^{cl} = 0$) is a δ-function: $\rho^{cl}(\xi) = \delta(\xi)$.

At the minimal energy E_0 of the quantum oscillator the classical oscillator would move in the region $-\xi_0 < \xi < +\xi_0$ $\left(U(\pm\xi_0) = E_0\right)$. The character distinction of the quantum oscillator from the classical one is that it penetrates in the classically forbidden domain.

The lowest energy is another difference, but very essential one between both oscillators. For the classical oscillator it is $E_{\min}^{cl} = 0$ and corresponds to the energy of the rested particle in the equilibrium point. For this state the probability density is δ-function $\rho^{cl}(\xi) = \delta(\xi)$ and the probability to find the particle in this point is a unity:

$$W(\xi) = \int_{-\infty}^{\infty} \rho^{cl}(\xi)d\xi = \int_{-\infty}^{\infty} \delta(\xi)d\xi = 1. \qquad (13.34)$$

The minimal energy of the quantum oscillator E_0, called zero-point energy, is its intrinsic characteristic. This is the lowest energy, which the quantum oscillator in general can have. This energy can not be decreased or removed. At the first glance the decreasing of the natural angular frequency $\omega_0 = \sqrt{\kappa / m}$ would decrease the energy $E_0 = \hbar\omega_0 / 2$. But this means either decreasing the force constant κ or increasing the mass *m*. This is equivalent to the change the same oscillator, the its essence.

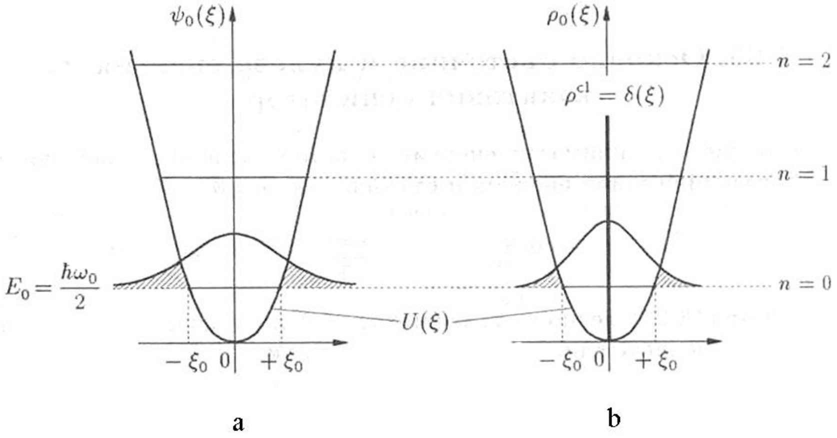


Figure 13-1. Wave function $\psi_0(\xi)$ (a) and the probability density $\rho_0(\xi)$ (b) of the ground state. The points $\pm\xi_0$ $(U(\xi_0) = E_0)$ are turning points of the classical oscillator of energy $E^{cl} = E_0$; the region $-\xi < \xi < +\xi$ - a permissible domain for such an oscillator, $\xi^2 > \xi_0^2$ - a forbidden domain.

The zero-point energy is proven experimentally by the crystal scattering of light. With the decreasing the crystal temperature T_0 according to the classical theory the oscillation amplitude has to decrease and to vanish finally. The experiment shows that at decreasing T_0 the scattering frequency tends to a threshold value, from which one concludes the atom oscillations do not stop.

The zero-point energy of the quantum oscillator can be obtained from the Heisenberg uncertainty condition (Section 10.9): $\Delta p \Delta x \geqq \hbar / 2$, which can be written in the form:

$$(\Delta p)^2(\Delta x)^2 \geq \hbar^2/4. \tag{13.35}$$

We admit that $\overline{p}=0$ and hence $\delta p = p - \overline{p}$. Then the dispersion square will be $(\Delta p)^2 = \overline{p^2}$ (see Section 10.8). By analogy for the co-ordinate *x*, admitting $\overline{x}=0$, we obtain $(\Delta x)^2 = \overline{x^2}$. Hence (13.35) can be written as

$$\overline{p^2}\,\overline{x^2} \geq \frac{\hbar^2}{4}, \quad \text{or} \tag{13.36a}$$

$$\overline{x}^2 = \frac{\hbar^2}{4\overline{p^2}}. \tag{13.36b}$$

We substitute $\overline{x^2}$ from (13.36b) in the expression for the average oscillator energy:

$$\overline{E} = \frac{\overline{p^2}}{2m} + \frac{m\omega_0^2\overline{x^2}}{2} = \frac{\overline{p^2}}{2m} + \frac{m\omega_0^2\hbar^2}{8\overline{p^2}}. \tag{13.37}$$

We calculate the derivative of $\overline{E} = \overline{E}\left(\overline{p^2}\right)$ with respect to $\overline{p^2}$ and equal it to zero. From here we determine that at $\overline{p^2} = m\omega_0\hbar/2$ the average energy of the oscillator is minimal:

$$\overline{E}_{\min} = \frac{m\omega_0\hbar}{4m} + \frac{m\omega_0^2\hbar^2 2}{8m\omega_0\hbar} = \frac{\hbar\omega_0}{2} = E_0. \tag{13.38}$$

This pure quantum effect - the minimal energy, different from zero - we have established for the square infinite well.

13.3 EIGENSTATES OF THE HARMONIC OSCILLATOR

Let us consider $n=1$ state. From (13.27) we determine a polynomial $\mathscr{H}_1$

$$\mathscr{H}_1 = (-1)e^{\xi^2}\frac{d}{d\xi}e^{-\xi^2} = 2e^{\xi^2}e^{-\xi^2}\xi = 2\xi. \tag{13.39}$$

The wave function $\psi_1(\xi)$, the probability density $\rho_1(\xi)$ and the energy E_1 in this are, relatively:

$$\psi_1(\xi) = 2A_1\xi e^{-\frac{\xi^2}{2}},$$
$$\rho_1(\xi) = \left|\psi_1(\xi)\right|^2 = 4A_1^2\xi^2 e^{-\xi^2}, \tag{13.40}$$
$$E_1 = \frac{3}{2}\hbar\omega_0.$$

The wave function $\psi_1(\xi)$ has one node at $\xi = 0$, i.e. $\psi_1(0) = 0$. Its plot as well as the plot of $\rho_1(\xi)$ are shown in Fig. 13-2.

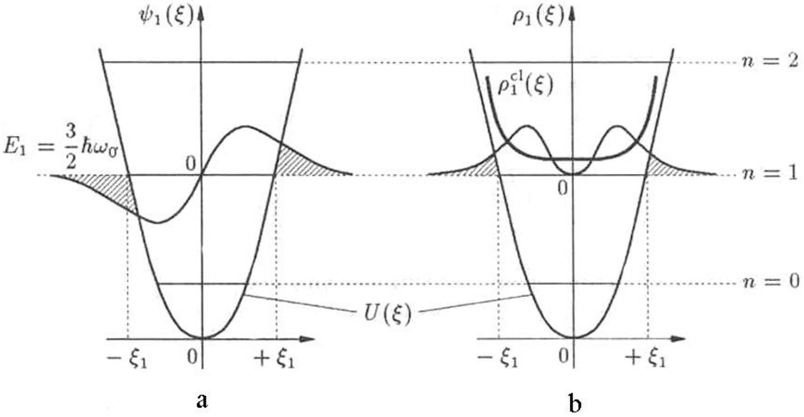


Figure 13-2. The wave function $\psi_1(\xi)$ (a) and the probability density $\rho_1(\xi)$ of the state with $n=1$: the quantum one $\rho_1(\xi)$ and the classical one $\rho_1^{\text{cl}}(\xi)$ (b): $-\xi_1 < \xi < +\xi_1$ - a classical permissible domain.

Let determine the probability of the classical oscillator of energy $E = E_1$. The probability to find the particle in the region between x and $x + dx$ is

$$dW(x) = \frac{dt}{\tau} = \frac{\omega_0}{2\pi}\frac{dx}{v}, \tag{13.41}$$

where $\tau = 2\pi/\omega$ is the period of the oscillations and v is the particle velocity. Its energy is $E = mv^2/2 + U(x)$ and expressing v through E we obtain for $\rho_1(\xi)$:

$$\rho^{cl}(x)=\frac{dW(x)}{dx}=\frac{\text{const}}{\sqrt{\frac{2}{m}\left[E-U(x)\right]}}\Rightarrow\rho^{cl}(\xi)=\frac{\text{const}}{\sqrt{\mathcal{E}-\xi^2}}. \tag{13.42}$$

The plot of the classical probability density is shown in Fig.13-2b. At $n=2$ from (13.23b) we get for the polynomial $\mathcal{H}_2$

$$\mathcal{H}_2=e^{\xi^2}\frac{d^2}{d\xi^2}e^{-\xi^2}=-2e^{\xi^2}\frac{d}{d\xi}\xi e^{-\xi^2}=4\xi^2-2. \tag{13.43}$$

The wave function and the energy of the state with $n=2$ are relatively:

$$\begin{aligned}&\psi_2(\xi)=A_2\left(4\xi^2-2\right)e^{-\frac{\xi^2}{2}},\\&E_2=\frac{5}{2}\hbar\omega_{0.}\end{aligned} \tag{13.44}$$

The function $\psi_2(\xi)$ has two nodes (Fig. 13-3):

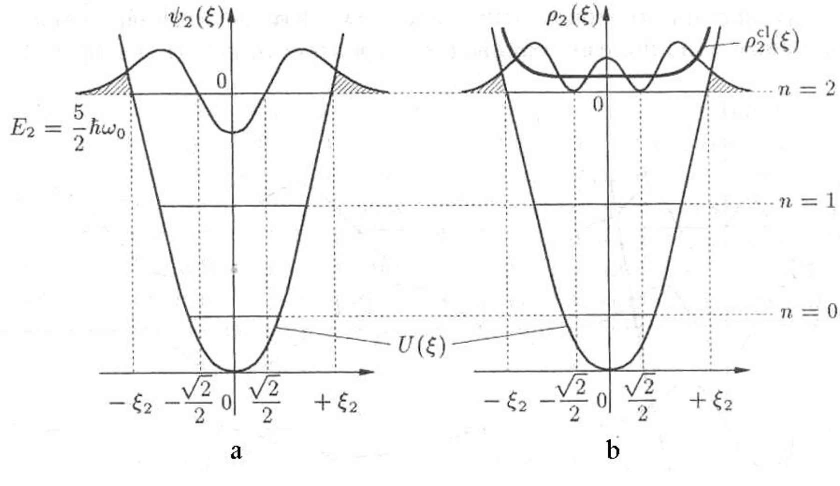


Figure 13-3. The state of the quantum oscillator with n=2: a) the wave function $\psi_2(\xi)$; b) the probability density: the quantum one $\rho_2(\xi)$ and the classical one $\rho_2^{cl}(\xi)$.

$$\xi=\pm\frac{\sqrt{2}}{2}\Rightarrow\psi\left(\pm\frac{\sqrt{2}}{2}\right)=0. \tag{13.45}$$

In the states with large values of the quantum number n the distribution of the quantum probability density $\rho_n(\xi)$ approaches the classical one (Fig. 13-4).

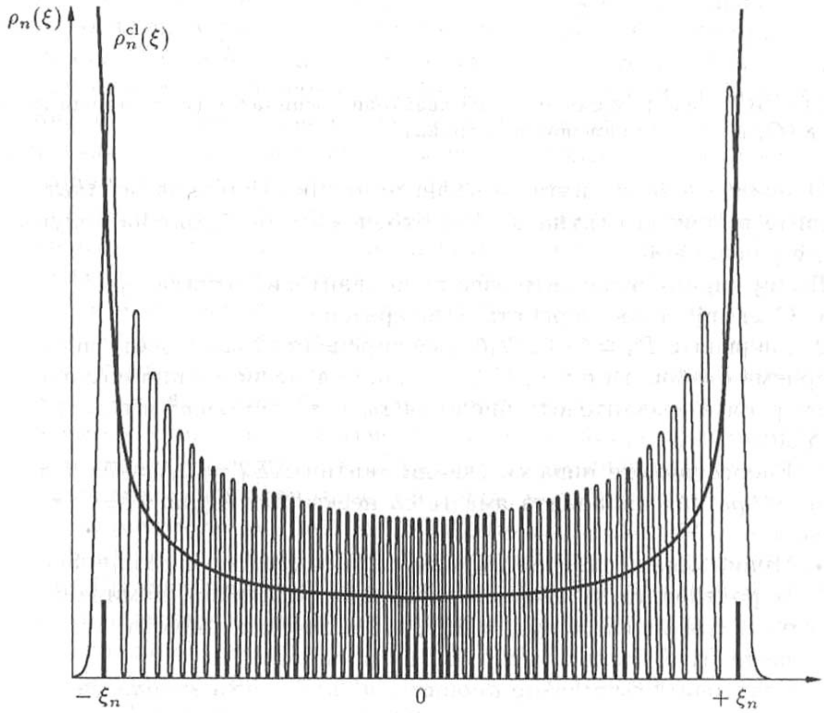


Figure 13-4. The probability density of the quantum oscillator $\rho_n(\xi)$ and of the classical oscillator $\rho_n^{\mathrm{cl}}(\xi)$ of the same energy at a great number n ($n = 61$).

And before summarizing the basic results of the quantum oscillator we shall make one useful comparison with the string oscillation (Fig. 13-5).

The analogy between the de Broglie waves and the string waves is obvious. We note that the number of the half waves $\psi_n(x)$ is equal to n.

We shall summarize the basic results of the quantum oscillator:

1. The energy spectrum is discrete.
2. The energy $E_n = (n+1/2)\hbar\omega_0$ is determined by the quantum number *n*, which has the values $n = 0, 1, 2, 3 \ldots$ (compare with the infinite well of the energy $E_n = (\pi^2\hbar^2 / 2ma^2)n^2$ and the quantum number $n = 1, 2, 3 \ldots$ (see Section 12.2).

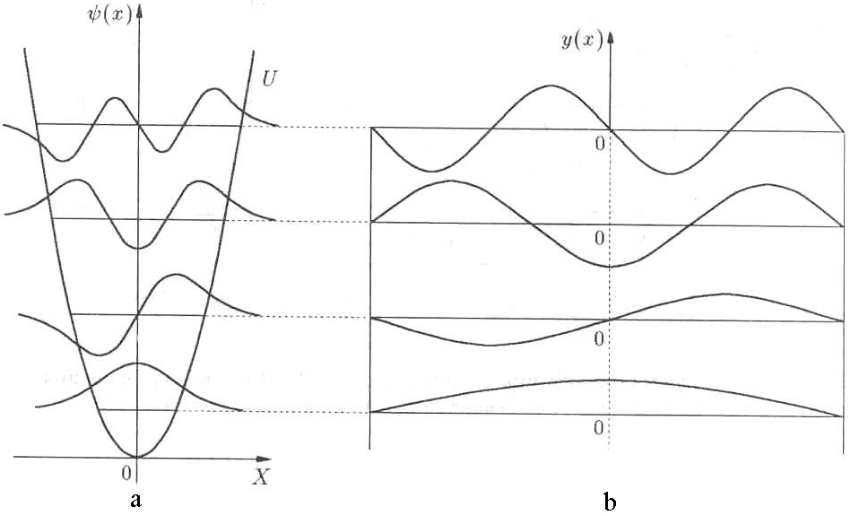


Figure 13-5. Wave function $\psi_n(\xi)$ of the quantum oscillator (a) and the standing waves of the string (b); $y(x)$ is the string deviation.

3. The energy levels are equidistant, $\Delta E_n = \Delta E = \hbar\omega_0$ (compare with the infinite well, where they are nonequidistant, $\Delta E_n = (\pi^2\hbar^2/2ma^2)(2n+1)$).
4. The minimal possible energy is different from zero, $E_{\min} = E_0 \neq 0$.
5. In the ground state ($E = E_{\min} = E_0$) the probability to find the quantum oscillator in every point of the classically permissible domain is different from zero.
6. The quantum oscillator penetrates in the classically forbidden domain.

13.4* COUPLED QUANTUM-MECHANICAL OSCILLATORS AND VAN DER WAALS FORCES

The solution of the quantum oscillator problem in Section 13.2 leads us to the conclusion that even at the absolute zero temperature the oscillator possesses the energy $E = \hbar\omega_0/2$ called zero-point energy. This fact is curiously enough from the classical point of view, but the experiment verifies its existence. It is particularly interesting that the existence of the zero-point energy unexpectedly explains the intermolecular and the interatomic attractive forces, known as van der Waals forces. They are well known in classical physics and are expressed through the known equation of van der Waals:

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT_0, \tag{13.46}$$

where $p,\ V\ and\ T_0$ are the pressure, the volume and the temperature of the fluid, a and b are constants and R is the universal gas constant. The term a/V^2 describes the attractive force between the molecules.

In the frames of classical physics many attempts are made to explain these forces, prescribing them an electrical origin. The neutral molecules are considered as electric dipoles and in more power systems as quadrupoles. But the consistence of the theoretical and experimental results meets the insuperable obstacles. Moreover, with such a concept cannot be explained the attractive forces between the inertial gases. They possess the high degree of the electrical symmetry and is impossible to have a permanent dipole or quadrupole moment. But all of them can be condensed into liquids and hence their molecules interact with the van der Waals forces.

The difficulties can be removed if one considers not only the permanent electrical dipoles but also the induced, due to the oscillations, dipole moments. Let consider two molecules, which charges in rest are spherically symmetrically distributed, so they do not interact. If we displace the charged, the molecule will acquire a dipole moment and will begin to interact. Such a displacement arises at zero-oscillations, which always exist. The appearance of the dipole moment in one molecule induces a dipole moment in another one, the quickly changing moments are found to be in phase, which in its turn originates the attractive force. Such is the qualitative explanation of the attractive intermolecular forces. We shall show that this simple physical picture allows maintaining the quantitative law for interaction between the molecules.

Let consider the idealized model of the coupled oscillator, using the two dipoles situated along the line of the distant r each from other. The masses of the charged are equal $m_1=m_2=m$. Because of the oscillations the electric charges are displaced correspondingly to x_1 and x_2 (Fig. 13-6). Every charge interacts with the all others. The energy of the interaction is determined by the attraction of the opposite charges and the repulsion of the like charges. According to the Coulomb law it is

$$\begin{aligned}U_{12}&=-\frac{k_0e^2}{r-x_1}-\frac{k_0e^2}{r+x_2}+\frac{k_0e^2}{r+x_2-x_1}+\frac{k_0e^2}{r}\\&=\frac{k_0e^2}{r}\left(-\frac{1}{1-\frac{x_1}{r}}-\frac{1}{1+\frac{x_2}{r}}+\frac{1}{1+\frac{x_2-x_1}{r}}+1\right).\end{aligned} \tag{13.47}$$

(For k_0 see (4.20)). As $r >> x_1, x_2$, we can represent the fraction in the brackets as power series, according to the formula

$$(1 \pm x)^{-1} = 1 \mp x + x^2 \mp x^3 + ... \tag{13.48}$$

Restricting only to the first three terms, we get for the potential energy of the dipole interaction:

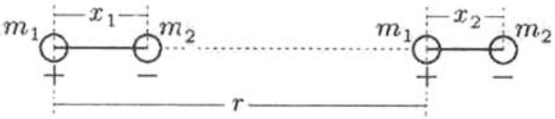


Figure 13-6. Two molecules interact as two electrical dipoles, which are due to the molecule oscillations.

$$U_{12} = -\frac{2k_0e^2}{r^3}x_1x_2 = -\kappa x_1x_2. \tag{13.49}$$

Here we set $\kappa = 2k_0e^2 / r^3 = 2e^2 / 4\pi\varepsilon_0 r^3$.

Separately every one of the dipoles represents the quantum oscillator with the force constant κ_1, the natural frequency ω_0 and the following potential energies:

$$U_1 = \frac{1}{2}\kappa_1 x_1^2 = \frac{1}{2}m\omega_0^2 x_1^2, \quad U_2 = \frac{1}{2}\kappa_1 x_2^2 = \frac{1}{2}m\omega_0^2 x_2^2, \tag{13.50}$$

where

$$\omega_0^2 = \frac{\kappa_1}{\tilde{m}} = \frac{2\kappa_1}{m} \quad \text{and} \quad \tilde{m} = \frac{m_1m_2}{m_1+m_2} = \frac{m}{2} \quad \text{(see (5.27) and (5.32)).}$$

The potential energy of two coupled oscillators is a sum of the potential energies of the separate oscillators and the energy of the dipole interaction:

$$U = U_1 + U_2 + U_{12} = \frac{1}{2}m\omega_0^2 x_1^2 + \frac{1}{2}m\omega_0^2 x_2 - \kappa x_1x_2\,. \tag{13.51}$$

Now we can write the function of Hamilton for the coupled oscillators:

$$H = T_1 + T_2 + U = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2} m\omega_0^2 \left(x_1^2 + x_2^2 \right) - \kappa x_1 x_2. \qquad (13.52)$$

Hence the operator of Hamilton is

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{1}{2} m\omega_0^2 \left(x_1^2 + x_2^2 \right) - \kappa x_1 x_2. \qquad (13.53)$$

Here x_1 and x_2 are displacements of the both oscillators from the equilibrium position and ω_0 is the natural frequency of every one of these (equal) oscillators with mass m.

We introduce normal co-ordinates (see Section 5.4):

$$\begin{aligned} x_1 &= \frac{1}{\sqrt{2}} (\xi_1 + \xi_2), \\ x_2 &= \frac{1}{\sqrt{2}} (\xi_1 - \xi_2). \end{aligned} \qquad (13.54)$$

From these expressions we can obtain two useful relations for $x_1^2 + x_2^2$ and $x_1 x_2$, squaring the two equalities and then summing them up and multiplying them:

$$\begin{aligned} x_1^2 + x_1^2 &= \xi_1^2 + \xi_2^2, \\ x_1^2 x_1^2 &= \frac{1}{2} (\xi_1^2 - \xi_2^2). \end{aligned} \qquad (13.55)$$

The Hamiltonian is expressed through the derivatives with respect to x_1 and x_2. It is necessary to pass to the derivative of the new co-ordinates ξ_1 and ξ_2. We determine the derivative $\partial / \partial \xi_1$ of the function $\psi = \psi \left[x_1 (\xi_1, \xi_2), x_2 (\xi_1, \xi_2) \right]$:

$$\frac{\partial \psi}{\partial \xi_1} = \frac{\partial \psi}{\partial x_1} \frac{\partial x_1}{\partial \xi_1} + \frac{\partial \psi}{\partial x_2} \frac{\partial x_2}{\partial \xi_1}. \qquad (13.56)$$

According to (13.54)

$$\frac{\partial x_1}{\partial \xi_1}=\frac{1}{\sqrt{2}},\quad \frac{\partial x_2}{\partial \xi_1}=\frac{1}{\sqrt{2}}. \tag{13.57}$$

Substituting (13.57) into (13.56), we get:

$$\frac{\partial \psi}{\partial \xi_1}=\frac{1}{2}\left(\frac{\partial \psi}{\partial x_1}+\frac{\partial \psi}{\partial x_2}\right). \tag{13.58}$$

Differentiating on ξ_1 and taking into account (13.57), for the second derivation on ξ_1 we obtain the following expression:

$$\frac{\partial^2 \psi}{\partial \xi_1^2}=\frac{1}{2}\left(\frac{\partial^2 \psi}{\partial x_1^2}+2\frac{\partial^2 \psi}{\partial x_1 \partial x_2}+\frac{\partial^2 \psi}{\partial x_2^2}\right) \tag{13.59}$$

and similarly with respect to ξ_2

$$\frac{\partial^2 \psi}{\partial \xi_2^2}=\frac{1}{2}\left(\frac{\partial^2 \psi}{\partial x_1^2}-2\frac{\partial^2 \psi}{\partial x_1 \partial x_2}+\frac{\partial^2 \psi}{\partial x_2^2}\right). \tag{13.60}$$

From the last two equalities it follows that

$$\frac{\partial^2}{\partial \xi_1^2}+\frac{\partial^2}{\partial \xi_2^2}=\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}\right). \tag{13.61}$$

Using (13.55) and (13.61), we may write the Hamiltonian (13.53) through the variables ξ_1 and ξ_2:

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial}{\partial \xi_1^2}-\frac{\hbar^2}{2m}\frac{\partial}{\partial \xi_2^2}+\frac{m\omega_0^2}{2}\left(\xi_1^2+\xi_2^2\right)-\frac{\kappa}{2}\left(\xi_1^2-\xi_2^2\right) \tag{13.62a}$$

or

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \xi_1^2}+\frac{m}{2}\left(\omega_0^2-\frac{\kappa}{m}\right)\xi_1^2-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \xi_2^2}+\frac{m}{2}\left(\omega_0^2+\frac{\kappa}{m}\right)\xi_2^2. \tag{13.62b}$$

The operator $\hat{H}$ is a sum of the operators $\hat{H}_1$ and $\hat{H}_2$:

$$\begin{aligned}
&\hat{H} = \hat{H}_1 + \hat{H}_2, \\
&\hat{H}_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \xi_1^2} + \frac{1}{2} m\omega_1^2 \xi_1^2, \\
&\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial \xi_2^2} + \frac{1}{2} m\omega_2^2 \xi_2^2,
\end{aligned} \tag{13.63}$$

where we have set

$$\omega_1^2 = \omega_0^2 - \frac{\kappa}{m}, \quad \omega_2^2 = \omega_0^2 + \frac{\kappa}{m}. \tag{13.64}$$

The operators $\hat{H}_1$ and $\hat{H}_2$ are Hamiltonian, describing the normal oscillations ξ_1 and ξ_2, i.e. the oscillations of harmonic oscillator with natural frequencies ω_1 and ω_2 and with equations

$$\begin{aligned}
&\hat{H}_1 \psi_1(\xi_1) = E^1 \psi_1(\xi_1), \\
&\hat{H}_2 \psi_2(\xi_2) = E^2 \psi_2(\xi_2).
\end{aligned} \tag{13.65}$$

The energies of these two oscillators according to (13.28) are

$$\begin{aligned}
&E_{n_1}^1 = \left(n_1 + \frac{1}{2}\right)\hbar\omega_1, \qquad n_1 = 0, 1, 2, ... \\
&E_{n_2}^2 = \left(n_2 + \frac{1}{2}\right)\hbar\omega_2, \qquad n_2 = 0, 1, 2, ...
\end{aligned} \tag{13.66}$$

These energies $E_{n_1}^1$ and $E_{n_2}^2$ are eigenvalues of the operators $\hat{H}_1$ and $\hat{H}_2$ and the eigenvalues E_n of the operator $\hat{H} = \hat{H}_1 + \hat{H}_2$ are the sum of $E_{n_1}^1$ and $E_{n_2}^2$:

$$E_n = E_{n_1}^1 + E_{n_2}^2 . \tag{13.67}$$

Hence for the minimal energy of the coupled oscillator we can write:

$$E_0 = E_0^1 + E_0^2 = \frac{\hbar}{2}(\omega_1 + \omega_2) = \frac{\hbar\omega_0}{2}\left(\sqrt{1 - \frac{\kappa}{m\omega_0^2}} + \sqrt{1 + \frac{\kappa}{m\omega_0^2}}\right). \quad (13.68)$$

Because the potential energy of the interaction is significantly lower than the potential energy of each of the oscillator (the connection is weak) the second terms in the radicals are small $\kappa << m\omega_0^2$ and we can expand (13.68) according to the formula

$$(1 \pm x)^{\frac{1}{2}} = 1 \pm \frac{1}{2}x - \frac{1}{8}x^2 \pm \frac{1}{16}x^3 - ... \quad (13.69)$$

As a result of this we obtain:

$$E_0 = \hbar\omega_0 - \frac{\hbar\kappa^2}{8m^2\omega_0^3} = \hbar\omega_0 - \frac{\hbar e^4}{2(4\pi\varepsilon_0)^2 m^2\omega_0^3 r^6}. \quad (13.70)$$

If the both oscillators of the natural frequencies ω_0 do not interact their common energy would be:

$$E_0 = \frac{\hbar\omega_0}{2} + \frac{\hbar\omega_0}{2} = \hbar\omega_0. \quad (13.71)$$

The comparison of (13.71) and (13.70) leads to a very important result. *Because of the interaction of two quantum oscillators their energy decreases. The additional term in* (13.70*) is a function on the distance between the both oscillators and plays the role of a potential energy between them*:

$$U(r) = -\frac{\hbar e^4}{2(4\pi\varepsilon_0)^2 m^2\omega_0^3}\frac{1}{r^6}. \quad (13.72)$$

This potential energy corresponds to the additional force of the attraction (the minus sign!) between the oscillators:

$$F = -\frac{\partial U(r)}{\partial r} = -\frac{3\hbar e^4}{(4\pi\varepsilon_0)^2 m^2\omega_0^3}\frac{1}{r^7} \propto -\frac{1}{r^7}. \quad (13.73)$$

Namely this additional force is the force of van der Waals of the attraction between the atoms and/or the molecules.

The atomic systems (the atoms and the molecules) represent quantum oscillators, which minimal energy even in the ground state is different from zero. Owing to this zero-point energy their dipole moments (which according to classical physics are equal to zero) have finite values, nevertheless they are very small. These dipole moments interact with the attractive forces. *The attractive forces* (*the forces of van der Waals*) *are owed to the existence of the zero-point energy of the quantum oscillators.*

SUMMARY

Replacing p_x in the function of Hamilton of the classical oscillator with the operator $\hat{p}_x$ we determine the operator of Hamilton of the quantum harmonic oscillator:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{m\omega_0^2 x^2}{2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega_0^2 x^2}{2}.$$

The solution of the stationary Schroedinger equation with such Hamiltonian is:

$$\psi_n(\xi) = A_n e^{-\frac{\xi^2}{2}} \mathcal{H}_n(\xi),$$

where $\mathcal{H}_n(\xi)$ are the Hermite polynomials.

The energy of the quantum oscillator is quantizied and its values are determined by the quantum number n:

$$E = \left(n + \frac{1}{2}\right)\hbar\omega_0 = \left(n + \frac{1}{2}\right)h\nu_0 . \qquad n = 0, 1, 2, 3, ...$$

The energy levels are equidistant:

$$\Delta E_n = E_{n+1} - E_n = \hbar\omega_0 = h\nu_0 .$$

The ground state of the quantum oscillator, i.e. the state with the minimal energy, is the state with the quantum number $n = 0$. The minimal energy of the quantum oscillator

$$E = \frac{1}{2}\hbar\omega_0,$$

which is called zero-point energy, is its intrinsic (or internal) characteristic. This is the lowest energy, which the given oscillator *in general* can possess.

The minimal energy of the classical oscillator is equal to zero. The zero-point energy is an essential distinction of the quantum oscillator from the classical one. Another characteristic distinction is that the wave function and the probability density are different from zero in the classically forbidden domain. This means that the quantum oscillator penetrates into the classically forbidden domain.

The existence of the zero energy explains the attractive intermolecular and interatomic forces, known as van der Waals forces. According to classical physics the atoms and the molecules with high degree of symmetry have zero permanent dipole moment and between them attractive forces do not act. From the point of view of quantum mechanics the atoms and the molecules represent quantum oscillators, which lowest energy in the ground state is different from zero. Due to this zero-point energy their dipole moments have finite values, nevertheless they are very small. These dipole moments interact with the attractive forces, i.e. the attractive forces (the forces of van der Waals) are due to the zero-point energy of the quantum oscillators.

QUESTIONS

1. Which is the Hamiltonian of the quantum harmonic oscillator?
2. What are the eigenfunctions of the quantum harmonic oscillator?
3. Which is the energy spectrum of the quantum harmonic oscillator?
4. Compare the ground state of the quantum oscillator with that of the classical one, which has: a) the same energy; b) the lowest energy.
5. Which values are possible for the quantum numbers of the oscillator and the particle in an infinite well?
6. Compare the energy spectrum of a quantum harmonic oscillator and a particle in infinite potential well.
7. Compare the probability density of the first three states of the quantum oscillator and a particle in: a) an infinite potential well; b) a potential well of finite depth.
8. What is a zero-point energy?
9. How does the energy of the oscillator change with increasing the numbers of the wave-function nodes?

PROBLEMS

1. Calculate the zero-point energy of the mathematical pendulum of a length 10 m in the gravitational field of the Earth.
2. The mathematical pendulum of mass $m = 0,5$ kg and a length $l = 1$ oscillates with an amplitude 0,05 m. Estimate the following quantities: a) the frequency of oscillation; b) the energy of oscillation; c) the approximate value of the quantum number of the oscillation; d) the energy space between adjacent allowed energy.
3. The force constant of the HF molecule is $\kappa = 9.10^2$ N/m (we shall note that the force constant of a typical diatomic molecule is in the order of 10^3 N/m). Estimate the zero-point energy of the molecule oscillation.
4. For the HF molecule from the problem 3. estimate: a) the energy difference between the ground and the first excited level; b) the energy of the photon, emitted from the transition of the molecule from the first excited level to the ground one; c) the photon frequency and compare it with the frequency of the classical oscillations of the system; d) the wavelength of the emitted electromagnetic wave.
5. The distance between the excited vibrational states of CO molecule is 2170 cm^{-1} (the distance is given with the numbers of the wavelength in 1 cm). Calculate the force constant of the molecule.
6. Find the first five eigenfunctions $\psi_n(x)$ of the quantum oscillator using the dependence (13.29) for $\psi_n(\xi)$.
7. With direct replacing into the Eq. (13.9) prove that the eigenfunction $\psi_2(x)$ and the eigenvalue E_2 are its solution.
8. The initial state of the quantum oscillator is described by the wave function $\psi(x,0) = \varphi(x)$. Which is the wave function $\psi_n(x,t)$?
9. The superposition state of the quantum oscillator is described by the wave function $\psi(x,t) = \frac{1}{\sqrt{2}}\left(\psi_0(x,t) + \psi_1(x,t)\right)$. Prove that the average value of x is $\bar{x} = \text{const}\cos\omega_0 t$.

Chapter 14

THE TWO-BODY PROBLEM - A HYDROGEN ATOM AND A DIATOMIC MOLECULE

SUGGESTED READING

1. Arya, A., Elementary modern physics, Addison-Wesley Publishing Co., 1976, Chapter 6.
2. Eisberg, R. and R. Resnic, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, John Wiley & Sons, 1974, Chapter 7, Sections 12-4÷12-7.
3. Blokhintsev, D. I., Principles of Quantum Mechanics, Allyn and Bacon, 1964, §47, Appendix IX
4. Spolsky, E. V., Atomic Physics, Vol. 1, Mir Publishing House, 1963, §158-§160.
5. Beiser, A., Perspectives of Modern Physics, McGraw-Hill Book Co., 1973, Chapter 14.

14.1* PARTICLE MOTION IN A CENTRAL SYMMETRIC FIELD

In Chapter 3 we have considered the motion in a central symmetric field (CSF). In such a field the potential energy depends only on the distance to the force centre - . We have presented energy E of the particle as a sum of the radial kinetic energy T_r, the centrifugal energy $L^2/2m_0r^2$ and the potential energy $U(r)$:

$$E = T + U = T_r + \frac{L^2}{2m_0 r^2} + U(r). \tag{14.1}$$

Here m_0 is a particle mass and L is its angular moment.

Going to the quantum-mechanical problem we firstly write the Hamilton's operator. According to (14.1) its form is

$$\hat{H} = \hat{T}_r + \frac{\hat{L}^2}{2m_0 r^2} + U(r) \tag{14.2}$$

or (see Section 10.8)

$$\hat{H} = -\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2m_0}\frac{\Delta_{\theta,\varphi}}{r^2} + U(r). \tag{14.3}$$

The Hamiltonian does not depend on shalland therefore the wave function in CSF satisfies the stationary Schroedinger equation:

$$\hat{H}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi). \tag{14.4}$$

We already know three *constants of the motion* for the Hamiltonian (14.3) (see Example 3 in Section 11.4). In fact the operators $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ commute with $\hat{H}$:

$$\left[\hat{H}', \hat{H}\right] = 0, \quad \left[\hat{L}^2, \hat{H}\right] = 0, \quad \left[\hat{L}_z, \hat{H}\right] = 0 \tag{14.5}$$

and the quantities E, L^2 and L_z are constants of the motion. We shall also notice that they are simultaneously measured. When two operators commute they have common eigenfunctions. Hence, the eigenfunctions of the operators L^2 and L_z are eigenfunctions of the Hamiltonian $\hat{H}$. We have found these functions in Section 10.6 - these are the spherical functions $Y_{lm}(\theta,\varphi)$ (10.96). They can be presented explicitly by Legendre polynomials (for details see Appendix V in [3]):

$$\varphi(\theta,\varphi) = Y_{lm}(\theta,\varphi) = \mathrm{A}_l^{|m|}\mathrm{P}_l^{|m|}(\cos\theta)\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\mathrm{A}_l^{|m|}\mathrm{P}_l^{|m|}(\cos\theta)e^{im\varphi},$$

$$\mathrm{P}_l^{|m|}(\xi) = \frac{1}{2^l l!}\left(\xi^2 - 1\right)^{\frac{|m|}{2}}\frac{d^{l+|m|}}{d\xi^{l+|m|}}\left(\xi^2 - 1\right)^l, \quad \mathrm{A}_l^{|m|} = \sqrt{\frac{(\mathrm{l}\text{-}|\mathrm{m}|)!(2l+1)}{(\mathrm{l}\text{-}|\mathrm{m}|)!4\pi}}. \tag{14.6}$$

The eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ are determined correspondingly by orbital l and by magnetic m quantum numbers:

$$\begin{aligned} &L^2 = \hbar^2 l(l+1), \qquad l = 0, 1, 2, ... \\ &L_z = m\hbar, \qquad\qquad m = 0, \pm 1, \pm 2, ..., \pm l. \end{aligned} \tag{14.7}$$

We shall seek the solution of the Schroedinger equation

$$-\frac{\hbar^2}{2m_0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{\hbar^2}{2m_0}\frac{\Delta_{\theta,\varphi}}{r^2}\psi + U(r)\psi = E\psi \tag{14.8}$$

in the form:

$$\psi = \psi(r,\theta,\varphi) = R(r)Y_{lm}(\theta,\varphi). \tag{14.9}$$

Substituting from (14.9) into (14.8) and taking into account (14.6) and (10.99), we obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{2m_0}{\hbar^2}\left[E - \frac{\hbar^2 l(l+1)}{2m_0 r^2} - U(r)\right]R(r) = 0. \tag{14.10}$$

This is the equation for the unknown radial part of the wave function (14.9). It does not depend on the magnetic quantum number. From this we can make an important conclusion. If in any CSF the particle moves with a fixed angular moment ($L = \hbar\sqrt{l(l+1)}$), i.e. with a fixed l, ($2l+1$) different spherical functions $Y_{lm}(\theta,\varphi)$ with magnetic quantum numbers $m = 0,\ \pm 1,\ \pm 2,\ ...,\ \pm l$ will correspond to this moment. In other words $2l+1$ eigenfunctions have one eigenvalue $L = \hbar\sqrt{l(l+1)}$ of the angular moment. *In every CSF there is* ($2l+1$)*-fold degeneracy with respect to m - this generation is called normal. The physical meaning of this degeneracy is clear - at a fixed angular moment (fixed orbital quantum number l) are possible* $2l+1$ *components along the Z-axis, i.e.* $2l+1$ *different orientation of the angular momentum.*

The general statement for stationary states is valid for the CSF: at $E > 0$ the energy spectrum is continuos and at $E < 0$ the spectrum is discrete.

To solve the equation (14.10) we have to know the concrete field, i.e. the form of $U(r)$. Some conclusions can be made from the general equation -

for example that of the motion with constant radius $r = r_0 = \text{const}$. The system with such a motion is called the quantum rotator. Setting $U(r) = \text{const} = 0$ we obtain from (14.8) the equation of the quantum rotator:

$$\frac{\hat{L}^2}{2m_0 r_0^2}\psi(\theta,\varphi) = E\psi(\theta,\varphi). \tag{14.11}$$

Here the total energy coincides with the centrifugal energy $L^2/2m_0 r_0^2$ (see the last two paragraphs of the Section 3.3). In quantum mechanics it is called rotational energy and we may write it in the form:

$$E_l = \frac{L^2}{2m_0 r_0^2} == \frac{\hbar^2 l(l+1)}{2m_0 r_0^2} = \frac{\hbar^2 l(l+1)}{2I}. \tag{14.12}$$

Here $I = m_0 r_0^2$ is the inertial moment. The spectrum of the rotational energy is discrete. It is determined by the orbital quantum number *l*. The rotational energy levels are nonequidistant:

$$\Delta E_l = E_{l+1} - E_l = \frac{\hbar^2 l(l+1)}{m_0 r_0^2}. \tag{14.13}$$

The distance between them increases with the increasing the number *l*.

14.2* ELECTRON IN A COULOMB FIELD

We shall consider the motion of the electron in a Coulomb field. If we assume that the nucleus is infinitely massive, i.e. it remains fixed in space this will be the motion of the electron in the atom of the hydrogen, and in so called hydrogen-like ions: a singly ionized helium atom, a doubly ionized lithium atom, etc. Such is the motion of a negative charged meson with a mass $m_\mu = 207 m_e$ around the proton in the atom of the meson-hydrogen.

The potential energy of the electron in the field of the point charge *Ze* depends only on the distance *r* between the both charges:

$$U(r) = -\frac{k_0 Ze^2}{r}, \quad k_0 \equiv \frac{1}{4\pi\varepsilon_0}. \tag{14.14}$$

Then, according to (14.3), for the Hamltonian of the electron we get:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2m_e}\frac{\Delta_{\theta,\varphi}}{r^2} + \frac{k_0 Ze^2}{r}. \tag{14.15}$$

In this case for the equation of the radial wave function we can write:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{2m_0}{\hbar^2}\left[E - \frac{\hbar^2 l(l+1)}{2m_0 r^2} + \frac{k_0 Ze^2}{r}\right]R(r) = 0. \tag{14.16}$$

We shall look for the solution in the form:

$$R(r) = \frac{X(r)}{r}. \tag{14.17}$$

For the first term of the Eq. (14.16) after substituting *R*, we get:

$$\begin{aligned}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) &= \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\frac{1}{r}\frac{\partial X(r)}{\partial r} - \frac{X(r)}{r^2}\right)\right] \\ &= \frac{1}{r^2}\left(\frac{\partial X(r)}{\partial r} + r\frac{\partial^2 X(r)}{\partial r^2} - \frac{\partial X(r)}{\partial r}\right) = \frac{1}{r}\frac{\partial^2 X(r)}{\partial r^2}.\end{aligned} \tag{14.18}$$

We return to the Eq. (14.16) and taking into account (14.17) and (14.18) we obtain the equation for the function $X(r)$:

$$\frac{\partial^2 X(r)}{\partial r^2} + \frac{2m_e}{\hbar^2}\left[E - \frac{\hbar^2 l(l+1)}{2m_0 r^2} + \frac{k_0 Ze^2}{r}\right]X(r) = 0. \tag{14.19}$$

This equation can be simplified if we pass to the dimensionless parameters. We shall use for the dimensionless values the combination of constants $m_e, \hbar, e$ and k_0. The value a has a dimension of a length ($[a] = \mathrm{L}$):

$$a = \frac{\hbar^2}{k_0 Z m_e e^2}. \tag{14.20}$$

At $Z = 1$, i.e. for the H atom $a = a_0 = 0{,}5.10^{-10}$ m is the Bohr radius. Let designate the value of the potential energy on the distance *a* with U_a:

$$U_a = \frac{k_0 Z e^2}{a} = \frac{Z^2 m_e k_0^2 e^4}{\hbar^2} = 2Z^2\Re,$$
$$U_{a_0} = 27{,}2 \text{ eV}, \qquad (Z = 1,\ \ a = a_0). \tag{14.21}$$

For the transition to the Rydberg's constant $\Re$ see (8.10).

We introduce the dimensionless variables - energy $\mathcal{E}$ and the radius ξ :

$$\mathcal{E} = \frac{E}{U_a} = \frac{\hbar^2 E}{Z^2 m_e k_0^2 e^4} = \frac{m_e a^2 E}{\hbar^2} = -\frac{1}{2n^2}, \qquad \xi = \frac{2r}{na}. \tag{14.22}$$

Here *n* is a number. We write the sign minus in $\mathcal{E} = -1/2n^2$ because we consider the bound state and expect the negative values of the energy.

Multiplying the Eq. (14.19) to $n^2 a^2/4$, we get:

$$\frac{n^2 a^2}{4}\frac{\partial^2 X(r)}{\partial r^2} + \frac{n^2 a^2}{4}\left[\frac{2m_e}{\hbar^2}E - \frac{l(l+1)}{r^2} + \frac{2m_e}{\hbar^2}\frac{k_0 Z e^2}{r}\right]X(r) = 0. \tag{14.23}$$

Using the Eqs. (14.22) and (14.20) in this equation we obtain the dimensionless equation for the function $X(\xi)$:

$$\frac{\partial^2 X(\xi)}{\partial \xi^2} + \left[-\frac{1}{4} - \frac{l(l+1)}{\xi^2} + \frac{n}{\xi}\right]X(\xi) = 0. \tag{14.24}$$

As in the problem with the quantum oscillator we firstly determine the asymptotic behaviour of the function $X(\xi)$ at large ξ. For $\xi \to \infty$ function $X(\xi \to \infty) \equiv X_\infty$ satisfies the next equation

$$\frac{\partial^2 X_\infty}{\partial \xi^2} + -\frac{1}{4} X_\infty = 0, \tag{14.25}$$

which is obtained from (14.24) neglecting the terms $\propto 1/\xi^2$, $1/\xi$. The solution of (14.25) is:

$$X = \exp(-\xi/2). \tag{14.26}$$

By an analogy we find the asymptote of X at small ξ . For $\xi \to 0$ the function $X(\xi \to 0) \equiv X_0$ satisfies the equation

$$\frac{\partial^2 X_0}{\partial \xi^2} - \frac{l(l+1)}{\xi^2} X_0 = 0, \tag{14.27}$$

which has the partial solution

$$X_0 = \xi^{l+1}. \tag{14.28}$$

In this case we are convinced to take the second derivative of X_0 ($X_0'' = l(l+1)\xi^{l-1}$) and to substitute it in (14.27). (The partial solution $\xi^{-(l+1)}$ at small ξ increases indefinitely and does not satisfy the property for the finiteness of the wave function (Section 9.2) and therefore we do not consider it). The solution of (14.24) for every ξ is looked for similarly to the problem for the oscillator as the product of the asymptotic functions $X_\infty . X_0$ to an unknown function $\eta(\xi) = \sum_{k=0}^{\infty} C_k \xi^k$:

$$X(\xi) = \eta(\xi)\xi^{l+1} e^{-\frac{\xi}{2}} = e^{-\frac{\xi}{2}} \sum_{k=0}^{\infty} C_k \xi^{k+l+1}. \tag{14.29}$$

To determine the unknown coefficients C_k we shall find $X''(\xi)$ and shall substitute this quantity in (14.24). For the derivatives we obtain:

$$\frac{\partial X(\xi)}{\partial \xi}=-\frac{1}{2}e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\xi^{k+l+1}+e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\xi^{k+l},$$

$$\frac{\partial^2 X(\xi)}{\partial \xi^2}=\frac{1}{4}e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\xi^{k+l+1}-\frac{1}{2}e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\xi^{k+l} \tag{14.30}$$

$$-\frac{1}{2}e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\xi^{k+l}+e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\left(k+l\right)\xi^{k+l-1}.$$

Substituting (14.29) and (14.30) into (14.24), we have:

$$-\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\xi^{k+l}+\sum_{k=0}^{\infty}C_k\left(k+l+1\right)\left(k+l\right)\xi^{k+l-1}$$
$$-l\left(l+1\right)\sum_{k=0}^{\infty}C_k\xi^{k+l-1}+n\sum_{k=0}^{\infty}C_k\xi^{k+l}=0\,. \tag{14.31}$$

The equation (14.31) has a nontrivial solution for C_k when the coefficients before the same powers of ξ are equal to zero. For the coefficients before ξ^{k+1} we have:

$$-C_k\left(k+l+1\right)+C_{k+1}\left(k+l+2\right)\left(k+l+1\right)-l\left(l+1\right)C_{k+1}+nC_k=0. \tag{14.32}$$

From here we find the recurrence formula for the coefficients C_k and C_{k+1}:

$$C_{k+1}=\frac{\left(k+l+1\right)-n}{\left(k+l+2\right)\left(k+l+1\right)-l\left(l+1\right)}C_k. \tag{14.33}$$

In such a way, according to the Eqs. (14.16) and (14.29) we obtain for the dimensionless radial function:

$$R(\xi)=\frac{X(\xi)}{\xi}=e^{-\frac{\xi}{2}}\sum_{k=0}^{\infty}C_k\xi^{k+l}, \tag{14.34}$$

where the coefficients C_k are determined by (14.33). According to the properties of the wave function this radial function is limited. But the obtained by us a radial wave function $R(\xi)$ at $\xi \to \infty$ increases indefinitely as $\sum_{k=0}^{\infty} C_k \xi^k \xrightarrow[\xi\to\infty]{} e^{\xi}$ and $R(\xi) \propto e^{\frac{\xi}{2}}$.

To avoid this divergence, we shall interrupt the power series $\eta(\xi) = \sum_{k=0}^{\infty} C_k \xi^k$ as we did in the problem of the oscillator.

Let at $k = n_r$ (here n_r is an integer) the coefficient $C_{n_r} \neq 0$, but the coefficient $C_{n_{r+1}} = 0$, i.e. according to (14.33)

$$n_r + l + 1 - n = 0. \tag{14.35}$$

The number n_r is called the radial quantum number.

Because n_r and l are integers, the number *n*, introduced in the relation (14.22) is also an integer:

$$\begin{gathered} n = n_r + l + 1, \quad n = 1,\ 2,\ 3,\ ... \\ n \geqq l + 1. \end{gathered} \tag{14.36}$$

Finally for the solution of the radial wave function equation we get (see (14.34)):

$$R_{n_r L}(\xi) = e^{-\frac{\xi}{2}} \xi^l \sum_{k=0}^{n_r} C_k \xi^k \ . \tag{14.37}$$

The power series $\sum_{k=0}^{n_r} C_k \xi^k$ can be expressed through the polynomials of Laguerre:

$$\begin{gathered} \sum_{k=0}^{n_r} C_k \xi^k \equiv \mathrm{A}_{\mathrm{n_r}} \mathrm{L}_{n_r}^{2l+1}(\xi), \\ \mathrm{L}_{n_r}^{2l+1}(\xi) = \frac{1}{n_r!} \xi^{-(2l+1)} e^{\xi} \frac{d^{n_r}}{d\xi^{n_r}} \left(\xi^{2l+1+n_r} e^{-\xi} \right). \end{gathered} \tag{14.38}$$

In the dimensional variables $(\xi = 2r/na)$ the function $R_{n_r l}(r)$ is

$$R_{n_r l}(r) = e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \sum_{k=0}^{n_r} C_k \frac{2r}{na}^k . \qquad (14.39a)$$

At fixed n_r and l the number n is uniquely determined by (14.36) and the radial function can be expressed by it:

$$R_{n_r l}(r) = \mathrm{A}_{nl} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \mathrm{L}_{n\text{-}l\text{-}1}^{2l+1}\left(\frac{2r}{na}\right). \qquad (14.39b)$$

Finally, according to (14.9), for the wave function $\psi(r,\theta,\varphi)$ of the particle in a Coulomb field we obtain:

$$\psi_{nlm}(r,\theta,\varphi) = \mathrm{A}_{nl} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \mathrm{L}_{n\text{-}l\text{-}1}^{2l+1}\left(\frac{2r}{na}\right) Y_{lm}(\theta,\varphi). \qquad (14.40)$$

Here the constants A_{nl} are determined by the condition of the normalization.

The obtained functions are eigenfunctions of the operator of Hamilton (14.15). For their eigenvalues, according to (14.21) and (14.22), we get

$$E_n = -\frac{Z^2 m_e k_0^2 e^4}{\hbar^2} \frac{1}{n^2} = -\frac{Z^2 \Re}{n^2}, \quad n = 1, 2, 3, ... \qquad (14.41)$$

The values of the number n are written according to (14.36). *The energy of the charged particle in a Coulomb field is quantizied. It is uniquely determined by the integer n, which is called a principle quantum number.*

14.3 SPECTRUM OF THE ENERGY OF THE HYDROGEN ATOM AND THE HYDROGEN-LIKE IONS

Up to here the hydrogen-like ions have been analysed without taking into account the motion of the nucleus. Therefore the expressed theory is valid only for the infinite mass of the nucleus. Strictly speaking, even more for light elements as hydrogen and singly ionized helium, this can be accepted only as first order of approximation of the problem. The finite nucleus mass leads to the explanation of many experimental results.

The one-electron atom contains two particles. This fact causes no difficulty at all, if it used the reduced mass technique. In Section 3.2 we have proved, that in the frame of centre of the mass the two-body problem reduces to the one-dimensional problem of the particle with reduced mass $\tilde{m}$. According to the obtained results for the electron of mass m_e and radius-vector $\mathbf{r}_e$ about the nucleus of mass M and radius-vector $\mathbf{r}_n$ in the CM-frame we can write

$$H = \frac{p^2}{2\tilde{m}} - \frac{k_0 Z e^2}{r}, \quad \tilde{m} \equiv \frac{m_e M}{m_e + M}. \tag{14.42}$$

Here $\tilde{m}$ is the reduced mass of the electron and the nucleus, Z is the nucleus charge number, $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_n$ is the relative radius-vector of the electron in respect to the nucleus and p is the momentum of the particle with mass $\tilde{m}$. The Hamiltonian in this case with the accuracy of replacing the mass m_e with $\tilde{m}$ coincides with the Hamiltonian (14.15):

$$\hat{H} = -\frac{\hbar^2}{2\tilde{m}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2\tilde{m}} \frac{\Delta_{\theta,\varphi}}{r^2} - \frac{k_0 Z e^2}{r}. \tag{14.43}$$

It is clear that the equation for the radial wave function of hydrogen-like atoms is obtained from the equation (14.16) for this wave function in a Coulomb field, replacing m_e with $\tilde{m}$. The same, of course, is valid for all relations in Section 14.2. Therefore the eigenfunctions of the Hamiltonian (14.43) are the functions (14.40) and we obtain its eigenvalues E_n as replacing m_e with $\tilde{m}$ in the relations of Section 14.2.

$$E_n = -\frac{Z^2 \tilde{m} k_0^2 e^4}{\hbar^2} \frac{1}{n^2} = -\frac{\mathfrak{R}_{\tilde{m}}}{n^2} = -13{,}6 \text{ eV}, \quad n = 1, 2, 3, ... \tag{14.44}$$

For the H atom the Rydberg's constant $\mathfrak{R}_{\tilde{m}} = (\tilde{m}/m_e)\mathfrak{R} = \left(m_p / \left(m_e + m_p\right)\right)\mathfrak{R}$ slightly differs from $\mathfrak{R}$ - in the numerical value the difference is in the fourth sign; here m_p is the proton mass.

The energy spectrum of the hydrogen atom is discrete. The energy levels of the atom are determined by the principal quantum number n. Energy of the ground state (n=1) is

$$E_1 = -\Re_{\tilde{m}} = -13{,}6\ \text{eV}. \tag{14.45}$$

From here it becomes clear the physical meaning of the Rydberg's constant - it is equal to the value of the minimal energy of H atom, i.e. to the energy in the ground state with $n=1$.

The energy levels are nonequidistant. The space between them decreases with increasing *n*:

$$\Delta E_n = E_{n+1} - E_n = \Re_{\tilde{m}} \left(\frac{1}{n^2} - \frac{1}{(n-1)^2} \right) = \Re_{\tilde{m}} \frac{2n+1}{n^2 (n+1)^2} \propto \frac{1}{n^3}. \tag{14.46}$$

When the energy of the electron is positive $E \geq 0$, it is in the free state. The condition $E_n = 0$ is valid for $n \to \infty$. The minimal energy, which has to give to the electron up in order to pass from the bound ground state into a free one , is called an ionization energy E_i of the H atom:

$$E_i = E_\infty - E_1 = |E_1| = 13{,}6\ \text{eV}. \tag{14.47}$$

In a free state $(E > 0)$ the energy has a continuos spectrum.

As we have already underlined that the H atom is described by the wave functions $\psi_{nlm}(r,\theta,\varphi)$ (14.10), which are the eigenfunctions of the operator of Hamilton (14.43). The fact, that three quantum numbers arise, is a consequence of the fact that the stationary Schroedinger equation for the hydrogen contains three independent variables - one for each space coordinates. The eigenfunctions are determined by the numbers n, l, m, while the eigenvalues of $\hat{H}$ depend only on the principal quantum number. At this for fixed *n* the maximum allowed value of the orbital quantum number *l* according to (14.36) is

$$l_{\max} = n - 1. \tag{14.48}$$

The number of the allowed values of *l* is

$$l = 0, 1, 2, 3, ..., n-1. \tag{14.49}$$

Its wave function corresponds to each *l* at a given *n*. Therefore to *n* different wave functions correspond one eigenvalue E_n of the energy. There is *n*-fold degeneracy on the orbital quantum number *l*. This is unexpected, because in the process of the problem solution we reached to the equation (14.24) and it depends on the l. *This degeneracy is called accidental or anomalous*. It is characteristic only for a Coulomb field. Physically it expresses the independence of the electron energy on the angular momentum L. Of course, the Coulomb field is CSF and the normal degeneracy on m is also characteristic for it. In fact E_n depends neither on l, nor on m. To every l correspond $2l+1$ states with different orientation of the angular momentum $\mathbf{L}$. *As at a given n the orbital quantum number l accepts the values from 0 to* $n-1$ *the general number of the states is* n^2. Really, using the formula for the arithmetic progression we readily obtain

$$\sum_{l=0}^{n-1}(2l+1)=\frac{1+2(n-1)+1}{2}n=n^2. \tag{14.50}$$

Allowed values of the orbital and of the magnetic quantum numbers and the multiplicity of the degeneracy at fixed n are shown in Table 14-1.

Table 14-1. Quantum numbers, states and the multiplicity of the degeneracy of the H atom

<table>
<tr><td>n</td><td>1</td><td colspan="2">2</td><td colspan="3">3</td></tr>
<tr><td>l</td><td>0</td><td>0</td><td>1</td><td>0</td><td>1</td><td>2</td></tr>
<tr><td>Spectroscopic notation</td><td>1S</td><td>2S</td><td>2P</td><td>3S</td><td>3P</td><td>3D</td></tr>
<tr><td>m</td><td>0</td><td>0</td><td>-1, 0, 1</td><td>0</td><td>-1, 0, 1</td><td>-2, -1, 0, 1, 2</td></tr>
<tr><td>Multiplicity of the degeneracy</td><td>1</td><td colspan="2">1 + 3
4</td><td colspan="3">1 + 3 + 5
9</td></tr>
</table>

The letter indication for different values of l is the same as in Section 10.7. But when it relates to the spectral indication of the state one uses capital letters (see below (16.34), Fig. 17-7, Fig. 17-8 etc.). For example, $3p$-electron denotes an electron of a level $3p$, but P-electron - one of the electrons in the p-state independently which is the value of its energy (P is a part of the spectral term $n\,{}^{2s+1}P_j$ (see 16.34)).

The state of H atom $\psi_{nlm}(r,\theta,\varphi)$ is completely defined if we know the quantum numbers n, l and m. This is equivalently to know the three physical quantities E, L^2 and L_z:

$$n, \qquad\qquad l, \qquad\qquad m,$$

$$E_n=\frac{\Re_m}{n^2}, \qquad L^2=\hbar^2 l(l+1), \qquad L_z=m\hbar.$$

Here E, L^2 and L_z form a complete set of physical quantities. The Table 14-1 and the diagram of the states (Fig 14-1) together with the energy spectrum permit us to build the diagram of the energetic level (Fig. 14-2). If the electron is in an excited state $n > 1$, then at the transition to the lower energetic level it radiates. The quantum theory of the radiation allows to state that not all transitions are allowed, but only such for which the orbital quantum number changes with unity: $\Delta l = \pm 1$. *The conditions, defining which transitions are allowed, are called selection rules.* The allowed transitions to the levels $1s$, $2s$, $2p, 3d$ and $4f$ are shown in Fig 14-2.

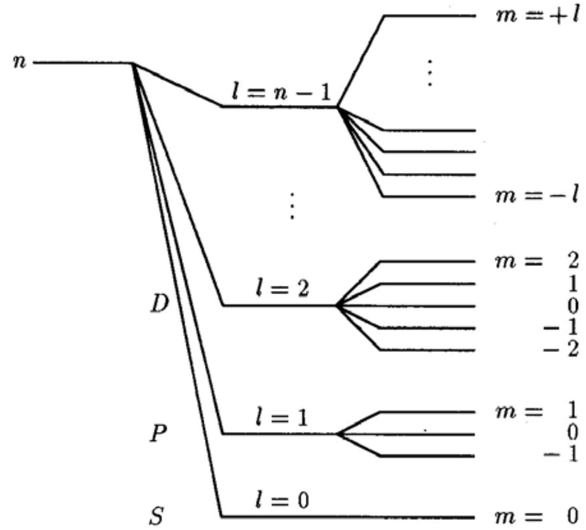


Figure 14-1. Diagram of the states for the H atom, illustrating n^2-fold degenerate states corresponding to the principal quantum number n.

At the transition from level n to level m the energy E_{mn} and the spectroscopic frequency are respectively

$$\left.\begin{aligned} E_m &= \Re_{\tilde{m}}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \\ \nu_m^* &= R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \end{aligned}\right\} n = m+1, m+2, m+3, ... \qquad (14.51)$$

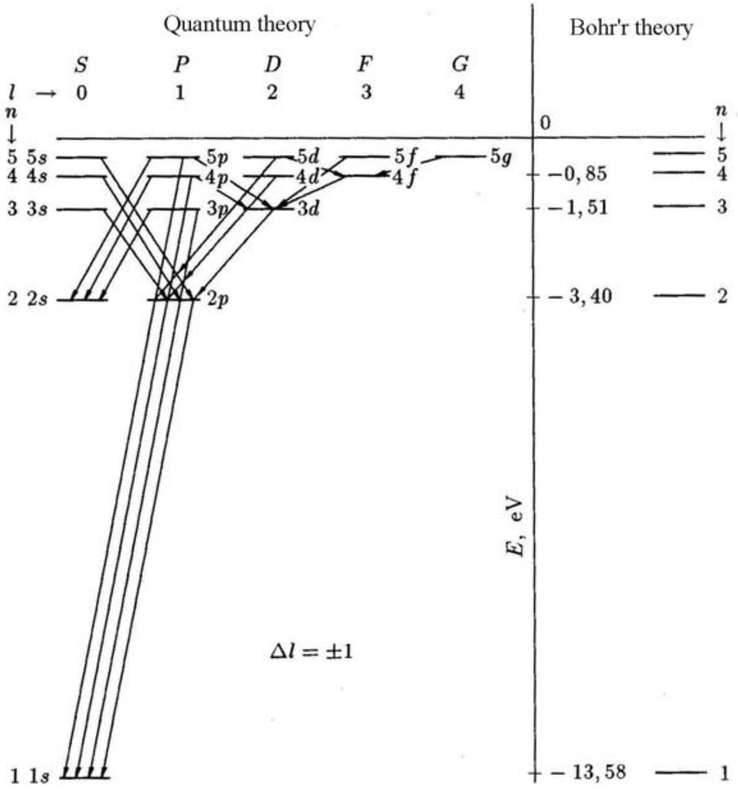


Figure 14-2. Energy levels and some allowed transitions in the H atom.

At the transitions to the level 1*s* *one obtains Lyman series*

$$\left.\begin{aligned} E_m &= \Re_{\tilde{m}}\left(1-\frac{1}{n^2}\right) \\ \nu_m^* &= R\left(1-\frac{1}{n^2}\right) \end{aligned}\right\} n = 2, 3, 4, ... \qquad (14.52))$$

The energy of the transition is given in the first row and its spectroscopic frequency $\nu^* = \nu / c$ - in the second row. The analogous dependencies can be written for the energy and the spectroscopic frequency at: $m = 2$ - Balmer series, $m = 3$ - Paschen series, $m = 4$ - Brackett series, $m = 5$ - Pfund series etc.

The lowest spectroscopic frequency (*respectively the greatest wavelength*) *for the given series is called a resonance frequency* (*resonance* *wavelength*). The resonance frequencies and wavelengths of the series of Lyman and Balmer are

$$
\begin{aligned}
&\nu_r^* = \frac{1}{\lambda_{\max}} = R\left(1-\frac{1}{4}\right) = \frac{3}{4}R, \quad \lambda_{\mathrm{r}} = \lambda_{\max} = \frac{4}{3R}, \\
&\nu_r^* = \frac{1}{\lambda_{\max}} = R\left(\frac{1}{4}-\frac{1}{9}\right) = \frac{4}{36}R, \quad \lambda_{\mathrm{r}} = \lambda_{\max} = \frac{36}{4R}.
\end{aligned}
\qquad (14.53)
$$

The highest spectroscopic frequency (respectively the lowest wavelength) is called threshold frequency (wavelength). The threshold frequencies and wavelengths of the series of Lyman and Balmer are

$$
\begin{aligned}
&\nu_\infty^* = \frac{1}{\lambda_{\min}} = R, \quad \lambda_\infty = \lambda_{\min} = \frac{1}{R}, \\
&\nu_\infty^* = \frac{1}{\lambda_{\min}} = \frac{R}{4}, \quad \lambda_\infty = \lambda_{inin} = \frac{4}{R}.
\end{aligned}
\qquad (14.54)
$$

The spectral line of the resonance and threshold wavelength (respectively $\lambda_r = 6562{,}8$ Å and $\lambda_\infty = 3645{,}6$ Å) of the Balmer series are shown in Fig 7-4.

At the beginning of this Chapter we have underlined that conducted above analysis is valid for the hydrogen-like ions He^+, Li^{++} etc. and for meson-hydrogen. Using the consideration at the beginning of this section, we obtain their energy replacing in (14.41) m_e with $\tilde{m} = m_e M / \left(m_e + M\right)$:

$$
E_n = -\frac{Z^2 m_e k_0^2 e^4}{\hbar^2}\frac{1}{n^2} = -\frac{Z^2 \mathfrak{R}_{\tilde{m}}}{n^2}, \quad n = 1, 2, 3, \ldots \qquad (14.55)
$$

(Note that the Rydberg constant for the hydrogen-like ions of mass of the nucleus M differs from that of the hydrogen atom (compare with Eq. (14.44) and the relations after it). As the Rydberg's constant $\mathfrak{R}_{\tilde{m}}$ for the hydrogen-like ions slightly differs from $\mathfrak{R}$, the values of the energy and of the spectroscopic frequency is Z^2 times greater than these of the hydrogen: for He^+ $\left(Z=2\right)$ - 4 times, for Li^{++} $\left(Z=3\right)$ - 9 times etc.

In the atom of meson-hydrogen there is a negatively charged μ-meson with mass $m_\mu = 207 m_e$ instead of an electron. In both cases the reduced masses are equal to masses of the light particles: for the hydrogen $\tilde{m} \approx m_e$ and for the meson-hydrogen $\tilde{m} \approx m_\mu$. Therefore the values of the Rydberg's constant for both atoms are proportional to these masses - for the hydrogen $\Re \propto m_e$ and for the meson-hydrogen $\Re_\mu \propto m_\mu$. Hence the values of the energy and of the spectroscopic frequencies of the meson-hydrogen atom are 207 times larger than the corresponding values of the hydrogen.

14.4 PROBABILITY DISTRIBUTION OF THE ELECTRON

The found in Section 14.2 wave functions $\psi_{nlm}(r,\theta,\varphi)$ allow to be determined radial and angular distribution of the hydrogen electron. In the analysis of these distributions very often are used terms "orbital" and "electron cloud". *The orbital is synonym of the wave function* $\psi_{nlm}(r,\theta,\varphi)$. The orbital of H atom is

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)=A_{lm}R_{nl}(r)P_l^{|m|}(\cos\theta)e^{im\varphi}. \qquad (14.56)$$

The distribution of the density $\rho_{nlm}(r,\theta,\varphi)$ *of the probability is illustrated with an electron cloud.* Let us determine the radial and angular electron clouds, i.e. the radial and the angular distribution of the probability density. The probability to find the electron in the volume element dV near the point r,θ,φ is

$$dW_{nlm}(r,\theta,\varphi)=dW_{nl}(r)dW_{lm}(\theta,\varphi)=R_{nl}^2(r)\left|Y_{lm}(\theta,\varphi)\right|^2 dV. \qquad (14.57)$$

The volume element dV in spherical co-ordinates has following form (see Fig. 1-6):

$$dV=r^2\sin\theta d\theta d\varphi dr=r^2 d\Omega dr, \qquad (14.58)$$

where $d\Omega$ stands for the space angle: $d\Omega=\sin\theta d\theta d\varphi$.

$$dW_{nl}(r)=R_{nl}^2(r)r^2dr. \qquad (14.59)$$

It is clear that for radial density of the probability $\rho_{nl}(r)$ we can write

$$\rho_{nl}(r)=\frac{dW_{nl}(r)}{dr}R_{nl}^2(r)r^2. \qquad (14.60)$$

Taking into account (14.40) we can easy determine the wave function for the ground state with the quantum numbers $n = 1$ and $l = 0$:

$$R_{10}(r) = \frac{2}{a_0^{\frac{3}{2}}} e^{-\frac{r}{a_0}}. \tag{14.61a}$$

Consequently for the electron cloud $\rho_{10}(r)$ in the ground state we can write:

$$\rho_{10}(r) = \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2. \tag{14.61b}$$

The radial wave function $R_{10}(r)$ and the electron cloud $\rho_{10}(r)$ are shown in Fig. 14-3.

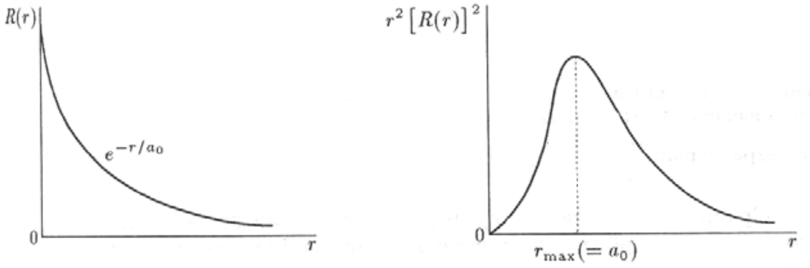


Figure 14-3. Radial wave function $R_{10}(r)$ and radial probability density (electron cloud) $\rho_{10}(r)$ for the ground state of the H atom ($n = 1$ and $l = 0$).

The radius of the maximal radial density of the probability is determined by equalling to zero the derivative $\rho_{10}(r)$:

$$\frac{d\rho_{10}(r)}{dr} = \frac{4}{a_0^3}\left(2r - \frac{2r^2}{a_0}\right) e^{-\frac{2r}{a_0}} r^2 = 0,$$
$$\rho_{10}(r) = \rho_{10\max} \quad \text{at} \quad r = a_0. \tag{14.62}$$

The radius of Bohr determines the position of the electron-cloud maximum in the ground state of H atom.

The results, obtained in Section 14.2, allow to determine similarly to $R_{10}(r)$ and $\rho_{10}(r)$ the wave functions and the electron clouds of the states with any n and l. For $n=3$ they are shown in Fig. 14-4.

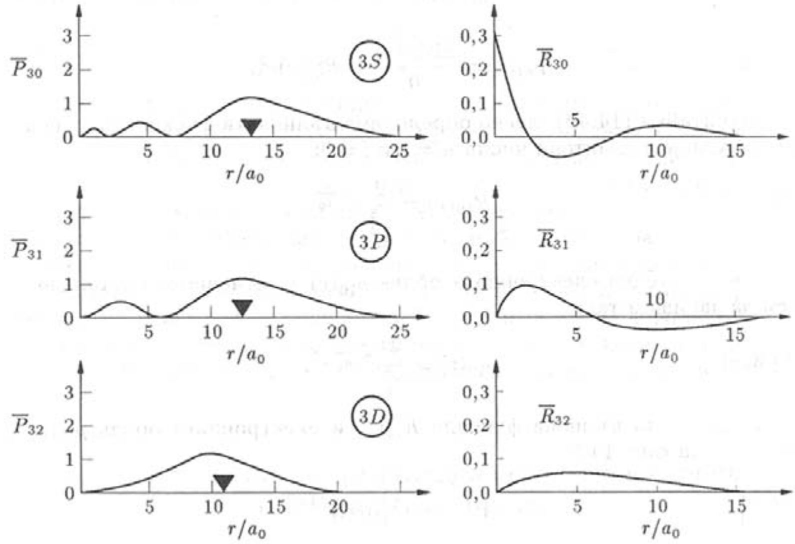


Figure 14-4. Radial wave function $R_{10}(r)$ and radial probability density (electron cloud) $\rho_{10}(r)$ at $n=3$ for the states: $3S$ $(l=0)$, $3P$ $(l=1)$ and $3D$ $(l=2)$; for convenience at the comparison they are non-dimensional: $\overline{P}_{nl}=a_0\rho_{nl}(r/a_0)$ and $\overline{R}_{nl}=a_0^{3/2}R_{nl}(r/a_0)$.

Comparing the cloud ρ_{30} and ρ_{32}, it is not difficult to note that with increasing the orbital quantum number the region of the cloud decreases. We shall give quality explanation of this effect using the semi-classical concept. The region of the particle position at given energy is defined by the effective potential energy $\tilde{U}(r)$ of the both particles, which are interacted by the central forces (see (3.33)). Taking into account the quantization of the angular momentum $L=\hbar\sqrt{l(l+1)}$, we get:

$$E=T_r+\frac{\hbar^2 l(l+1)}{2\tilde{m}r^2}-\frac{k_0e^2}{r}\equiv T_r+\tilde{U}_l(r). \qquad (14.63)$$

This is a classical formula and behind the *r* we have to understand the average radius of the electron cloud. The using of the classical formula helps to build the useful qualitative idea. In fact, as we have persuaded ourselves, in quantum mechanics it is not possible to divide the atom energy to the kinetic and potential ones. Because of the wave character of the object we can not merely determine which part of the energy is kinetic and which - potential. The effective potential energy depends on the orbital quantum number *l.* It increases with the increasing *l* and at a fixed E_n the radial region of the cloud decreases (Fig. 14.5). At a fixed electron energy, i.e. at fixed principal quantum number *n,* with a changing of *l* the redistribution of the energy form in (14.63) takes place. Not only the rotational energy changes, but also the potential energy of the interaction due to the changing of the average radius (with the increasing *l* it decreases).

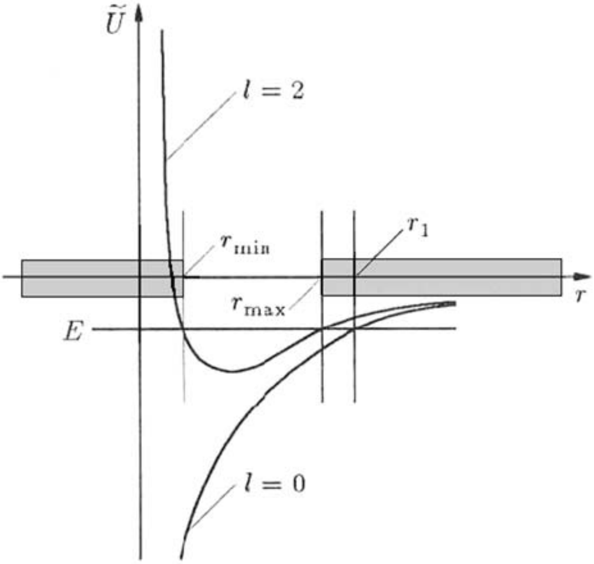


Figure 14-5. "Shrinkage" of the electron cloud with the *increasing l* (from $l=0$ to $l=2$); in the state with $l=0$ the cloud fills the region $0 \div r_1$, but with $l=2$ - the region $r_{\min} \div r_{\max}$ and $\left(r_{\max} - r_{\min}\right) < \left(r_1 - 0\right)$. The shaded regions define classically forbidden domain for the electron in the state ψ_{n2} with energy $E = E_{n2}$.

Really, from the strictly quantum treatment we can determine the average radius of the electron in the ψ_{nl} - state as $\overline{r} = \int\limits_0^{+\infty} r\rho_{nl}\left(r\right)dr$ and obtain:

$$\overline{r}_{nl} = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right]. \tag{14.64}$$

The average radius of the state with $n=3$ is shown with an arrow in Fig. 14-4. It is interesting to compare the average radius with Bohr formula (8.3). We can see that the average radius of the cloud has approximately the size of the Bohr-orbital radius.

Now we shall go to the angular distribution of the electron cloud. From (14.5) it is easy to determine the probability $dW_{lm}(\theta)$:

$$dW_{lm}(\theta)=\left|Y_{lm}(\theta,\varphi)\right|^2 d\Omega. \tag{14.65}$$

It is clear that the angular density depends only on the angle θ and for the cloud $\rho_{lm}(\theta)$ we have

$$\rho_{lm}(\theta)=\frac{dW_{lm}(\theta)}{d\Omega}=\left|Y_{lm}(\theta,\varphi)\right|^2. \tag{14.66}$$

The concrete form of the functions $Y_{lm}(\theta,\varphi)$ we define through the associated Legendre polynomials (see Section 10.6). For the states with the principal quantum number $n=0,1,2,3$ the functions $Y_{lm}(\theta,\varphi)$ are shown in Table 14-2.

Table 14-2. First few angular functions of the H atom

$$Y_{lm}(\theta,\varphi)=\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]P_l^{|m|}(\cos\theta)\,e^{im\varphi}$$

$$Y_{0,0}=\left(\frac{1}{4\pi}\right)^{\frac{1}{2}},\qquad Y_{1,0}=\frac{1}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{2}}\cos\,\theta,\qquad Y_{1,\pm1}=\frac{1}{2}\left(\frac{3}{2\pi}\right)^{\frac{1}{2}}\sin\,\theta\,e^{\pm i\varphi},$$

$$Y_{2,0}=\frac{1}{4}\left(\frac{5}{\pi}\right)^{\frac{1}{2}}\left(3\cos^2\theta-1\right),\ Y_{2,\pm1}=\mp\frac{1}{2}\left(\frac{15}{2\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\,e^{\pm i\varphi},\ Y_{2,\pm2}=\frac{1}{4}\left(\frac{15}{2\pi}\right)^{\frac{1}{2}}\sin^2\theta\,e^{\pm2i\varphi},$$

$$Y_{3,0}=\frac{1}{4}\left(\frac{7}{\pi}\right)^{\frac{1}{2}}\left(5\cos^3\theta-3\cos\theta\right),\qquad Y_{3,\pm1}=\mp\frac{1}{8}\left(\frac{21}{\pi}\right)^{\frac{1}{2}}\sin\theta\left(5\cos^2\theta-1\right)e^{\pm i\varphi},$$

$$Y_{3,\pm2}=\frac{1}{4}\left(\frac{105}{2\pi}\right)^{\frac{1}{2}}\sin^2\theta\cos\,\theta\,e^{\pm2i\varphi},\qquad Y_{3,\pm3}=\frac{1}{8}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}\sin^3\theta\,e^{\pm3i\varphi},$$

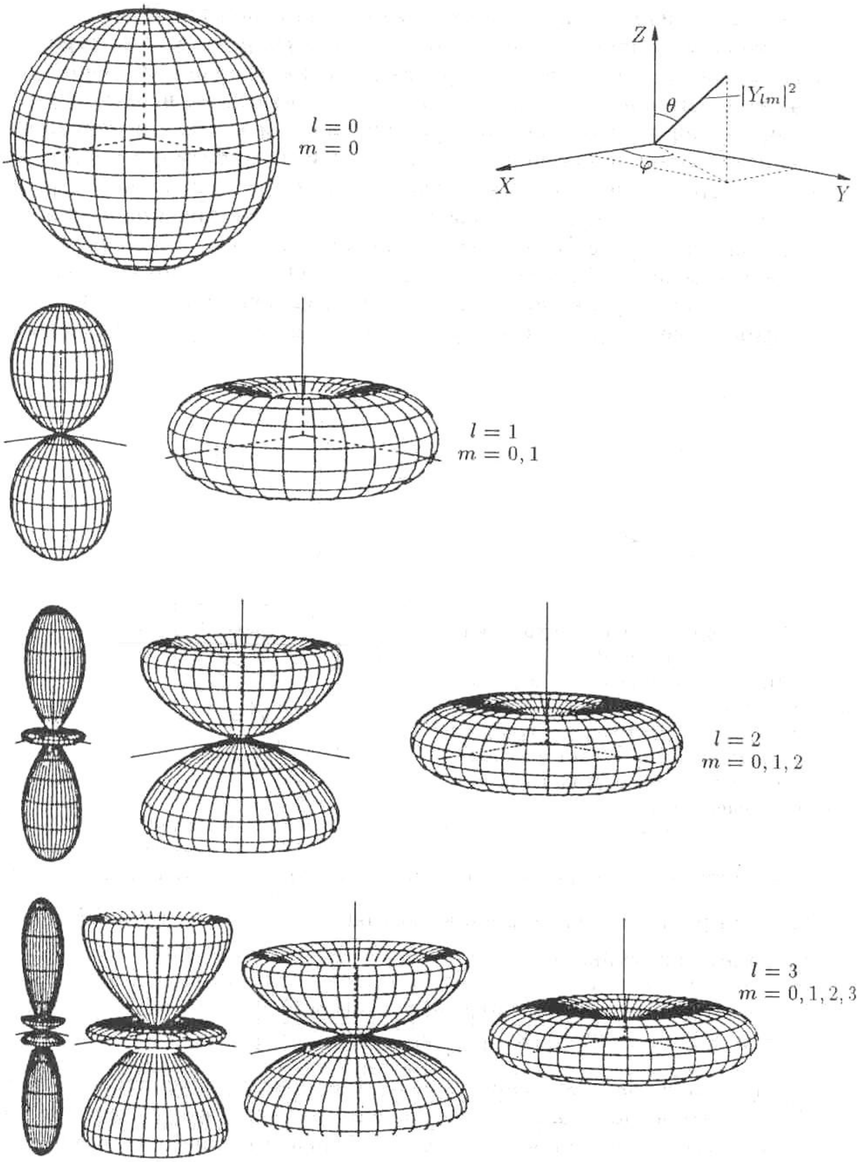


Fig. 14-6. Polar diagrams of the electron cloud of the H atom: the distance from the origin of the co-ordinate system to a point on the surface seen under the angles θ and φ is equal to $|Y_{lm}(\theta,\varphi|^2$.

The cloud ρ_{lm} does not depend on the polar angle φ because of the exponential dependence of Y_{lm} on φ - $Y_{lm}(\theta,\varphi)\propto e^{im\varphi}$. Hence, the angular distributions of the cloud in the different states are rotational surfaces (r is fixed). For the states s, p, d and f they are shown in Fig.14-6. We shall note, however, that the dependence of the magnetic quantum number m remains, because the associated Legendre polynomials and consequently the spherical functions depend on this number.

14.5 HYDROGEN-LIKE ATOMS

The hydrogen-like atoms are atoms with one outer electron, which is called valence or optic one. These are alkali metals Li $(Z=3)$, Na $(Z=11)$, K $(Z=19)$, Rb $(Z=37)$ and Cs $(Z=55)$. The common properties, which united the hydrogen-like atoms, are following:

1. The chemical properties are determined mainly by the valence electron.
2. The optical properties (the optical levels and the transitions between them: emission and absorption ones) are determined by the optical electron.
3. The inner electrons form the stable inert core, which is similar to those of the inert elements and slightly is influenced by the outer electron.
4. The core of electrons is spherically symmetric.

In the hydrogen-like ions ($\mathrm{He}^{+}, \mathrm{Li}^{++}$etc.) the single electron moves in the nucleus Coulomb field. *In the hydrogen-like atoms the outer electron moves in the net field of the nucleus and the core electrons.* Strictly seen, the problem of the hydrogen-like atoms is a multielectron problem. However the properties 3. and 4. allow this problem to be reduced approximately to the problem of the electron motion in the central symmetric field. Really, the theory and the experiment show that if we remove from the hydrogen-like atoms the outer electron it is formed the stable shell of the inert gas (e.g., for Li^{+} - the electron shell of He), which has spherical symmetry and very slightly is influenced by the outer actions. Therefore approximately we can assume that the outer electron does not influence the core electrons and consider its motion in the central symmetric field of the nucleus and of the spherically symmetrical distributed core electrons.

The problem will be solved if the potential energy of the valence electron is known. Taking into account this reason we can represent it in the form

$$U(r)=-\frac{k_0\tilde{Z}e^2}{r}. \tag{14.67}$$

Here $\tilde{Z}e$ is the effective charge, determined by the nucleus charge $+Ze$ and the core-electrons charge $-Z(r)$, which is restricted by a sphere of a radius *r*:

$$\tilde{Z}e = Ze - Z(r)e, \quad -Z(r)e = -e4\pi\int_0^r \rho(r)r^2dr. \qquad 14.68)$$

The radial probability density of the inner electrons $\rho(r)$ can be determined by quantum mechanics. For example, for Li^+ this is the solution of the motion of the two electrons in the nucleus field (see Section 18.2). Moreover, $\rho(r)$ can be measured experimentally (see [3], Section 79).

The inner electrons shield the nucleus field. This shielding plays very important role. It removes the accidental degeneracy, i.e. the degeneracy on *l*. For the explanation of this interesting fact we shall use the qualitative semi-classically ideas based on the Bohr-Sommerfeld model. The electron in the H atom moves in the Coulomb field of the nucleus, turning it to circle or elliptic orbits. In the hydrogen-like atoms *the valence electron, moving around the nucleus can penetrate the core of the inner electrons (penetrating orbit) or avoid completely it non-penetrating orbit.* When the orbit is non-penetrating, the electron moves in a Coulomb field:

$$\tilde{Z} = Z - (Z-1) = 1, \quad U(r) = -\frac{k_0e^2}{r}. \qquad (14.69)$$

Hence the problem reduces to the hydrogen-atom problem and we would expect the same energetic spectrum. *For the penetrating orbit the effective charge is larger than unity* $\tilde{Z} > 1$ *and depends on the power of the penetration*. An example with the penetrating of 3*s*- and 3*p*-orbits and the non-penetrating 3*d*-orbit of the sodium atom Na is shown in Fig. 14-7 (for comparison we show in the same figure the orbits of the hydrogen atom). Here we shall note that this is a qualitative picture. In the semi-classical model of Bohr-Sommerfeld the electron cannot have the angular momentum $L = 0$. But from the rigorous quantum mechanical treatment we are persuaded that this is possible (*s*-state). It is obvious that the "orbit" of this state can be represented by the line passing through the nucleus (there is no rotation and $L = 0$).

From the figure we see that with decreasing the angular momentum *L* the power penetration increases and $\tilde{Z}$ also increases from 1 to *Z*. In other words the effective charge $\tilde{Z}$ shows dependence of *l*, i.e. $\tilde{Z} = \tilde{Z}_l$. Hence, according to (14.67) the potential energy of the penetrating orbit also depends on the orbital number:

$$U_l(r) = -\frac{k_0 \tilde{Z}_l e^2}{r}. \tag{14.70}$$

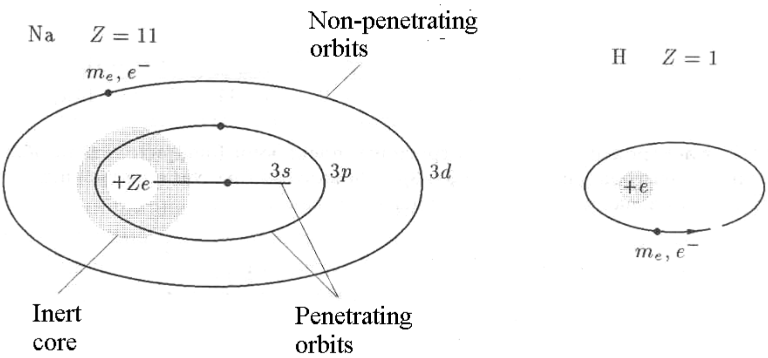


Figure 14-7. Semi-classical picture of: a) the electron core and the penetrating 3*s*- 3*p*-orbits and the non-penetrating 3*d*-orbit of Bohr of the valence electron of Na atom; the electron orbit of the atom of H, which unlike the atom of Na has no inner shell.

With decreasing l the potential energy becomes more negative. In the frames of this concepts the total energy also depends on l and instead of energy $E_n = -Z^2 R/n^2$ of Coulomb field it may be written as

$$E_{n,l} = -\tilde{Z}_l^2 \frac{R}{n^2}. \tag{14.71}$$

The actual probability-density distributions ρ_{3l} ($l = 0, 1, 2$) of the valence electron as well as the inner electrons of Na atom (Fig. 14-8) justify the use of the semi-classical orbits for the explanation of the energy spectrum. The last ones merely illustrate the actual penetrating and non-penetrating of the radial charge-density distributions $\rho^{nl}(r)$ (of the valence electron) into the charge-density distribution of core electrons. Or saying with others words, the visualised semi-classical representation of the penetrating and non-penetrating orbits corresponds to the penetrating and non-penetrating valence electron cloud.

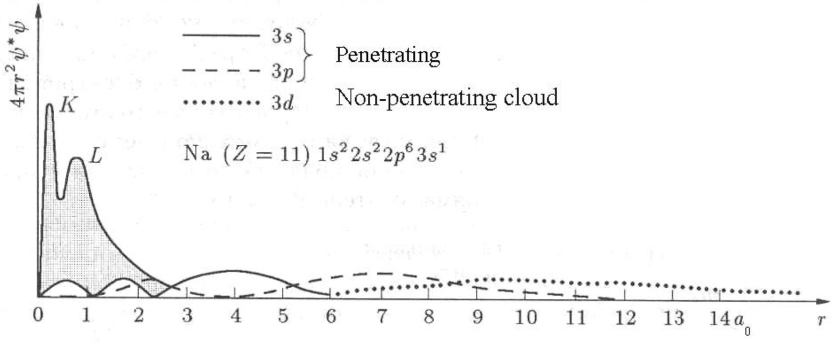


Figure 14-8. The radial charge-probability-density distribution (the electrons clouds) of the inner electrons (shaded area) and of the state 3*s*, 3*p* and 3*d* of the valence electron of Na atom; the electrons clouds 3s and 3p are penetrating and 3d is non-penetrating one.

The energy levels of the sodium atom are shown in Fig. 14-9. For the states 3*d*, 4*d*, 5*d* etc., 4*f*, 5*f* etc. they coincide with the energy levels of the

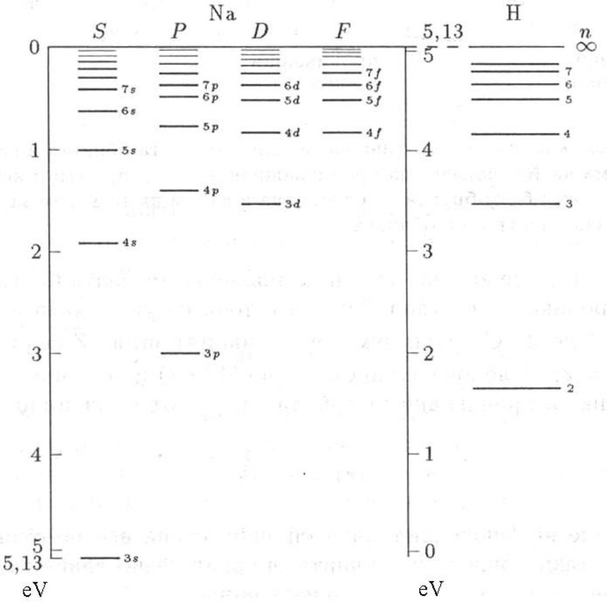


Figure 14-9. Diagram of the energy levels of Na atom - for non-penetrating orbits (clouds) they coincide with the energy levels of the H atom and for penetrating orbits (clouds) the anomalous degeneracy is removed.

H atom. These are non-penetrating clouds. For the penetrating electron clouds (for example, of the states $3s$ and $3p$) the role of the removing the degeneracy on the l through the shielding of nucleus field by core electrons is obvious - then $E_{3s} \neq E_{3p}$ (compare with $E_{4s} = E_{4p}$).

14.6 POTENTIAL ENERGY OF A DIATOMIC MOLECULES

The obtained results of the analysis of the two-body system, interacting through the central forces, permit us to determine the diatomic molecule spectrum. We shall not analyze in details the complicate and wide topics of the diatomic molecule. The molecule consists of many particle and for the solution of such systems different approximation theory are used. We shall give the idea for one of them, qualitatively considering the potential energy of the diatomic molecule and then considering in details its spectrum.

The atomic nuclei are heavier than electrons. Therefore *the motion of the molecule particles can be divided into two kinds: the slow motion of the nuclei and the quick motion of the electrons. During the motion of the electrons the co-ordinates of the nuclei are changed so slowly that they can be considered as fixed. This approximation is called adiabatic or an approximation of Born-Oppenheimer.*

The adiabatic approximation permits to "divide" the motion of the electrons and the nuclei and to reduce the origin equation of the molecule into two simpler equations: for the electron subsystem and for the nuclei. Important peculiarity of the nucleus equation is that the electron-subsystem energy plays the role of the potential energy for the nuclei.

Let note this potential energy with $U(r)$. From the physical point of view we may found its qualitative kind. At a small distance $r \to 0$ the repulsive force between the nuclei predominate and $U \to \infty$. At large distance the atoms are independent - they don't interact each other and $U \to 0$. As at some distance the atoms are in the bound state, it is obvious that $U(r)$ has a minimum. The Born-Oppenheimer theory permits to determine with high accuracy the dependence $U(r)$. The typical dependence of the potential energy versus the destination between the atoms is shown in Fig. 14-10.

Let return to the adiabatic model. After dividing the motion we have two particles (nuclei) with masses m_A and m_B, the potential interaction force being define by the potential $U(r)$. We can solve such a problem - it reduces to the motion of the particle with the reduced mass $\tilde{m} = m_A m_B / (m_A + m_B)$ in a central symmetric field (Sections 14.1 and 14.3).

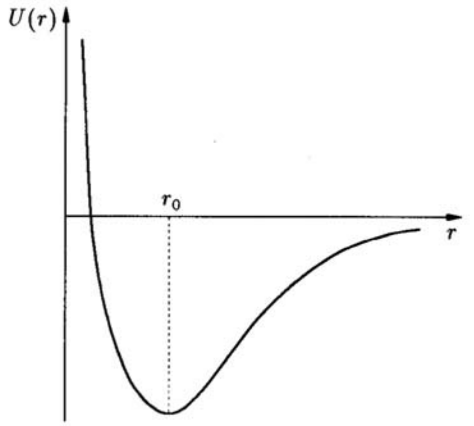


Figure 14-10. Potential energy of the diatomic molecule versus the distance between the atoms; the equilibrium position is denoted with r_0.

The Hamiltonian of the molecule is:

$$\hat{H} = \hat{T}_r + \frac{\hat{L}^2}{2\tilde{m}r^2} + U(r) = -\frac{\hbar^2}{2\tilde{m}}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2\tilde{m}}\frac{\Delta_{\theta,\varphi}}{r^2} + U(r). \quad (14.72)$$

The wave function satisfies the stationary Schroedinger equation and the variables can be divided:

$$\begin{aligned} &\hat{H}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi), \\ &\psi = \psi(r,\theta,\varphi) = R(r)Y_{lm}(\theta,\varphi). \end{aligned} \quad (14.73)$$

Using the results of Section 14.2 we can write the equation of the function $X(r) = rR(r)$:

$$\frac{\partial^2 X(r)}{\partial r^2} + \frac{2\tilde{m}}{\hbar^2}\left[E - U(r) - \frac{\hbar^2 K(K+1)}{2\tilde{m}r^2}\right]X(r) = 0. \quad (14.74)$$

Here instead of *l* we write *K*, which is *the orbital number of the molecule.* Similar to the electron orbital number it takes the values $K = 0, 1, 2, \dots$ This number very often is called a rotational quantum number of the molecule. The effective potential energy depends on the rotational number:

$$\tilde{U}_k = U(r) + \frac{\hbar^2 K(K+1)}{2\tilde{m}r^2}. \tag{14.75}$$

At small K ($K \sim 1$) the position of the potential energy minimum is changed negligibly (Fig. 14.11a) and we can consider that

$$r_k \approx r_0 \tag{14.76}$$

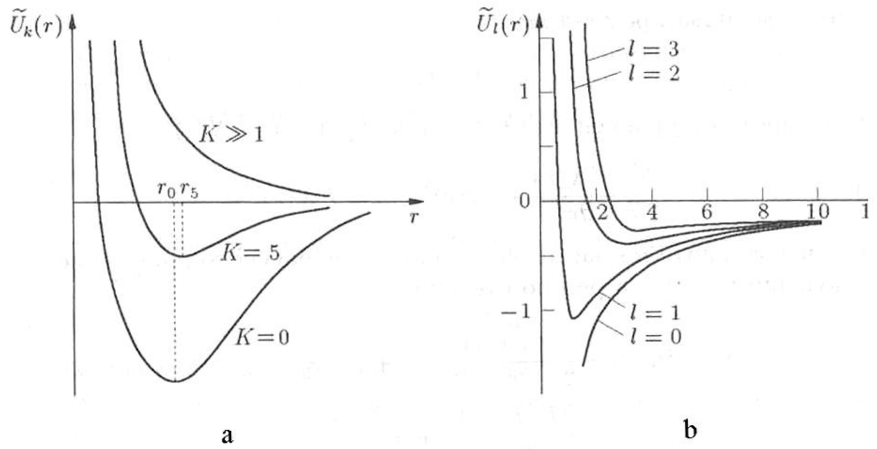


Figure 14-11. Effective potential energy of two particles: a) of a diatomic molecule for different rotational numbers ($K \sim 1, r_k \approx r_0 \Rightarrow 2\tilde{m}r_k^2 \approx 2\tilde{m}r_0^2 = 2I$ ($I \equiv I_0$)); b) of the H atom for different orbital number l; (at $K = 0$ the function $\tilde{U}_0(r)$ of the molecule has a minimum, but at $l = 0$ the function $\tilde{U}_0(r)$ of the H atom coincides with the Coulomb attractive energy!).

For example, for the molecule of HF we have $r_0 = 0{,}929$ Å, $r_5 = 0{,}94$ Å and $r_{10} = 0{,}969$ Å. At higher *K* values the effective potential energy becomes positive and the molecule dissociates. We shall underline that *despite of the qualitative resemble of the dependencies of the effective potential energies of the diatomic molecule and the hydrogen atom and the electrical character of the interaction between the two compound particles the mechanism is different and in the ground states* (*relatively at*) $K = 0$ *and* $l = 0$ *the curves* $\tilde{U}(r)$ *are different.*

14.7* VIBRATIONAL AND ROTATIONAL LEVELS OF A DIATOMIC MOLECULE

Let us treat the case when the rotational energy is not large $(K \sim 1)$, i.e. when the effective potential energy $\tilde{U}_k(r)$ slightly differs from $\tilde{U}(r)$. Then the equilibrium radius of the molecule r_k can be found by the minimum of the $\tilde{U}(r)$:

$$\frac{d\tilde{U}_k}{dr} = \frac{dU(r)}{dr} - \frac{\hbar^2 K(K+1)}{\tilde{m}r^3} = 0. \tag{14.77}$$

The solution of this equation is r_k and at small K we have $r_k \approx r_0$ (14.76).

Let us consider the small deviations from the equilibrium position:

$$r - r_k \approx r - r_0 << r. \tag{14.78}$$

We introduce a new variable

$$\tilde{r} \equiv r - r_k. \tag{14.79}$$

Through it the equation (14.74) for the function $X(r)$ is:

$$-\frac{\hbar^2}{2\tilde{m}} \frac{\partial^2 X(\tilde{r})}{\partial \tilde{r}^2} + \tilde{U}_k(\tilde{r}) X(\tilde{r}) = EX(\tilde{r}). \tag{14.80}$$

For the considered small deviations from the equilibrium states we expand in series the function $\tilde{U}_k(r)$:

$$\begin{aligned} \tilde{U}_k(\tilde{r}) &= \tilde{U}_k(0) + \frac{1}{2} \left. \frac{\partial^2 \tilde{U}_k(\tilde{r})}{\partial \tilde{r}^2} \right|_{\tilde{r}=0} \tilde{r}^2 + \ldots \\ &= U(0) + \frac{\hbar^2 K(K+1)}{2\tilde{m}r_k^2} + \frac{1}{2} \left. \frac{\partial^2 \tilde{U}_k(\tilde{r})}{\partial \tilde{r}^2} \right|_{\tilde{r}=0} \tilde{r}^2 + \ldots \end{aligned} \tag{14.81}$$

As an essence the restriction with the terms $\propto \tilde{r}^2$ is a parabolic approximation and it is valid for small $\tilde{r}$, i.e. near the r_k. In the expansion we have taken into consideration that in point $\tilde{r} = 0$ the effective potential energy has a minimum (14.76). The coefficient before $\tilde{r}^2$ is constant, which we set equal to $\tilde{m}\omega_k^2/2$, i.e.

$$\left.\frac{\partial^2 \tilde{U}_k(\tilde{r})}{\partial \tilde{r}^2}\right|_{\tilde{r}=0} = \tilde{m}\omega_k^2. \tag{14.82}$$

The substitution of (14.81) and (14.82) into Eq. (14.74) reduces it to the following one:

$$-\frac{\hbar^2}{2\tilde{m}}\frac{\partial^2 X(\tilde{r})}{\partial \tilde{r}^2} + \left[U(0) + \frac{\hbar^2 K(K+1)}{2I_k} + \frac{\tilde{m}\omega_k^2\tilde{r}^2}{2}\right] X(\tilde{r}) = EX(\tilde{r}). \tag{14.83}$$

Here $I_k = \tilde{m}r_k^2$ is the inertial moment of the particle of reduced mass $\tilde{m}$ and destination from the centre of mass equal to r_k. After substituting

$$\tilde{E} \equiv E - U(0) - \frac{\hbar^2 K(K+1)}{2I_k}, \tag{14.84}$$

the Eq. (14.83) becomes:

$$-\frac{\hbar^2}{2\tilde{m}}\frac{\partial^2 X(\tilde{r})}{\partial \tilde{r}^2} + \frac{\tilde{m}\omega_k^2\tilde{r}^2}{2} X(\tilde{r}) = \tilde{E}X(\tilde{r}). \tag{14.85}$$

This is the equation for the quantum oscillator of the natural frequency ω_k (see Section 13.1). Hence the functions (13.29) are its solution:

$$X_v(\xi) = A_v e^{-\frac{\xi^2}{2}} \mathcal{H}_v(\xi), \qquad \xi \equiv \frac{\tilde{r}}{\sqrt{\frac{\hbar}{\tilde{m}\omega_k}}}. \tag{14.86}$$

Here $\mathcal{H}_v(\xi)$ are the Hermite polynomials and the constants A_v are determined by (13.27a) according to the normalization condition. The analysis of the quantum oscillator, conducted in Section 13.1, allows us to write the energy of the molecule oscillation as a half-integer of quanta $\hbar\omega_k$:

$$\tilde{E}_v = \left(v + \frac{1}{2} \right) \hbar \omega_k . \tag{14.87}$$

The number *v*, which is an analog to the quantum number *n* of the harmonic oscillator, takes the values

$$v = 0, 1, 2, ... \tag{14.88}$$

and is called *a vibrational quantum n*umber.

Substituting (14.87) into (14.84) we obtain the total molecule energy:

$$\tilde{E}_{vk} = U(r_k) + \left(v + \frac{1}{2} \right) \hbar \omega_k + \frac{\hbar^2 K(K+1)}{2 I_k} . \tag{14.89}$$

Here the potential energy $U(0) \equiv U(\tilde{r} = 0)$ again is expressed through the variable *r*, i.e. $U(0) \to U(r)$.

At fixed rotational energy, i.e. at fixed rotational number *K*, changing the vibrational number $v = 0, 1, 2, ...,$ we obtain *the vibrational energy* levels of the diatomic molecule (Fig. 14.12).

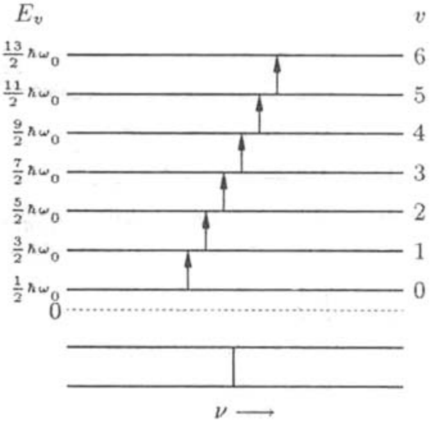


Figure 14-12. Vibrational levels of a diatomic molecule are equidistant. At vibrational transitions (allowed are the transitions $\Delta v = \pm 1$) the spectral line of the emission ($\Delta v = +1$) and the absorption ($\Delta v = -1$) is single one (the absorption spectral line is shown).

The harmonic vibrational levels are equally spaced one from another and those transitions are allowed for where v changes by unity:

$$\Delta v = \pm 1. \tag{14.90}$$

The energy $\hbar\omega_k$ is emitted or absorbed ones. At small K according to (14.82) and (14.76) the vibrational quantum $\hbar\omega_k$ very slightly differs from the vibartional quantum of the ground state:

$$\Delta E_v = \hbar\omega_k \approx \hbar\omega_0. \tag{14.91}$$

The wavelengths of the vibrational lines of the diatomic molecules are in infrared region and most of them are between 2500 *and* 50000 Å.

For the excited molecules with large v the vibrational levels do not satisfy Eq. (14.87) as with the increasing energy the parabolic approximation becomes of the less and less applied. But when v is not great this approximation is good enough for molecules with nuclei much heavier than the hydrogen nucleus. For the ion H_2^+ this approximation is unsatisfactory as the vibrational motion is spread on the distance almost coinciding with the potential well width at $v = 0$. The oscillations no longer satisfy the harmonic law - they become anharmonics. In this case the precise values of the vibrational energetic levels can be obtained at numerically solving the Eq. (14.74). Other initial approximations, better than the parabolic one, are used to model the potential energy near the real curve. A good approximation is the potential of Morse. In Fig. (14.13) it is compared the real potential with the Morse's one. It is obvious that this potential is an excellent approximation in the region $\tilde{U}(r) < 0$. A remarkable property of

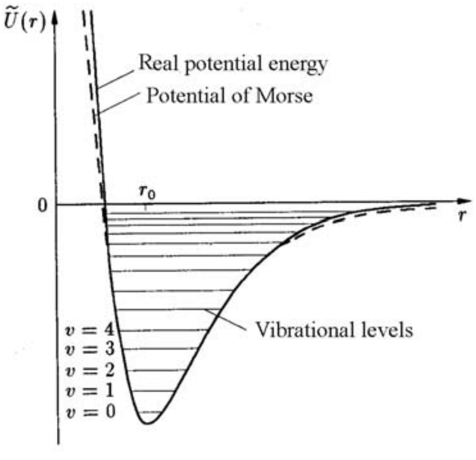


Figure 14-13. The Morse potential is an excellent approximation to the real potential energy of diatomics. At high energy the molecule oscillations are anharmonic and the energy levels are not equidistant.

Morse's potential is that the Schroedinger equation can be explicitly solved with it. Anharmonic corrections, erased in this approximation (also in other approximations) and allowing decrease of the slope of the right part of the curve $\tilde{U}(r)$) are proportional to $-(v+1/2)^2$. Because of the negative corrections of the energy the distance between the vibrational levels decreases and they become nonequidistants.

At a fixed vibrational energy, i.e. at a fixed vibrational number v, changing $K = 0, 1, 2, ...,$ we obtain the *rotational energy levels* (Fig.14-14):

$$E_r = E_k = K(K+1)\frac{\hbar^2}{2I_k} \approx \frac{\hbar^2}{2I}K(K+1), \quad I_0 \equiv I. \tag{14.92}$$

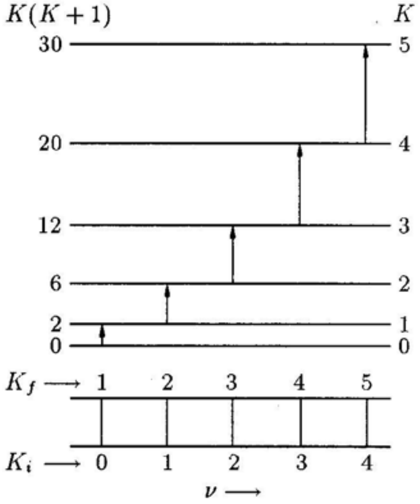


Figure 14-14. The rotational energy levels of a diatomic molecule are nonequidistants. The transitions with ΔK=±1 are allowed - only absorption transitions and corresponding spectral lines are shown.

*Rotational levels are nonequidistants and the distance between two neighboring levels increases while increasi*ng *K*:

$$\Delta E_k = E_{k+1} - E_k = \frac{\hbar^2}{2I_k}\left[(K+1)(K+2) - K(K+1)\right] = \frac{\hbar^2}{2I_k}(K+1). \tag{14.93}$$

The difference between the levels is measured in units $\hbar^2/I \ (I \approx I_k)$. This quantity represents the smallest possible rotational energy at $K=1$ and hence determines the value of the rotational quantum. For the most molecules the rotational quantum has the value from 10^{-5} to 10^{-4} eV. For example, for the molecule of CO, which equilibrium radius and inertial moment are relatively $r_0 = 1{,}13$ Å and $I = \tilde{m}r_0^2 = 1{,}46.10^{-46}$ kg. m^2, the lowest rotational level has energy $E_1 = 7{,}61.10^{-23}$ J $= 5{,}07.10^{-4}$ eV (as a comparison for the CO molecule we have $\hbar\omega_0 \sim 8{,}4.10^{-2}$ eV).

Only those rotational transitions are allowed, for which the quantum number K changes with unity:

$$\Delta K = \pm 1. \tag{14.94}$$

The wavelength of the rotational lines of the diatomic molecules are in the region 1mm - 1 cm (*as a comparison at vibrational spectrum* $\lambda \sim 1$ μm).

Both the experimental and the theoretical results from the research of the energy of the diatomic molecule show that the vibrational quantum (14.91) is essentially greater than the rotational one $\hbar\omega_r \equiv \hbar^2/I$:

$$\hbar\omega_0 : \frac{\hbar^2}{I} \sim \hbar\omega_0 : \hbar\omega_r \sim 100:1. \tag{14.95}$$

For example, for the molecule of CO we have $\hbar\omega_0 = 8{,}84.10^{-2}$ eV and $\hbar\omega_0 : \hbar^2/I = 1{,}6.10^2$.

Taking into account the vibrational and the rotational energies of the molecule we can find its *vibrational-rotational* levels of it:

$$E_{vr} = E_v + E_r = \left(v + \frac{1}{2}\right)\hbar\omega_0 + K(K+1)\frac{\hbar^2}{2I_k}. \tag{14.96}$$

We shall underline once again that $\hbar\omega_0 \sim 10^{-2}$ eV, while $\hbar^2/I \sim 10^{-4}$ eV. Consequently, every vibrational level has its "fine" structure, which is shown on Fig. 14-15.

We shall pay attention that (14.96) determines only the vibrational-rotational levels, but not the energy of the molecule. The potential energy $U(r)$ of the interaction between the atoms (14.89) enters into the total energy. The energy of the ground state of the molecule we determine from (14.89) at $v=0$ and $K=0$:

$$E_{00} = U(r_0) + \hbar\omega_0/2. \tag{14.97}$$

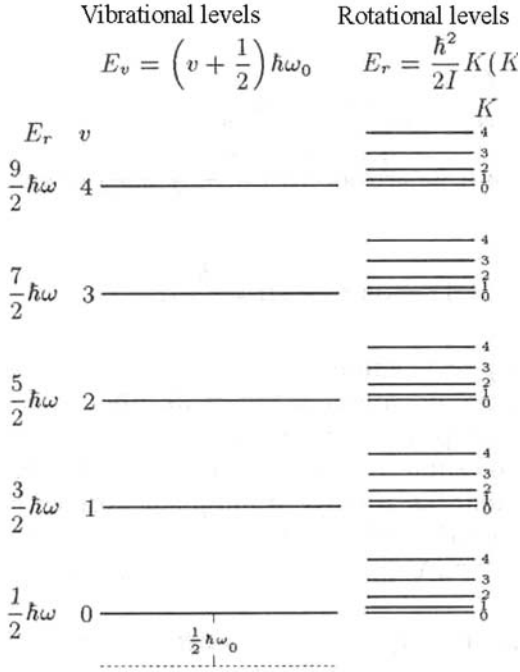


Figure 14.15. Vibrational-rotational energy levels of a diatomic molecule - to each vibrational level correspond many rotational levels.

The energy of the dissociation E_d is equal to $-E_{00}$. Taking into account that $U(r) < 0$ (the atoms are attracted) we can write for E_d the following

$$E_d = -E_{00} = |U(r_0)| - \hbar\omega_0/2. \tag{14.98}$$

For the hydrogen molecule $E_d \approx 4{,}38$ eV.

14.8 SPECTRA OF A DIATOMIC MOLECULE

The quantum of the photon, which is absorbed at the transition from the initial state of energy $(E_{vr})_i \equiv E_{v_i r_i}$ to the final state of energy $(E_{vr})_f \equiv E_{v_f r_f}$ $\left(E_{v_i r_i} < E_{v_f r_f}\right)$, is determined by the vibrational and rotational quantum numbers of the both states. For the energy of the quantum of the absorption at a vibrational-rotational transition we obtain

$$\hbar\omega = E_{v_f r_f} - E_{v_i r_i} = \hbar\omega_0\left(v_f - v_i\right) + \frac{\hbar^2}{2I}\left[K_f\left(K_f+1\right) - K_i\left(K_i+1\right)\right]. \quad (14.99)$$

We shall pay attention that we treat only the motion of the nuclei, i.e. we consider that the electron state is not changed. In other words, at the transitions (14.99) the electron term of the molecule remains constant.

The selection rules, defining the allowed *vibrational-rotational transitions* are following:

$$\Delta v = \pm 1, \qquad \Delta K = \pm 1. \qquad (14.100)$$

Fig. 14-16 illustrates both the levels of the diatomic molecule with

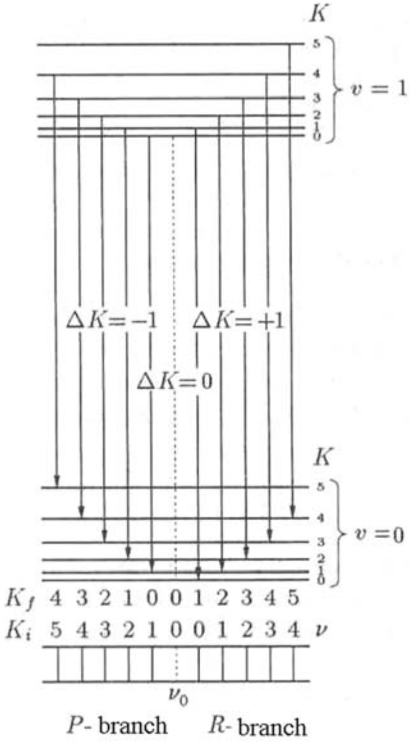


Figure 14-16. Vibrational-rotational transitions of the diatomic molecule between the vibrational levels $v = 0$ and $v = 1$. The spectral line v_0 does not exist, because the transition ΔK=0 (the dashed line) is forbidden. The lines in right of v_0 belong to the R-branch and in the left of v_0 - to the P-branch.

$K < 1, 2, 3, 4, 5$ for the vibrational levels with $v = 0$ and $v = 1$ and the spectral lines, corresponding to $\Delta v = 1$ and $\Delta \mathrm{K} = \pm 1$. *The vibrational-rotational transitions are divided into two branches: P-branch, for which* $\Delta K = -1$, and R-branch, *for which* $\Delta K = +1$ *the two branches differ from* *each other in polarization of the radiation.* From (14.99) we obtain the spectral lines ν_P and ν_R of both branches:

$$\begin{aligned} \nu_P &= \nu_0 - K_i \frac{\hbar}{2\pi I}, \qquad K_i = 1, 2, 3, \dots, \\ \nu_R &= \nu_0 + \left(K_i + 1\right) \frac{\hbar}{2\pi I}, \qquad K_i = 0, 1, 2, 3 \dots. \end{aligned} \tag{14.101}$$

The line ν_0 does not exit, as in the diatomic molecule the transitions for which $\Delta K = 0$ are not allowed. The spaces between the lines both in *P*- and in *R*-branch are equal to $\Delta\nu = \hbar/2\pi I$. Hence, from the spectral lines of the vibrational-rotational transition we can find the distance between atoms in the molecule. This, of course, is possible, and at for the rotational transition - see (14.93).

In Section 14.6 we have underlined that the energy of electrons defines the potential energy of the nuclei. If the electrons of the atoms are in the state with the principal quantum number *n*, the energy level will be defined by the electron energy E_n, the vibrational E_v and the rotational E_r:

$$E = E_n + \left(v + \frac{1}{2} \right) \hbar\omega_0 + K\left(K+1\right) \frac{\hbar^2}{2I_k}. \tag{14.102}$$

The space between the levels of the molecule electrons is few electronvolts, i.e. it is of the order of the space between atom-electron levels. The transitions lead to absorption or emission of the photons, the frequency of which is in the visible and ultraviolet spectra. The electron transition changes the configuration of the electron cover and hence changes the attractive force between the nuclei. This leads to changing of their vibrational and rotational motions. Therefore at an electron transition the vibrational-rotational states of the molecules are changed.

The selection rules of these transitions are

$$\begin{aligned} &\Delta K = \pm 1, 0, \\ &\text{at } K = 0 \ \ \Delta K = 0 \text{ - forbidden}, \\ &\Delta v \text{ - arbitrary}. \end{aligned} \tag{14.103}$$

At a transition from the state with quantum numbers n, v and K and energy (14.102) to the state with quantum numbers n', v' and K' and energy

$$E' = E_{n'} + \left(v' + \frac{1}{2} \right) \hbar\omega_0 + K'(K'+1)\frac{\hbar^2}{2I_k} \tag{14.104}$$

is emitted a quantum $\hbar\omega_{nn'}$:

$$\begin{aligned} \hbar\omega_{nn'} &= E - E' = \Delta E_e + \Delta E_v + \Delta E_r \\ &= \hbar\omega_{nn'}^e + \hbar\omega_0 \Delta v + \frac{\hbar\omega_r}{2}\left[K(K+1) - K'(K'-1) \right]. \end{aligned} \tag{14.105}$$

It is clear that the spectral line is defined not only by the rotational and vibrational quanta but also by optical one $\hbar\omega_{nn'}^e$, *which is due to the change of the molecule-electron state.*

For the electron transitions is valid Frank-Condon principle, according to which during the transition the distance between the nuclei remains constant. We shall not analyze this principle (for details see [5], Section 14.8). We shall notice only that due to the transitions $\Delta K = 0$ to the known *R*- and *P*-branches of the spectrum a new branch appears - *Q*-branch.

The diatomic molecule spectrum is defined by three kinds of quanta: optical, vibrational and rotational. The energy of these quanta differs very much, the largest energy belonging of the optical transition:

$$\hbar\omega^e : \hbar\omega_0 : \hbar\omega_r \sim 1 : \sqrt{\frac{m_e}{m_{mol}}} : \frac{m_e}{m_{mol}} \sim 1 : 10^{-2} : 10^{-4}. \tag{14.106}$$

Therefore *the spectrum has a band character* (Fig. 14.17). The optical line of the electron transition stands at the head of every series of bands. Near such a line many vibrational lines are situated and to every of the vibrational lines there is a great number of rotational ones.

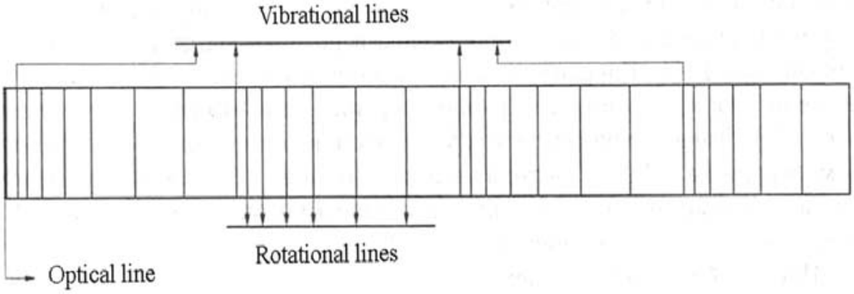


Figure 14-17. Band spectrum of the diatomic molecule. The bands consist from great number of spectral lines situated near one to another.

According to the spectroscopic combination principle (see (7.8)) the frequency of every spectral line can be represented as a difference of two terms: $\nu_{mn} = T(m) - T(n)$. Not every combination of terms gives the frequency corresponding to the observed spectral line. The analysis of the spectra shows that in the most cases there are peculiar "selection rules": only some transitions are found to be "allowed". The others are "forbidden", i.e. the corresponding spectral lines are not observed. The quantum radiation theory (which is out of scope of this book; see, for example [3], Chapter 15 or [R23], Chapter 22)) defines rigorously the transitions between which states are allowed or forbidden. The transitions are accomplished with determined probability, if so-called matrix elements of dipole moment (see Section 15.1) of the corresponding states ψ_m and ψ_n differ from zero:

$$er_{mn} = \int \psi_m^* \left| e\mathbf{r} \right| \psi_n dV \neq 0. \tag{14.107}$$

This matrix element for a combination of many states is equal to zero. The transition between them is not possible as its probability (of the transition) is equal to zero. Only in determined cases the matrix element appears to be different from zero and the transition is possible. Such transitions are called allowed. The conditions for the possibility to realize such transitions impose some requirements on the quantum numbers. *These requirements - the restrictions, on the quantum numbers of the initial and the final state of the possible transition are called selection rules*. In every concrete system (quantum oscillator, hydrogen atom, hydrogen-like ion, diatomic molecule etc.) they are obtained from (14.107) taking the corresponding wave functions of the system states. Namely in such way the used selection rules of the analyzed system are obtained.

The quantum character of the diatomic molecule spectrum permits to be explained the behavior of the specific heat of the diatomic gases at a temperature change. The diatomic molecule posses 6 degrees of freedom - 3 translational, 2 rotational and 1 vibrational. According to the classical theory energy of each translational and rotational degree of freedom is equal to $kT_0/2$. The energy of the vibrational degree is kT_0 because two equal kinds of energy - kinetic and potential $\left(2\left(kT_0/2\right)\right)$, correspond to it. So at temperature T_0 one expects the diatomic molecule energy to be $7kT_0/2$ and the specific heat - $7k/2$. But the experiment shows such specific heat only at very high temperatures. At intermediate temperatures the specific heat is $5k/2$ and at low ones falls to $3k/2$.

We have persuaded ourselves that the value of the vibrational motion energy, i.e. the vibrational quantum $\hbar\omega_0$, is much higher than the one of the rotational motion. If at the temperature T_0 the average energy of the translational molecule motion $3kT_0/2$ is less than $\hbar\omega_0$, the molecule oscillations canot be excited. In this case we can consider the molecule as a solid state ("a weight") with 5 degrees of freedom. Very often it is said that the oscillations "freeze". The temperature of "freezing" T_0, i.e. the temperature at which the oscillations cannot be excited, is determined by the condition

$$\frac{3}{2}kT_{0v} \leqq \hbar\omega_0. \tag{14.108}$$

For the H_2 molecule the temperature of "freezing" is $T_{0v} = 4300\ \mathrm{K}$. Namely, this high value is the reason the specific heat of the gas to be equal not to $7k/2$, but to $5k/2$ at the usual temperatures.

With decreasing the temperature we reach the point at which the energy of the translational motion appears less than the rotational quantum $\hbar^2/I$. Then the rotation cannot be excited and by analogy with the vibrational motion we say that the rotation "freezes". In this case the molecule remains only with 3 degrees of freedom (namely these of the translational motion). The temperature of the "freezing" of the rotational motion T_{0r} is determined by the inequality

$$\frac{3}{2}kT_{0r} \leqq \frac{\hbar^2}{I}. \tag{14.109}$$

At this condition the specific heat of the diatomic molecule is $3k/2$ and it is due only to the translational motion.

SUMMARY

The Hamiltonian of two particles, being interacted with central forces is

$$\hat{H} = \hat{T}_r + \frac{\hat{L}^2}{2\tilde{m}r^2} + U(r) = -\frac{\hbar^2}{2\tilde{m}}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2\tilde{m}}\frac{\Delta_{\theta,\varphi}}{r^2} + U(r).$$

The Schroedinger equation $\hat{H}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$ for such Hamiltonian allows obtaining an explicit solution for the angular part of the wave function even when the explicit potential energy $U(r)$ is not known:

$$\psi(\theta,\varphi) = Y_{lm}(\theta,\varphi) = A_l^{|m|}P_l^{|m|}(\cos\theta)\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}A_l^{|m|}P_l^{|m|}(\cos\theta)e^{im\varphi}.$$

In every CSF one observes $(2l+1)$-fold degeneracy on *m*, which is called normal degeneracy. To a given value *L* of the angular moment corresponds 2*l*+1 wave functions with a different dependence on the polar angle φ. Physically this degeneracy means that at a fixed angular momentum (fixed orbital quantum number l) $2l+1$ components on the Z-axis are possible, i.e. L has $2l+1$ different orientations in the space.

The motion of the particle with mass m_0 in CSF on a sphere of radius $r_0 = \text{const}$ is called quantum rotator. The energy levels of the quantum rotator are nonequidistant and they are defined by the orbital quantum number l:

$$E_l = \frac{L^2}{2m_0 r_0^2} = \frac{\hbar^2 l(l+1)}{2m_0 r_0^2} = \frac{\hbar^2 l(l+1)}{2I}.$$

The Schroedeinger equation of motion of the electron of mass m_e in the Coulomb field of the nucleus of mass M and charge Ze yields for the wave functions and the energy levels:

$$\psi_{nlm}(r,\theta,\varphi) = \mathrm{A}e^{-\frac{r}{na}}\left(\frac{2r}{na}\right)^l \mathrm{L}_{\text{n-l-1}}^{2l+1}\left(\frac{2r}{na}\right)Y_{lm}(\theta,\varphi),$$

$$E_n = -\frac{Z^2 \tilde{m} k_0^2 e^4}{2\hbar^2}\frac{1}{n^2} = \frac{Z^2 R_{\tilde{m}}}{n^2}, \qquad n = 1, 2, 3, \ldots$$

At a given n to every l corresponds its one eigenfunction. Consequently n different wave functions correspond to the eigenvalue E_n of the energy. N-fold degeneracy on the orbital quantum number l is observed in every Coulomb field. It is called accidental or anomalous. Physically this degeneracy expresses the independence of the electron energy on the angular momentum L.

According to the selection rules those transitions are allowed, for which the orbital quantum number changes with unity, i.e. $\Delta l = \pm 1$. The spectral lines of given series of H atom are formed at the transition of the electron to the given fixed level. The lowest frequency from the given series is called resonance frequency and the highest - the threshold frequency.

The probability-density distribution $\rho_{nlm}(r,\theta,\varphi)$ of the atom electron is called electron cloud and the wave function $\psi_{nlm}(r,\theta,\varphi)$ - orbital.

In the hydrogen-like atoms the single outer electron (valence electron) moves in the net field of the nucleus and the inner electrons. The penetrating outer electron in the core of inner electrons removes the anomalous degeneracy on l. For the states with a nonpenetrating electron the valence electron has the energy of the corresponding state of the H atom.

Both the electron motion and the rotation and the oscillation of their nuclei define energy level of the diatomic molecule:

$$E = E_n + \left(v + \frac{1}{2} \right) \hbar \omega_0 + K(K+1) \frac{\hbar^2}{2I_k}.$$

Here E_n is the energy of the electron state, $(v+1/2)\hbar\omega_0$ is the vibrational one and $K(K+1)\hbar^2/2I_k$ - rotational energy of the molecule.

If the electron state of the molecule is not changed, the next vibrational-rotational transitions are allowed:

$$\Delta v = \pm 1, \qquad \Delta K = \pm 1.$$

At the changing of the electron state of the molecule the selection rules are the following:

$\Delta K = \pm 1, 0,$

at $K = 0$ $\Delta K = 0$ - forbidden,

Δv - arbitrary.

As the quanta, corresponding to the different kinds of motion, differ essentially

$$\hbar\omega^e : \hbar\omega_0 : \hbar\omega_r \sim 1 : \sqrt{\frac{m_e}{m_{mol}}} : \frac{m_e}{m_{mol}} \sim 1 : 10^{-2} : 10^{-4},$$

the spectrum has a band character (Fig. 14.17).

The results of the considered in the last chapters quantum mechanical systems are summarized in Table 14-3.

QUESTIONS

1. Which quantum numbers does the rotator energy depend on?
2. What kind of degeneracy is observed in a central symmetric field?
3. What kind of degeneracy is observed in a Coulomb field?
4. What is the physical meaning of the normal and anomalous degeneracy?
5. Which quantum numbers determine the particle in a Coulomb field?
6. What are the eigenfunctons of the quantum rotator?
7. What values can the quantum numbers *n, l, m* take and what quantity they determine?
8. By which quantum number is described the hydrogen atom?
9. What is an orbital? What is an electron cloud?
10. Which state is ground?
11. What is the ground state of the H atom characterised with?

Table 14-3. Basic quantum mechanical systems

System	Wave functions	Energy levels	Quantum numbers	Equi-distance	Degeneracy
Infinite square well	$\psi_n = A \sin \frac{n\pi}{a} x$	$E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2$	quantum number n $n = 1, 2, 3, \ldots$	no	no
Oscillator	$\psi_n = A_n e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)} \mathcal{H}\left(\frac{x}{x_0}\right)$ $x_0 = \sqrt{\hbar / m\omega_0}$	$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0$	quantum number n $n = 0, 1, 2, 3, \ldots$	yes	no
Rotator	$\psi_{lm}(\theta, \varphi) = Y_{lm}(\theta, \varphi) =$ $\frac{1}{\sqrt{2\pi}} A_l^{\lvert m \rvert} P_l^{\lvert m \rvert}(\cos\theta) e^{im\varphi}$	$E_l = \frac{\hbar^2 l(l+1)}{2I}$	orbital q. n. l $l = 0, 1, 2, 3, \ldots$ magnetic q. n. m $m = 0, \pm 1, \pm 2, \ldots, \pm l$	no	normal: $(2l+1)$ – fold on m
Electron in Coulomb field of charge Ze (H atom)	$\psi_{nlm}(r, \theta, \varphi) = A_{nl} e^{-\frac{r}{na}}$ $\times \left(\frac{2r}{na}\right)^l \mathrm{L}_{\mathrm{n}}^{2l+1}\left(\frac{2r}{na}\right) Y_{lm}(\theta, \varphi)$ $a \equiv \hbar^2 / k_0 Z m_e e^2$ $(a = a_0)$	$E_n = -\frac{Z^2 \Re}{n^2}$ $\left(E_n = -\frac{\Re}{n^2} = -\frac{13{,}6}{n^2} \mathrm{eV}\right)$	principal q. n. n $n = 1, 2, 3, \ldots$ orbital q. n. l $l = 0, 1, 2, 3, \ldots$ magnetic q. n. m $m = 0, \pm 1, \pm 2, \ldots, \pm l$ radial q. n. n_r $n_r = 0, 1, 2, \ldots n - l - 1$	no	normal: $(2l+1)$ – fold on m : anomalous: n – fold on l ; common: n^2 – fold
Diatomic molecule	for small deviations from the equilibrium $\psi(\xi, \theta, \varphi) = A_n e^{-\frac{\xi^2}{2}} \mathcal{H}_n(\xi) Y_{lm}(\theta, \varphi)$ $\xi \equiv (r - r_0) / \sqrt{\hbar / \widetilde{m}\omega_0}$	$E = E_n$ $+ \left(v + \frac{1}{2}\right)\hbar\omega_0$ $+ K(K+1)\frac{\hbar^2}{2I_k}$	principal q. n. n $n = 1, 2, 3, \ldots$ vibrational q. n. v $v = 0, 1, 2, 3, \ldots$ rotational q. n. K $K = 1, 2, 3, \ldots$	electron levels-no , vibrational levels-yes, rotational levels-no	normal: $(2l+1)$ – fold on m

12. What is the radius of the maximal probability density of the ground state?
13. Which ions are hydrogen-like?
14. What is the difference between the hydrogen-like ions and atoms?
15. What are penetrating and non-penetrating orbits?
16. When do the energy levels of the hydrogen-like atoms coincide with the levels of the hydrogen?
17. What is common and different in the spectra of the hydrogen and the hydrogen-like atoms?
18. What is the essence of Born-Oppenheimer theory?
19. Show the form of the effective potential energy of the diatomic molecule when: a) there is no rotation; b) there is weak rotation; c) there is force rotation.
20. What determines the rotational energy?
21. What determines the vibrational energy?
22. How the rotational and the vibrational levels are situated?
23. What are the selection rules for vibrational-rotational transitions?
24. What are the selection rules for transitions, including changes of the electron state of the diatomic molecule?

PROBLEMS

1. Find the angular wave functions $\psi(\theta,\varphi)$ for the electron charge in CSF for the states with $l=0$ and $l=1$, i.e. $\psi_{00}(\theta,\varphi)$, $\psi_{10}(\theta,\varphi)$, $\psi_{11}(\theta,\varphi)$, $\psi_{1-1}(\theta,\varphi)$, knowing

$$P_l^{|m|}(\xi)=\frac{1}{2^l l!}\left(1-\xi^2\right)^{\frac{|m|}{2}}\frac{d^{l+|m|}}{d\xi^{l+|m|}}\left(\xi^2-1\right)^l, \qquad \xi=\cos\theta.$$

2. For the electron of H atom find the radial wave function $R_{10}(r)$, the orbital ψ_{100} and the radial charge distribution $\rho\left({}_{10}r\right)$, knowing

$$R_{nl}(r)=A_{nl}e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l \mathrm{L}_{\mathrm{n_r}}^{21+1}\left(\frac{2r}{na_0}\right),$$

$$\mathrm{L}_{\mathrm{n_r}}^{21+1}(\xi)=\frac{1}{n_r!}\xi^{-(2l+1)}e^{\xi}\frac{d^{n_r}}{d\xi^{n_r}}\left(\xi^{2l+1+n_r}e^{-\xi}\right), \qquad n_r=n-l-1.$$

3. Find the average radius of the electron and the radius of the maximum density of the electron cloud in the ground state of H atom $(n=1, l=0, m=0)$, which is described by the wave function
$$\psi_{100}=\frac{1}{\sqrt{4\pi}}\frac{2}{a_0^{3/2}}e^{-\frac{r}{a_0}}.$$
4. The electron in the proton Coulomb field is in a state, which is described by a wave function
$$\varphi(r)=\frac{1}{6}\left[4\psi_{100}(r)+3\psi_{211}(r)-\psi_{210}(r)+\sqrt{10}\psi_{21-1}(r)\right].$$
What are the expectation and the average values of: a) the energy E ; b) the square of the orbital angular momentum L^2 ; c) the component of the L_z ?
5. For the electron in H atom in a state with $n=3$ find:
   - the multiplicity of the degeneracy;
   - the number of wave-function nodes;
   - the energy of the state (also for the electron in He^+);
   - the wavelengths of the allowed emission transitions.
6. Find the ionization energy of the ions He^+ and Li^{++} .
7. For hydrogen find the most probable distance of the electron from the nucleus in the state $2s$.
8. Calculate semi-classically the rotational energy of the diatomic molecule with the masses of atoms m_A and m_B and distance r between them.
9. The molecule HCl shows a strong absorption line of $\lambda=3465\ \mu\mathrm{m}$. Accepting that this is due to the vibrational motion, calculate the force constant of the molecule.
10. The equilibrium distance between two nuclei of H_2 molecule is $r_0=0,75$ Å and its force constant is $\kappa=5,136.10^3$ N/m. Calculate: a) the moment of inertia and the energy of the lowest rotational level; b) angular velocity of rotation; the emission frequency at the rotational transition from a level $K=2$ to a level $K=1$; c) the distance between the nuclei in the states; d) the frequency of oscillations; e) the space between the vibrational levels.
11. Solve the problem 10. for CO molecule, which has a length $r_0=1,13$ Å and a force constant $\kappa=1,87.10^2$ N/m.
12. The distance between two adjacent lines of the emission spectrum of $^{1}\mathrm{H}^{35}\mathrm{Cl}$ molecule is 20,68 cm^{-1} . Calculate the distance between the spectral lines of $^{2}\mathrm{H}^{35}\mathrm{Cl}$ molecule.

Chapter 15

PERTURBATION THEORY AND STARK EFFECT

SUGGESTED READING

1. Blokhintsev, D. I., Principles of Quantum Mechanics, Allyn and Bacon, 1964, Sections 8, 12.
2. W. Greiner, Quantum Mechanics, An Introduction, Vol. 1, Springer-Verlag, 1989, Chapters 10, 11.
3. Messiah, A., Quantum Mechanics, Vol. 1, John Wiley & Sons, 1968, Chapter VII.
4. Messiah, A., Quantum Mechanics, Vol. 2, John Wiley & Sons, 1968, Chapter XVI.

15.1* ELEMENTS OF MATRIX MECHANICS

In Section 9.6 we have touched a very important question - we have seen that the state of a given system can be described by two different functions, $\psi(x)$ and $C(p)$. Essentially this is the wave function *in different representations.* The state of the system, described by the wave function $\psi(x)$, can be represented as a superposition of the eigenstates of free particles with momentum p which are described by the functions $\psi_p(x)$ of the form (10.57):

$$\psi(x)=\int_{-\infty}^{\infty} C(p)\psi_p(x)dp=\frac{1}{\sqrt{2\pi h}}\int_{-\infty}^{\infty} C(p)\exp\left(\frac{i}{\hbar}px\right)dp, \qquad (15.1)$$

where

$$C(p)=\int_{-\infty}^{\infty} \psi(x)\psi_p^*(x)dx=\frac{1}{\sqrt{2\pi h}}\int_{-\infty}^{\infty} \psi(x)\exp\left(-\frac{i}{\hbar}px\right)dx. \qquad (15.2)$$

The function $\psi(x)$ is a wave function in *co-ordinate representation*. If we know $\psi(x)$ we can determine $C(p)$ using (15.2) and vice versa - if we know $C(p)$ we can determine $\psi(x)$ from (15.1), i.e. with the equal success we can use the one or the another function. The function $C(p)$ is determined in the momentum space and is called the wave function in *momentum representation*. Equations (15.1) and (15.2) determine the rules for transformation of the wave function from one representation into another one (in this case from x-representation (co-ordinate representation) to p-representation (momentum representation)) and vice versa). (We note that the example is for the state with the continuous quantity.)

Before discussing the wave function in arbitrary representation, we shall say a few words about the eigenfunctions of a continuous quantity A in A-representation, i.e. in eigenrepresentation. Above we have written the wave functions in co-ordinate representation. In eigenrepresentation they are always δ -functions. For example, the eigenfunction of a free particle (one-dimensional motion) with a momentum p' in x-representation and p-representation is respectively:

$$\begin{aligned} \psi_{p'}(x) &= \frac{1}{\sqrt{2\pi\hbar}} \exp\left(+\frac{i}{\hbar} p' x \right), && x\text{-representation;} \\ \varphi_{p'}(p) &= \delta(p - p'), && p\text{-representation.} \end{aligned} \tag{15.3}$$

Let us consider the state with the physical quantity *M*, which has discrete values. The operator of this quantity has the eigenfunctions

$$\psi_1(x), \psi_2(x), \psi_3(x), \ldots \psi_n(x), \ldots \tag{15.4}$$

We shall note that in the general case the number of the ψ -functions is infinite (in Section 9.6 we have underlined that these functions form infinite vector space). The ψ -functions form a complete set, which can be used as a basis. Any wave function in co-ordinate representation may be expanded in terms of the basis functions $\psi_n(x)$:

$$\psi(x) = \sum_k C_{M_k} \psi_k(x). \tag{15.5}$$

The eigenfunctions $\psi_n(x)$ are also in co-ordinate representation. The coefficients C_{M_k} determine uniquely the wave function $\psi(x)$, i.e. they determine uniquely the state. In this sense they are equivealent to the wave function, however in *M*-representation. (If we had the eigenfunctions $\psi_{f_k}(x)$ of the operator $\hat{f}$, the coefficient C_{f_k} of the expantion $\psi(x) = \sum C_{f_k} \psi_{f_k}(x)$ would determine the wave function $\psi(x)$ in *f*-representation.)

It is obvious that *the wave function* $\psi(x)$ *may be represented as a column matrix*:

$$\psi(x)=\begin{vmatrix} C_{M_1} \\ C_{M_2} \\ C_{M3} \\ . \\ . \\ . \end{vmatrix}, \tag{15.6}$$

which determines the function in M-representation. So, the wave function $\psi(x)$ in *M*-representation is a column matrix, whose terms are the superposition coefficients in the expansion of $\psi(x)$ in the eigenfunctions of the operator of this quantity.

It turns out that using the Fourier transformation (for the continuous quantity) or the matrix (15.6) we may describe the state of a system in different representation. The following question arises: how does an operator change under such a transformation?

We will determine the form of the operator $\hat{N}$ of the quantity N in *x*-representation, starting from the dependence $N(x,p)$ and going to the operator form, $\hat{N}(x,-i\hbar\partial/\partial x)$ (see Section 10.5). Acting with the operator $\hat{N}$ on the function $\psi(x)$ we obtain the function $\varphi(x)$:

$$\varphi(x)=\hat{N}\left(x,-i\frac{\partial}{\partial x}\right)\psi(x). \tag{15.7}$$

Here the functions $\psi(x)$ and $\varphi(x)$ and the operator $\hat{N}$ are given in *x*-representation. Let's find $\hat{N}$, for example, in *M*-representation. Label the eigenfunctions and the eigenvalues of the operator $\hat{M}$ as follows:

$$\begin{matrix} \psi_1(x), \psi_2(x), \psi_3(x), \ldots \psi_n(x), \ldots \\ M_1, \quad M_2, \quad M_3, \quad \ldots M_n, \quad \ldots \end{matrix} \tag{15.8}$$

Then, expand the wave functions $\varphi(x)$ and $\psi(x)$ in terms of the basis functions $\psi_k(x)$:

$$\begin{gathered} \varphi(x)=\sum_k b_k\psi_k(x), \\ \psi(x)=\sum_k c_k\psi_k(x). \end{gathered} \tag{15.9}$$

Here $b_1, b_2, ..., b_n$ and $c_1, c_2, ..., c_n$ are the functions $\varphi(x)$ and $\psi(x)$ in *M*-representation. After taking into account (15.9), Eq. (15.7) can be written in the following form:

$$\sum_k b_k\psi_k(x) = \hat{N}\sum_k c_k\psi_k(x), \tag{15.10a}$$

or $$\sum_k b_k\psi_k(x) = \sum_k c_k\hat{N}\psi_k(x). \tag{15.10b}$$

Multiplying by $\psi_i^*(x)$ and integrating over dx, we obtain as a result

$$\sum_k b_k\int_{-\infty}^{\infty}\psi_i^*(x)\psi_k(x)dx = \sum_k c_k\int_{-\infty}^{\infty}\psi_i^*(x)\hat{N}\psi_k(x)dx. \tag{15.11}$$

The eigenfunctions $\psi_k(x)$ of the operator $\hat{M}$ form a complete set and the integral from the left-hand side is equal to δ_{ik}. Hence,

$$\sum_k b_k\int_{-\infty}^{\infty}\psi_i^*(x)\psi_k(x)dx = \sum_k b_k\delta_{ik} = b_i. \tag{15.12}$$

We set

$$\int_{-\infty}^{\infty}\psi_i^*(x)\hat{N}\psi_k(x)dx \equiv N_{ik}. \tag{15.13}$$

After taking into account (15.12) and (15.13), the relation (15.11) becomes

$$b_i = \sum_k N_{ik}c_k. \tag{15.14}$$

Here b_i is the function $\varphi(x)$ in *M*-representation and c_k - the function $\psi(x)$ in *M*-representation. It is logically to consider *the matrix* N_{ik} (15.13*) as the operator* $\hat{N}$ *in M-representation*, which in explicit form is

$$\hat{N} = \|N\| = \begin{vmatrix} N_{11} & N_{12} & N_{13} & \ldots \\ N_{21} & N_{22} & N_{23} & \ldots \\ N_{31} & N_{32} & N_{33} & \ldots \\ . & . & . & . \\ . & . & . & . \\ . & . & . & . \end{vmatrix}. \tag{15.15}$$

We shall underline that in order to obtain the matrix elements N_{ik}, i.e. in order to obtain $\hat{N}$ in *M*-representation, it is necessary to use in (15.13) the eigenfunctions of the operator $\hat{M}$.

We have settled that in quantum mechanics is possible to a given quantity N instead of the operator to correspond the matrix $\|N\|$. This idea was first suggested by Heisenberg. Together with the matrix $\|N\|$ the following matrices are considered:

1. *The matrix* $\|N\|^*$ *is the complex conjugate matrix* of $\|N\|$, if each element of the matrix $\|N\|^*$ is obtained in the following way from the corresponding element of the matrix $\|N\|$:

$$\left(\|N\|^*\right)_{ik} = N^*_{ik}. \tag{15.16}$$

2. *The matrix* $\|\tilde{N}\|$ *is transposed of* $\|N\|$, if the rows of $\|\tilde{N}\|$ are obtained from the columns of $\|N\|$ and the columns of $\|\tilde{N}\|$ from the rows of $\|N\|$:

$$\left(\|\tilde{N}\|\right)_{ik} \equiv \tilde{N}_{ik} = N_{ki}. \tag{15.17}$$

3. *The matrix* $\|N\|^+$ *is the adjoint of* $\|N\|$, if $\|N\|^+$ is obtained from $\|N\|$ by complex conjugating and then transposing:

$$\left(\|N\|^+\right)_{ik} \equiv N^+_{ik} = \tilde{N}^*_{ik} = N^*_{ki}. \tag{15.18}$$

4. *Self-adjoint or Hermitian is a matrix* $\|N\|$ which is equal to his adjoint matrix $\|N\|^+$:

$$\|N\| = \|N\|^+. \tag{15.19}$$

We shall show that at this condition the operator $\hat{N}$ is Hermtian. For every element of the Hermitian matrix we can write

$$N_{ik} = \left(\|N\|^{+} \right)_{ik} = N_{ki}^{*}. \tag{15.20}$$

According to (15.13) for the matrix elements N_{ik} and N_{ik}^{*} we have

$$\begin{aligned} N_{ik} &= \int_{-\infty}^{\infty} \psi_i^*(x) \hat{N} \psi_k(x) dx, \\ N_{ki}^* &= \left(\int_{-\infty}^{\infty} \psi_k^*(x) \hat{N} \psi_i(x) dx \right)^* = \int_{-\infty}^{\infty} \psi_k(x) \hat{N}^* \psi_i^*(x) dx. \end{aligned} \tag{15.21}$$

Substituting it into (15.20) we obtain

$$\int_{-\infty}^{\infty} \psi_i^*(x) \hat{N} \psi_k(x) dx = \int_{-\infty}^{\infty} \psi_k(x) \hat{N}^* \psi_i^*(x) dx. \tag{15.22}$$

This is the condition (10.21) for Hermitian character of $\hat{N}$.

Now let us consider how to find an operator in its eigenrepresentation. We shall start from the matrix elements N_{mn} (15.13) of the operator $\hat{N}$. In its eigenrepresentation the functions $\psi_i(x)$ are eigenfunctions of the same operator $\hat{N}$. Then

$$\int_{-\infty}^{\infty} \psi_i^*(x) \hat{N} \psi_k(x) dx = \int_{-\infty}^{\infty} \psi_i^*(x) N_k \psi_k(x) dx = N_k \delta_{ik}. \tag{15.23}$$

where N_i are the eigenvalues of the operator $\hat{N}$.

Therefore in its eigenrepresentation the matrix of the operator has a diagonal form and the values of the diagonal elements are equal to the eigenvalues of the operator:

$$\hat{N} = \|N\| = \begin{vmatrix} N_1 & 0 & . & . & . & . \\ 0 & N_2 & 0 & . & . & . \\ . & 0 & N_3 & 0 & . & . \\ . & . & 0 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{vmatrix}. \tag{15.24}$$

We shall consider two concrete examples of operators in their eigenrepresentation - the operators $\hat{H}$ of a particle in an infinite square well and the quantum harmonic oscillator.

The energy levels in the infinite well (Section 12.2), i.e. the eigenvalues of the Hamiltonian have the form:

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2} = n^2 E_1. \tag{15.25}$$

Hence in *E*-representation the operator $\hat{H}$ has the following form

$$\hat{N} = \|N\| = E_1 \begin{vmatrix} 1 & 0 & . & . & . & . \\ 0 & 4 & 0 & . & . & . \\ . & 0 & 9 & 0 & . & . \\ . & . & 0 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{vmatrix}. \tag{15.26}$$

For the oscillator the eigenvalues of the energy are $E_n = \hbar\omega_0 \left(n + 1/2\right)$ and the matrix of the Hamiltonian in eigenrepresentation is

$$\hat{N} = \|N\| = \hbar\omega_0 \begin{vmatrix} 1/2 & 0 & . & . & . & . \\ 0 & 3/2 & 0 & . & . & . \\ . & 0 & 5 & 0 & . & . \\ . & . & 0 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{vmatrix}. \tag{15.27}$$

The more interested reader can find a more detailed presentation in [1].

15.2* PERTURBATION THEORY

In many practical problems encountered in quantum mechanics, the Hamiltonian of the analyzed system can be represented as a sum of two operators:

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}', \tag{15.28}$$

where the eigenfunction of the operator $\hat{H}^0$ are known and the operators $\hat{H}$ and $\hat{H}^0$ do not differ appreciably. The additional operator $\lambda\hat{H}'$ is in some sense small compared to $\hat{H}^0$. This means that under the action of the operators $\lambda\hat{H}'$ the system state, described by the eigenfunctions of $\hat{H}^0$, changes weakly. The criterion, that establishes the smallness of $\lambda\hat{H}'$ compared to $\hat{H}^0$ will emerge further. Mathematically this is ensured by the dimensionless parameter λ, which is an infinitesimal parameter, so that $\lambda >> \lambda^2 >> \lambda^3 ...$ The operator $\lambda\hat{H}'$ is called *perturbation Hamiltonian* or merely *perturbation* and the operator $\hat{H}^0$ *unperturbed Hamiltonian.* The theory that seeks the approximate eigenfunctions of the total operator $\hat{H}$ is called *perturbation theory.*

Perturbation theory begins with the statement that the eigenfunctions and eigenvalues of the unperturbed Hamiltonian are known - they are solutions of the Schroedinger equation with $\hat{H}^0$:

$$\hat{H}^0\psi_k^0 = E_k^0\psi_k^0. \tag{15.29}$$

The functions ψ_k^0 are the eigenfunctions of the operator $\hat{H}^0$ and E_k^0 are its eigenvalues (further we shall consider discrete eigenvalues only). The functions ψ_k^0 form a complete set of orthonormal functions.

We seek the solution of the Schroedinger equation with $\hat{H}$:

$$\hat{H}\psi = E\psi \Rightarrow \left(\hat{H}^0 + \lambda\hat{H}'\right)\psi = E\psi. \tag{15.30}$$

Let's assume that the unperturbed system is in the state ψ_i^0 with energy E_i^0. In other words we seek the eigenfunctions and the eigenvalues of Eq. (15.30), which at $\hat{H}'=0$ transform to the eigenfunctions ψ_i^0, when the eigenvalues E_i^0 of Eq. (15.29) describe the unperturbed system. Let's label the unknown eigenfunctions and eigenvalues with ψ_i and E_i, respectively.

We expand the unknown wave function ψ_i in terms of the basis functions ψ_k^0, i.e. in terms of known functions of the unperturbed system:

$$\psi_i = \sum_k C_k\psi_k^0. \tag{15.31}$$

Replacing this into (15.30) and taking into account (15.29), we obtain

$$\sum_k \lambda \hat{H}' C_k \psi_k^0 = \sum_k C_k \left(E_i - E_k^0\right)\psi_k^0. \tag{15.32}$$

Multiplying the equation by ψ_m^{0*} and integrating over the whole space of changing of the nondependent variables (for a simplicity they are omitted in the further expressions), we obtain:

$$\sum_k \lambda C_k \int \psi_m^{0*} \hat{H}' \psi_k^0 dV = \sum_k C_k \left(E_i - E_k^0\right)\delta_{km}. \tag{15.33}$$

We have used the fact that the eigenfuctions are orthonormal:

$$\int \psi_m^{0*} \psi_k^0 dV = \delta_{km}. \tag{15.34}$$

The integral in the left-hand side of (15.33) according to (15.13) determines the matrix elements $H_{mk}^{'}$ of the operator $\hat{H}'$ in E^0-representation:

$$H'_{mk} = \int \psi_m^{0*} \hat{H}' \psi_k^0 dV. \tag{15.35}$$

Taking this into account into (15.33), we obtain the Schroedinger equation (15.30) in a matrix form:

$$\left(E_m^0 + \lambda H'_{mm} - E_i\right)C_m + \lambda \sum_{k \neq m} H'_{mk} C_k = 0. \tag{15.36}$$

Here according to (15.6) the coefficients C_k form a column matrix for the function ψ in E^0-representation. (For convenience we have separated the term $\lambda H_{mm}^{'} C_m$ from the sum.)

As we have already underlined, we shall consider small perturbations under which the system does not change appreciably. This means that the energy levels and the wave function of the perturbed system (i.e. the coefficients C_i in E^0-representation are close to the values for the unperturbed system. We expand the unknown quantities E_i and C_k in power series of the small parameter λ:

$$E_i = E_i^0 + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ..., \tag{15.37a}$$

$$C_k = C_k^0 + \lambda C_k^{(1)} + \lambda^2 C_k^{(2)} + ..., \quad k = 1,2,3,... \tag{15.37b}$$

The unknown wave functions ψ_i also can be expanded in similar powers

$$\psi_i = \psi_i^0 + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \ldots \tag{15.37c}$$

To avoid further misunderstanding we shall emphasize that E_k^0 (see (15.29)) are the eigenenergies of the corresponding unperturbed states ψ_k^0, and the value $E_i^{(0)}$ are the zeroth order approximations of the energies E_i of the perturbed state! In general the number in the parenthesis shows the order of the approximation. For example, $E^{(2)}$ means the second order in the expansion of the small parameter λ.

We substitute (15.37) into (15.36) up to the order λ, and omitting the higher powers:

$$\left(E_m^0 - E_i^{(0)}\right)C_m^{(0)} + \lambda\Big[\left(H'_{mm} - E_i^{(1)}\right)C_m^{(0)} \tag{15.38}$$
$$+\left(E_m^0 - E_i^{(0)}\right)C_m^{(1)} + \sum_{k\neq m} H'_{mk}C_k^{(0)}\Big] + 0\left(\lambda^2\right) = 0.$$

This equation can be solved by the method of successive approximations. Setting $\lambda = 0$ we obtain the solution in zeroth order approximation:

$$\left(E_m^0 - E_i^{(0)}\right)C_m^{(0)} = 0, \quad m = 1,2,3,\ldots \tag{15.39}$$

This is the matrix Schroedinger equation of the unperturbed system and E_m^0 are the diagonal matrix elements of the operator $\hat{H}^0$ in its eigenrepresentation. We are interested in the change of eigenvalue and the eigenfunction of the *i*th state, i.e. E_i^0 and ψ_i^0 under the perturbation $\hat{H}'$. It is clear from (15.39) (and also from (15.29) and (15.31)) that the solution is

$$E_i^{(0)} = E_i^0, \quad C_m^{(0)} = \delta_{mi}. \tag{15. 40}$$

To find the first order approximation we substitute $E_i^{(0)}$ and $C_m^{(0)}$ into (15.38), and then equate the coefficients before λ to zero:

$$\left(H'_{mm} - E_i^{(1)}\right)\delta_{mi} + \left(E_m^0 - E_i^{(0)}\right)C_m^{(1)} + \sum_{k\neq m} H'_{mk}\delta_{ki} = 0, \quad m = 1,2,3,\ldots,n. \tag{15.41}$$

For $m = i$ we obtain the first-order corrections $E_i^{(1)}$ to the unperturbed energies $E_i^{(0)}$:

$$E_i^{(1)} = H'_{ii}, \quad i = 1, 2, 3, ..., \tag{15.42}$$

and for $m \neq i$ we obtain the coefficients $C_m^{(1)}$:

$$C_m^{(1)} = \frac{H'_{mi}}{E_i^{(0)} - E_m^0}, \quad m \neq i. \tag{15.43}$$

For the application of the perturbation theory we assumed that the perturbation is "small", i.e. the energy levels, the coefficients and the wave functions are not changed significantly. We can express this in the following way (see (15.37b):

$$\lambda \frac{H'_{mi}}{E_i^0 - E_m^0} << 1, \tag{15.44}$$

i.e. *the method of the perturbations theory is applicable if the matrix elements of the perturbation are small compared to the difference between the corresponding unperturbed energy levels.*

The coefficients $C_i^{(1)}$ cannot be determined by this formula. We shall find them from the normalization of the perturbed wave functions ψ_i. Taking into account (15.31), (15.37b) and (15.43), we readily show that within first-order approximation these functions take the following form:

$$\psi_i = \psi_i^0 + \lambda \left(C_i^{(1)} \psi_i^0 + \sum_{m \neq i} \frac{H'_{mi}}{E_i^{(0)} - E_m^0} \psi_m^0 \right). \tag{15.45}$$

From the normalization of these functions follows that (see, for example, [2], Section 67) that

$$C_i^{(1)} = 0. \tag{15.46}$$

Substituting this into (15.45) we obtain the first-order correction $\psi_i^{(1)}$ to the wave function ψ_i:

$$\psi_i^{(1)} = \lambda \sum_{m \neq i} \frac{H'_{mi}}{E_i^0 - E_m^0} \psi_m^0. \tag{15.47}$$

According to this equation, the expansion (15.37c) would make sense if the coefficients of expansion are much smaller than 1, i.e. $\lambda H'_{mi} << E_i^0 - E_{mi}^0$. We obtain the same condition as (15.44).

Taking into account (15.42), (15.37a) and (15.35), we obtain the energy of the *i*th state in the first-order approximation:

$$E_i = E_i^{(0)} + \lambda H'_{ii} = E_i^0 + \int \psi_i^{0*} \lambda \hat{H}' \psi_i^0 dV. \tag{15.48}$$

By analogy with the first-order approximation of the eigenfunctions (15.45) and the eigenenergy (15.48), we can obtain the approximations of second order, third order etc.

Finally, we shall underline that the described method is applicable if the levels E_i^0 are not degenerate. For degenerate states the perturbation method must be modified, which we shall do in the next section.

15.3* TIME-INDEPENDENT DEGENERATE PERTURBATION THEORY

Let $\hat{H}^0$ describe degenerate eigenstates. Suppose, for example, that in unperturbed system the level E_i^0 is *f*-fold degenerate. Then the eigefunctions $\psi_{i1}^0, \psi_{i2}^0, ..., \psi_{if}^0$ $\left(\text{or } \psi_{i\alpha}^0, \alpha = 1, 2, ..., f\right)$ correspond to the eigenenergy E_i^0. What will happen at the presence of a perturbation?

We can give following qualitative answer. The degeneracy can always be traced to some symmetry of the system. This symmetry is also a characteristic of the Hamitonian. For example, the Hamiltonian in central symmetric field does not depend on the angular-momentum direction - we observe normal degeneracy. In the most general case the perturbation does not posses such symmetry. Therefore, the interaction energy of the different states with the perturbation in the degenerate system is not the same, hence splitting of the degenerate levels is observed.

The change in energy levels under the influence of the perturbation accompanies by a change in the wave functions of the degenerate state.

Let us consider a concrete example. The states $2p$ of the H atom with three different orientations of the angular momentum (at $m=-1,0,1$) is degenerate (see Section 14.3). In an external magnetic field **B,** because of the its interaction with the orbital magnetic moment $\boldsymbol{\mu}_l$, the atom receives additional energy $\Delta U=-\boldsymbol{\mu}_l\mathbf{B}$ (4.40). The vectors of the magnetic moment and the orbital angular momentum are collinear (Section 4.4). The energy of the state, in which **L** and **B** are parallel $(m=1)$ increases - $\Delta U=-\boldsymbol{\mu}_l\mathbf{B}=\left(e\mathbf{LB}/2m_e\right)$; the energy of the state, in which **L** and **B** are antiparallel $(m=-1)$ decreases and in the state, in which they are perpendicular ($m=0$), the energy is not changing.

In degenerate states the functions which form the complete set depend on both indices *k* (15.31) and on the indices *α*. Therefore, in the expansion of the wave functionσ ψ_i of the perturbed system to the eigenfunctions $\psi_{i\alpha}^0$ of the unperturbed system, the sum is double and the coefficients depend on both indices (compare with (15.31):

$$\psi_i=\sum_{\alpha,k}C_{k\alpha}\psi_{k\alpha}^0,\qquad k=1,2,3,\dots,n,\qquad \alpha=1,2,3,\dots,f. \tag{15.49}$$

In Eq. (15.36) we did not impose constraints, concerning the degeneracy for the unknown energies and the coefficients of the perturbed system. That equation is valid both for nondegenerate and for degenerate states. The comparison of the expansions of the nondegenerate states (15.31) and degenerate states ((15.49) shows that it is necessary a replacement, for nongenerate systems in Eq. (15.36) the single indices with double ones: $m\rightarrow m,\alpha$ and $k\rightarrow k,\beta$. We shall recall that α and β change from 1 to *f* and *m* and *k* - from 1 to *n*. With this replacement in non-generate system the Eq. (15.36) becomes

$$\left(E_m^0+\lambda H_{m\alpha,m\alpha}-E_i\right)C_{m\alpha}+\lambda\sum_{k\beta\neq m\alpha}H'_{m\alpha,k\beta}C_{k\beta}=0, \tag{15.50}$$

where

$$\lambda H'_{m\alpha,k\beta}=\int\psi_{m\alpha}^{0*}\lambda\hat{H}'\psi_{k\beta}^0dV \tag{15.51}$$

are the matrix elements of the perturbation.

Let us analyze the *i*th state as in the previous section. When the degeneracy is absent, the function of the perturbed system in 0th order approximation coincides with the one of the unperturbed system. Due to the lack of a perturbation the degenerate system can appear in every one of the states $\psi_{i\alpha}^{0}$ $(\alpha = 1, 2, 3, ..., f)$ or in a superposition of them. (All (!) these states have an energy E^{0}.) Therefore here all coefficients $C^{(0)}$ are different from zero:

$$C_{i\alpha}^{(0)} = C_{i\alpha}^{0} \neq 0, \quad \alpha = 1, 2, 3, \dots, f, \tag{15.52.a}$$

$$C_{m\alpha}^{(0)} = 0, \qquad m \neq i. \tag{15.52b}$$

As in the nondegenerate states, the energy in the 0th order approximation is equal to that of the energy of unperturbed system: $E_{i}^{(0)} = E_{i}^{0}$.

We could proceed as in the previous section - to substitute $C_{m\alpha}^{(0)}$ and E_{i}^{0} into (15.50) (we would obtain the analogue of Eq. (15.38)). However we shall proceed a little differently. We shall substitute in Eq. (15.50) only the coefficients (15.52). After taking into account the terms different than zero, we obtain

$$\left(E_{i}^{0} + \lambda H'_{i\alpha,i\alpha} - E_{i}\right) C_{i\alpha}^{(0)} + \lambda \sum_{\beta,\alpha} H'_{i\alpha,i\beta} C_{i\beta}^{(0)} = 0. \tag{15.53}$$

In these equations E_{i} is assumed to be energy of the 1st order approximation, i.e. unperturbed energy plus the correction in the 1st approximation. To be clear we write the equations for different alpha's:

$$\begin{gathered}
\left(E_{i}^{0} + \lambda H'_{i1,i1} - E_{i}\right) C_{i1}^{(0)} + \lambda H'_{i1,i2} C_{i2}^{(0)} + \dots + \lambda H'_{i1,if} C_{if}^{(0)} = 0, \quad \alpha = 1, \\
\lambda H'_{i2,i1} C_{i1}^{(0)} + \left(E_{i}^{0} + \lambda H'_{i2,i2} - E_{i}\right) C_{i2}^{(0)} + \dots + \lambda H'_{i1,if} C_{if}^{(0)} = 0, \quad \alpha = 2, \\
\cdot \\
\cdot \\
\cdot \\
\lambda H'_{if,i1} C_{i1}^{(0)} + \lambda H'_{if,i2} C_{i2}^{(0)} + \dots + \left(E_{i}^{0} + \lambda H'_{if,if} - E_{i}\right) C_{if}^{(0)} = 0, \quad \alpha = f.
\end{gathered} \tag{15.54}$$

This is a linear homogeneous system of equations for the unknown coefficients $C_{i\alpha}^{(0)}$. It has a nontrivial solution if its determinant is equal to zero:

$$\begin{vmatrix} E_i^0+\lambda H'_{i1,i1}-E_i & \lambda H'_{i1,i2} & \dots & \lambda H'_{i1,if} \\ \lambda H'_{i2,i1} & E_i^0+\lambda H'_{i2,i2}-E_i & \dots & \lambda H'_{i2,if} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \lambda H'_{if,i1} & \lambda H'_{if,i2} & \dots & E_i^0+\lambda H'_{if,if}-E_i \end{vmatrix} = 0 . \quad (15.55)$$

We have obtained an algebraic equation of *f*th power for the energies E_i, which is often called a secular equation. This equation has f solutions:

$$E_i = E_{i1}, E_{i2}, E_{13}, \dots, E_{if} . \quad (15.56)$$

As the matrix elements are small, proportional to λ, these solutions are very close to each other. Thus, under the influence of the perturbation, the *f*-fold degenerate state of energy E_i^0 splits up into f close-lying states. Thus, the perturbation removes the degeneracy. If some solutions are equal to zero, then the degeneracy is partly removed.

To obtain the wave functions of the perturbed states of energies $E_{i\alpha}$, we substitute the solutions $E_{i\alpha}$ (15.56) into Eqs. (15.53). The obtained system of equations enables us to determine the coefficients $C_{i\alpha}^{(0)}$. For each $C_{i\alpha}^{(0)}$ we get f solutions $C_{i\alpha\beta}^{(0)}$ ($\beta = 1, 2, ..., f$). The wave function is determined from (15.49), taking into account that the sum on k drops out since according to (15.52b) for $k \neq i$ the coefficients $C_{k\alpha}^{(0)}$ are equal to zero:

$$\psi_{i\alpha}^{(0)} = \sum_{\beta=1}^{f} C_{i\alpha\beta}^{(0)} \psi_{i\beta}^{0} . \quad (15.57)$$

To 0th order approximation the eigenfunctions of the perturbed degenerate states are a linear combination of the eigenfunctions of the unperturbed states.

15.4* THE STARK EFFECT

As an example of the splitting of the degenerate levels we shall consider the H atom in an electric field. Experiments show that under the influence of an electric field, the spectral lines of an atom split. This phenomenon was first noticed by Stark in 1913 (he observed the splitting of Balmer lines in an electric field of a strength $\mathscr{E} = 1\,000\,000$ V/m) and it is called the Stark effect.

The experiments have shown that the influence of the electric field on hydrogen and other atoms depends on the electric field strength. Moreover, the result of this influence is different for hydrogen and other atoms. *The energy levels of H atom in weak field* $\mathscr{E}$ *split proportionally to the first power of* $\mathscr{E}$ (*i.e.* $\propto \mathscr{E}$; *this is so-called linear Stark effect*) *but those of all other atoms - proportionally to the second power of the* $\mathscr{E}^2$ *(i.e.* $\propto \mathscr{E}^2$; *this is the so-called quadratic Stark effect).* Physically this difference can be easily understood. The electric dipole moment **d** of the hydrogen atom is different than zero. The electric field $\boldsymbol{\mathscr{E}}$ interacts with the dipole and it receives an additional energy $\Delta E = \mathbf{d}\boldsymbol{\mathscr{E}}$. Typically, in the multielectron atom there is not a degeneracy in l and the average dipole moment is zero. Therefore the Stark effect is not observed in weak electric fields. In strong fields, however, the atoms are polarized and the induced dipole moment is proportional to the $\mathscr{E}$, i.e. $d \propto \mathscr{E}$. The energy is proportional to $\mathscr{E}^2$, i.e. $\Delta E = \mathbf{d}\boldsymbol{\mathscr{E}} \propto \mathscr{E}^2$ as a result of the interaction of the field with this induced dipole moment.

The Stark effect is inexplicable in the framework of classical theory. Only quantum mechanics can give an explanation of this phenomenon. We shall treat in details the linear Stark effect for the second level of the H atom. The external electric field $\mathscr{E} \sim 10^8 \div 10^9$ V/m, which is necessary for the Stark effect, is much smaller than the inner field $\mathscr{E}_{\text{nucl}}$, caused by the nucleas of the H atom: $\mathscr{E}_{\text{nucl}} = ek_0 / a_o^2 \approx 5.10^{11}$ V/m. The potential energy W of the electron in the external field is treated as the perturbation. The states with $n = 2$ have an energy $E_2^0 = -R/4$ (the index "0" notices that there is no perturbation). These are the $2s$ - and $2p$ -states, which are described by the wave functions

$$\psi_{200}, \psi_{210}, \psi_{211} \text{ and } \psi_{21-1}. \tag{15.58}$$

The level E_2^0 is 4-fold degenerate. Using for convenience the designation from the previous sections, we set

$$\psi_{200} \equiv \psi_{21}^0, \quad \psi_{210} \equiv \psi_{22}^0, \quad \psi_{211} \equiv \psi_{23}^0, \quad \psi_{21-1} \equiv \psi_{24}^0. \tag{15.59}$$

In other words, we have labeled the functions of the degenerate states as $\psi_{i\alpha}^0$, where i=2, and $\alpha = 1, 2, 3, 4$. Using (14.40) and Table 14-1, we can express these functions in an explicit form:

$$\psi_{21}^0=\frac{1}{2\sqrt{2\pi a_0^3}}e^{-r/2a_0}\left(1-\frac{r}{2a_0}\right)\quad \psi_{23}^0=\frac{1}{4\sqrt{\pi a_0^3}}e^{-r/2a_0}\frac{r}{2a_0}\sin\theta e^{i\varphi},$$
$$\psi_{22}^0=\frac{1}{2\sqrt{2\pi a_0^3}}e^{-r/2a_0}\frac{r}{2a_0}\cos\theta,\quad \psi_{24}^0=\frac{1}{4\sqrt{\pi a_0^3}}e^{-r/2a_0}\frac{r}{2a_0}\sin\theta e^{-i\varphi}. \tag{15.60}$$

Before writing the secular equation for this system, we shall determine more accurately the perturbation operator. The electron of the hydrogen atom in homogeneous electric field along the *Z*-axis (the centre of the co-ordinate system coincides with the nucleus) acquires an additional potential energy $\Delta E = e\mathbf{r}\mathscr{E} = e\mathscr{E}z = e\mathscr{E}r\cos\theta$. Hence, its Hamiltonian is

$$\hat{H}=\frac{\hat{p}^2}{2m_e}+U(r)+e\mathscr{E}r\cos\theta=H^0+\lambda\hat{H}',$$
$$\lambda\hat{H}'\equiv e\mathscr{E}r\cos\theta. \tag{15.61}$$

For its matrix elements (see (15.51)) we can write:

$$W_{\alpha,\beta}\equiv\lambda H_{2\alpha,2\beta}=\frac{e\mathscr{E}}{16\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi_{2\alpha}^{0*}e\mathscr{E}r\cos\theta\psi_{2\beta}^{0*}r^2\sin\theta drd\theta d\varphi,$$
$$\alpha,\beta=1,2,3,4. \tag{15.62}$$

At the integration over the polar angle φ leads to zero for all integrals with different magnetic quantum numbers because of the orthonormality of the wave functions on φ. From all matrix elelments only W_{12} and W_{21} are different than zero, i.e. those which contain in their integrands the states with magnetic quantum number $m=0$, namely ψ_{21}^0 and ψ_{22}^0. As the functions ψ_{21}^0 and ψ_{22}^0 are real, these two matrix elements are equal:

$$W_{12}=W_{21}=\frac{e\mathscr{E}}{16\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}e^{-r/a_0}\left(1-\frac{r}{2a_0}\right)\frac{r^4}{a_0^4}\cos^2\theta\sin\theta drd\theta d\varphi=-3e\mathscr{E}a_0. \tag{15.63}$$

The final result is obtained after the 5-fold integration by parts over *r* (the integration over φ and θ is trivial).

After taking into account this result and the zeros for the remaining matrix elements, the secular equation reduces to the following:

$$\Delta(E)=\begin{vmatrix} E_2-E & W_{21} & 0 & 0 \\ W_{12} & E_2-E & 0 & 0 \\ 0 & 0 & E_2-E & 0 \\ 0 & 0 & 0 & E_2-E \end{vmatrix} \tag{15.64}$$
$$=(E_2-E)^2\left[(E_2-E)^2-W_{12}{}^2\right]=0.$$

This equation has 4 roots:

$$\begin{aligned} &E_{21}\equiv E_+ = E_2^0-3e\mathscr{E}a_0, \\ &E_{22}\equiv E_- = E_2^0+3e\mathscr{E}a_0, \\ &E_{23}=E_3=E_4^0=E_2^0. \end{aligned} \tag{15.65}$$

The degeneracy is partly removed - only in *l.* For example, consider the state with fixed l for the above system with $l=1$. Then, substituting the functions ψ_{22}^0, ψ_{23}^0 and ψ_{24}^0 into (15.61) we see that all matrix elements $W_{\alpha\beta}$, which in this case strongly depend on the magnetic number *m,* are equal to zero. From physical point of view the partial removal of the degeneracy could be expected for the following reason. Without an electric field unperturbed Hamiltonian is spherically symmetric. Namely, the degeneracy is due to this symmetry. The perturbation posseses an axial symmetry over the elctrical-field vector $\mathscr{E}$, i.e. along the axis *Z.* The perturbation does not remove entirely the symmetry and part of the degeneracy remains.

In Fig. 15-1 are shown both the splitting of the level $n=2$ and of the

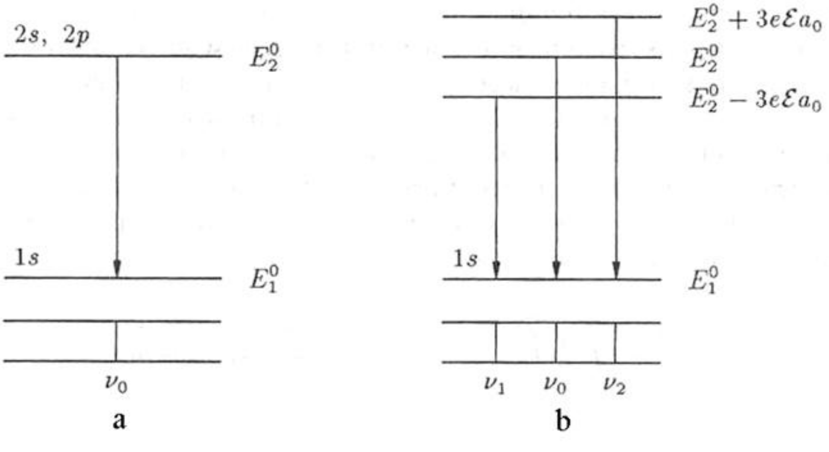


Figure 15-1. Splitting of the level n = 2 of the H atom in an electric field $\mathscr{E}$. As a consequence the Stark effect is observed - the splitting of the spectral line: a) without an electric field, b) with a constant elctric field.

resonance Lyman line. The energy level E_2^0 splits in three sublevels and the resonance line in three lines , which is the Stark effect.

The condition (15.45) for the applicability of perturbation theory is satisfied even for a very strong field. For example, for $\mathscr{E} = 10^9$ V/m we have $\Delta E = 3a_0 e\mathscr{E} \approx 3.10^{-1}\,\text{eV}$. At the same time $E_2^0 - E_1^0 \approx 10\,\text{eV}$ and, consequently, $\Delta E << E_2^0 - E_1^0$, which is the condition of applicability in this case.

SUMMARY

A function $\psi(x)$ can always be expanded over a complete set of eigenfunctions $\psi_k(x)$ of an operator $\hat{M}$:

$$\psi(x) = \sum C_{M_k} \psi_k(x).$$

The set of coefficients C_k completely determines the function $\psi(x)$. Therefore we can use these coefficients instead of the function $\psi(x)$. We say that the set C_k is the function $\psi(x)$ in *M*-representation. An arbitrary function $\psi(x)$ in *M*-representation is a one column matrix, whose elements are superposition coefficients in the expansion of $\psi(x)$ over the eigenfunctions of the operator $\hat{M}$ of the quantity *M*. The eigenfunctions of the operator in an eigenrepresentation are always δ -function.

Not only the functions, but also the operators can be given in different representations. Operator $\hat{N}$ in *M*-representation is given by a matrix, whose elements are determined in the following way:

$$\int_{-\infty}^{\infty} \psi_i^*(x) \hat{N} \psi_k(x) dx \equiv N_{ik}.$$

Here $\psi_i(x)$ and $\psi_k(x)$ are eigenfunctions of the operator $\hat{M}$.

In eigenrepresentation the operator matrix is diagonal and the values of its elements are equal to the eigenvalues of the operator.

Very often the Hamiltonian of a quantum system can be represented as a sum of two operators:

$$\hat{H} = \hat{H}^0 + \lambda H',$$

where λ is a small parameter. The operator $\lambda\hat{H}'$ is called a perturbation operator and the operator $\hat{H}^0$ - an unperturbed Hamiltonian. The theory for the determination of the total-Hamiltonian's approximate eigenfunctions is called perturbation theory. The perturbation method is applicable if the matrix elements of the perturbation operator are small with respect to the distance between the corresponding levels of the unperturbed system:

$$\lambda\frac{H'_{mi}}{E_i^0 - E_m^0} << 1.$$

Perturbation theory shows that in the first order approximation the perturbed ith state is described by all eigenfunctions ψ_k^0 of the unperturbed Hamiltonian:

$$\psi_i = \psi_i^0 + \lambda\left(C_i^{(1)}\psi_i^0 + \sum_{m\neq i}\frac{H'_{mi}}{E_i^{(0)} - E_m^0}\psi_m^0 \right).$$

(The unperturbed state is described by the function ψ_i^0.) Its energy is changed by a small correction $\lambda H'_{ii}$

$$E_i = E_i^{(0)} + \lambda H'_{ii} = E_i^0 + \int \psi_i^{0*}\lambda\hat{H}'\psi_i^0 dV.$$

For a degenerate system under the influence of perturbation the degenerate level E_i^0 is split in sublevels. The perturbation removes the degeneracy fully or partly. A degenerate system has always some degree of symmetry. This symmetry is characteristic also for its Hamiltonian. In the most general case perturbations do not posses such symmetry. Therefore, the influence of the perturbation on the different states of the degenerate system is not the same. A result of this perturbation influence is the splitting of the degenerate levels. If the perturbation does not have any symmetry the degeneracy is fully removed. If its symmetry is of lower degree than the system, the removal is partial. If its symmetry is the same as the system the degeneracy remains.

When an atom (for example hydrogen) is located in electric field $\mathscr{E}$ the last plays a role of a perturbation. Without electric field unperturbed Hamiltonian of the atom is spherically symmetric and its states are degenerate. The perturbation posseses the axial symmetry along the vector of the electric field $\mathscr{E}$. Due to the electric field the degenerate levels split and the degeneracy is partly removed. This splitting is known as Stark effect.

QUESTIONS

1. What does it mean to have a function in different representations?
2. How does a function look in *A*-representation?
3. What does an eigenrepresentation mean?
4. What are the wave eigenfunctions of a state of a continuous physical variable in an eigenrepresentation?
5. Give the operator $\hat{N}$ in *M*-representation.
6. What is the form of an operator in an eigenrepresentation?
7. What is the essence of perturbation theory?
8. How do we determine the solution of the perturbed Schrodienger equation?
9. What is the criterion of validity of perturbation theory?
10. What is the change of the energy levels of a nondegenerate state and a degenerate state within the first order approximation?
11. What is the change of the wave function of a non-degenerate state and a degenerate state in first order approximation in the presence of a perturbation?
12. How does a perturbation influence the degeneracy of a system?
13. What is the Stark effect?
14. How does the level $n = 2$ of the H-atom split in electric field?
15. How does the Stark effect in the hydrogen and other atoms differ?
16. Why does the electric field remove only partly the degeneracy of the hydrogen?
17. Starting from the interaction between a dipole and an electric field, explain physically why the matrix elements of the state $m \neq 0$ for the linear Stark effect are equal to zero.

PROBLEMS

1. Determine in the energy representation the Hamilton operators of: a) a particle in an infinite square potential well; b) a quantum rotator; c) a quantum harmonic oscillator; d) a hydrogen atom.
2. The H atom in its ground state is in constant homogeneous electric field $\mathscr{E}$, which is directed along the *Z*-axis. Prove that with an accuracy within the first order approximation the energy of the ground state is not changed.
3. The energy of interaction between an electric dipole with a dipole moment **d** and an electric field is $E = -\mathbf{d}\boldsymbol{\mathscr{E}}$. Using the result of Section 15.4, determine the dipole moments of the states with energies E_+ and E_- (15.65).

4. Find the wave functions of the perturbed levels with energy E_+ and E_- (15.65) of the hydrogen atom in electric field.
5. Find the correction ΔE to the energy E_1 of the ground state of the hydrogen-atom electron, which is due to the gravitational interaction between the proton and the electron. Determine the relation $\Delta E / E_1$.

Chapter 16

SPIN

SUGGESTED READING

1. W. Greiner, Quantum Mechanics, An Introduction, Vol. 1, Springer-Verlag, 1989, Chapters 12.
2. Messiah, A., Quantum Mechanics, Vol. 2, John Wiley & Sons, 1968, Chapter XIII- Section I, IV, V - §24÷§26.
3. Blokhintsev, D. I., Principles of Quantum Mechanics, Allyn and Bacon, 1964, § 58÷60.

16.1 SPIN, SPIN MATRICES AND SPIN FUNCTIONS

In classical mechanic we have been persuaded that an electron with an orbital angular momentum **L** has a magnetic dipole moment **μ**. Due to this magnetic moment an electron interacts with a magnetic field. It is logical to expect that an electron with an orbital angular momentum equal to zero, $l=0$, will not interact with a magnetic field. This is true both for a free electron and an electron in an atom in *s*-state. In 1922 Otto Stern and Walter Gerlach conducted an experiment, whose results were unexpected. Their experimental scheme is shown in Fig. 16-1. A beam of Ag atoms passes through an inhomogeneous magnetic field. The outer electrons of the atoms are in *s*-state. Their orbital angular momentum is zero (the total orbital angular momenta of the remain electrons, which form a completely filled subshell, is equal to zero - this question is discussed in detail in Chapter 19). After passing through the inhomogeneous magnetic field the electron beam

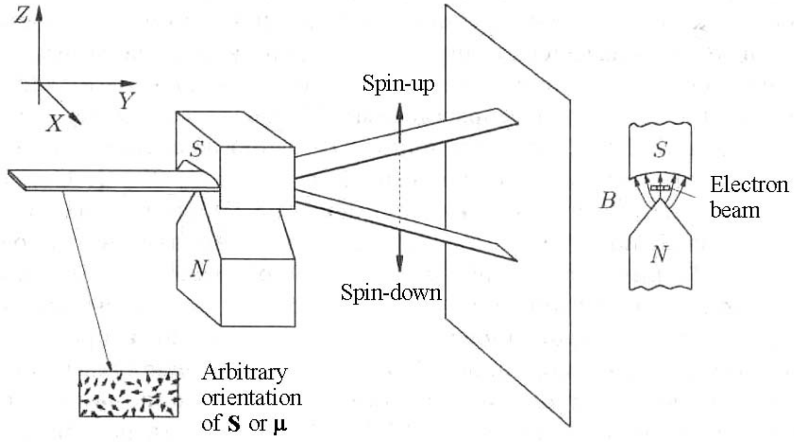


Figure 16-1. The Stern-Gerlach experiment.

is registered by the screen on which two bright traces are observed. This experimental result could not be explained with the known until then quantum-mechanics methods. It was clear that something is not accounted for.

Another experimental result confirmed this doubt. An observation with a sensitive apparatus proved that many spectral lines are actually doublets. Instead of the Lyman line, a double line is observed (see Fig. 17-8). The transition of the first excited level of Na to the ground state ($3p \to 3s$; see Fig. 17-9) leads not to a single line but to a well known yellow doublet, consisting of two very close lines 5890 Å and 5896 Å. The distance $\Delta\lambda$ between the lines is very small in comparison to the wave length λ, i.e. $\Delta\lambda / \lambda \sim 10^{-3}$. When we obtained the energy levels (Chapter 13) we accounted for the electrostatic interaction between the nucleus and the electron, but not for the magnetic one. The interaction energy of the nuclear electric and the magnetic fields with the electrons are of the order $v / c \sim 10^{-3}$ (v is the electron velocity), i.e. of the order $\Delta\lambda / \lambda$. It is logical to assume that the line splitting is due to the magnetic interaction.

Both the effect of Stern-Gerlach and the doublet lines can be explained if the electron in s-state possesses another (besides the orbital) angular momentum. These facts and several other experimental results motivated Goudsmit and Uhlebeck in 1925 to hypothesize that *every electron has, in addition to the orbital angular momentum L, an intrinsic angular momentum S* (*spin*). The picture is analogous to the motion of the Earth - it has an orbital angular momentum, because of the rotation around the Sun and an intrinsic angular momentum, because of its spinning about its own axis. The spin of electron is a quantum quantity which has no the classical analog.

The intrinsic angular momentum of the electron is an inner characteristic It cannot be taken away, like its charge *e*. This intrinsic characteristic has vector property - it may have different orientations. Judging by the experimental results of Stern and Gerlach, the spin can have two components over the *Z*-axis (over the physically given direction). The spin is mechanical moment of the momentum. Because of this its mathematical description is equivalent to the formalism of the orbital angular momentum (we shall underline that every quantum mechanical moment obeys this formalism). *The number analogous to the orbital number l defines the spin magnitude - this quantum number s is called a spin quantum number*. The number of the components of **L** is equal to $2l+1$. Consequently, taking into account the result of the Stern-Gerlach experiment for the component number of **S**, we obtain $2s+1=2$. From here we determine the spin quantum number $s=1/2$. Unlike the orbital number *l*, which is an integer, the spin number is half-integer. (In general, from the equality $2a+1=k$ it is clear that for an odd *k* (odd number of components) the number a is an integer and for an even k (even number of components) a is half-integer.) The components are defined by the magnetic spin number m_s (an analog of the orbital number m). It takes the values from $-s$ to $+s$ through the unity, i.e. $m_s = \pm 1/2$. For *the magnitude of the spin and its components over the Z-axis* we can write

$$\begin{aligned} &S = \hbar\sqrt{s(s+1)} = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \frac{\hbar}{2}\sqrt{3}, \\ &S_z = m_s\hbar = \pm\frac{\hbar}{2}. \end{aligned} \tag{16.1}$$

The spin is described by the operator $\hat{\mathbf{S}}$, which has three components: $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$. Two allowed orientations of the spin vector are shown in Fig. 16-2a. Similarly to the orbital angular momentum the quantities S^2 and S_z are compatible, while $\hat{S}_x$ and $\hat{S}_y$ are incompatible (Fig. 16-2b).

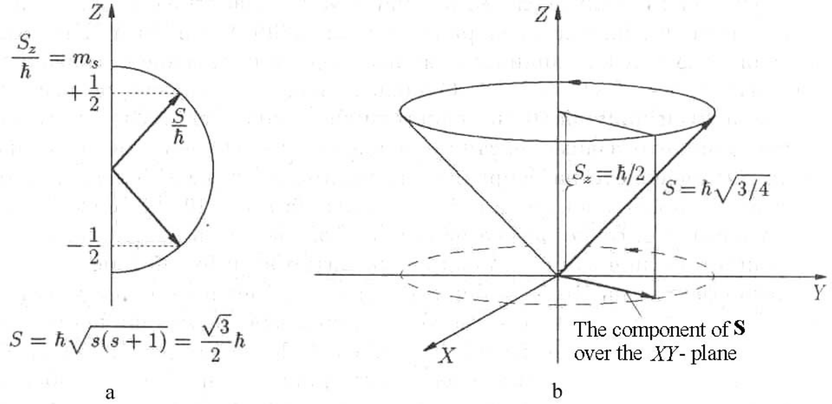


Figure 16-2. The vector diagram (a) and the vector interpretation of the electron spin (b). Two orientations of the spin are allowed; the magnitudes of the spin S and of the component S_z are determined, while S_x and S_y can vary.

The characteristic feature of one angular momentum operator is its commutation with the operators of its components. Therefore the operators $\hat{S}^2, \hat{S}_x, \hat{S}_y$ and $\hat{S}_z$ obey the same commutation relations as the operators $\hat{L}^2, \hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ do.

The analogy between the spin and the orbital angular momentum allows us to write the following:

Orbital angular momentum	Spin angular momentum	
$\hat{\mathbf{L}}\,(\hat{L}_x, \hat{L}_y, \hat{L}_z),$	$\hat{\mathbf{S}}\,(\hat{S}_x, \hat{S}_y, \hat{S}_z),$	
$L = \hbar\sqrt{l(l+1)},$	$S = \hbar\sqrt{s(s+1)},$	
$l = 0,\ 1,\ 2, ...,$	$s = 1/2,$	
$L_z = m\hbar,$	$S_z = m_s\hbar,$	
m- magnetic number,	m_s- magnetic spin number	
$m = 0,\ \pm 1,\ \pm 2, ...,$	$m_s = \pm 1/2$	(16.2)
$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2,$	$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,$	
$[\hat{L}^2 \hat{L}_{x_j}] = 0,\ x_j = x,\ y,\ \mathrm{z},$	$[\hat{S}^2 \hat{S}_{x_j}] = 0,\ x_j = x,\ y,\ \mathrm{z},$	
$[\hat{L}_x \hat{L}_y] = i\hbar \hat{L}_z,$	$[\hat{S}_x \hat{S}_y] = i\hbar \hat{S}_z,$	
$[\hat{L}_z \hat{L}_x] = i\hbar \hat{L}_y,$	$[\hat{S}_z \hat{S}_x] = i\hbar \hat{S}_y,$	
$[\hat{L}_y \hat{L}_z] = i\hbar \hat{L}_x,$	$[\hat{S}_y \hat{S}_z] = i\hbar \hat{S}_x.$	

According to the shown analogy the operator of the *z*-component of spin $\hat{S}_z$ has two eigenvalues: $\hbar/2$ and $-\hbar/2$. According to the representation theory (Section 15.1) the operator $\hat{S}_z$ in eigenrepresentation (see (15.15) has the following form:

$$\hat{S}_z = \|S_z\| = \begin{vmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{vmatrix}. \tag{16.3}$$

In the same S_z-representation the $\hat{S}_x$ and $\hat{S}_y$ are written as follows:

$$\hat{S}_x = \|S_x\| = \begin{vmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{vmatrix}, \quad \hat{S}_y = \|S_y\| = \begin{vmatrix} 0 & -i\frac{\hbar}{2} \\ i\frac{\hbar}{2} & 0 \end{vmatrix}. \tag{16.4}$$

Very often the matrices $\|\sigma_x\|$, $\|\sigma_y\|$ and $\|\sigma_z\|$ are used instead of the matrices (16.3) and (16.4), which are connected with the corresponding operators in the following way:

$$\hat{S}_{xj} = \frac{\hbar}{2}\hat{\sigma}_{xj}, \quad x_j = x, y, z. \tag{16.5}$$

Comparing (16.5) with (16.3) and (16.4) we obtain

$$\hat{\sigma}_x = \|\sigma_x\| = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad \hat{\sigma}_y = \|\sigma_y\| = \begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix}, \quad \hat{\sigma}_z = \|\sigma_z\| = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}. \tag{16.6}$$

These are called *Pauli matrices*.

Until now we have described the state of an atom electron by the wave function $\psi_{nlm}(x, y, z)$ or equivalently, by the three quantities E, L^2 and L_z. The discovery of the intrinsic angular momentum S of the electron shows that it has a fourth degree of freedom. Its state can be characterized by the fourth quantities E, L^2, L_z and S_z, correspondingly by the quantum numbers n, l, m and m_s. They form a complete set of physical quantities. As S is singly expressed by S_z (this is not the case for the orbital angular momentum) the giving of S_z defines S and generally speaking the spin state. Then the wave function will depend on one more argument S_z:

$$\psi = \psi_{nlmm_s}(x, y, z, S_z). \tag{16.7}$$

The spin variable has only two values $\hbar/2$ and $-\hbar/2$ and therefore we could say that instead of the function (16.7) there are two wave functions. Commonly they are represented as a column matrix:

$$\psi = \begin{vmatrix} \psi_1 \\ \psi_2 \end{vmatrix}, \qquad \begin{aligned} \psi_1 &= \psi\left(x, y, z, \frac{\hbar}{2}\right), \\ \psi_2 &= \psi\left(x, y, z, -\frac{\hbar}{2}\right). \end{aligned} \tag{16.8}$$

The energy of the spin motion is negligible compared to the orbital motion. This allows us to consider both motions independently and to present the function (16.7) as a product of the coordinate wave function $\psi_{nlm}(x, y, z)$ and the spin function $X(S_z)$:

$$\psi = \psi_{nlmm_s}(x, y, z, S_z) = \psi_{nlm}(x, y, z) X(S_z). \tag{16.9}$$

We can write an analogous equality for the functions ψ_1 and ψ_2 in (16.8). They differ by the spin functions: $X_+(S_z)$, for the spin-up (further we shall call it the positive orientation of the spin - $S_z = \frac{\hbar}{2}$) and $X_-(S_z)$, for the spin-down (further we shall call it the negative orientation of the spin - $S_z = -\frac{\hbar}{2}$):

$$\begin{aligned} \psi_1 &= \psi\left(x, y, z, {}^{h}\!/_{2}\right) = \psi_{nlm}(x, y, z)X_+(S_z), \\ \psi_1 &= \psi\left(x, y, z, -{}^{h}\!/_{2}\right) = \psi_{nlm}(x, y, z)X_-(S_z). \end{aligned} \tag{16.10}$$

The functions $X_\pm(S_z)$ are eigenfunctions of the operator $\hat{S}_z$:

$$\begin{aligned} &\hat{S}_z X(S_z) = m_s \hbar X(S_z), \\ &m_s = \frac{1}{2}, \quad S_z = \frac{h}{2}, \quad X(S_z) = X_+(S_z), \\ &m_s = -\frac{1}{2}, \quad S_z = -\frac{h}{2}, \quad X(S_z) = X_-(S_z). \end{aligned} \tag{16.11}$$

If the electron is in a state described by the wave function ψ_1, the probability to measure a spin $S_z = \hbar/2$ is equal to unity, and a spin $S_z = \hbar/2$ - to zero. Taking into account that the function $\psi_{nlm}(x, y, z)$ is normalized we easy obtain

$$\begin{aligned} W\left(S_z = +\frac{h}{2}\right) &= \left|X_+\left(\frac{\hbar}{2}\right)\right|^2 \int_{-\infty}^{+\infty} \left|\psi_{nlm}(x, y, z)\right|^2 dV = \left|X_+\left(\frac{\hbar}{2}\right)\right|^2 .1 = 1, \\ W\left(S_z = -\frac{h}{2}\right) &= \left|X_+\left(\frac{\hbar}{2}\right)\right|^2 \int_{-\infty}^{+\infty} \left|\psi_{nlm}(x, y, z)\right|^2 dV = \left|X_+\left(-\frac{\hbar}{2}\right)\right|^2 .1 = 0. \end{aligned} \tag{16.12}$$

This, together with similar considerations for $X_-(S_z)$, allows us to write

$$\begin{aligned} &X_+\left(\frac{\hbar}{2}\right) = 1, \quad X_+\left(-\frac{\hbar}{2}\right) = 0, \\ &X_-\left(+\frac{\hbar}{2}\right) = 0, \quad X_-\left(-\frac{\hbar}{2}\right) = 1. \end{aligned} \tag{16.13}$$

The eigenfunctions $X_+(S_z)$ and $X_-(S_z)$ of the operator $\hat{S}_z$ can be used as a basis. For such a basis the expansion (15.5) for $X_+(S_z)$ and $X_-(S_z)$ takes the following form:

$$\begin{aligned} X_+(S_z) &= \sum_k C_k X_k(S_z) = 1.X_+(S_z) + 0.X_-(S_z), \\ X_-(S_z) &= \sum_k C_k X_k(S_z) = 0.X_+(S_z) + 1.X_-(S_z). \end{aligned} \tag{16.14}$$

Hence, according to (15.6) the functions $X_+(S_z)$ and $X_-(S_z)$ in S_z-representation can be written as follows:

$$\left\| X_+(S_z) \right\| = \begin{vmatrix} 1 \\ 0 \end{vmatrix}, \quad \left\| X_-(S_z) \right\| = \begin{vmatrix} 0 \\ 1 \end{vmatrix}. \tag{16.15}$$

Very often they are written in the form of the Pauli matrices (16.6)

$$\left\| X_+(S_z) \right\| = \begin{vmatrix} 1 & 0 \\ 0 & 0 \end{vmatrix}, \quad \left\| X_-(S_z) \right\| = \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix}. \tag{16.16}$$

and are called *spinors*.

16.2 ADDITION OF ANGULAR MOMENTA IN QUANTUM MECHANICS

In the previous section we established that the electron has two angular momenta: **L** and **S**. It is natural to pose the question for its total angular momentum, which is a sum of both angular momenta. But for the sum of two angular momenta, because of their quantum character (more accurately said, because of their space quantization), we cannot use the rule for summation of two vectors from classical mechanics. Therefore, first we shall establish the rules for summation of two orbital angular momenta $\mathbf{L}_1$ and $\mathbf{L}_2$ in quantum mechanics.

In classical mechanics the total angular momentum **L** is a vector sum of $\mathbf{L}_1$ and $\mathbf{L}_2$ (Fig. 16-3).

In quantum mechanics the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ can accept only discrete directions. Depending of their orientation in space we obtain different orientations and correspondingly different magnitudes of the total vectors **L**.

In addition, the total vector $\mathbf{L}$ also cannot be arbitrary oriented, but its

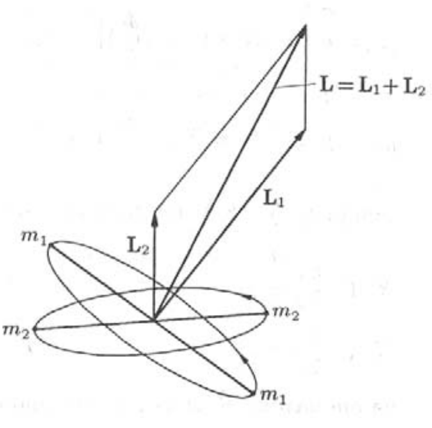


Figure 16-3. The classical addition of the angular momenta. The addition of the both vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ gives the resultant vector $\mathbf{L}$.

components over the Z-axis must be integer multiples of $\hbar$. So, we add the angular momentum $\mathbf{L}_1$ with quantum numbers l_1 and m_1 to the angular momentum $\mathbf{L}_2$ with quantum numbers l_2 and m_2 and expect to obtain the angular momentum $\mathbf{L}$ with quantum numbers l and m:

$$\begin{aligned} &l_1 : L_1 = \hbar\sqrt{l_1(l_1+1)}, && L_{1z} = m_1\hbar, && m_1 = -l_1, -l_1+1, \ldots, 0, \ldots, l_1, \\ &l_2 : L_2 = \hbar\sqrt{l_2(l_2+1)}, && L_{2z} = m_2\hbar, && m_2 = -l_2, -l_2+1, \ldots, 0, .., l_2, \\ &l : L = \hbar\sqrt{l(l+1)}, && L_z = m\hbar, && m = -l, -l+1, \ldots, 0, \ldots, l. \end{aligned} \tag{16.17}$$

Let us try to connect the unknown l and m with the given l_1, l_2, and m_1, m_2. We shall note that the maximum possible projection of an orbital angular momentum with the quantum number l is

$$L_{z_{\max}} = m_{\max}\hbar = l\hbar. \tag{16.18}$$

We have already underlined that depending on the orientation of $\mathbf{L}_1$ and $\mathbf{L}_2$ the different total vectors are obtained. First, we shall determine among them these with maximal and minimal magnitudes $\mathbf{L}_{\max}$ and $\mathbf{L}_{\min}$. Orient the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ in a way to have maximal projections over the Z-axis. If these projections are with equal directions the sum $\mathbf{L}_1 + \mathbf{L}_2$ will determine the vector **L** with the maximal magnitude $\mathbf{L}_{\max}$. If the projections are with opposite directions the sum $\mathbf{L}_1 + \mathbf{L}_2$ will determine the vector **L** with the minimal magnitude $\mathbf{L}_{\min}$. Every other combination of possible orientations of the two angular momenta $\mathbf{L}_1 + \mathbf{L}_2$ will give the total vector with a magnitude lower than $\mathbf{L}_{\max}$ and larger than $\mathbf{L}_{\min}$.

Let's find the maximal projection $L_{\max z_{\max}}$ of the vector $\mathbf{L}_{\max}$, which is a sum of maximal projections $L_{1 z_{\max}}$ and $L_{2 z_{\max}}$ of the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ (Fig. 16-4):

$$L_{\max z_{\max}} = L_{1 z_{\max}} + L_{2 z_{\max}}. \tag{16.19}$$

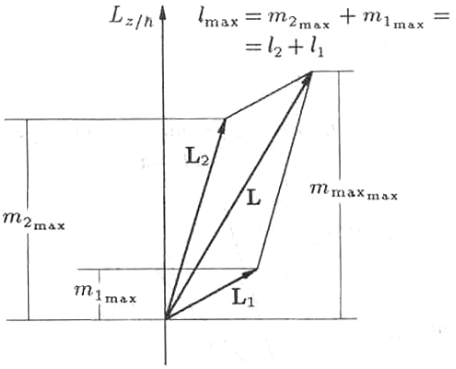


Figure 16-4. Adding of $\mathbf{L_1}$ and $\mathbf{L_2}$, oriented so that their projections over *Z*-axis are maximal and with equal directions, we obtain the maximal possible angular momentum $\mathbf{L}_{\max}$. This angular momentum with the orbital number $l_{\max} = l_1 + l_2$ can have $2l_{\max}+1$ orientations with respect to the *Z*-axis.

According to (16.18) these projections can be determined by the orbital quantum numbers:

$$\begin{aligned} L_{\max z_{\max}} &= m_{\max_{\max}}\hbar = l_{\max}\hbar, \\ L_{1 z_{\max}} &= m_{1_{\max}}\hbar = l_1\hbar, \\ L_{2 z_{\max}} &= m_{2_{\max}}\hbar = l_2\hbar. \end{aligned} \tag{16.20}$$

After substituting these values in (16.19) we obtain

$$L_{\max z_{\max}} = l_{\max}\hbar = (l_1 + i_2)\hbar \Rightarrow l_{\max} = l_1 + l_2. \tag{16.21}$$

The resultant vector $\mathbf{L}_{\max}$ is an orbital angular momentum and it can be oriented in $2l_{\max}+1$ different ways with respect to the *Z*-axis. Hence, the magnitude of the vector is

$$L_{\max} = \hbar\sqrt{l_{\max}\left(l_{\max}+1\right)}, \quad l_{\max} = l_1 + l_2 . \tag{16.22}$$

Now, let's determine the minimal summed up vector $\mathbf{L}_{\min}$, which as we have already mentioned, is obtained when $\mathbf{L}_1$ and $\mathbf{L}_2$ have maximal, but oppositely oriented projections. Its maximal projection $L_{\min\, z_{\max}}$ over *Z*-axis (Fig. 16-5) is

$$\begin{aligned} L_{\min\, z_{\max}} &= L_{2\, z_{\max}} - L_{1\, z_{\max}}, \\ l_{\min}\hbar &= m_{2_{\max}}\hbar - m_{1_{\max}}\hbar. \end{aligned} \tag{16.23}$$

Substituting (16.18) in the right-hand side of the last equality, we deter mine the orbital number $l_{\min}$ of the minimal orbital angular moment:

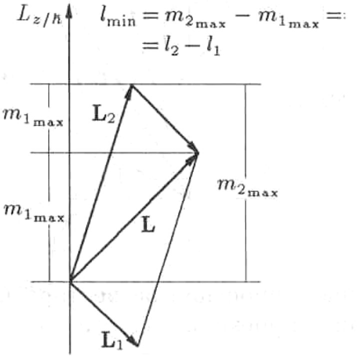


Figure 16-5. Adding $\mathbf{L}_1$ and $\mathbf{L}_2$, oriented so that their projections with respect to the *Z*-axis are maximal but with opposite directions, we obtain minimal possible total angular momentum $\mathbf{L}_{\min}$ with orbital number $l_{\min} = l_1 + l_2$, which can have $2l_{\min}+1$ orientations with respect Z-axis.

$$l_{\min} = l_2 - l_1 . \tag{16.24}$$

For our discussion we choose $l_2 > l_1$ (see Fig. 16-4 and Fig. 16-5). If $l_1 > l_2$ instead of (16.24) we can write $l_{\min} = l_1 - l_2$. It is clear that in the general case we shall write

$$l_{\min} = |l_2 - l_1| . \tag{16.25}$$

All other possible orientations of $\mathbf{L}_1$ and $\mathbf{L}_2$ give the remaining total angular momenta **L** with orbital numbers *l*, whose values are integers in the interval $l_{\min} \div l_{\max}$, i.e.

$$\begin{aligned} l &= l_1 - l_2, l_1 - l_2 + 1, \; l_1 - l_2 + 2, \ldots, \; l_1 + l_2, \\ l &= l_2 - l_1, l_2 - l_1 + 1, \; l_2 - l_1 + 2, \ldots, \; l_1 + l_2. \end{aligned} \tag{16.26}$$

Adding two quantum mechanical moments with orbital numbers l_1 and l_2 we obtain $2l_1 + 1$ (for $l_1 < l_2$) or $2l_2 + 1$ (for $l_2 < l_1$) different total moments.

Let us summarize: *adding two quantum angular momenta with orbital numbers* l_1 *and* l_2 *we obtain different angular momenta with the quantum numbers l, which have values*

$$|l_1 - l_2|, \quad |l_1 - l_2| + 1, \quad |l_1 - l_2| + 2, \; \ldots, \quad l_1 + l_2. \tag{16.27}$$

Constants of the system motion, whose parts have the angular momenta $\mathbf{L}_1$ and $\mathbf{L}_2$, are L^2, L_z, L_1^2 and L_2^2. Both components L_x and L_y and the *x* and *y*-components of $\mathbf{L}_1$ and $\mathbf{L}_2$ are indeterminated. The vector interpretation (Fig. 16-6) visually illustrates this. In the figure the vector **L** precesses

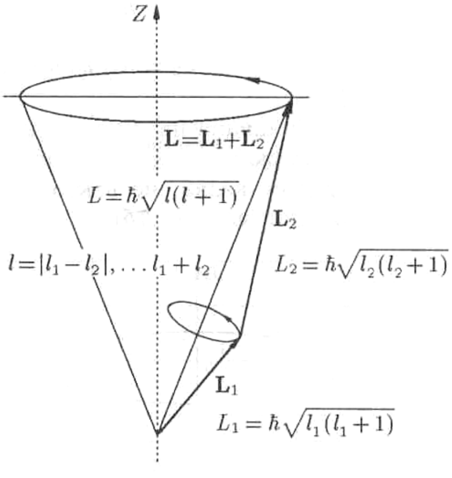


Figure 16-6. Vector interpretation of the sum $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ of two angular momenta - the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ precess around the vector $\mathbf{L}$, and $\mathbf{L}$ - around the axis Z.

about the *Z*-axis, because L and L_1 are determined; $\mathbf{L}_1$ and $\mathbf{L}_2$ precess about **L,** because L_1 and L_2 are determined, but all their components are undetermined.

16.3 TOTAL ANGULAR MOMENTUM

The electron has an orbital angular momentum **L** and a spin angular momentum **S**. From the summation of these momenta we obtain the total angular momentum of the electron, which is denoted as **J**:

$$\mathbf{L}+\mathbf{S}=\mathbf{J}\,. \tag{16.28}$$

According to the rule of quantization of angular momentum *the total angular momentum is*

$$J=\hbar\sqrt{j\left(j+1\right)} \tag{16.29}$$

and the number j, which is called total quantum number, takes values from $|l-s|$ *to* $|1+\mathrm{s}|$ *through the unity*, i.e.

$$\begin{aligned} &j=\frac{1}{2} \text{ for } l=0,\\ &j_1=l-\frac{1}{2}\,,\quad j_2=l+\frac{1}{2}\quad \text{for}\quad l\neq 0. \end{aligned} \tag{16.30}$$

The case $l=0$ is trivial - simply there is no summation (the one of the vectors is zero). In the general case we obtain two different total angular momenta with the corresponding quantum numbers

$$\begin{aligned} &J_1=\hbar\sqrt{j_1\left(j_1+1\right)},\quad j_1=l-\frac{1}{2},\\ &J_2=\hbar\sqrt{j_2\left(j_2+1\right)},\quad j_2=l+\frac{1}{2}. \end{aligned} \tag{16.31}$$

The angular momentum J_1 is obtained when the components of the vectors **L** and **S** are with opposite directions and the angular momentum J_2 when the components are with equal directions. One can say that in the sum J_2 the vectors **L** and **S** are parallel (Fig. 16-7a) and in the sum J_1 - antiparallel (Fig. 16-7b).

It can be shown strictly that J, J_z, L and S are constants of the motion. This is clear from the vector interpretation in Fig 16-7.

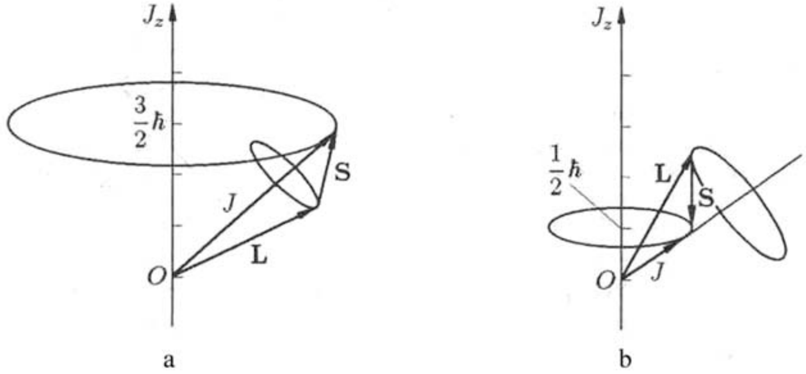


Figure 16-7. The total angular momentum of the electron has two values: a) J_2 (for $j_2=l+1/2$), when **L** and **S** are parallel; b) J_1 (at $j_1=l-1/2$), when **L** and **S** are antiparallel.

The components of the total angular momentum, similarly the orbital and spin angular momenta, *are determined by a number, which is called the total magnetic quantum number and denoted by* m_j:

$$J_z = m_j\hbar. \tag{16.32}$$

The possible values of m_j are from *-j* to *+j* through the unity. For m_{j_1} and m_{j_2} they are respectively (see (16.31))

$$\begin{aligned} m_{j_1} &= -\left(l-\frac{1}{2}\right), -\left(l-\frac{1}{2}\right)+1, \ldots, -\frac{1}{2}, +\frac{1}{2}, \ldots, \left(l-\frac{1}{2}\right), \\ m_{j_2} &= -\left(l+\frac{1}{2}\right), -\left(l+\frac{1}{2}\right)+1, \ldots, -\frac{1}{2}, +\frac{1}{2}, \ldots, \left(l+\frac{1}{2}\right). \end{aligned} \tag{16.33}$$

We shall note that the total angular momentum of an electron is half-integer and therefore has not a zero component (similarly to its spin angular moment.

Let's make a brief summary for the quantum numbers, which characterized the state of the electron in H-atom, using the results from the previous and present chapters. It is presented in Table 16-1.

Table 16-1. Quantum numbers and the corresponding physcal quantities

Notation	Quantum numbers	Values	Characterized quantity	Dependence of the quantity
n	principal	1, 2, 3, ...	E	$E_n = -\mathfrak{R}/n^2$
l	orbital	0, 1, 2, 3,..., n - 1	L	$L=\hbar\sqrt{l(l+1)}$
m	magnetic	-l, -l + 1,..., 0,..., l	L_z	$L_z = m\hbar$
s	spin	1/2	S	$S=\hbar\sqrt{s(s+1)}$
m_s	magnetic spin	-1/2, 1/2	S_z	$S_z = m_s\hbar$
j	total	l - 1/2, l + 1/2	J	$J=\hbar\sqrt{j(j+1)}$
m_j	total magnetic	-j, -j + 1,..., i1/2, 1/2, , j	J_z	$J_z = m_j\hbar$

In spectroscopy the electron state is denoted with so called terms, which are of the following kind:

$$\overset{2s+1}{n}\;L_j\,, \tag{16.34}$$

where L is the letter notation of the orbital quantum number: *S, P, D, F* etc. The origin of these letters is spectroscopic. In the analysis of the hydrogen spectrum we have seen that the spectral-line series are obtained from the transition to fixed level. Similar series were observed for the other elements even before quantum mechanics. The series were called: **s**harp *s*, **p**rincipal *p*, **d**iffuse *d,* **f**undamental *f* etc. With the development of quantum mechanics it became clear that these series correspond to the transitions to the states with corresponding orbital numbers: $s-0,\ \ p-1,\ \ d-2,\ \ f-3$ etc.

The number $2s+1$ in the term notation shows the multiplicity of the energy level.

Now, let us find the total angular momentum for two specific cases - the electron states with $l=0$ and $l=1$. For the state $l=0$ the quantum numbers and the angular momenta are as follows:

$$\begin{aligned} &l=0, \quad s=\frac{1}{2}, \qquad j=\frac{1}{2}, \qquad\qquad\qquad m_j=\pm\frac{1}{2}, \\ &L=0, \quad S=\frac{\hbar}{2}\sqrt{3}, \quad J=\hbar\sqrt{\frac{1}{2}\left(1+\frac{1}{2}\right)}=\frac{\hbar}{2}\sqrt{3}, \quad J_z=\pm\frac{\hbar}{2}. \end{aligned} \tag{16.35}$$

For $L=0$ the vector diagram does not differ from that in Fig. 16.2, which is expected - the total angular momentum coincides with spin. For the p-state we get

$$\begin{aligned} &l=1, \quad s=\frac{1}{2}, \quad j_1=\frac{1}{2}, \quad j_2=\frac{3}{2}, \quad m_{j1}=\pm\frac{1}{2}, \quad m_{j2}=\pm\frac{1}{2},\pm\frac{3}{2}, \\ &L=\hbar\sqrt{3}, \; S=\frac{\hbar\sqrt{3}}{2}, \; J_1=\frac{\hbar\sqrt{3}}{2} \; J_2=\frac{\hbar\sqrt{15}}{2}, \; J_{1z}=\pm\frac{\hbar}{2}, \quad J_{2z}=\pm\frac{\hbar}{2},\pm\frac{3\hbar}{2}. \end{aligned} \tag{16.36}$$

The terms of the states with quantum numbers j_1 and j_2 are ${}^2P_{1/2}$ and ${}^2P_{3/2}$. The vector diagrams of both terms are shown in Fig. 16-8.

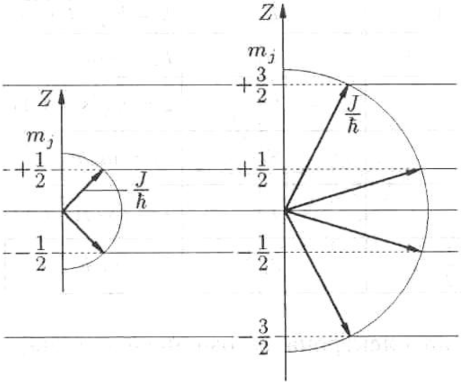


Figure 16-8. Vector diagrams of the total angular momentum of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ terms.

Both total angular momenta do not have a zero projection.

16.4 *LS* AND *JJ* COUPLING

In the atom of helium there are two electrons. The angular momenta are four: L_1, S_1 of the one electron and L_2, S_2 of the other electron. Their sum determines the total momentum of the system with two electrons. In classical mechanics the sum of the angular momentum vectors does not depend on their order. In quantum mechanics because of the specific rule for the summation of the angular momenta, due to their quantum character, the result depends on the order of the addition. The order of addition is determined by the nature of interaction between the electrons. If the energy of the interaction is small, the orbital motion of each of the electrons is practically not perturbed by the other and it may be considered as independent. Then, the orbital and spin angular momenta of each electron are added and the total angular momentum is a sum of the total momenta of both electrons:

$$\left.\begin{array}{l} \mathbf{L}_1 + \mathbf{S}_1 = \mathbf{J}_1 \\ \mathbf{L}_2 + \mathbf{S}_2 = \mathbf{J}_2 \end{array}\right\} \Rightarrow \mathbf{J}_1 + \mathbf{J}_2 = \mathbf{J}. \qquad (16.37)$$

Such kind of interaction is called *JJ coupling*. It is illustrated in Fig. 16-9. The electrons retain their independence and the vectors $\mathbf{L}_i$ and $\mathbf{S}_i$ of each of them precess about the corresponding total angular momentum $\mathbf{J}_i$. On the other hand, the total momentum precesses about *Z*-axis to satisfy the angular momentum uncertainty principle (not shown in the figure). The total angular momentum *J* and its *z*-component J_z are constants of the motion.

When the interaction between two electrons is very strong, the orbital angular momenta and the spin angular momenta unite separately in the vectors of the total orbital angular momentum **L** and the total spin angular momentum **S,** and then the last are summed to form the total angular momentum of the system:

$$\left.\begin{array}{l} \mathbf{L}_1 + \mathbf{L}_2 = \mathbf{L} \\ \mathbf{S}_1 + \mathbf{S}_2 = \mathbf{S} \end{array}\right\} \Rightarrow \mathbf{L} + \mathbf{S} = \mathbf{J}. \qquad (16.38)$$

This kind of interaction is called *LS coupling*. It is shown in Fig. 16-10.

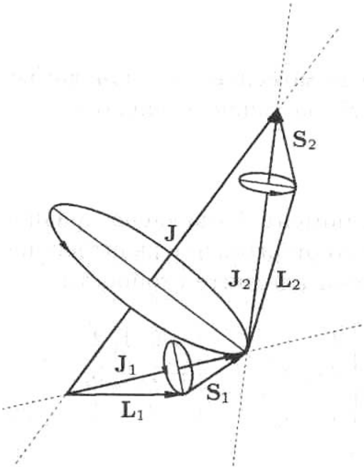


Figure 16-9. The scheme of the *JJ* coupling.

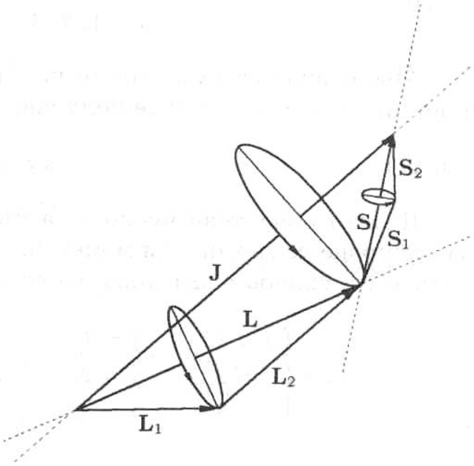


Figure 16-10. The scheme of the *LS* coupling.

The vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ precess about the vector **L** and the spin angular momenta $\mathbf{S}_1$ and $\mathbf{S}_2$ about **S.** On the other hand the angular momenta **L** and **S** precess about **J**, which in its turn precesses about the *Z*-axis. As in the *JJ* coupling, here J and J_z are constants of motion. This coupling is often called Russel-Sounders coupling by the names of its discoverers.

The *LS* coupling dominates in the atoms in the beginning and the middle of the periodic table. It is encountered more often. The *JJ* coupling dominates at the heavy elements.

We shall consider the *LS* coupling between two electrons, one in *p*-state and another in *d*-state. Addition of both angular momenta $\mathbf{L}_1$ and $\mathbf{L}_2$ with quantum numbers

$$l_1 = 1 \quad \text{and} \quad l_2 = 2, \tag{16.39}$$

according to the rule of summation of the mechanical moments (16.27) leads to an angular momenta with the following orbital numbers l

$$\begin{aligned} &l = |l_2 - l_1|, \ldots, l_1 + l_2, \\ &l = 1, 2, 3. \end{aligned} \tag{16.40}$$

Similarly, the addition of the spin angular momenta with the spin quantum numbers $s_1 = s_2 = 1/2$ leads to spin S with the spin numbers:

$$s = 0, 1. \tag{16.41}$$

The total quantum number j of the total angular momentum J according to the rule of a summation of mechanical moments, namely of the orbital angular momentum with a quantum number l (16.40) and the spin angular momentum with a number s, has the following values:

$$s = 0 \begin{cases} l = 1, & j = 1, \\ l = 2, & j = 2, \\ l = 3, & j = 3, \end{cases} \qquad s = 1 \begin{cases} l = 1, & j = 0, 1, 2, \\ l = 2, & j = 1, 2, 3, \\ l = 3, & j = 2, 3, 4. \end{cases}$$

In general 12 terms are obtained:

$$s = 0 \rightarrow {}^1P_1, {}^1D_2, {}^1F_3, \qquad s = 1 \rightarrow \begin{cases} {}^3P_0, & {}^3P_1, & {}^3P_2, \\ {}^3D_1, & {}^3D_2, & {}^3D_3, \\ {}^3F_2, & {}^3F_3, & {}^3F_4. \end{cases}$$

The vector interpretation of the *LS* coupling between two electrons, whose terms are $^3D_1$, $^3D_2$ and $^3D_3$, is illustrated in Fig. 16-11.

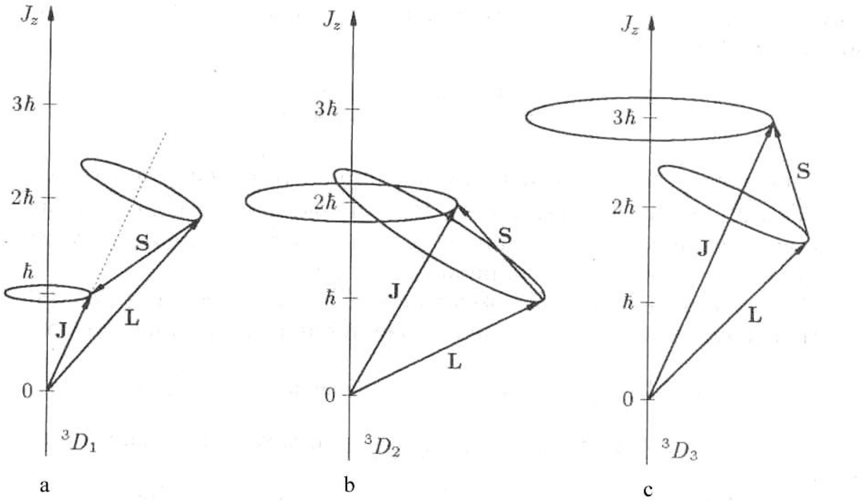


Figure 16-11. Vector model of the *LS* coupling for *D*-terms of two electrons: a) $^3D_1$; b) $^3D_2$; c) $^3D_3$.

We shall note that in Fig. 16-11 the terms $^3D_1$ and $^3D_3$ are obtained for the same orientation of **L** (with $m = 2$) and $^3D_2$ for a different orientation of **L** (with $m = 1$).

The term $^3D_2$ can be obtained also for an orientation with $m = 2$. In that case the vector of the spin angular momentum will have a zero projection, i.e. $m_s = 0$.

SUMMARY

To explain the results of the Stern-Gerlach experiments and the presence of many doublet lines in the atom spectrum Goudsmit and Uhlebeck hypothesized that every electron has an intrinsic angular momentum **S**, which is called spin. The spin is a quantum quantity which does not have a classical analog (therefore the operator of the spin cannot be obtained in a standard way, like for example, the operators $\hat{L}$ and $\hat{H}$, and cannot be expressed through the co-ordinates).

All kinds of quantum mechanical angular momenta obey the same laws and are described with equal mathematical formalism. Both their magnitude and the magnitude of their components are determined by quantum numbers. For the spin they are the spin quantum number $s=1/2$ and magnetic spin quantum numbers $m_s=\pm 1/2$. Analogously to the known orbital angular momentum, for the magnitudes of the spin angular momentum and its components we obtain:

$$S=\hbar\sqrt{s(s+1)}=\hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}=\frac{\hbar}{2}\sqrt{3}, \qquad S_z=m_s\hbar=\pm\frac{\hbar}{2}.$$

The spin is described by the operators of the square of the spin $\hat{S}^2$ and of its components $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$. Usually the operators $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ are given in S_z-representation (two-dimensional matrices). These matrices, divided by $\hbar/2$, give the Pauli matrices $\left\|\sigma_{x_j}\right\|$:

$$\left\|S_{xj}\right\|=\frac{\hbar}{2}\left\|\sigma_{xj}\right\|, \qquad x_j=x,y,z.$$

The spin state is completely determined by the eigenfunctions $X_+(S_z)$ and $X_-(S_z)$ of the operator $\hat{S}_z$. In S_z-representation these functions, which are column matrices, are written in the form of Pauli matrices and are called spinors.

By a summation of two angular momenta with quantum numbers l_1 and l_2 total angular momenta with quantum numbers l

$$|l_1-l_2|,\quad |l_1-l_2|+1,\quad |l_1-l_2|+2,\ \ldots,\quad l_1+l_2$$

are obtained.

This is the rule of the angular-momenta addition in quantum mechanics.

By an addition of the orbital angular momentum **L** and the spin angular momentum **S** of an electron, the total angular momentum of the electron **J** is obtained. The magnitude and components of the total angular momentum are determined by the total quantum number j and the total magnetic number m_j:

$$J=\hbar\sqrt{j(j+1)}, \qquad J_z=m_j\hbar.$$

In the spectroscopic notation the electron state is given by the following terms:

$$n\,{}^{2s+1}L_j\,,$$

where L is the letter notation of the orbital quantum number and $2s+1$ determines the multiplicity of the energy levels.

The total angular momentum of two or more electrons depends on the kind of their interaction. If the energy of the interaction is small, the electrons can be considered as independent. Then the orbital and spin angular momenta of each electron are added and the total angular momentum of the system is the sum of the total angular momenta of the both electrons. Such an interaction is called *JJ* coupling. It is characteristic of the heavy elements and dominates at the end of the periodic table.

When the interaction between two electrons is very strong the orbital and spin angular momenta are united separately in vectors called orbital angular momenta **L**, and spin angular momenta **S**, of the atom. Such an interaction is called *LS* coupling. It dominates in the beginning and the middle of the Mendeleev table.

QUESTIONS

1. What is a spin?
2. Why do we conclude from the Stern-Gerlach experiment that the spin quantum number is half-integer?
3. What are the values of the spin number and the magnetic spin number?
4. What are the possible orientations of the spin vector and what is its magnitude?
5. What is the form of the operator $\hat{S}_z$ in eigenrepresentation?
6. How are angular momenta added in quantum mechanics?
7. What is the total angular momentum of an electron called and what are the possible values of its total quantum number?
8. What is the difference between the vectors of the total angular momentum and the orbital angular momentum?
9. What is the vector model of the total angular momentum?
10. Which quantum numbers do we use for a description of the electron state of the atom and which quantities do they determine?
11. What is a spectral term and what is the meanings of its notations?
12. What is the difference between the *JJ* coupling and the *LS* coupling?
13. What are the vector interpretations of the *JJ* coupling and the *LS* coupling?

PROBLEMS

1. Find the angle between the spin vector and the *Z*-axis.
2. For *d*-electron in single-electron atom find:
    - a) the quantum numbers l, s and j;
    - b) the angular momenta L, S and J, and plot their vector diagrams;
    - c) the angles between **L** and **S**.
3. For the term $D_{5/2}$ find the possible values of m_j and J_z. Can the spin number of this term take the value $s = 1/2,\ s = 0$?
4. For an *s*-electron and a *p*-electron find the spectral terms for *LS* coupling and plot the vector diagrams of the angular momenta **L**, **S** and **J**.
5. Calculate the total angular momentum of two electrons with orbital quantum numbers $l_1 = 1$ and $l_2 = 2$ for *JJ* coupling. Plot the vector diagrams for the total angular momenta and their vector interpretation.
6. What are the possible values of l of three *p*-electrons?
7. Prove that $\mathbf{LS} = \frac{\hbar}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$.

Chapter 17

INTERACTION OF AN ELECTRON IN AN ATOM WITH A MAGNETIC FIELD

17.1 A Magnetic Field and an Electron in an Atom

Rotational move of an electron – current, magnetic dipole, orbital angular momentum; Lande g-factor, spin and orbital magnetic moments; precessions of the moments – frequency; potential energy of interaction; an explanation of the Stern-Gerlach experiment. 432

17.2 The Spin-Orbit Interaction

The interaction of the magnetic field of the nucleus with the spin of the electron; spin-orbit interaction – fine structure; examples – H and Na; relativistic effects for H; selection rules and their application to H and Na; doublets and triplets of the spectral lines. 438

17.3 Normal Zeeman Effect

Normal Zeeman effect at $S = 0$ *and* $S \neq 0$*; energy levels; transitions and spectral lines of the normal Zeeman effect for s-, p- and d-states for* $S=0$*; energy levels and transition between 3p- and 3s-states of Na in strong magnetic field.* 444

17.4* Coupling to the Electromagnetic Field

Schroedinger equation for an electron with a spin – Pauli equation; nonstationary Pauli equation in uniform magnetic field; linearization; stationary solutions – eigenfunctions and eigenvalues of the energy. 448

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17.1 A MAGNETIC FIELD AND AN ELECTRON IN AN ATOM

In Section 4.4 we have realised that the motion of a charge particle in a loop is equivalent to a circle current, which has magnetic dipole moment $\boldsymbol{\mu}$ (4.30). This magnetic moment is explicitly connected with the angular momentum of the particle (4.33). Hence, an electron with the charge *e* and an orbital angular momentum *L* produces a magnetic field of a magnetic dipole (Fig. 17-1) with magnetic moment

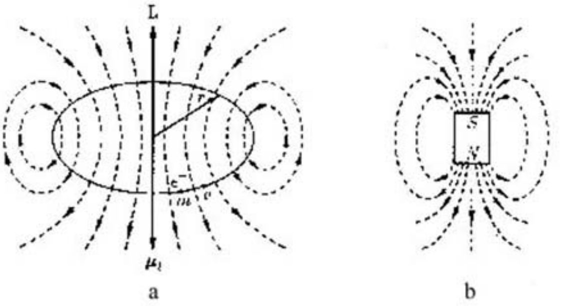


Figure 17-1. The orbital motion of the electron in the atom is equivalent to the current in a loop (a). This current produces a field of a magnetic dipole, which lines of force are in analogy with those of the current magnetic dipole (b).

$$\boldsymbol{\mu}_l = -\frac{e\mathbf{L}}{2m_e}. \tag{17.1}$$

This permits us to interpret the electron in the atom as a small magnet (Fig. 17-1b), which turns out to be a very useful qualitative description.

The formula (17.1) determines the magnetic moment, which is due to the orbital angular momentum (according to Bohr to the orbital motion). It has been established in Chapter 16 that the electron in an atom possesses two more angular momenta - spin angular momentum **S** and total angular momentum **J**. The magnetic dipole moments are also associated with them by analogy with (17.1), namely - $\boldsymbol{\mu}_s$ due to the spin motion and $\boldsymbol{\mu}_j$ due to the total (the orbital + the spin) circular motions.

Because the angular momenta **L**, **S** and **J** are quantizied, the corresponding magnetic dipole moments also take discrete values. According to (17.1) the orbital magnetic moment $\boldsymbol{\mu}_l$ and its component μ_{lz} take the following values:

$$\mu_l = \frac{e\hbar}{2m_e}\sqrt{l(l+1)}, \quad \mu_{lz} = \frac{e\hbar}{2m_e}m. \tag{17.2}$$

Hence, for $l=0 \rightarrow \mu_l = 0,$ for $l=1 \rightarrow \mu_l = \sqrt{2}e\hbar/2m_e,$ for $l=2 \rightarrow$ $\mu_l = \sqrt{6}e\hbar/2m_e$ etc. The values of the z-component are multiplied by $e\hbar/2m_e$. The quantity $e\hbar/2m_e$ consists only of universal constants and is used as the unit of magnetic moment. It is called Bohr magneton and is equal to

$$\mu_B = \frac{e\hbar}{2m_e} = \frac{eh}{4\pi m_e} = 0{,}927.10^{-23}\,\text{J/T} \quad (\text{or A.m}^2). \tag{17.3}$$

Using (17.1) and (17.3) we can present the magnetic dipole moment of the electron in the following form:

$$\boldsymbol{\mu}_l = \frac{\mu_B}{\hbar}L. \tag{17.4}$$

Here we shall underline that this relationship is written for the values μ_l and L. The vectors $\boldsymbol{\mu}_l$ and **L** have opposite directions (Section 4.4) because of the negative charge of the electron. According to (17.4) the ratio μ_l / L does not depend on the electron state. The ratio (17.4) can be written in the form:

$$\frac{\mu_l / \mu_B}{L / \hbar} = 1. \tag{17.5}$$

On the left-hand side we have the ratio of two quantities, taken in their quantum units. The ratio of the magnetic moment in Bohr-magneton units to the angular momentum in $\hbar$ units is called giromagnetic ratio *g* or *g*-factor of Lande. For the orbital magnetic moment the giromagnetic ratio *g* is equal to unit

$$\frac{\mu_l / \mu_B}{L / \hbar} = g_l, \quad g_l = 1. \tag{17.6}$$

For the magnetic dipole moment we have

$$\mu_l = \frac{\mu_l \mu_B}{\hbar} L \Rightarrow \mu_l = g_l \mu_B \sqrt{l(l+1)}. \tag{17.7}$$

By analogy with (17.6) we can write for the spin magnetic moment

$$\frac{\mu_s / \mu_B}{S / \hbar} = g_s, \tag{17.8a}$$

or in a vector form

$$\frac{\boldsymbol{\mu}_s}{\mu_B} = -g_s \frac{\mathbf{S}}{\hbar}. \tag{17.8b}$$

The magnetic moment can be measured very precisely. In its expression g_s remains the only unknown quantity, i.e. we can determine the spin *g*-factor. It appears to be equal to 2 (more accurately to 2,00231923). In respect to the magnetic moment the spin motion is twice more effective than the orbital one: $g_s = 2g_l$. For the spin magnetic moment it follows from (17.8) that

$$\mu_s = g_s \mu_B \frac{S}{\hbar} = g_s \mu_B \sqrt{s(s+1)}\,. \tag{17.9}$$

As we have already mentioned, the total angular momentum relates to the total magnetic dipole moment μ_j. The relationship (17.6) is also valid for it, i.e. the ratio of the magnetic dipole moment μ_j in units of μ_B to the total angular momentum J in units of $\hbar$ is equal to the Lande factor g_j:

$$\frac{\mu_j / \mu_B}{J / \hbar} = g_j \Rightarrow \mu_j = \frac{g_j \mu_B}{\hbar} = g_j \mu_B \sqrt{j(j+1)}. \tag{17.10}$$

In this case the Lande factor g_j can be calculated (see for example [4], Section 14.7). It depends on quantum numbers s, l and j, as follows:

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \tag{17.11}$$

Finally, making a summary of the three different cases, we can write:

$$l \neq 0, \quad s = 0 \rightarrow \mu_l = g_l \mu_B \sqrt{l(l+1)}, \qquad g_1 = 1; \tag{17.12a}$$

$$l = 0, \quad s \neq 0 \ \rightarrow \ \mu_s = g_s \mu_B \sqrt{s(s+1)}, \qquad g_s = 2; \tag{17.12b}$$

$$l \neq 0, \quad s \neq 0 \rightarrow \mu_j = g_j \mu_B \sqrt{j(j+1)}, \quad g_j = g_j(j, l\, s). \tag{17.12c}$$

Considering an electron in an atom as a magnetic dipole moment permits us to answer the question of what is going to happen to it as a result of the application of an external magnetic field **B**. From the analysis of Section 4.4 it follows, that the dipole would experience a torque **N (**4.25) and it would start to precess. The precession frequency of the orbital magnetic moment μ_l is equal to its Larmor frequency ω_L (4.28). The precession is shown in Fig. 17-2, where the electron is shown as a small magnet.

The exact analysis shows that the frequencies of the precession of the vectors **L**, **S** and **J** during the interaction of the external magnetic field with the corresponding dipole moments differs in their *g*-factors:

$$\omega_l = g_l \omega_L = g_l \frac{eB}{2m_e}; \omega_s = g_s \omega_L = g_s \frac{eB}{2m_e}; \omega_j = g_j \omega_L = g_j \frac{eB}{2m_e}. \tag{17.13}$$

As $g_s = 2g_l$, it follows that **S** precesses around **B** twice more quickly than **L**. The precession frequency of **J** depends on the g_j-factor (17.11). Under

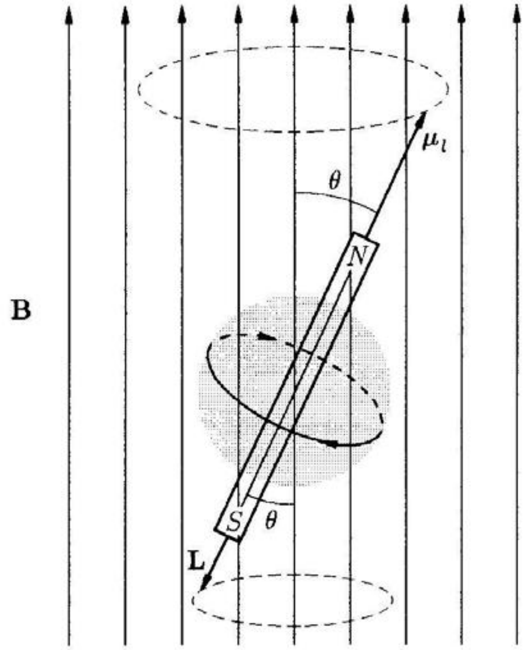


Figure 17-2. Under the influence of the magnetic field **B** the electron orbital angular momentum **L** precesses with an angular frequency $\omega_l = g_l\omega_L$ at an angle θ around *Z*-axis ($\cos\theta = L_z/L$).

the influence of the magnetic field **B** the magnetic dipole receives an additional potential energy (4.40). For this additional energy of interaction of the magnetic field with the orbital magnetic dipole we get:

$$\begin{aligned}\Delta U_l &= -\boldsymbol{\mu}_l\mathbf{B} = g_l\frac{e\mathbf{LB}}{2m_e} = g_l\frac{e\hbar}{2m_e}\frac{LB\cos\theta}{\hbar}\\ &= g_1\mu_B\frac{L_z}{\hbar}B = mg_l\mu_B B = mg_1\omega_L\hbar.\end{aligned} \tag{17.14}$$

By analogy, for the interaction of the spin with the total magnetic dipole, we obtain for the additional potential energy:

$$\Delta U_s = m_s g_s \mu_B B = m_s g_s \omega_L \hbar, \tag{17.15a}$$

$$\Delta U_j = m_j g_j \mu_B B = m_j g_j \omega_L \hbar. \tag{17.15b}$$

Performed semi-classical analysis (classical law + the Bohr rule of quantization) allows us to explain the Stern-Gerlach experiment, i.e. to answer the question what is happening to an electron in an inhomogeneous external field. In an uniform field the couple of forces $\mathbf{F}_m^N$ and $\mathbf{F}_m^S$ (Fig. 17-3a) acts on the magnetic dipole, which is due to the spin angular momentum **S**.

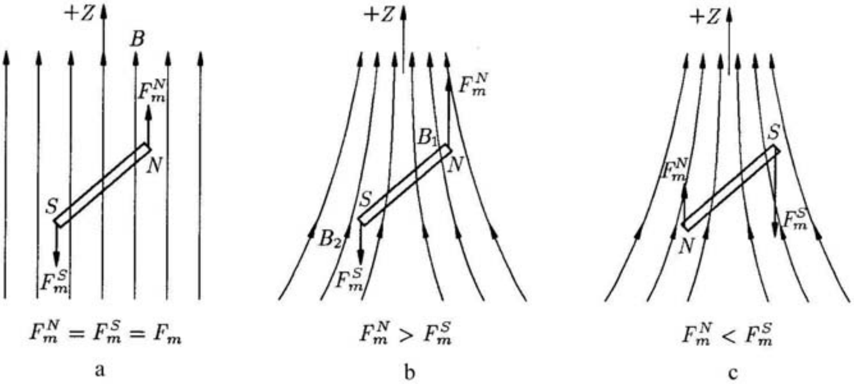


Figure 17-3. A magnetic bar equivalent to the spin magnetic dipole of an electron (L = 0 and S≠0) in a magnetic field. In a uniform magnetic field (a) there is only precession but not a translational motion. In an inhomogeneous field the bar moves along the +Z-axis (b) or along the -Z-axis (c) depending on the spin orientation.

The magnitudes of these forces are equal (because of the uniformity of the field) but they are antiparallel. They cause the precession of the spin angular momentum **S**, without changing the position of the electron. When the field is inhomogeneous (Fig. 17-3b,c) the two forces are different. (Note that here the form of the poles is vice versa of that one in Fig. 16-1.) Some of the electrons in the magnetic field have a negatively orientated spin, such that the northern pole of the equivalent magnet bar is turn upwards (Fig. 17-3b). For them $\left|\mathbf{F}_m^N\right| > \left|\mathbf{F}_m^S\right|$ and the electron (the atom) moves along the +*Z*-axis. When some of the electrons have a positively oriented spin, the southern pole of the equivalent magnet bar is in the stronger field (Fig. 17-3c) and $\left|\mathbf{F}_m^N\right| < \left|\mathbf{F}_m^S\right|$ - the electron (the atom) moves along the -*Z*-axis.

We can easily determine the net force, which acts on the equivalent magnetic bar, i.e. the force, acting on the electron. According to (17.15a) the electron in **B**-field gains an additional potential energy ΔU_s. This additional potential energy is equivalent to a force, which act to the electron. In the Stern-Gerlach experiment the inhomogeneity determines the field gradient $\text{grad}\mathbf{B} = \left(\text{dB/dz}\right)\mathbf{s}^0$. Consequently, for the force acting on the electrons we have

$$F_z = \frac{d}{dz}(\Delta U_s) = -m_s g_s \mu_B \frac{dB}{dz}. \qquad (17.16)$$

As a result of the action of this force on the two possible orientations of the spin ($m_s = \pm 1/2$) with respect to **B**, the electron beam is divided in two beams and we observe two tracks on the registering screen (Fig. 16-1).

17.2 THE SPIN-ORBIT INTERACTION

The basic interaction between the electron and the nucleus, which is realised through their charges, is electrostatic. But there is another additional interaction, due to the nuclear charge's relative motion with respect to the electron, and its spin. It is qualitatively explained by the semi-classical theory of Bohr. If for simplicity we take the atom of hydrogen and consider the electron motion in a circle, then the orbital motion of this negative charge produces at the nucleus a magnetic field $\mathbf{B}_e$. In the rest frame of the electron, in which the nucleus moves with respect to it (Fig.17-4), the positive charge of the last produces at the electron the magnetic field $\mathbf{B}_n$.

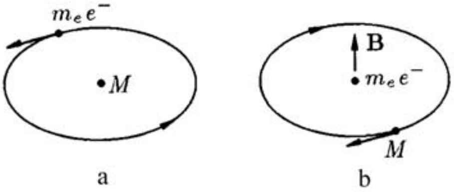


Figure 17-4. The motion of an electron in a Bohr-type orbit in a nuclear reference frame (a). The same motion in the electron reference frame (b) - from the electron point of view the nucleus moves around it and creates a magnetic field $\mathbf{B}_n$.

Because the charges of the electron and the nucleus are equal but opposite and the velocity directions of the electron and the nucleus in the given moment are opposite, both fields are equal $\mathbf{B}_e = \mathbf{B}_n = \mathbf{B}$. We can formally talk about the interaction between the spin and orbital (equal to one of the nuclear!) magnetic moment. *The interaction between the nucleus magnetic field and the electron spin magnetic moment is called a spin-orbit interaction.*

Let us consider these topics quantitatively. The motion of the charged nucleus in the fixed frame with the velocity $-v$ is equivalent to the current element $\mathbf{j} = -e\mathbf{v}$. According to Ampere's law it produces a magnetic field

$$\mathbf{B} = \frac{\mu_0}{4\pi}\frac{\mathbf{j}\times\mathbf{r}}{r^3} = -\frac{e\mu_0}{4\pi}\frac{\mathbf{v}\times\mathbf{r}}{r^3}. \tag{17.17}$$

As a result of the interaction of this magnetic field with the spin magnetic dipole of the electron, the latest receives an additional energy:

$$\Delta U = -\boldsymbol{\mu}_s\mathbf{B}. \tag{17.18}$$

This energy is, however, in the reference frame in which the electron is at rest. Meanwhile we are interested in the energy in the reference frame, in which the nucleus is at rest. As the motion is relativistic, it is necessary to do a Lorentz transformation. In the frame of the nucleus the additional energy is twice less:

$$\Delta U = -\frac{1}{2}\boldsymbol{\mu}_s\mathbf{B}. \tag{17.19}$$

This magnetic field can be expressed through the electron orbital angular momentum $\mathbf{L} = \mathbf{r}\times m_e\mathbf{v} = -m_e\mathbf{v}\times\mathbf{r}$. Multiplying the numerator and the denominator of (17.17) by m_e, we obtain:

$$\mathbf{B} = -\frac{e\mu_0}{4\pi}\frac{\mathbf{v}\times\mathbf{r}}{r^3}\frac{m_e}{m_e} = \frac{e\mu_0}{4\pi r^3 m_e}\mathbf{L}. \tag{17.20}$$

Substituting $\mathbf{B}$ in (17.19) and taking into account that $g_s = 2$ in the relation for μ_s, we get:

$$\Delta U = \frac{e^2}{4\pi\varepsilon_0 2m_e^2c^2}\frac{1}{r^3}\mathbf{SL}. \tag{17.21}$$

This formula is equivalent to (17.15a), where the nuclear magnetic field is in the implicit form:

$$\Delta U_s = m_s g_s \mu_B B = m_s g_s \omega_L \hbar, \quad m_s = -\frac{1}{2}, +\frac{1}{2}. \tag{17.22}$$

The spin and the orbital angular momentum (through the scalar product **SB** in (17.21)) determine quantitatively the interaction of an electron with the magnetic field of a nucleus, which is the reason to call it spin-orbit interaction.

As we can see from (17.22), for the positively orientated spin the energy of the state $l \neq 0$ increases by $\Delta U_s = \mu_B B$, and for the negatively orientated spin it decreases by $\Delta U_s = -\mu_B B$. Of course, this can be obtained from (17.21). This addition is essentially less than the state energy of the electron: $\Delta U << E_n$. Actually, determining in (17.21) the product **SL** (for example for $l=1$ (see problem 16.2)) and substituting r from (8.3), we obtain for the ratio $\frac{\Delta U}{E_n}$ at $n \sim 1$ (for E see (14.41)):

$$\frac{\Delta U}{E_1} \approx \left(\frac{k_0 c^2}{\hbar e}\right)^2 \equiv \alpha^2 = \frac{1}{137^2} = 5{,}325.10^{-5}. \qquad (17.23)$$

All levels with $l \neq 0$ are split in two very close levels (Fig. 17-5). The energy of the s-state does not change:

$$l = 0 \;\Rightarrow\; B = 0 \;\Rightarrow\; \Delta U = 0. \qquad (17.24)$$

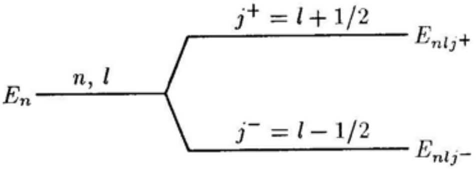


Figure 17-5. Due to the spin-orbit interaction the singlet level of the state $l \neq 0$ becomes a doublet.

The set of the energy levels without taking into account the spin gives the energy structure of the atom. The levels, formed by splitting of the level of the energy are called multiplet. The set of the energy levels, which are obtained by taking account the spin-orbit interaction, is called a fine structure. The splitting of the levels is quadratic in the constant α, which is determined only by the universal constants and is called *the fine structure constant.*

The energy levels of the hydrogen at $n = 2$ are shown in Fig. 17-6. Because of the spin-orbit interaction the degeneracy in l is removed - the energy of the term ${}^2P_{3/2}$ (a positive spin, $m_s = 1/2$) increases and of the term ${}^2P_{1/2}$ (a negative spin, $m_s = -1/2$) decreases. At the same time the energy of the s-state remains unchanged.

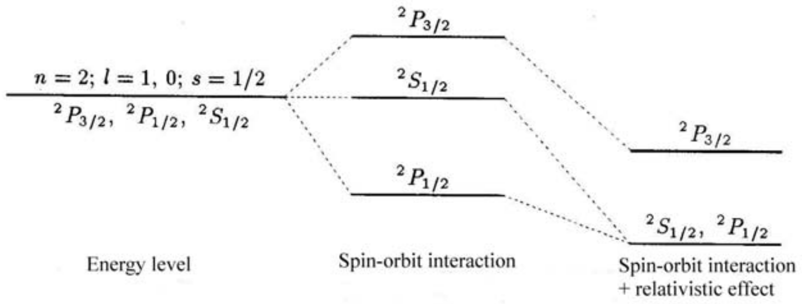


Figure 17-6. Splitting of the level n =2 of the hydrogen atom as a result of the spin-orbit interaction and the relativistic effects.

We have already determined that the relative change of energy is proportional to α^2. From (8.37) and (8.4) it is obvious that $\alpha = v/c$, where v is the velocity of the hydrogen electron in the first Bohr orbit. Hence, the splitting is an effect $\propto (v/c)^2$, i.e. it is of the order of the relativistic corrections of its mass. Therefore it is correct to analyze the spin-orbit interaction in the relativistic approximation. For this it is necessary to solve the wave equation of Dirac, which is out of the scope of this book. Due to these relativistic effects and the spin-orbit interaction the level $n = 2$ does not split in three, but in two sublevels (Fig.17-6). The influence of the spin-orbit interaction on some levels of the valence electron of Na is illustrated in Fig. 17-7.

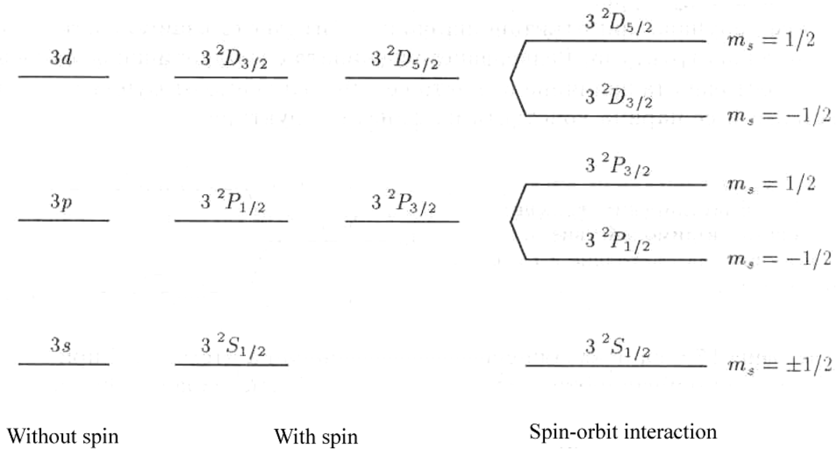


Figure 17-7. Fine structure of the levels with n = 3 of the Na atom.

We have already discussed (Chapter 14, Sections 14.3 and 14.5) the selection rules which give the possibility to determine the allowed transitions in the energy structure of H atom and the hydrogen-like atom. The picture becomes more complicated for the transitions between the sublevels of the fine structure as the energy depends already on the quantum numbers s and j. The allowed transitions in this case determined by quantum mechanics. But like in Chapter 14, we will not derive them. The theory shows that for the allowed transitions the quantum numbers change as follows:

– the total quantum number j and the total magnetic quantum number m_j:

$\Delta j = \pm 1, 0$,

but the transition from $j_{in} = 0$ to $j_f = 0$ is forbidden,

$\Delta m_j = \pm 1, 0$;

– the orbital quantum number l and the magnetic quantum number m_j:

$\Delta l = \pm 1$,

$\Delta m = \pm 1, 0$;

– the spin number:

$\Delta s = 0$.

We shall underline that during an absorption or an emission of a photon, the spin of the electron does not change. The transition $\Delta l = 0$ of the H atom is always forbidden.

Let us apply the selection rules to the fine structure in Fig. 17-6 and Fig.17-7. In the H atom without taking into account the spin, for the transition from 2p to 1s we observe the resonance line of Lyman ν_α^* (Fig. 17-8).

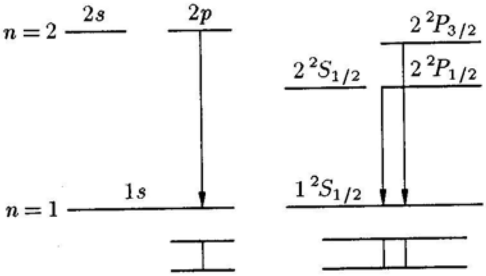


Figure 17-8. Taking into account the spin-orbit interaction (and the relativistic effects) the line ν_α^* of the Lyman series transforms into a doublet.

With the *LS* coupling the level 1s does not change – we obtain the singlet state ${}^1S_{1/2}$, but the level 2p becomes a doublet: ${}^2P_{3/2}$ and ${}^2P_{1/2}$. As a result of this, the singlet line of the structure without spin appears as a doublet with frequencies ν_1^* and ν_2^* of the corresponding transitions:

$$\begin{aligned} &\nu_1^* \quad {}^2P_{1/2} \;\rightarrow\; {}^2S_{1/2,} \quad \Delta l = 1, \quad \Delta j = 0, \\ &\nu_2^* \quad {}^2P_{3/2} \;\rightarrow\; {}^2S_{1/2,} \quad \Delta l = 1, \quad \Delta j = 1. \end{aligned} \tag{17.25}$$

Here $\Delta\nu^* = \nu_2^* - \nu_1^* = 0{,}365\ \text{cm}^{-1}$ and in wavelength $\Delta\lambda = 5{,}3.10^{-4}$ nm. We shall underline that the splitting of the spectral line is a small quantity in a comparison to the wave length λ of the line ν_a^* ($\lambda = 121{,}6$ nm): $\Delta\lambda/\lambda \approx 0{,}45.10^{-5}$.

Here we shall note one peculiarity of the notation of the level multiplicity. The number $2s+1$ gives the real multiplicity only when $s<l$, but not when $s>l$. In the last case the notation $2s+1$ in the terms ${}^{2s+1}S$ is conditional.

And now let us see what are the possible transitions between the sublevels of the fine structure of the terms $3S, 3P$ and $3D$ in the Na atom (Fig. 17-9).

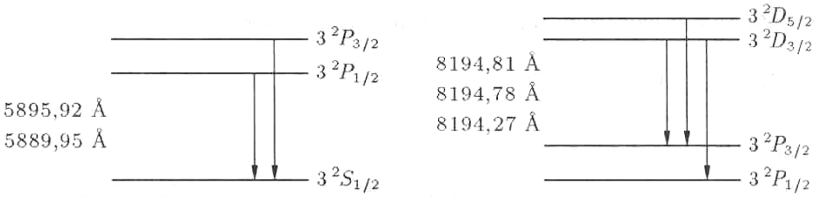


Figure 17-9. Allowed transitions between the levels 3*d*, 3*p* and 3*s* in the Na atom.

The line corresponding to the transition $3p \rightarrow 3s$, transforms into a doublet, which is due to the transitions:

$$\begin{aligned} &3\,^2P_{3/2} \rightarrow 3\,^2S_{1/2}, \qquad \Delta l = 1, \qquad \Delta j = 1, \\ &3\,^2P_{1/2} \rightarrow 3\,^2S_{1/2}, \qquad \Delta l = 1, \qquad \Delta j = 0. \end{aligned} \tag{17.26}$$

The line, corresponding to the transition $3d \rightarrow 3p$, transforms into a triplet, which is due to the next transitions:

$$\begin{aligned} &3\,^2D_{3/2} \rightarrow 3\,^2P_{1/2}, \qquad \Delta l = 1, \qquad \Delta j = 1, \\ &3\,^2D_{5/2} \rightarrow 3\,^2P_{3/2}, \qquad \Delta l = 1, \qquad \Delta j = 1, \\ &3\,^2D_{3/2} \rightarrow 3\,^2P_{3/2}, \qquad \Delta l = 1. \qquad \Delta j = 0. \end{aligned} \tag{17.27}$$

The transition $3^2D_{5/2} \rightarrow 3^2P_{5/2}$ is forbidden because $\Delta j = 2$. The both spectral lines corresponding to the transitions (17.26) are known as yellow doublet of Na with the wavelength $\lambda_1 = 5895{,}92$ Å and $\lambda_2 = 5889{,}95$ Å and $\Delta\lambda \approx 6$ Å.

And at last we shall underline that the multiplicity of the levels and of the spectral lines are different, which is obvious from Fig. 17-9.

17.3 NORMAL ZEEMAN EFFECT

The splitting of the singlet spectral line of the atomic structure without spin into a triplet in the fine structure under the influence of a magnetic field is called a normal (or a simple) Zeeman effect. Such a splitting is observed in two different cases:

1. when the summed spin of the electrons of the atom is equal to zero, but the orbital angular momentum is different than zero, $S = 0,\ L \neq 0$;
2. when the spin and the orbital angular momentum are different from zero and the external magnetic field is strong enough , $S \neq 0,\ L \neq 0$.

Let us consider the both cases in detail.

1. $S = 0, L \neq 0$

In this case the external magnetic field interacts with the orbital angular momentum. Each level of the atomic structure with energy E_{nl} will receive an additional energy ΔU :

$$\Delta U_l = m_l g_l \mu_B B = m_1 g_1 \omega_L \hbar. \qquad (17.28)$$

Here the index l in m_l underlines the fact that magnetic quantum numbers m_l corresponds to the fixed orbital number l. It is obvious that under the influence of the magnetic field this level splits in $2l+1$ sublevels.

Let us consider the two levels with the orbital quantum numbers l_1 and l_2. During the transition from the sublevels of l_2 to the sublevels of l_1 quanta will be emitted with energy:

$$\hbar\omega = \left(E_{nl_2} + \Delta U_{l_2}\right) - \left(E_{nl_1} + \Delta U_{l_1}\right) = \left(E_{nl_2} - E_{nl_1}\right) + g_l \left(m_{l_2} - m_{l_1}\right)\omega_L \hbar. \qquad (17.29)$$

Taking into account that the $g_l = 1$ and $E_{nl_2} - E_{nl_1} = \hbar\omega_0$ (here ω_0 stands for the frequency of the spectral line without the magnetic field), we obtain for the frequency ω :

$$\omega = \omega_0 + \left(m_{l_2} - m_{l_1}\right)\omega_L = \omega_0 + \Delta m \omega_L. \qquad (17.30)$$

But according to the selection rules $\Delta m = \pm 1, 0$, i.e. the transitions are allowed where $m_{l_2} - m_{l_1}$ takes values $-1, 0, 1$. Hence the spectral line ω_0 splits into three lines:

$$\begin{gathered} \omega_0 \\ \downarrow \\ \overbrace{\omega_0 - \omega_L, \quad \omega_0, \quad \omega_0 - \omega_L} . \end{gathered} \tag{17.31}$$

Such a triple line is called a triplet of Lorentz. We shall emphasize that this splitting for $S = 0$ is obtained independently of the magnitude of the magnetic field, while for $S \neq 0$ - only for a strong field.

2. $S \neq 0$, $L \neq 0$

For a strong enough magnetic field the energy of the interaction with the orbital angular momentum (with the orbital magnetic dipole) and the spin angular momentum (the spin magnetic dipole) is essentially greater than the energy of the spin-orbit interaction. Then we can neglect the last, i.e. the sublevels of the fine structure, and we can think that an energy level without spin in an external magnetic field splits as a result of the interaction of the magnetic field with the orbital and spin angular momenta. In other words, the magnetic field is so strong, that it breaks the *LS* coupling and interacts separately with **L** and **S.**

Without and with a weak magnetic field **B** the vectors **L** and **S** precess around **J** and J, J_z, L and S are constants of the motion, but in a strong magnetic field **B** they (the vectors **L** and **S)** precess around **B** and L, L_z, S and S_z are constants of the motion.

In a strong magnetic field **B** the levels (without spin and without magnetic field) with quantum numbers *l* and *s* receives an additional energy ΔU_l and ΔU_s as a result of its interaction with the spin and the orbital angular momentum:

$$\begin{aligned} \Delta U_l &= m_l g_l \omega_L \hbar, \\ \Delta U_s &= m_s g_s \omega_L \hbar. \end{aligned} \tag{17.32}$$

Or, in summary, the additional energy is

$$\Delta U = \Delta U_l + \Delta U_s = (m_l + 2m_s)\omega_L \hbar . \tag{17.33}$$

We have used that $g_l = 1$ and $g_s = 2$.

For the transition from the level with l_2 and s_2 to the level with l_1 and s_1 a quantum is emitted with energy:

$$\hbar\omega = [E_{nl_2} + (m_{l_2} + 2m_{s_2})\omega_L\hbar] - [E_{nl_1} + (m_{l_1} + 2m_{s_1})\omega_L\hbar]. \qquad (17.34)$$

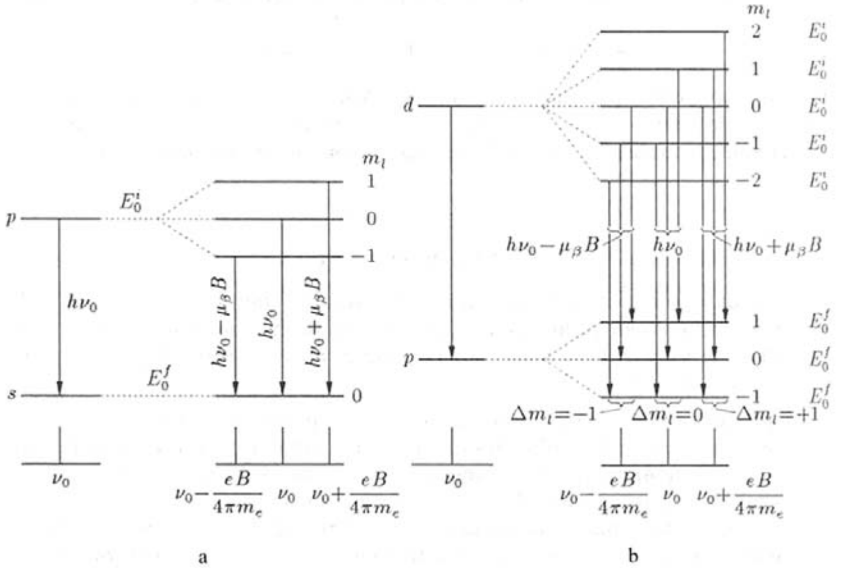


Figure 17-10. The normal Zeeman effect for $S = 0$ - arbitrary magnetic field: a) transitions from p-state ($l = 1$) to s-state ($l = 0$); b) nine allowed transitions from d-state to p-state give only three lines because the sublevels are equidistant.

If we denote with ω_0 the frequency of the transitions between the energy levels (without spin and without magnetic field), i.e. $\omega_0 = \left(E_{nl_2} - E_{nl_1}\right)/\hbar$, from (17.34) we get for ω:

$$\omega = \omega_0 + [(m_{l_2} - m_{l_1})] + 2(m_{s_2} - m_{s_1})]\omega_L\hbar. \qquad (17.35)$$

But according to the selection rules $\Delta m_s = 0$, $\Delta m_l = \pm 1,\ 0$. Hence, the spectral line splits into the Lorentz triplet $(\omega_0 - \omega_L)$, ω_0 and $(\omega_0 + \omega_L)$.

Let us consider the allowed transitions for the normal Zeeman effects both at $S = 0$ and at $S \neq 0$. In the first case ($S = 0$) we take three energy levels from the atom structure without magnetic field: *s*, *p* and *d*. When we apply the magnetic field the *s*-level remains unchanged, the *p*-level splits in three (three orientations of **L**) sublevels and the *d*-level splits in five (five orientations of **L**) sublevels - Fig. 17-10. The spaces between the sublevels of *p*- and *d*-states are equal and they are $\omega_L \hbar$.

According to the selection rules $(\Delta l = \pm 1, 0)$ the transitions from *p*- to *s*-sublevels and from *d*- to *p*-sublevels are allowed. Three transitions are allowed from *p*- to *s*-sublevels $(\Delta m = \pm 1, 0)$ and nine - from *d*- to *p*-sublevels.

The following transition are forbidden:

$$\begin{array}{lrrrrrr} m_d: & -2, & -2, & -1, & 1, & 2, & 2, \\ \downarrow & & & & & & \\ m_p: & 1, & 0, & 1, & -1, & 0, & -1, \\ & & & & & & \\ \Delta m: & -3, & -2, & -2, & 2, & 2, & 3. \end{array}$$

Besides, nine transitions $d \to p$ are allowed, the spectral lines are only three because of the equal spacing between the sublevels.

The normal Zeeman effects for $S \neq 0$ and $L \neq 0$ is illustrated with the levels 3*p* and 3*s* of the Na atom (Fig. 17-11).

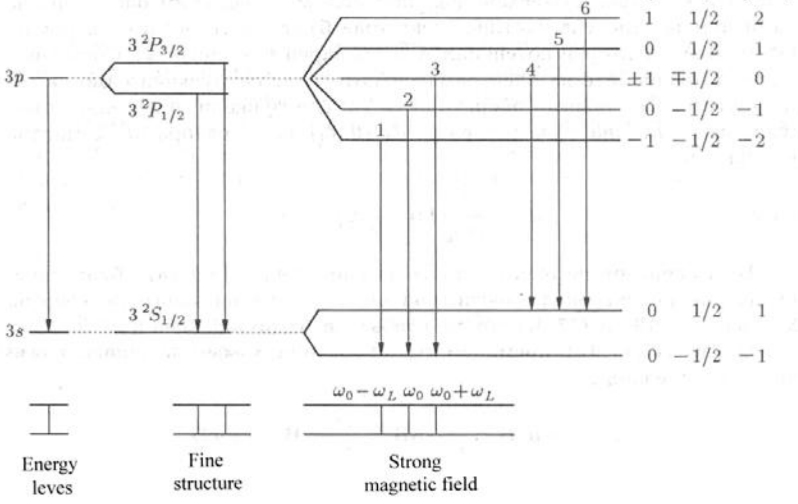


Figure 17-11. Normal Zeeman effect for the resonance line $3p \to 3s$ of the Na atom. Six transitions are allowed, but as they are two by two equal, only three spectral lines are observed. Note that only the transitions for which $\Delta m_s = 0$, i.e. without change of the spin state, are allowed.

Six transitions are allowed, which are two by two equals. They are the transitions between the sublevels with equal spins: the lines 1, 2, 3 with $m_s = -1/2$ and 4, 5, 6 with $m_s = 1/2$. Instead of line ω_0 of the transition $p \to s$ we obtain a Lorentz triplet.

17.4* COUPLING TO THE ELECTROMAGNETIC FIELD

In Section 6.3 we obtained the function of Hamilton of the charged particle in an electromagnetic field and in Section 10.8 - the operator of Hamilton. Using the result of the last section we can write the operator of Hamilton for the electron in an electromagnetic field:

$$\hat{H}_0 = \frac{1}{2m_e}(\hat{\mathbf{p}} - e\mathbf{A})^2 + e\Phi. \tag{17.36}$$

This operator does not take into account the electron spin. Because due to its spin an electron in a magnetic field gains additional energy ΔU (see (17.15a)), it has to be added to the Hamiltonian $\hat{H}_0$. (We neglect the spin-orbit interaction; from Section 17.2 it is clear that it is a subject to relativistic quantum mechanics, i.e. it is put of scope of this book). Using (17.8b) and passing to operators we can write this energy in the following form:

$$\Delta U = -\hat{\boldsymbol{\mu}}_s\mathbf{B} = \frac{e}{m_e}\hat{\mathbf{S}}\mathbf{B} = \frac{e\hbar}{m_e}\hat{\boldsymbol{\sigma}}\mathbf{B} = \mu_B\hat{\boldsymbol{\sigma}}\mathbf{B}. \tag{17.37}$$

(The quantity **B** depends only on the co-ordinates and its operator is equal to the same classical quantity.) For the transition from $\hat{\mathbf{S}}$ to the Pauli operator $\hat{\boldsymbol{\sigma}}$ we use (16.5). Then according to (17.34) the Hamiltonian of the electron with a spin takes the following form:

$$\hat{H} = \hat{H}_0 + \mu_B\hat{\boldsymbol{\sigma}}\mathbf{B}. \tag{17.38}$$

Substituting this operator in the Schrodinger equation we get the equation for an electron with a spin, which is known as Pauli equation:

$$i\hbar\frac{\partial\psi}{\partial t} = \left[\frac{1}{2m_e}(\hat{\mathbf{p}} - e\mathbf{A})^2 + e\Phi + \mu_B\hat{\boldsymbol{\sigma}}\mathbf{B}\right]\psi. \tag{17.39}$$

Now we shall consider an atom with a single valence electron in external uniform magnetic field. As in Chapter 14 we shall use the notation $U(r)$ for the potential energy in the electrostatic field of the nucleus, i.e. $U(r) \equiv e\Phi$. The external magnetic field is along the *Z*-axis, i.e. $\mathbf{B} = (0, 0, B)$. Then for the vector-potential components we can write

$$A_x = -\frac{B}{2}y, \quad A_y = \frac{B}{2}x, \quad A_z = 0. \tag{17.40}$$

Substituting (17.40) into $\mathbf{B} = \mathrm{rot}\mathbf{A} = \nabla \times \mathbf{A}$, we see that this vector potential corresponds to the magnetic field with components $B_x = 0,\ B_y = 0,$ $B_z = B$. For this vector potential the Pauli equation takes the form:

$$\begin{gathered} i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m_e}\nabla^2\psi + U(r)\psi - \frac{ie\hbar B}{2m_e}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi \\ + \frac{e^2}{8m_e}B^2\left(x^2 + y^2\right) + \psi\frac{e\hbar}{2m_e}(\hat{\sigma}_z B)\psi. \end{gathered} \tag{17.41}$$

For a very large interval of magnetic-field values the energy of its interaction with the electron is substantially smaller than the electrostatic energy of interaction. Therefore the quadratic term in the magnetic field ($\propto B^2$) can be neglected. According to (10.64) the operator $i\hbar\left(x\partial/\partial y - y\partial/\partial x\right)$ in the third term on the right-hand side of the equation is the operator of the *z*-component of the angular momentum

$$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \hat{L}_z. \tag{17.42}$$

Taking into account the above states and denoting by $\hat{H}_0$ the Hamiltonian of the electron without external magnetic field

$$\hat{H}_0 = \frac{\hbar^2}{2m_e}\nabla^2 + U(r), \tag{17.43}$$

we get from (17.41)

$$i\hbar\frac{\partial\psi}{\partial t}=\hat{H}_0\psi+\frac{eB}{2m_e}\left(\hat{L}_z+\hbar\hat{\sigma}_z\right)\psi. \tag{17.44}$$

Up to this section of the present chapter we considered the interaction of the electron in an atom with a magnetic field qualitatively on the basis of the Bohr theory. It is seen from (17.44), that actually this interaction leads to an additional energy of the orbital and the spin magnetic dipole, which has a total angular momentum $\hat{\mathbf{L}}+\hbar\hat{\boldsymbol{\sigma}}$:

$$\Delta U=-\boldsymbol{\mu}\mathbf{B}=-\left(\boldsymbol{\mu}_l+\boldsymbol{\mu}_s\right)\mathbf{B}=\frac{eB}{2m_e}\left(L_z+2S_z\right). \tag{17.45}$$

For the stationary states with energy E we shall search for a wave function in the following form:

$$\psi\left(x,y,z,t\right)=\psi\left(x,y,z,S_z\right)\exp\left(-i\frac{Et}{\hbar}\right). \tag{17.46}$$

Substituting this into (17.44) we obtain the stationary equation of the electron with spin in an external magnetic field:

$$\hat{H}_0\psi+\frac{eB}{2m_e}\left(\hat{L}_z+\hbar\hat{\sigma}_z\right)\psi=E\psi. \tag{17.47}$$

As from (16.16) and (16.8) it follows that

$$\hat{\sigma}_z\psi=\begin{vmatrix}1 & 0\\ 0 & -1\end{vmatrix}\begin{vmatrix}\psi_1\\ \psi_2\end{vmatrix}=\begin{vmatrix}+\psi_1\\ -\psi_2\end{vmatrix}, \tag{17.48}$$

Eq. (17.47) can be written as two separate equations for ψ_1 and ψ_2:

$$\begin{aligned}\hat{H}_0\psi_1+\omega_L(\hat{L}_z+\hbar)\psi_1&=E\psi_1,\\ \hat{H}_0\psi_2+\omega_L(\hat{L}_z-\hbar)\psi_2&=E\psi_2.\end{aligned} \tag{17.49}$$

Without electron spin and magnetic field ($\omega_L=0$) we obtain as solutions of these equations the eigenfunctions and the eigenvalues of $\hat{H}_0$. In both cases they are equal:

$$\begin{aligned} &\psi_1 = \psi_2 = \psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \varphi), \\ &E_1 = E_2 = E_{nl.} \end{aligned} \tag{17.50}$$

We must remember that in the general case the energy of an atom with a single valence electron depends also on the orbital number l (see Section 14.5).

As the wave function ψ_{nlm} is an eigenfunction of the operator $\hat{L}_z$ $\left(\hat{L}_z \psi_{nlm} = m\hbar \psi_{nlm}\right)$, it is a solution of Eqs. (17.49). But in the case of an external magnetic field the states with different spins have different eigenvalues of the energy:

$$\begin{aligned} &\psi_{nlm,} \quad E_1 = E_{nl} + \omega_L \hbar \left(m + 2.\frac{1}{2} \right) = E_{nl} + \omega_L \hbar (m+1), \quad S_z = \frac{\hbar}{2}, \\ &\psi_{nlm,} \quad E_2 = E_{nl} + \omega_L \hbar \left(m - 2.\frac{1}{2} \right) = E_{nl} + \omega_L \hbar (m-1), \quad S_z = -\frac{\hbar}{2}. \end{aligned} \tag{17.51}$$

Because of the magnetic field the energy depends on the orientation of the magnetic moment, i.e. of the angular momentum with respect to the field direction. As a result, the degenerate (without a field) levels split. And due to the selection rules, instead of a singlet line we obtain a Lorentz triplet (17.30). Finally we shall note that classical physics obtains a correct result for the energy of the electron of the atom in external magnetic field (4.40). It can explain the normal Zeeman effect (17.30) by the precession of the angular momentum about the magnetic field, which physically corresponds to the precession of the electron orbit. This quantum formula (17.30) does not contain the Planck constant $\hbar$ and therefore the result coincides with the classical one.

17.5 ANOMALOUS ZEEMAN EFFECT

In a weak magnetic field the additional potential energy of the electron is smaller than the energy difference between two adjacent levels of the fine structure. In this case the weak magnetic field interacts with the magnetic dipole moment μ_j or, i.e. with the total angular momentum. This interaction is called an anomalous Zeeman effect. The change of the energy is determined by the formulae:

$$\Delta U = m_j g_j \mu_B B = m_j g_j \omega_L \hbar . \tag{17.52}$$

For each term with a fixed total quantum number the orientation of the vector **J,** i.e. the number of m_j, determines the number of the splitting of the levels as a result of the influence of the field. In the general case, a state with an orbital number l, the level of which when taking into account spin-orbit interaction splits in two sublevels with $j = l + \frac{1}{2}$ и $j = l - \frac{1}{2}$. The result of the influence of the weak magnetic field is shown in Fig. 17-12.

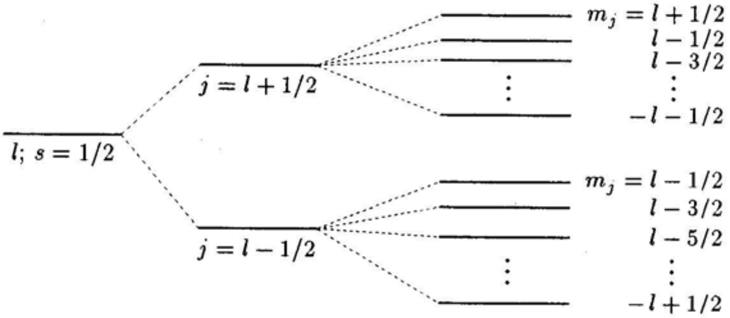


Figure 17-12. Anomalous Zeeman effect for the electron with orbital number l; the level $j = l + \frac{1}{2}$ splits in $2l + 2$ sublevels with an interval ΔU^+ and the level $j = l - \frac{1}{2}$ on $2l$ sublevels with an interval ΔU^- $\left(\Delta U^+ > \Delta U^-\right)$.

The state with a positive spin, i.e. with $j = l + 1/2$, has $2l + 2$ components of the total angular momentum **J**:

$$m_j = -\left(l + \frac{1}{2}\right),\ -l + \frac{1}{2},\ -l + \frac{3}{2},\ \ldots,\ -\frac{1}{2},\ +\frac{1}{2},\ \ldots,\ l + \frac{1}{2}. \qquad (17.53a)$$

The state with a negative spin, i.e. with $j = l - 1/2$, has $2l$ components of the total angular momentum **J**:

$$m_j = -\left(l - \frac{1}{2}\right),\ -l + \frac{3}{2},\ -l + \frac{5}{2},\ \ldots,\ -\frac{1}{2},\ +\frac{1}{2},\ \ldots,\ l - \frac{1}{2}. \qquad (17.53b)$$

Hence, in weak magnetic field **B** the two atomic levels of the fine structure split in $4l + 2$ sublevels.

Let us consider two concrete examples of an anomalous Zeeman effect for the states $1s$, $2s$ and $2p$ of the H atom and for $3s$, $3p$ and 3d of the Na atom.

The level with $n=2$ of the fine structure of the H atom splits in 2 sublevels with 3 terms (see Fig. 17-6) and the level with $n=1$ does not change. In a weak magnetic field the term $2^2P_{3/2}$ splits in 4 sublevels and the other three terms $1^2S_{1/2}$, $2^2S_{1/2}$, $2^2P_{1/2}$ - in 2 sublevels (Fig. 17-13). The change of the energy ΔU, and consequently the space between the levels, is different for each term, because ΔU depends on g_j and according to (17.11) the total g-factor is determined by the quantum numbers j, l and s. Let us determine g_j for the four terms. First, we shall note that the terms $1^2S_{1/2}$ and $2^2S_{1/2}$ have equal numbers j, l and s and, hence, the same g-factor. For g_j we easy obtain

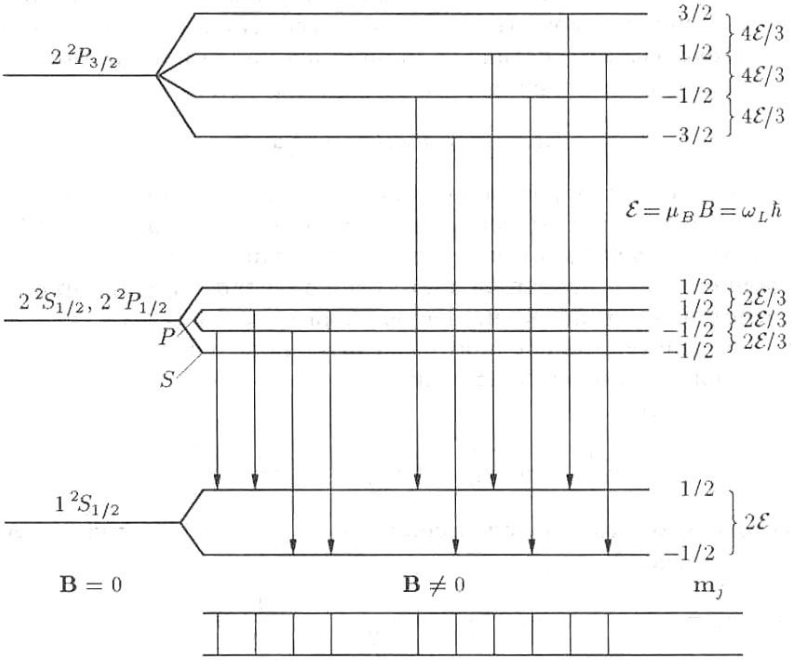


Figure 17-13. Anomalous Zeeman effect in the H atom ($\mathcal{E}=\mu_B B=\omega_L\hbar$). Transitions for which $\Delta l=1, \Delta m=\pm1, 0$ are allowed. The doublet (17.25) splits as follows: ν_1^* in 4 lines and ν_2^* in 6 lines.

$$2^2P_{3/2}, \quad g_j=1+\frac{15/4+3/4-2}{2.15/4}=\frac{4}{3}; \qquad (17.54)$$

$$2^2P_{1/2}, \quad g_j=2/3; \qquad 1^2S_{1/2},\ 2^2S_{1/2}, \quad g_j=2.$$

Substituting into (17.52), we obtain the change in energy for every value of m_j in all states and the spaces Δ between the sublevels of the terms:

$$\begin{aligned}&2^2P_{3/2} \rightarrow \Delta = \frac{4\mathcal{E}}{3}; \quad 2^2P_{1/2} \text{ and } 2^2S_{1/2} \rightarrow \Delta = \frac{2\mathcal{E}}{3};\\ &1^2S_{1/2} \rightarrow \Delta = 2\mathcal{E}.\end{aligned} \tag{17.55}$$

Here $\mathcal{E} = \mu_B B = \omega_L \hbar$.

The sublevels which are obtained due to the anomalous Zeeman effect in H atom, are shown in Fig. 17-13. We shall underline once again that they are not equidistant. Applying the selection rules (Section 17.2) we establish that instead of the doublet in Fig. 17-6, as a result of the influence of the magnetic field **B**, we obtain 10 lines.

In an analogous way we obtain the splitting of the levels of the three terms $3^2S_{1/2}$, $3^2P_{1/2}$, $3^2P_{3/2}$ and the allowed transitions of the anomalous Zeeman effect in the Na atom (Fig. 17-14). We have used the g-factors of hydrogen terms (17.54), because g_j does not depend on the principal quantum number.

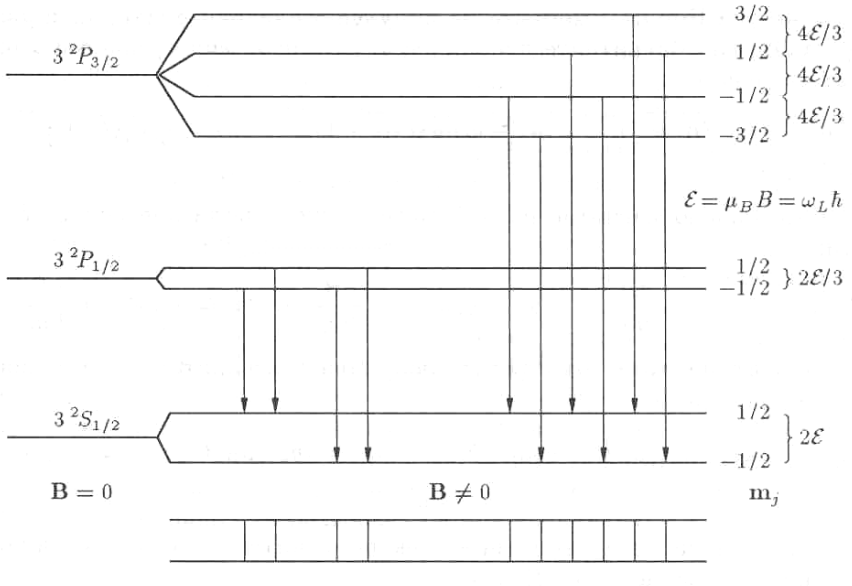


Figure 17-14. Anomalous Zeeman effect in Na. Both lines of the yellow doublet split correspondingly on 4 and 6 lines.

SUMMARY

Each rotation motion of a charged particle can be treated as a current in a loop, which corresponds to a magnetic dipole with a magnetic moment uniquely determined by the angular momentum, charge and mass of the particle. As the electron in the atom has three different angular momenta **L**, **S** and **J**, it possesses three magnetic moments corresponding to the orbital, spin and total rotation motions: μ_l, μ_s and μ_j. In atomic physics the magnetic moment is expressed in the units of $\mu_B = e\hbar / 2m_e$. This quantity is called a magneton of Bohr. The ratio between the magnetic dipole moment in units of the Bohr magneton and the angular momentum in units of $\hbar$ is called g-factor of Lande. The magnetic dipole moments have the following form:

$$\begin{array}{lll} \mu_l = g_l \mu_B \sqrt{l(l+1)}, & \mu_s = g_s \mu_B \sqrt{s(s+1)}, & \mu_j = g_j \mu_B \sqrt{j(j+1)}, \\ g_1 = 1; & g_s = 2; & g_j = g_j(j, l\, s). \end{array}$$

In an external magnetic field **B** the dipoles precess with frequencies:

$$\omega_l = g_l \omega_L = g_l \frac{eB}{2m_e}; \omega_s = g_s \omega_L = g_s \frac{eB}{2m_e}; \omega_j = g_j \omega_L = g_j \frac{eB}{2m_e}.$$

As a result the electron gains an additional potential energy:

$$\Delta U_l = m g_l \mu_B B = m g_1 \omega_L \hbar,$$
$$\Delta U_s = m_s g_s \mu_B B = m_s g_s \omega_L \hbar,$$
$$\Delta U_j = m_j g_j \mu_B B = m_j g_j \omega_L \hbar.$$

A charged particle with a spin in an electromagnetic field is described by the Pauli equation:

$$i\hbar \frac{\partial \psi}{\partial t} = \left[\frac{1}{2m_e} \left(\hat{\mathbf{p}} - e\mathbf{A} \right)^2 + e\Phi + \mu_B \hat{\boldsymbol{\sigma}} \mathbf{B} \right] \psi .$$

Applied to the stationary state of the electron, it is divided to two equations for positively and negatively oriented spin with respect to the Z-axis:

$$\hat{H}_0 \psi_1 + \omega_L \left(\hat{L}_z + \hbar \right) \psi_1 = E \psi_1, \qquad \hat{H}_0 \psi_2 + \omega_L \left(\hat{L}_z - \hbar \right) \psi_2 = E \psi_2.$$

In the frame in which the electron is at rest, the relative motion of the positively-charged nucleus produces a magnetic field. It interacts with the spin magnetic moment of the electron (spin-orbit interaction), so that all energy levels split in two very close energy sublevels. The set of the levels, which are obtained as the result of the spin-orbit interaction, is called a fine structure. The relative change in energy is proportional to the square of the fine-structure constant α^2. The interaction of the magnetic field with an electron in an atom is called the Zeeman effect. There are two Zeeman effects, normal and anomalous.

The normal effect of Zeeman defines the splitting of the singlet spectral line in triplet under the influence of the external magnetic field. It is observed at:

1. $S = 0,\ \mathrm{L} \neq 0$ and an arbitrary magnetic field;
2. $S \neq 0,\ \mathrm{L} \neq 0$ and a strong magnetic field.

In the first case the external magnetic field interacts with the orbital magnetic moment of the electrons. Each level of the atom structure with energy E_{nl} gains an additional energy ΔU_l and splits in $(2l+1)$ sublevels. In the second case the magnetic field is so strong that the interaction energy with the orbital and the spin moments is much greater than the energy of spin-orbit interaction. Here the magnetic field is strong enough to remove the *LS* coupling and to separately interact with **L** and **S**. The level with fixed *l* splits in $((2l+1)+2)$ sublevels.

Despite the multiplicity of the sublevels only three lines are observed in both cases. This is due to the equidistant levels and the selection rules.

The interaction of a weak magnetic field with an electron in a atom is called an anomalous Zeeman effect. In this case the potential energy which is gained by the electron, is less than the difference between the energies of two adjacent levels of the fine structure. The weak external magnetic field interacts with the magnetic dipole moment μ_j or, in other words, with the total angular momentum. As a result, the levels of the fine structure with fixed *l* splits in $(4l+2)$ sublevels.

QUESTIONS

1. What is the Bohr magneton?
2. Which are the dipole moments of the electron and what is their cause?
3. What is a Lande factor?
4. How can you explain the additional energy of an electron in an external magnetic field?
5. Why in an inhomogeneous magnetic field the electron beam is divided in two parts?

6. What is the physical nature of the spin-orbit interaction?
7. What is called a fine structure?
8. What are the selection rules for the transitions between the levels of the fine structure?
9. Are the *S*-terms doublets? Why?
10. In which cases is the normal Zeeman effect observed? What is the distance between the sublevels?
11. Why for the normal Zeeman effect for 9 allowed transitions we observe only three spectral lines?
12. What do we call an anomalous Zeeman effect?
13. What is the difference between the normal and the anomalous Zeeman effect from the energy point of view?
14. What are the distances between the sublevels for the anomalous Zeeman effect: a) for a fixed *j*; b) for different *j*'s?
15. What equation describes the state of the charged particle with a spin in an electromagnetic field?

PROBLEMS

1. Estimate the additional energy of an electron of an H atom in a state with $n = 2$ and $l = 1$ in the nuclear magnetic field. Estimate the field magnitude.
2. A line with $\lambda = 4226{,}73$ Å is radiated for the transition from *P*- to *S*-level in Ca atom. The normal Zeeman effect is observed when the Ca atom is in an external magnetic field with magnitude $B = 4.10^4$ Gs. Calculate the wavelengths of the spectral lines and the differences between them?
3. Determine the possible transitions from 3*p*-sublevels to 3*s*-sublevels for the Zeeman effect for the resonance line of Na in a strong magnetic field.
4. The resonance line of Lyman has a wavelength $\lambda = 1216$ Å. For the magnetic field $B = 10^4$ T find the splitting of its corresponding levels in units of $\mu_B B$, as well as the allowed transitions and the wavelengths of the spectral lines.
5. For the terms ${}^2S_{1/2}$, ${}^2P_{1/2}$ and ${}^2P_{3/2}$ for an anomalous Zeeman effect calculate: a) the splitting in the units of $\omega_L \hbar$; b) the allowed transitions; c) the splitting of the spectral lines for the transitions ${}^2P_{1/2} \to {}^2S_{1/2}$ and ${}^2P_{3/2} \to {}^2S_{1/2}$ in the units of $\omega_L \hbar$.
6. Express the Lande factor g_j for the interaction of a magnetic field with the total moment of an electron, with the quantum numbers.

Chapter 18

THE HELIUM ATOM

SUGGESTED READING

1. Greiner, W., Quantum Mechanics - An Introduction, Vol. 1, Springer-Verlag, 1989, Chapter 15.

2. Eisberg, R. and R. Resnic, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, John Wiley & Sons, 1974, Sections 9-2.
3. Gasiorowicz S., Quantum Physics, John-Wiley and Sons, 3rd ed., 2003., Chapter 18.
4. Blokhintsev, D. I., Principles of Quantum Mechanics, Allyn and Bacon, 1964, Section 121.

18.1 IDENTICAL PARTICLES

In classical mechanics particles with an identical nature (for example two molecules of oxygen) are distinguishable in principle. We can number or name them, for example *A* and *B* at the instant t_0 and then trace their trajectories. So, at the instant t_1 we can say which particle is *A* and which *B*.

In quantum mechanics the situation is totally different. Due to the uncertainty principle the term trajectory loses its meaning. Even if we identify particles at the instant t_0 as *A* and *B*, after some time at the instant t_1, because of the overlapping of the probability density, we cannot say where is *A* and where is *B* (Fig. 18.1).

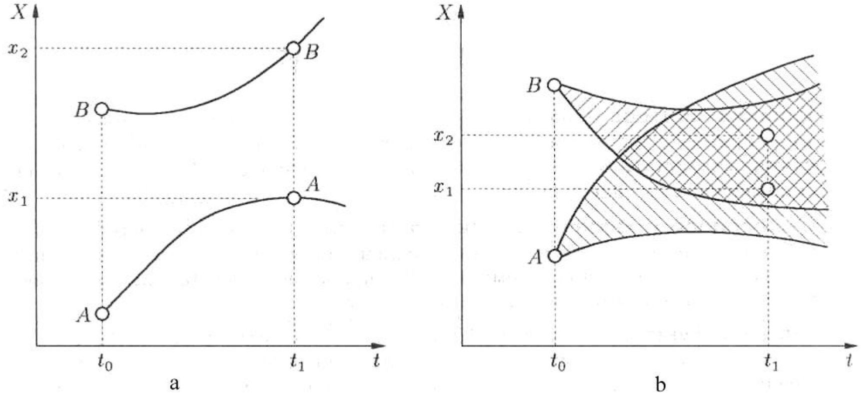


Figure 18-1. At the instant t_0 we identify: a) two classical particles *A* and *B*; b) two quantum particles *A* and *B*. At the instant t_1, tracing the trajectories of the classical particles, we can establish that *A* has co-ordinate x_1 and *B* - x_2. For the quantum particles at the instant t_1 we cannot say which of the them (*A* or *B*) has a co-ordinate x_1 and which - x_2, due to the overlap of the probability density.

In quantum mechanics particles lose their individuality and are indistinguishable. In classical physics we can follow the motion of a compound particle of a system by taking motion pictures of the system. Identical particles can be distinguished from each other by procedures which do not affect their behavior. In quantum mechanics this cannot be done because the uncertainty principle does not allow us to observe the motion of the particles (for example of an electron) without changing of the behavior of these particles. As we have seen in Section 9.4 the photon, which is used to illuminate the scene of a motion picture, interacts with an electron in an unpredictable manner. The behavior of the quantum particles (in this case electrons) is significantly affected by any attempt to distinguish them.

Consider a specifies example: two identical particles, each of them with mass *m*, are in an infinite square potential well of width *a*. Particle *A* is in the state with quantum number n_1 and *B* - with n_2 (Fig. 18-2). According to the conclusions in Section 12.2 we can write for wave functions, probability densities and energies of two particles

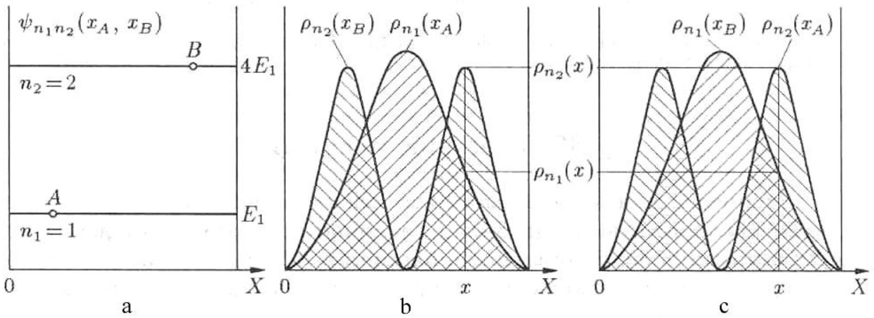


Figure 18-2. Two particles *A* and *B* in the states $n_1 = 1$ and $n_2 = 2$, respectively, in an infinite potential well (a); their probability densities in these states - *A* in n_1 and *B* in n_2 - (b); the same probability densities, when the states of *A* and *B* are exchanged, that is, *A* is in state n_2 and *B* is in state n_1 - (c).

$$\begin{aligned} \psi_{n_1}(x_A) &= \sqrt{\frac{2}{a}}\sin\frac{n_1\pi}{a}x_A, \quad \rho_{n_1}(x_A) = \frac{2}{a}\sin^2\frac{n_1\pi}{a}x_A, \quad E_{n_1} = n_1^2 E, \\ \psi_{n_2}(x_B) &= \sqrt{\frac{2}{a}}\sin\frac{n_2\pi}{a}x_B, \quad \rho_{n_2}(x_B) = \frac{2}{a}\sin^2\frac{n_2\pi}{a}x_B, \quad E = n_2^2 E, \end{aligned} \tag{18.1}$$

where $E = \pi^2\hbar^2/2ma^2$.

The distributions $\rho_{n_1}(x_A)$ and $\rho_{n_2}(x_B)$ for $n_1 = 1$ and $n_2 = 2$ are shown in Fig. 18-2b.

The wave function of the state of the two noninteracting particles $\psi_{n_1n_2}(x_A, x_B)$ is a product of the functions $\psi_{n_1}(x_A)$ and $\psi_{n_2}(x_B)$:

$$\psi_{n_1n_2} \equiv \psi_{n_1n_2}(x_A, x_B) = \frac{2}{a}\sin\frac{n_1\pi}{a}x_A \sin\frac{n_2\pi}{a}x_B. \tag{18.2}$$

Now let us exchange the positions of the particles - let *B* be in the state n_1 and *A* - in the state n_2. Then, instead of (18.1) we get:

$$\begin{aligned} &\psi_{n_1}(x_B)=\sqrt{\frac{2}{a}}\sin\frac{n_1\pi}{a}x_B,\ \rho_{n_1}(x_B)=\frac{2}{a}\sin^2\frac{n_1\pi}{a}x_B,\ E_{n_1}=n_1^2E_1,\\ &\psi_{n_2}(x_A)=\sqrt{\frac{2}{a}}\sin\frac{n_2\pi}{a}x_A,\ \rho_{n_2}(x_A)=\frac{2}{a}\sin^2\frac{n_2\pi}{a}x_A,\ E_{n_2}=n_2^2E_2. \end{aligned} \tag{18.3}$$

The distributions $\rho_{n1}(x_B)$ and $\rho_{n2}(x_A)$ for $n_1=1$ and $n_2=2$ are shown in Fig. 18-2c. The wave function $\psi_{n_2n_1}(x_A,x_B)$ is obtained by analogy with (18.2), i.e. with $\psi_{n_2n_1}(x_A,x_B)$:

$$\psi_{n_2n_1}\equiv\psi_{n_2n_1}(x_A,x_B)=\frac{2}{a}\sin\frac{n_2\pi}{a}x_A\sin\frac{n_1\pi}{a}x_B. \tag{18.4}$$

So, we have two states, in which the positions of the two identical particles have been exchanged. Let us try by physical means to distinguish the states from one another. If we position the measuring device for example in the point *x* (Fig. 18-2b, c) we shall register in both cases a particle with energy E_1 and a probability density $\rho_1(x)dx$ and a particle with energy E_2 and a probability density $\rho_2(x)dx$. But in both cases we cannot say which particle (*A* or *B*) has energy E_1 and which - $E_2=4E_1$. Both states are indistinguishable by physical means because of the indistinguishability of the particles.

Here we shall note one more interesting characteristic of these identical particles. The energies of the states $\psi_{n_1n_2}$ and $\psi_{n_2n_1}$ are

$$\begin{aligned} E_{n_1n_2}&=n_1^2E_1+n_2^2E_1=\left(n_1^2+n_2^2\right)E_1,\\ E_{n_2n_1}&=n_2^2E_1+n_1^2E_1=\left(n_2^2+n_1^2\right)E_1, \end{aligned} \tag{18.5}$$

i.e. they are equal. These energies are eigenvalues of the Hamiltonian of the system

$$\hat{H}_{AB}=\hat{H}_A+\hat{H}_B=\frac{\hat{p}_A^2}{2m}+\frac{\hat{p}_B^2}{2m}, \tag{18.6}$$

and functions $\psi_{n_1n_2}$ and $\psi_{n_2n_1}$ are its eigenfunctions. *One value of the energy* (18.5) *corresponds to two wave functions* (18.2) *and* (18.4). The energy is two-fold degenerated. *This degeneracy is called exchange degeneracy.*

Let us generalize the above discussion for two particles to a system of N identical particles in a state with a wave function $\psi(x_1, x_2, ..., x_i, ..., x_k, ..., x_N)$ and energy E. When we exchange the position of particles i and k the system is described by the wave function $\psi(x_1, x_2, ..., x_k, ..., x_i, ..., x_N)$, and it has the same energy. The exchange degeneracy is observed here too.

18.2 SYMMETRIC AND ANTISYMMETRIC STATES

For the exchange of two particles' co-ordinates we shall introduce the operator $\hat{\mathscr{P}}$, which is called the operator of permutation. Let us return to the example with the two-particle function $\psi(x_1, x_2)$. By definition the operator $\hat{\mathscr{P}}$ exchanges the co-ordinates of the two particles:

$$\hat{\mathscr{P}}\psi(x_1,x_2) = \psi(x_2,x_1). \tag{18.7}$$

If we designate the eigenvalue of this operator with λ we can write the equation for its eigenfunction:

$$\hat{\mathscr{P}}\psi(x_1,x_2) = \lambda\psi(x_1,x_2). \tag{18.8}$$

Then, applying the operator $\hat{\mathscr{P}}$ once again we get:

$$\hat{\mathscr{P}}[\hat{\mathscr{P}}(x_1,x_2)] = \lambda\hat{\mathscr{P}}\psi(x_1,x_2). \tag{18.9}$$

According to the definition of the operator (18.7), on the left-hand side we get $\psi(x_1, x_2)$ and on the right-hand side, using (18.8), we get $\lambda^2\psi(x_1, x_2)$:

$$\psi(x_1,x_2) = \lambda^2\psi(x_1,x_2) . \tag{18.10}$$

Therefore, the operator $\hat{\mathscr{P}}$ has two eigenvalues

$$\lambda_{1,2} = \pm 1. \tag{18.11}$$

So, we obtain

$$\hat{\mathscr{P}}\psi(x_1,x_2)=\psi(x_2,x_1)=\begin{cases}+\psi(x_1,x_2)\\ -\psi(x_1,x_2),\end{cases}\tag{18.12}$$

i.e. the wave function is symmetric or antisymmetric with respect to the exchange of the space co-ordinates of two particles. This means that two kinds of systems of particles exist: systems with wave function that change their sigh upon the exchange particles and system whose wave functions remain unchanged upon such an exchange. The functions $\psi_{n_1n_2}(x_A,x_B)$ (18.2) and $\psi_{n_2n_1}(x_A,x_B)$ (18.4) are neither symmetric nor antisymmetric. But by wave functions of individual particles we can construct linear combinations which will be the eigenfunctions of the Hamiltonian with eigenvalues $(n_1^2+n_2^2)E_1$. Two of these combinations have special meaning in physics. They are:

$$\begin{aligned}\psi_s(x_A,x_B)&=\frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_A)\psi_{n_2}(x_B)+\psi_{n_1}(x_B)\psi_{n_2}(x_A)\right],\\ \psi_a(x_A,x_B)&=\frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_A)\psi_{n_2}(x_B)-\psi_{n_1}(x_B)\psi_{n_2}(x_A)\right].\end{aligned}\tag{18.13}$$

The function $\psi_s(x_A,x_B)$ is symmetric:

$$\psi_s(x_A,x_B)=\psi_s(x_B,x_A),\tag{18.14}$$

an the function $\psi_a(x_A,x_B)$ is antisymmetric

$$\psi_a(x_A,x_B)=-\psi_a(x_B,x_A).\tag{18.15}$$

The Hamiltonian of the two particles does not change while interchanging of their positions. Then

$$\hat{\mathscr{P}}\left(\hat{H}\psi\right)=\hat{H}\left(\hat{\mathscr{P}}\psi\right),\tag{18.16}$$

from where we can conclude that the operator of the permutation commutes with the Hamiltonian:

$$\hat{H}\hat{\mathscr{P}}-\hat{\mathscr{P}}\hat{H}=0.\tag{18.17}$$

In Section 11.4 we have proved that if the operator of a given quantity does not depend on time and commutes with the Hamiltonian this quantity is a constant of the motion. Therefore, the parity of the ψ -function remains constant in time. In other words, a system of identical particles is described either by a symmetric wave function ψ_s, or by an antisymmetric ψ_a.

It is logically to suppose that the parity depends on the nature of the particles. Actually Pauli managed to prove that particles with an integer spin are described by the symmetric wave functions and with half-integer spin - by antisymmetric wave functions. The first obey the statistics of Bose-Einstein and are called *bosons*, and the second - the statistics of Fermi-Dirac and are called *fermions*. Fermions are the elementary particles with spin number $s = 1/2$ - electrons, positrons, protons, neutrons, neutrinos, muons, and bosons are the photons $(s = 1)$, π - and K-mesons $(s = 0)$. When we have a complex particle it is necessary to calculate its net spin. For example, for the H atom the net spin number according to the rules for addition of angular momenta can be either 0 or 1. Consequently, the hydrogen is a boson.

For fermions the following important result can be proved (see [2]): *In a system of identical fermions there can never be more than one fermion in the same quantum state.*

This is equivalent to the famous *Pauli's exclusion principle*, which was first empirically formulated for the electrons in multielectron atom on the basis of the atomic spectra.

Applied to the electrons in an atom, the Paul's principle states that *in an atom there can only be one electron in a quantum-mechanical state with the fixed numbers n, l, m and m_s. In the state with the fixed $n, l,$* and *m, there can be two electrons with the opposite spins $m_s = \pm 1/2$.* The exclusion principle is a consequence of the indistinguishability of identical particles.

18.3 SPIN FUNCTIONS OF HELIUM

Classical mechanics has been helpless trying to explain the atomic structure. The semi-classical mechanics of Borh, which in is a classical theory plus some rules for quantization, has been successfully applied to the H atom. But it has suffered a crash in its explanation of the helium atom, and generally, of multielectron atoms. The principal difficulties arose before it. Quantum mechanics did explain the structure of multielectron atoms, even though some difficulties also arose. But those are only some numerical difficulties.

The helium atom consists of a nucleus of charge $Z = 2$ and two electrons, which we can label 1 and 2. To solve the problem of the He atom it is necessary first to find its Hamiltonian. It can be written in the following form:

$$\hat{H} = \hat{T} + U_e + U_m, \tag{18.18}$$

where $\hat{T}$ is the operator of the kinetic energy of the two electrons, U_e is the electrostatic potential energy and U_m - the potential energy due to the magnetic interactions. The last include: the spin-orbit interaction of each of the electrons, the interaction of the magnetic field of one of electrons (due to its orbital motion) with the spin magnetic dipole moment of the other electron (the spin-other's orbit interactions $(l_1 s_2)$ and $(l_2 s_1)$), the interaction between their orbital angular momenta (orbit-orbit interactions), as well as the interactions between their spin angular momenta (spin-spin interaction), i.e.:

$$U_m = U_{l_1 s_1} + U_{l_2 s_2} + U_{l_1 s_2} + U_{l_2 s_1} + U_{l_1 l_2} + U_{s_1 s_2}. \tag{18.19}$$

In the previous chapter we convinced ourselves that the potential energy U_m of the magnetic interactions is substantially smaller than the electrostatic one:

$$U_m << U_e. \tag{18.20}$$

Neglecting the magnetic interactions of the electrons, which move in the nucleus Coulomb field (Fig. 18-3), we have for the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\Delta_{r_1} - \frac{\hbar^2}{2m_e}\Delta_{r_2} - \frac{2k_0 e^2}{r_1} - \frac{2k_0 e^2}{r_2} + \frac{k_0 e^2}{r_{12}}. \tag{18.21}$$

The neglect of the small magnetic interactions means also that the spins

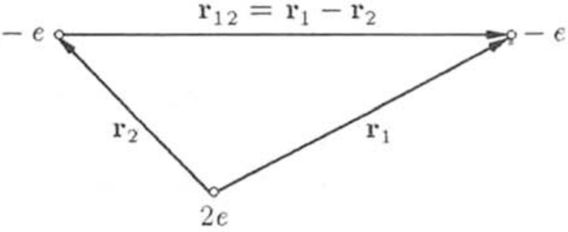


Figure 18-3. Atom of helium.

of the electrons do not influence their positions. Or, in others words, the space and spin variables are independent. Then we can seek the solution of the Schroedinger equation with a Hamiltonian (18.21) by the method of separation of variables:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, S_{1z}, S_{2z}) = \Phi(\mathbf{r}_1, \mathbf{r}_2) X(S_{1z}, S_{2z}), \tag{18.22}$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is a space wave function and $X(S_{1z}, S_{2z})$ a spin wave function.

We are not going to solve the Schroedinger equation, but we will restrict ourselves to finding the spin function $X(S_{1z}, S_{2z})$. The wave function ψ, which describes the state of both electrons is antisymmetric because they are fermions. Two cases are possible for antisymmetric ψ-function: antisymmetric space + symmetric spin functions and symmetric space + antisymmetric spin functions:

$$\begin{aligned} \psi_a^i(\mathbf{r}_1, \mathbf{r}_2, S_{1z}, S_{2z}) &= \Phi_a(\mathbf{r}_1, \mathbf{r}_2) X_s(S_{1z}, S_{2z}), \\ \psi_a^{ii}(\mathbf{r}_1, \mathbf{r}_2, S_{1z}, S_{2z}) &= \Phi_s(\mathbf{r}_1, \mathbf{r}_2) X_a(S_{1z}, S_{2z}). \end{aligned} \tag{18.23}$$

In Section 16.1 we have found that the spin state of an electron is described by two functions: $X_+(S_z)$ and $X_-(S_z)$, corresponding to the positively $(m = 1/2)$ and to the negatively $(m = -1/2)$ oriented spins. As we have neglected the spin interaction, we can present the spin function of the two electrons as a product of the spin functions of the different electrons:

$$X(S_{1z}, S_{2z}) = X_\alpha(S_{1z}) X_\alpha(S_{2z}), \tag{18.24}$$

where α takes the values ± for the one and for the other electron.

Hence, four combinations are possible:

$$\begin{aligned} X^i(S_{1z}, S_{2z}) &= X_+(S_{1z}) X_+(S_{2z}), && \uparrow\uparrow, \\ X^{ii}(S_{1z}, S_{2z}) &= X_-(S_{1z}) X_-(S_{2z}), && \downarrow\downarrow, \\ X^{iii}(S_{1z}, S_{2z}) &= X_+(S_{1z}) X_-(S_{2z}), && \uparrow\downarrow, \\ X^{iv}(S_{1z}, S_{2z}) &= X_-(S_{1z}) X_+(S_{2z}), && \downarrow\uparrow. \end{aligned} \tag{18.25}$$

In the right-hand side of each function are shown the directions of the two electron spins. The functions X^i and X^{ii} are symmetric, while the functions X^{iii} and X^{iv} are neither symmetric nor antisymmetric. But in the previous sections' example the situation has been fully analogous. Therefore, we shall use the symmetric and antisymmetric functions from example (18.13). By analogy, we can construct similar functions from X^{iii} and X^{iv}. As the result we have three symmetric spin functions (to which corresponds an antisymmetric space function) and one antisymmetric spin function (to which corresponds a symmetric space function):

$$\begin{aligned}
&X_s^{i}(S_{1z},S_{2z})=X_+(S_{1z})X_+(S_{2z}) \ ,\\
&X_s^{ii}(S_{1z},S_{2z})=X_-(S_{1z})X_-(S_{2z}) \ ,\\
&X_s^{iii}(S_{1z},S_{2z})=\frac{1}{\sqrt{2}}\left[X_+(S_{1z})X_-(S_{2z})+X_+(S_{2z})X_-(S_{1z})\right] \ ,\\
&X^{iv}(S_{1z},S_{2z})=\frac{1}{\sqrt{2}}\left[X_+(S_{1z})X_-(S_{2z})-X_+(S_{2z})X_-(S_{1z})\right] \ .
\end{aligned} \tag{18.26}$$

The physical meaning of the symmetric and antisymmetric spin states shall become clear through the vector interpretation in the next section.

18.4 VECTOR INTERPRETATION OF THE SPIN STATES. PARAHELIUM AND ORTHOHELIUM

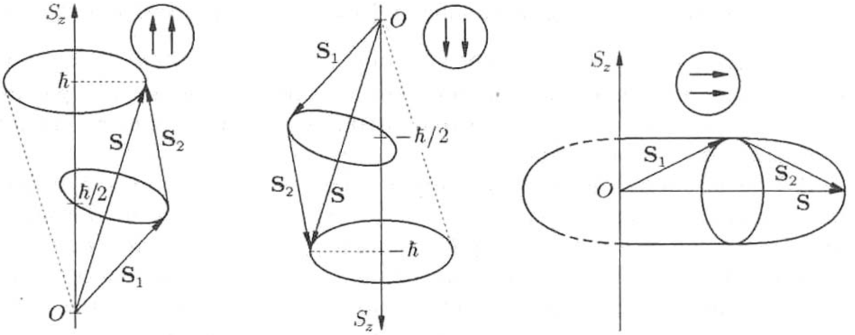
For each electron there are two possible states of its spin - positively and negatively oriented (Fig. 18-4). In both these cases the vector of the spin angular momentum precesses around the *Z*-axis (according to the vector interpretation of angular momentum - Fig. 10-2. Both the value of this angular momentum and its *Z*-component are determinate and the components S_x and S_y are indeterminate.

a) $m_s=1/2,\ S_z=\hbar/2,\ X_+(S_z)$; b) $m_s=-1/2,\ S_z=-\hbar/2,\ X_-(S_z)$.

Figure 18-4. Vector interpretation of the state of an electron with positive (a) and negative (b) spin.

And now to consider two electrons with spins $\mathbf{S}_1$ and $\mathbf{S}_2$. In the state with X_s^i both spins are positively oriented (Fig.18-5). Their vectors precess around the total spin **S** and it precesses around *Z*-axis. We shall note that the addition of both angular momenta with the spin numbers $s_1 = 1/2$ and $s_2 = 1/2$ results in two possible total momenta with numbers.

For $s = 1$ the vector $\mathbf{S}$ has three orientations, which are shown in Fig. 18-5. For these three states the quantities of S, S_z, S_1, S_2 are determinate and S_x, S_y and the three components of the spin of the each of the electrons are indeterminate. The symbolic notations of the spin are shown in circles (compare with (18.25)).



a) $m_s = 1,\ S_z = \hbar,\ X_s^i$; b) $m_s = -1,\ S_z = -\hbar,\ X_s^{ii}$; c) $m_s = -1,\ S_z = -\hbar,\ X_s^{iii}$.

Figure 18-5. Vector interpretation of the spin symmetric states of the electrons in He; S_z-component of the total spin is positive (a), negative (b) or zero (c).

As it can be seen from Fig. 18-5a,b, the spins of electrons are always positive in the state X_s^i and negative in the state X_s^{ii}. The state X_s^{iii} in Fig. 18-5c is a linear combination (a superposition) of two possible states of the spins and therefore S_{1z} and S_{2z} can be both positive and negative. The precession of the vectors $\mathbf{S}_1$ and $\mathbf{S}_2$ around the vector **S** ensures this.

The state with the total quantum number $s = 0$ is also a superposition. In it $S_1{=}S_2{=}\hbar\sqrt{3}/2,\ S{=}0,$ and $S_z{=}0$. Meanwhile the components S_{1x}, S_{1y}, S_{1z} and S_{2x}, S_{2y}, S_{2z} are indeterminate. The interpretation in Fig. 18-6 corresponds to these conditions. The precession around the *X*- and *Y*-axes ensures the indeterminacy of the components of the two spins.

This analysis allows us to make the conclusion that two states of helium exist:

a) the state symmetric by co-ordinates $(\Phi_s(\mathbf{r}_1, \mathbf{r}_2))$ and antisymmetric by spin $(X_a(S_{1z}, S_{2z}))$ with a total spin $S = 0$ (antiparallel spins);
b) the state antisymmetric by co-ordinates $(\Phi_a(\mathbf{r}_1, \mathbf{r}_2))$ and symmetric by spin $(X_s(S_{1z}, S_{2z}))$ with a total spin $S = 1$ (parallel spins); in this case the spin states are three and they correspond to three different orientation of the spin.

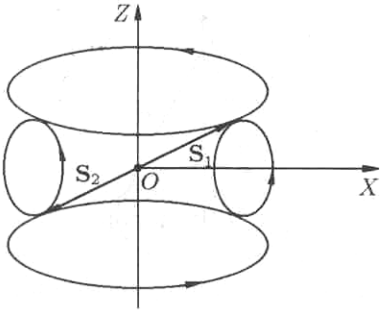


Figure 18-6. Vector interpretation of the antisymmetric spin state of the two electrons in the atom of helium.

The state with the antiparallel spins is a singlet and the one with parallels spins a triplet.

In Section 18.2 we have seen that because of the operator commutation of the permutation with the Hamiltonian, the character of the symmetry is preserved. Then, if the helium exists in antisymmetric spin state it cannot transform into a helium in a symmetric state. And vice versa, if the helium exists in a symmetric spin state it cannot transform into a helium in an antisymmetric state. The impression is created that there are two kinds of helium. This is verified by experiment. *The helium with antiparallel spins* (*antisymmetric spin state*) *is called parahelium. The helium with parallel spins* (*symmetric spin state*) *is called orthohelium.*

Which of these states is a ground state of the atom of helium? Recall that in all considered until now quantum-mechanical systems (a potential well, a rotator, a harmonic oscillator, and an atom of hydrogen) the lowest energy state is described by a spatial wave function without nodes. But the antisymmetric wave function of helium $\Phi_a(\mathbf{r}_1, \mathbf{r}_2)$ has a node at $\mathbf{r}_1 = \mathbf{r}_2$. In fact, because

$$\Phi_a(\mathbf{r}_1, \mathbf{r}_2) = -\Phi_a(\mathbf{r}_1, \mathbf{r}_2), \tag{18.27}$$

at $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$

$$\Phi_a(\mathbf{r},\mathbf{r}) = -\Phi_a(\mathbf{r},\mathbf{r}) \Rightarrow \Phi_a(\mathbf{r}) = 0. \qquad (18.28)$$

Hence, the symmetric spatial state has lower energy. This state is antisymmetric by spin, i.e. this is parahelium. So the ground state of the helium atom, i.e. the state with the minimal possible energy is parahelium. The energy levels of this state with $n \leqq 4$ are shown in Fig. 18.7. The energy of the ionization of He atom is 24,47 eV. The ground state, the term 1^1S_0 has energy 24,47 eV and the lower energetic level of the orthohelium, the term 2^3S_1 has an energy of 19,77 eV higher than it.

Naturally, a question arises how to obtain orthohelium. We already stated that the transition between the para- and orthohelium is impossible. However, we neglected the magnetic interactions. Only in that case the spatial and the spin variables are separated and the transition from the state ψ_a^i to the state ψ_a^{ii} (see (18.23)) is impossible. We described the states, respectively, by the spatial wave functions $\Phi_a(\mathbf{r}_1,\mathbf{r}_2)$ and $\Phi_s(\mathbf{r}_1,\mathbf{r}_2)$ and the transition between them would mean that the parity changed!). But the magnetic interactions, however weak, exist, i.e. theoretically the transition from the state ψ_a^i to the state ψ_a^{ii} is possible. In this case (taking into account the magnetic interactions) the wave functions (ψ_a^i and ψ_a^{ii}!) are antisymmetric and for such a transition the parity would be saved and the spin would remain unchanged. As magnetic interactions are very weak, the probability of such a transition is small.

As an illustration we shall consider a qualitative example of the photon impact on a He atom. It can be proved that the energy of the interaction of a photon with the magnetic moment of an electron E_m is v/c time smaller than the energy of its interaction with the charge of the electron E_e ([4], Section 121):

$$\frac{E_m}{E_e} \approx \frac{v}{c} \sim \frac{1}{100}. \qquad (18.29)$$

The probability of transition is proportional to the square of the perturbation energy. Therefore the ratio between the probabilities of the transition due to the magnetic interaction and of transition due to the electric interaction (without a change of the spin) is of the order of 10^{-4}. The probability of a transition accompanied by a change of the spin is negligible and the conversion of orthohelium into parahelium through the absorption of a photon is practically impossible.

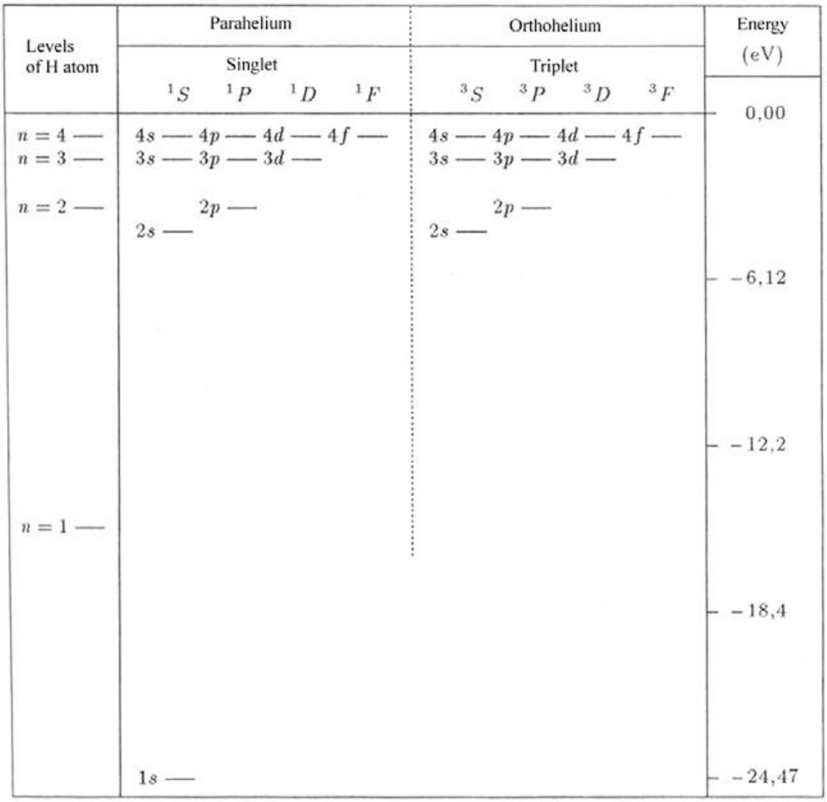


Figure 18.7. The energy levels of the two helium states: parahelium and orthohelium.

But it can occur due to a bombardment with an electron. Of course the above analysis cannot be used for such a case. This is already a problem of three electrons. The incident electron can take the place of one of the atomic electrons of the parahelium. In such an exchange the electron spin could be changed: the parahelium could transform into orthohelium.

SUMMARY

Identical particles in quantum mechanics lose their individuality and are indistinguishable. If in a potential well we have two particles *A* and *B* with energies E_1 and E_2, measuring the energy would produce either E_1 or E_2. But we cannot say which particle (*A* or *B*) has the energy E_1 and which E_2.

The both particles are indistinguishable by physical means.

If in a system of identical particles in a state described by a wave function $\psi(x_1, x_2, ..., x_i, ..., x_k, ..., x_N)$ and an energy E we could exchange the position of particles i and k, the system would be described by the wave function $\psi(x_1, x_2, ..., x_k, ..., x_i, ..., x_N)$ and would have the same energy. The energy is 2-fold degenerate. This degeneracy is called exchange degeneracy. It is observed in systems of identical particles when exchanging the positions of any two of them.

The parity is a constant of the motion. A system of identical particles can be either in a symmetric or in an antisymmetric state. Particles with an integer spin (bosons) are described by symmetric wave functions and particles with half-integer spin (fermions) - with antisymmetric ones. The fermions obey the principle of Pauli: two fermions of a given system cannot be in one and the same state.

For the addition of two spin moments with numbers $s_1 = 1/2$ and $s_2 = 1/2$ the total spin has two quantum numbers: $s = 0$ (antiparallel spins) and $s = 1$ (parallel spins). The state with antiparallel spins is a singlet and the one with parallel spin is a triplet. The helium atom with antiparallel spins of its electrons is called parahelium and the one with parallel spins of its electron - orthohelium. The ground state of helium, i.e. the state with minimal possible energy, is parahelium. The conversion of orthohelium into parahelium by an absorption of a photon is practically impossible to be achieved. But it is possible to achieve it by a bombardment of a He atom with an electron.

QUESTIONS

1. Why are identical particles in quantum mechanics indistinguishable?
2. What is exchange degeneracy?
3. What do the symmetric and antisymmetric wave functions represent?
4. Which are the eigenvalues of the operator of permutation?
5. Why cannot the parity of particles change?
6. Which particles are fermions and which bosons?
7. To which kind does the hydrogen atom belong?
8. Which kind of particles are obey the Pauli's principle? What does this principle state?
9. What is the relation between the energies of the magnetic and the Coulomb interactions in the He atom?
10. What are the character and the general form of the wave function of the electrons in a He atom?

11. Which spin functions characterize the possible orientations of the electron spins in the He atom?
12. How would you interpret in a vector form the spin of one electron and of the symmetric and the antisymmetyric states of the helium electrons?
13. Why are the levels of a parahelium singlets?
14. How can we conclude which kind of helium is in the ground state?
15. How can you explain that the symmetric states are three and the antisymmetric - one?
16. Are transitions from parahelium to orthohelium possible?

PROBLEMS

1. Prove that the number of bosons, filling an infinite potential well is proportional to its energy E and the number of photons is proportional to $E^{1/3}$.
2. What would be the energy of the ground state of a He atom if we neglect the spin-orbit interaction and the interaction between its electrons?
3. Within the same approximation as in problem 2, find the wave function of the ground state.
4. Determine the wavelength of the two lines in the spectrum of a single ionized He atom which correspond to the first two lines of the Balmer series of the H atom.
5. The energy of the full (double) ionization of He is equal to 78,98 eV. Find the energy of the single ionization of the He atom and the ionization energy of the ion He^{+}.

Chapter 19

PERIODIC TABLE

SUGGESTED READING

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3. Spolsky, E. V., Atomic Physics, Vol. 1, 2, Mir Publishing House, 1963, Sections 82, 90÷93.
4. Garcia, N. and A. Damask, Physics for Computer Science Students with Emphasis on Atomic and Semiconductor Physics, John Wiley & Sons, New York, 1986, 1st ed., Section 21.7.

19.1 MULTIELECTRON ATOMS – THE HARTREE THEORY

In the previous chapter, neglecting the magnetic interaction, we managed to analyze the spin state of He atom. For the full analysis it is necessary to solve the Schroedinger equation (18.21) of He atom. In that case we would find the two-particle wave function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$. As we have already mentioned in Section 18.3, the exact solution of this problem is impossible. This is true for all atoms with more than two electrons. We should note once more that these difficulties are only computational. Different approximation methods are developed for solving the Schroedinger equation. Here we shall consider the essence of one of them - the method of self-consistent field more called the field method of Hartree-Fock. The rigorous approach for obtaining the Hartree-Fock equations is based on the variational principle. We will adduce only the physical meaning of it. The spatial distribution of the electrons in an atom changes continuously, but in a stationary state the probability density remains constant. Therefore, each electron creates some field, which can be considered as constant. Then, the motion of each electron can be thought as being independent in the average field of the nucleus and of all other electrons. Or, in other words, each electron possesses its wave function and its set of quantum numbers. Then the N-particle wave function of an N-electron atom can be represented as a product of single-particle wave functions of the states of each one electron:

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_N)=\psi_{n_1}(\mathbf{r}_1)\,\psi_{n_2}(\mathbf{r}_2)\,\psi_{n_3}(\mathbf{r}_3)\,...\,\psi_{n_N}(\mathbf{r}_N)\,. \tag{19.1}$$

Here $\psi_{ni}(\mathbf{r}_i)$ is the wave function of the *i*th electron, which is in a state with quantum numbers n_i. The interaction between the electrons is taking into account by including it in the Hamiltonian. The operator of Hamilton for separate electron which moves in the field of the nucleus and all other electrons can be written as follows:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\Delta_i - U(r_i) + U_\Sigma(r_i). \tag{19.2}$$

Here $U(r_i)$ is the potential energy of the electron in the Coulomb field of the nucleus and $U_\Sigma(r_i)$ is the electrostatic energy of the interaction of the *i*th electron with the others. If the probability density of an arbitrary *k*th electron is $\left|\psi_{n_k}\right|^2$ its charge density $\rho_k^e(\mathbf{r}_k)$ is distributed in space according to the law $\rho_k^e(\mathbf{r}_k) = e\left|\psi_{n_k}\right|^2$.

According to the Coulomb law, the energy of interaction between the *i*th and the *k*th electron is

$$U_{ik}(r_i) = \int \frac{k_0 e^2 \left|\psi_{n_k}\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_k\right|} dV_k \ . \tag{19.3}$$

It is obvious that to determine the energy of interaction with all electrons it is necessary to sum up these energies:

$$U_\Sigma(r_i) = \sum_{k \neq i} \int \frac{k_0 e^2 \left|\psi_{n_k}\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_k\right|} dV_k \ . \tag{19.4}$$

Then the Hamiltonian takes the following form:

$$\hat{H}_i = -\frac{\hbar^2}{2m}\Delta_i - U(r_i) + \sum_{k \neq i} \int \frac{k_0 e^2 \left|\psi_{n_k}\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_k\right|} dV_k \ , \tag{19.5}$$

and the function $\psi_{n_i}(\mathbf{r}_i)$ satisfies the stationary Schroedinger equation

$$\hat{H}_i \psi_{n_i}(\mathbf{r_i}) = E_{n},\psi_{n_i}(\mathbf{r}_i), \quad i = 1, 2, 3, \ldots, N \,. \tag{19.6a}$$

The general form of this equation, written through the potential energy $U_s(r_i)$, which unites the potential energies in the field of the nucleus and the electrons $(U_s(r_i) = -U(r_i) + U_\Sigma(r_i))$, does not differ from the (14.10) for the H atom:

$$-\frac{\hbar^2}{2m}\Delta_i\psi_{n_i}(\mathbf{r}_i) + U_s(r_i)\psi_{n_i}(\mathbf{r}_i) = E_{n_i}\psi_{n_i}(\mathbf{r}_i), \quad i=1,2,3,...,N. \qquad (19.6b)$$

In this equation for the function $\psi_{n_i}(\mathbf{r}_i)$ the wave functions of the remaining electrons enter through the Hamiltonian $\hat{H}_i$, i.e. through $U_\Sigma(r_i)$, which in the potential energy $U_s(r_i)$. The function $\psi_{n_i}(\mathbf{r}_i)$ in its turn enters in the Schroedinger equation of the remaining electrons. The relations (19.6) are in essence a system of equations for the functions $\psi_{n_k}(\mathbf{r}_k)$ ($k = 1, 2, 3, ..., N$).

The system (19.6) for determining of the electron wave functions is known as the Hartee approximation. In it, the identity of the electrons is not taken into account. To account for it, it is necessary to use the antisymmetric wave functions similar to those of the atom of He. Fock did this. Therefore the method carries the names of the both scientists.

The following method is used to solve the system (19.6). We choose an initial wave function for each electron separately. Usually they are chosen as wave functions of the hydrogen electron. Then, we use them to determine the energy of interaction $U_\Sigma(r_i)$ (19.4) and the Hamiltonians (19.5). Then, with the new Hamiltonians $\hat{H}_i$ we find the functions $\psi_{n_i}(\mathbf{r}_i)$, which differ from the starting ones (the functions of the hydrogen atom) These wave functions represent the next approximation to the exact wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)$. With their help we again calculate the potential (19.4) and the Hamiltonian (19.5) and then solve the system (19.6). We repeat these operations until the results converge, that is, the results have to be self-consisted.

The method of the self-consistent field allows us to describe the state of a multielectron atom with single-particle wave function instead of a multiparticle one $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)$. This gives us the possibility to describe the state of an atom with the quantum numbers n, l, m and $\mathrm{m_s}$ of separate electrons.

We shall present a short review of the results of Hartree-Fock theory: **1)** the angular dependence; **2)** the radial dependence and **3)** the electron energy in multielectron atom.

1) The wave functions, which are obtained by the Hartree-Fock method, are closely connected with the eigenfunctions considered in Chapter 14 for a one-electron atom. Actually the eigenfunctions of Hartree can be written as

$$\psi_{n_i}(\mathbf{r}_i) \equiv \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\omega, \varphi). \qquad (19.7)$$

For the sake of brevity the index *i* after the sign $\equiv$ has been omitted.

The spherical functions $Y_{lm}(\theta, \varphi)$, describing the angular dependence, are the same as in a one-electron atom. This is so because the Schroedinger equation (19.6) for a multielectron atom does not differ from the Shroedinger equation (14.10) for a one-electron atom as far as angular dependencies on θ and φ are concerned. Hence, all conclusions, related to the θ - and φ -dependencies of the eigenfunctions of a one-electron atom can be applied directly to the θ - and φ -dependencies of the eigenfunctions of a multielectron atom.

The sum of the probability density of states with single-electron wave functions of fixed n and l and all possible *m,* is spherically symmetric (see problem 1 for $n = 2$ and $l = 1$). According to the previous paragraph this is also true for the wave functions of a multielectron atom. When a multielectron atom is in its ground state, the quantum states with low energies are filled with electrons. This means that for almost all values of n and l there are electrons in states with all possible values of *m.* Hence, the sum of the probability densities of these electrons is spherically symmetric; such is their charge distribution. At least a few electrons in the highest energetic states, for which not all-possible values of *m* are filled, can make a contribution to the asymmetry of the charge distribution.

2) The dependence of the eigenfunctions of an electron in a multielectron atom on *r* is not the same as in a one-electron atom. The reason is that the net potential U_s which enters in the differential equation for $R_{nl}(r)$, does not have the same *r*-dependence as the Coulomb potential in a one-electron atom. A typical example for the radial distribution of a multielectron atom is shown in Fig. 19-1. These are the results of the Hartree-Fock method for the atom of argon with $Z = 18$. The value $2(2l+1)R_{nl}^2(r)r^2 = 2(2l+1)\rho_{nl}(r)$ is plotted on the vertical axis. Here $\rho_{nl}(r)$ is the radial probability density to find the electron with the quantum numbers *n* and *l* in the position with radial co-ordinate *r*. As for each fixed *l* there are $2l+1$ possible values of *m* and for each of them there are two values of m_s, the value $2(2l+1)\rho_{nl}(r)$ is a radial probability density for the states with quantum numbers *n* and *l,* multiplied by the numbers of electrons for which the Pauli's principle permits to occupy these states. In the ground states of the argon two electrons are in the state with $n = 1$ and $l = 0$, two - with $n = 2$ and $l = 0$, six - with $n = 2$ and $l = 1$, two - with $n = 3$ and $l = 0$ and six - with $n = 3$ and $l = 1$. These are the states, which are filled in the ground state of the atom, because as how we shall see later they have the lowest possible energy.

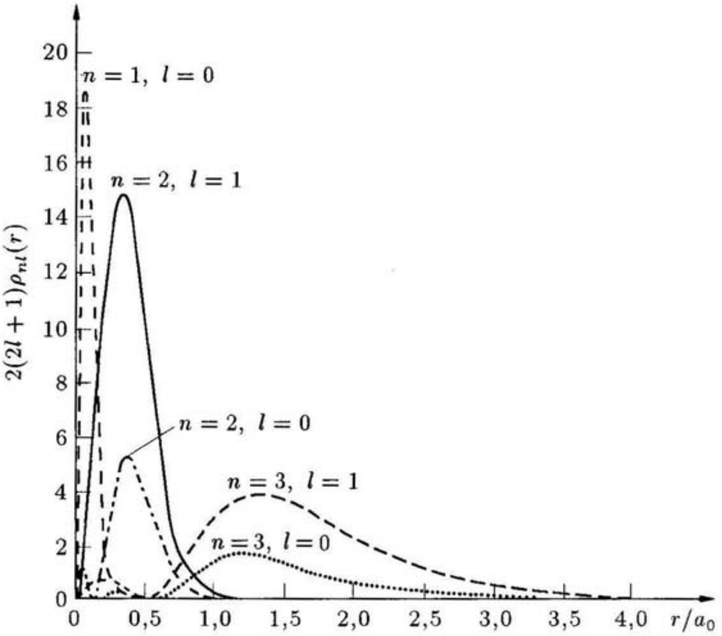


Figure 19-1. The radial probability densities for the filled quantum states of argon, according to the Hartree-Fock theory, as a function of *r*, which is normalized with the Bohr radius a_0. For each fixed value of *n* the probability density is concentrated mainly in a limit layer called a shell.

The radial probability density $\rho(r)$ of the atom ^{18}Ar is shown in Fig. 19-2. It is a sum of the probability densities of each populated state, multiplied by the number of electrons in it. Physically $\rho(r)$ gives the probability to find an arbitrary electron in the region between r and $r+dr$. The figure also shows indirectly through the effective charge number $Z(r)$, the net potential $U_s(r)$. The relationship between these two quantities (see also (14.67)) is as follows:

$$U_s(r) = -\frac{k_0 Z(r) e^2}{r}. \tag{19.8}$$

3) The results of the Hartree-Fock theory show that the energy of the electron in a multielectron atom depends both on the principal number *n* and on the orbital number *l*, i.e. $E = E_{nl}$. We have already reached such con-

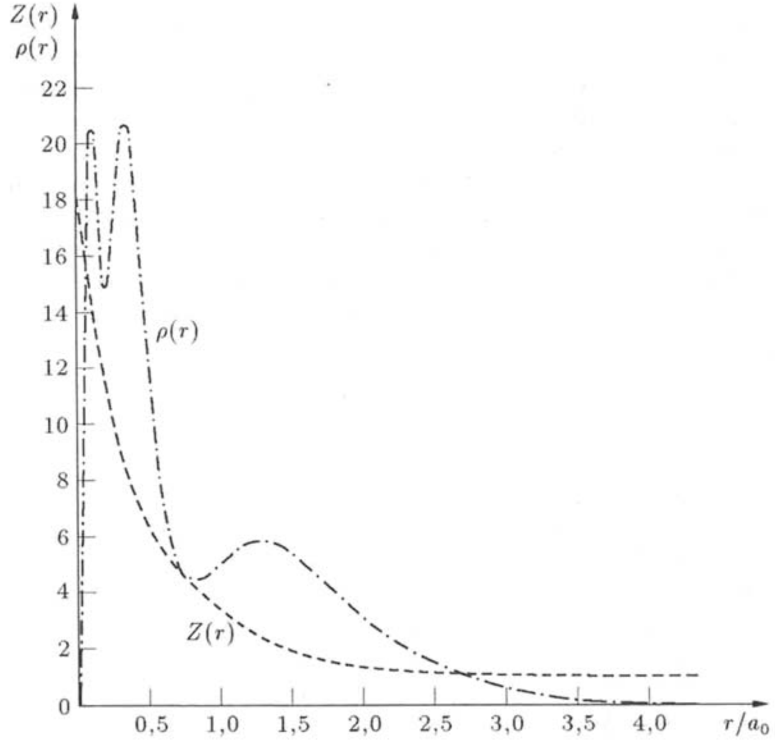


Figure 19-2. The total radial probability densities $\rho(r)$ of the argon and the effective charge $Z(r)$, which determines the net potential $U_s(r)$.

clusion in Section 14.5 for a special case of the multielectron atoms namely, the hydrogen-like atoms.

19.2 SHELL STRUCTURE OF THE ATOM

Theory and experiment show that the electrons which have the same energy are characterized by approximately the same average distance from the nucleus. In this sense the electrons with states of equal energy produce layer structures from the nucleus. The atom has a layered structure.

A shell is called a set of the quantum states with fixed principal quantum number n. The shell with given *n* is denoted with capital Latin letter:

$n=$	1	2	3	4	5	6	7,
letter notation	*K*	*L*	*M*	*N*	*O*	*P*	*Q*.

In fact, from the plots of $\rho_{nl}(r)$ in Fig. 19-1 it is clear that the probability density of all electrons with an equal number *n* is significant in the same range of *r*. These electrons are situated in a spherical layer, which as we have already said, is called a shell.

For the estimation of the shells we shall use formula (19.8). For the argon atom we shall take the values of $Z(r)$ from Fig. 19-2. This approach gives a rough but very useful approximation of the results of the Hartree-Fock theory. In this approach all electrons from the shell *n* are moving in the field of the Coulomb potential:

$$U_s(r) = -\frac{k_0 Z_n e^2}{r}, \tag{19.9}$$

where Z_n is a constant equal to the effective charge number $Z(r)$ for the average value of *r* for the shell (for "the radius" of the shell). Very often Z_n is called the effective charge number of the shell. For the argon atom $(Z = 18)$ from Fig. 19-2 we find:

$$Z_1 \approx 16, \quad Z_2 \approx 8, \quad Z_1 \approx 3. \tag{19.10}$$

The Schroedinger equation (19.6) for the potential (19.9) has a solution for the eigenvalues of the energy, coinciding with the energy (14.55) of the one-electron atom:

$$E \approx -\frac{\tilde{m} k_0^2 Z(r)\, e^4}{2\hbar^2 n^2} \approx -\frac{m_e k_0^2 Z_n^2 e^4}{2\hbar^2 n^2} = -\frac{Z_n^2}{n^2} R = -\frac{Z_n^2}{n^2} 13{,}6 \text{ eV}. \tag{19.11}$$

After substituting (19.10) for the atom of Ar we obtain $E_1 \approx -16^2 \times 13{,}6$ eV ≈ -3500 eV, $E_2 \approx -4^2 \times 13{,}6$ eV ≈ -220 eV and $E_3 \approx -1^2 \times 13{,}6$ eV ≈ -14 eV. This estimate differs from the exact results, obtained by the Hartree-Fock theory by about 20%.

In the example which we considered for the argon atom $(Z = 18)$, the effective charge of the inner shell $(n = 1)$ is $Z_1 = 16$. The calculations within the Hartree-Fock theory show that in all multielectron atoms $Z_1 \approx Z - 2$. For the outermost shell of the argon ($n = 3$) we have obtained small number for the effective charge: $Z_3 \approx 3$. This is so, because an electron in the outermost shell is almost completely shielded from the nuclear charge by the inner electrons. It appears that for all multielectron atoms the effective charge of the outermost shell with the quantum number *n* is $Z_n \approx n$.

In the multielectron atoms, inner shells with small *n* have very small radius because for these shell the shielding by the remain electrons is weak and the electrons are attracted almost fully by the positively charged nucleus. The Hartree-Fock theory predicts that the radius of the *K*-shell $(n=1)$ is approximately $(Z-2)$ times smaller than the hydrogen radius. (This result is a very rough approximation for large *Z*, because of the relativistic effects which are not taken into account. In this case the relativistic effects are very important because the electrons of the inner shells of atoms with large *Z* have energies comparable to the rest energy $m_e c^2 \approx 5.10^5\ \text{eV}$.) Using the same rough method, we substitute in the equation for an one-electron atom $Z_1 \approx Z-2$ and $n \approx 1$ and obtain for the average radius:

$$\bar{r} \approx \frac{n^2 a_0}{Z_1} \approx \frac{\bar{r}_H}{Z-2}. \qquad (19.12)$$

The index *H* relates to the hydrogen; here $\bar{r}_H$ stands for its average radius. For the outermost shell, substituting in (19.12) for Z_1 the effective charge $Z_n \approx n$ we obtain the following:

$$\bar{r} \approx \frac{n^2 a_0}{Z_n} \approx \frac{n^2 a_0}{n} \approx n a_0. \qquad (19.13)$$

This is a very interesting result. Although it is a crude estimate, it correctly expresses the fact that the radius of the outermost shell increases very slowly with the atomic number. Hartree calculations show that *even for elements of highest atomic number, their outermost shell radius is only three times larger than the radius of the hydrogen.* Since the average radius of the outermost shell defines the size of the atom, the above statement can be used to estimate atomic sizes.

Using the crude method we can find the energy of the innermost and the outermost shells. For the *K*-shell, according to (19.11) it is equal to $(Z-2)^2$ times the energy of the hydrogen electron with quantum number $n=1$:

$$E_z \approx -\frac{\widetilde{m} k_0^2 (Z-2)^2 e^4}{2\hbar^2} = (Z-2)^2 E_{1H}. \qquad (19.14)$$

Similarly, for an electron of the outermost *n*th shell we get

$$E_z \approx -\frac{\tilde{m}k_0^2 Z_n{}^2 e^4}{2\hbar^2 n^2} \approx -\frac{\tilde{m}k_0^2 e^4}{2\hbar^2} = E_{1H}\,. \tag{19.15}$$

The energy of an electron from the outermost populated shell is comparable to the energy of the electron in the ground state of the hydrogen.

A subshell - a set of the quantum state with fixed principal quantum number n and orbital quantum number l.

Electrons with equal quantum numbers n and l are called equivalent electrons. Relationship (14.64) shows that the average radii of equivalent electrons, i.e. the electrons of a subshell, are exactly equal to each other. And according to the curve $Z(r)$ in Fig. 19-2 this means that they have equal effective charges. Using (19.11), this in its turn means that the states of a subshell possess equal energy E_{nl}, which depends on both the principal and the orbital quantum numbers.

The number of states in a subshell is defined by the allowed orientations of the orbital angular momentum. For a fixed orbital number they are $N_l = 2l+1$ states with equal n and l, but with different m. Taking into account the exclusion Pauli's principle that in every state n, l and m there can be two electrons, we can determine the number of electrons in a given shell. The states in a given shell, their number and the number of electrons are presented in Table 19-1.

Table 19-1. The states, the numbers of states and the electrons in the subshells

Subshell		The states with the magnetic quantum number m=	Number of states	Number of electrons
l	Letter notation			
0	*s*	0	1	2
1	*p*	−1, 0, 1	3	6
2	*d*	−2, −1, 0, 1, 2	5	10
3	*f*	−3, −2, −1, 0, 1, 2, 3	7	14
4	*g*	−4, −3, −2, −1, 0, 1, 2, 3, 4	9	18

The number of the subhells in a shell n is equal to the number of the shell, i.e. n. The states in a given shell differ by their orbital angular momentum and its orientations. While calculating the multiplicity of the degeneracy of the hydrogen atom (Section 14.3) we determined the number of possible states $N_n = n^2$. According to the Pauli's principle the number of electrons in the shell is $N_n^e = 2n^2$.

The shells, subshells, number of the states and number of electrons in them are given in Table 19-2.

The order of subshells in increasing energy will allow us to establish the order of filling them with electrons. To within first order, it is natural to neglect the energy of the electrons and consider that the energy of the atom is equal to the sum of the electron energies in the Coulomb field of the nucleus. The energy of the electron in the Coulomb field of the nucleus is well known (14.41) and therefore it is not difficult to find the distribution (with minimal energy) of the electrons in different states, taking into account the Pauli's exclusion principle. As a result we obtain the ideal scheme of the shell filling, which essentially differs from the real scheme, but its consideration is useful.

We know from the hydrogen atom that the energy of the state increases with n. Therefore we expect in the ideal scheme to subsequently fill the shells K, L, M, N, O, P, Q (here we pointed the shells, which are observed in the real existing elements in Nature and artificial created ones).

Table 19-2. The subshells and the numbers of states and electrons in sells

Shell		Subshells in a shell	Number of states	Number of electrons
n	Letter notation			
1	K	$1s$	1	2
2	L	$2s,\ 2p$	4	8
3	M	$3s,\ 3p,\ 3d$	9	18
4	N	$4s,\ 4p,\ 4d,\ 4f$	16	32
5	O	$5s,\ 5p,\ 5d,\ 5f,\ 5g$	25	50

On the basis of the states of three hydrogen-like atoms considered in Section 14.5, we would expect inside the shell, i.e. at fixed n, the filling would "ideally" form s, p, g, f, g, etc. subshells. The ideal filling would occur when subshells are ordered in an increasing order in the following way:

$$\begin{array}{ccccc} K & L & M & N & O \end{array}$$
$$\xrightarrow{\begin{array}{ccccc} 1s & 1s,2p & 3s,3p,3d & 4s,4p,4d,4f & 5s,5p,5d,5f,5g \end{array}} E. \tag{19.16}$$

This ideal order however is in contradiction with the rule of filling that every subsequent electron fills the state with a minimal possible energy (rule 2. in the next Section 19.3).

In fact, the energy increases with both n and l. But to answer the question, how are the states ordered, we must solve the quantum-mechanical problem of N electrons in an atom. We know that this is very difficult problem. Therefore, we are forced to use empirical data in particular chemical and spectroscopic data, for the ionisation potentials of the atoms. This attaches to the periodic-table theory a semi-empirical descriptive character. Therefore, it is better not to speak about a theory but about an explanation of the periodic system.

One of the most important semi-empirical rules, which allow us to order the subshells in increasing energy, is the *rule of Madelung*. It states:

The energy of the subshell increases with increasing the sum $n+l$ *and for subshells with the same* $n+l$*, the subshell with the larger n has larger energy.*

Let's order the subshells according to the increasing the sum $n+l$ (Table19-3), applying the second part of the Madelung's rule to the sum with equal $n+l$.

Table 19-3. The subshells ordering according to the Madelung's rule, i.e. to the real scheme

$n+l$ of the state	Subshells
7	$4s$, $5d$, $6p$, $7s$
6	$4d$, $5p$, $6s$
5	$3d$, $4p$, $5s$
4	$3p$, $4s$ $\uparrow E$
3	$2p$, $4p$, $5s$
2	$2s$
1	$1s$

The subshells, ordered by increasing energy have the following order:

$$\underset{\xrightarrow{\hspace{30em}} E.}{1s, 2s, 2p, 3s, 3p, 4s, \underline{3d}, 4p, 5s, \underline{4d}, 5p, 6s, \underline{4f}, \underline{5d}, 6p, 7s, \underline{5f}, \underline{6d}} \tag{19.17}$$

Comparing to the ideal order (19.8) we note the deviation at the subshells $3d, 4d, 4f, 5d, 5f, 6d$, which are underlined. The breaking of the ideal order is observed in *d*- and *f*-subshells.

How can we explain the breaking of the ideal order of filling? It can be readily explained by the presence of the orbital angular momentum $L = \hbar\sqrt{\left(l(l+1)\right)}$ of the electron. In essence, this is the same qualitative explanation, which we used in Section 14.4. The energy of an atomic electron depends not only on its potential energy in the net field of the nucleus and the electron core, but also on its rotational energy

$$E_r = \frac{L^2}{2m_e r^2} = \frac{l(l+1)\hbar^2}{2m_e r^2}. \tag{19.18}$$

In such a way we can consider its motion in a central symmetric field with an effective energy $\widetilde{U}^l(r)$ (see Section 3.3):

$$\widetilde{U}^l(r) = -U(r) + \frac{l(l+1)\hbar^2}{2m_e r^2}, \tag{19.19}$$

where $-U(r)$ is the potential energy of the field of the nucleus and the electron core. With increasing *l*, as the electrostatic and the rotational energies are with opposite sign, the effective energy increases, i.e. it becomes less negative. This means that the bond of the electron with the nucleus decreases. For this reason the electrons from the 3*d*-subshell have smaller energy than the electron of 4*s*-subshell. The rotational energy of the electrons of the *d*- and *f*-subshell is a few times larger than that of the *p*-subshell (we are not speaking of rotational energy of *s*-electrons, which is zero).

The orbital angular momentum changes not only the electron energy. The curve of the effective potential energy $\widetilde{U}^l(r)$, which determines qualitatively the motion, is also changed. Therefore, another interesting phenomenon is observed - the immersion of the *d*- and *f*-subshell. Both the order and the immersion of these subshells are plotted in Fig. 19-3. Both phenomena are connected with the change of $\widetilde{U}^l(r)$ at different *l* (compare with Fig. 14-11b).

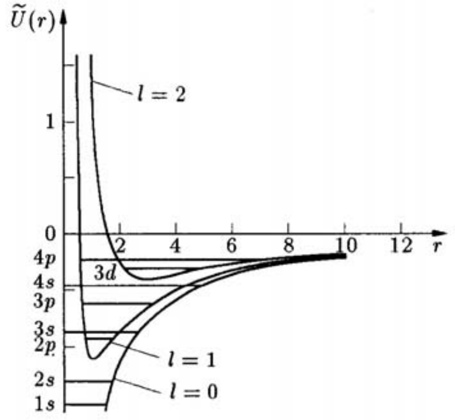


Figure 19-3. With increasing *l* the curve of the effective potential changes due to the increasing of the rotational energy. Therefore, the level 3*d* appears above the level 4*s* (in breaking the ideal order) and the electrons of this subshell are inner in respect to close *s*- and *p*-electrons (from the subshell 4*s* and 4*p*), i.e., the *d*-subshell sinks.

We have to underline once more that the analysis done above is qualitative. This analysis and the well-known chemical and physical properties of the atoms allow us to make a number of conclusions. We shall not consider them in detail, but shall only summarize them:

1. The subshells *s* and *p* are outer.
2. The number of electrons in the outer subshells is from 1 to 8 - they are called valence electrons; the outer subshell can not have more than 8 electrons.
3. The subshells *d* and *f* are inner.
4. Many chemical and physical properties of atoms with the same outer subshells differ insignificantly.
5. The periods of the Mendeleev system are defined by filling of the outer subshells.

19.3 ELECTRONIC CONFIGURATION AND THE PERIODIC TABLE

The preceding analysis allows us to formulate the following general rules for the structure of the Mendeleev table:

1. The structure of the atoms is defined by the atom number *Z*, i.e. by the charge of the nucleus. The isotopes of a given element have one and the same electronic structure.
2. With the increasing of the atomic number, i.e. increasing the electrons in the atom, the electrons gradually fill the states with minimal possible energy.
3. The number of electrons filling of the energy levels is limited by the Pauli's exclusion principle.
4. The energy of the *k*th electron, being in the net field of the nucleus and the remaining electrons, i.e. in spherically symmetric field, is determined by the principal quantum number n_k and the orbital quantum number l_k. Electrons with equal n and l have the same energy.
5. The electrons in the atom have a layered structure - they are grouped in shells and subshells.

Here we shall underline the important role of the Pauli's exclusion principle. The subshell 1*s* is the subshell with lowest energy. If the exclusion principle did not existed, all electrons in multielectron atoms would be in the subshell of lowest energy, i.e. in the subshell 1*s*. Then, all atoms would have spherically symmetrical distributions of their charge. Such a distribution would not produce an external electric field and according to Fig. 19-5 the atoms would have a very high first exited state. In other words, all atoms would be similar to the noble gases and therefore there would be no chemical compounds. So, if electrons did not obey the Pauli's exclusion principle the entire universe would be completely different.

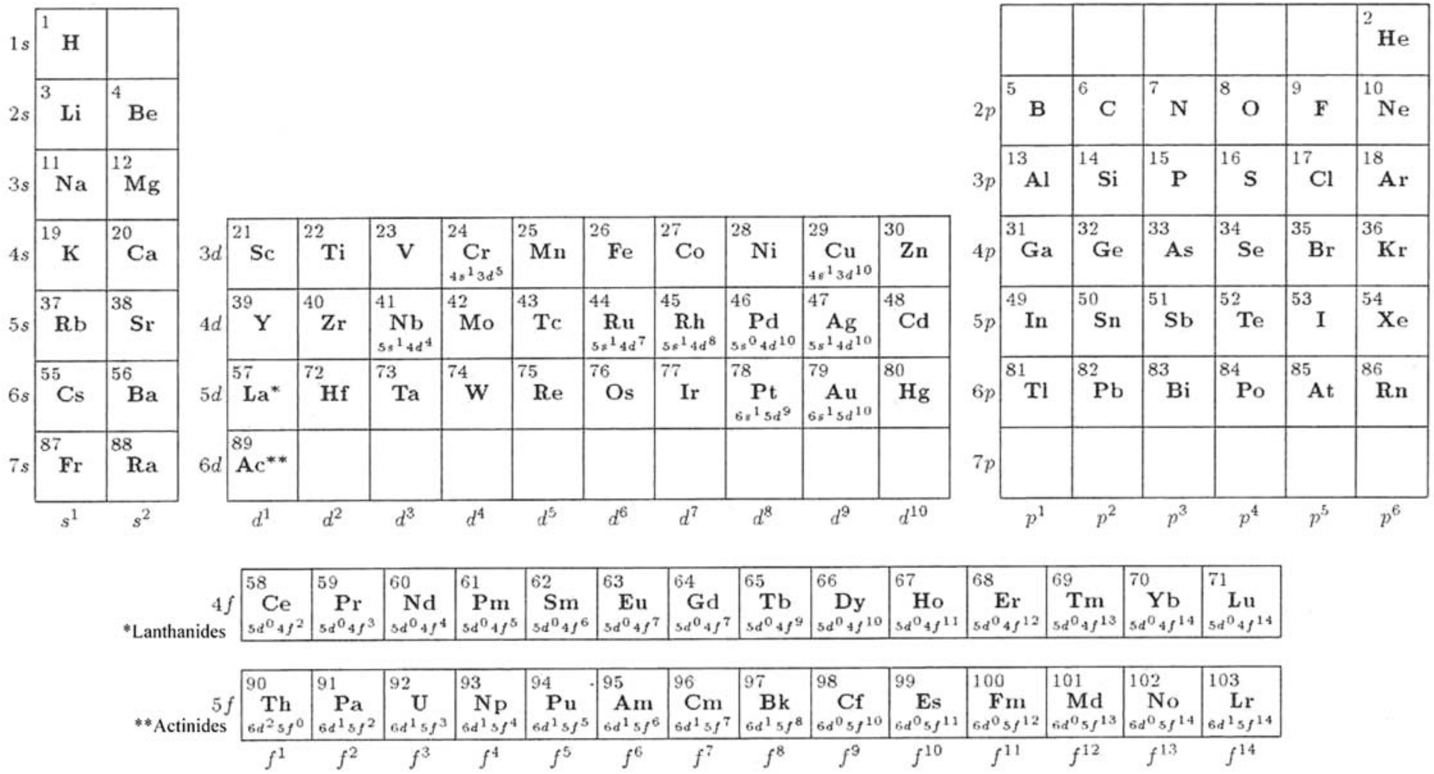
Most of the properties of the chemical elements are periodic functions of their atomic number Z. First, Mendeleev in 1869 suggested that this periodicity could be made most apparent and convincing by the periodic table of the elements. A present-day version of this table is shown in Fig.19.4. Let us consider two columns of elements in this table. The elements in the first column are alkalis and have a valence of plus one. The elements in the last column are noble gases and have a valence of zero. Generally, the elements with similar chemical and physical properties are in the same column. The discovery of the periodic table has been a great event in the history of chemistry and its interpretation has been a significant contribution to the development of physics. Here our task is to interpret the properties of the multielectron atoms within the Hartree-Fock theory. This represents the quantum mechanical interpretation of the basis of inorganic chemistry and of much of organic chemistry, atomic physics and solid state physics.

The distribution of the electrons by the subshells is called *an electron configuration.* When the energy order in the subshells is known (19.17), it is easy to find the electron configuration. The configuration is denoted by the quantum numbers n and l of the subshell, which in the self-consistent theory define its energy and number of electrons. We have to emphasize that the real scheme (19.17) does not give the order of all subshells in every atom but only of those, which are outer. For example, the energy of $4s$-subshell is lower than the energy of $3d$-subshell in the atom of K and in the following few atoms in the periodic table. But for the atoms following even further in the table, the subshell $3d$ has lower energy than the $4s$-subshell, because for these atoms it is inner (Fig. 19-5). From this figure it is clear that the completely filled d- and f-subshells obey the ideal scheme of order (19.16). The considered example allows us to conclude that *if the d- and f-subshells are outer, the electrons are ordered by the real scheme* (19.17)*, but if d- and f-subshells are inner the electrons are ordered by the ideal scheme* (19.16).

The configuration of the elements of the first two periods of the Mendeleev table is the following:

1. H							2. He
$1s^1$							$1s^2$
3. Li	4. Be	5. B	6. C	7. N	8. O	9. F	10. Ne
$1s^22s^1$	$1s^22s^2$	$1s^22s^22p^1$	$1s^22s^22p^2$	$1s^22s^22p^3$	$1s^22s^22p^4$	$1s^22s^22p^5$	$1s^22s^22p^6$

The periodic table in Fig. 19-4 is divided vertically into columns. Each column has a label of the subshell, which is filled by the elements of this column according to the real scheme (19.17). But there are certain exceptions in which the last few electrons of the atoms have a different subshell than would be predicted by the real scheme. The configurations of these exceptional atoms in Fig. 19-4 are labeled below their chemical symbol.



	s^1	s^2
$1s$	1 **H**	
$2s$	3 **Li**	4 **Be**
$3s$	11 **Na**	12 **Mg**
$4s$	19 **K**	20 **Ca**
$5s$	37 **Rb**	38 **Sr**
$6s$	55 **Cs**	56 **Ba**
$7s$	87 **Fr**	88 **Ra**

	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$3d$	21 **Sc**	22 **Ti**	23 **V**	24 **Cr** $4s^1 3d^5$	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu** $4s^1 3d^{10}$	30 **Zn**
$4d$	39 **Y**	40 **Zr**	41 **Nb** $5s^1 4d^4$	42 **Mo**	43 **Tc**	44 **Ru** $5s^1 4d^7$	45 **Rh** $5s^1 4d^8$	46 **Pd** $5s^0 4d^{10}$	47 **Ag** $5s^1 4d^{10}$	48 **Cd**
$5d$	57 **La***	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt** $6s^1 5d^9$	79 **Au** $6s^1 5d^{10}$	80 **Hg**
$6d$	89 **Ac****									

	p^1	p^2	p^3	p^4	p^5	p^6
						2 **He**
$2p$	5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
$3p$	13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
$4p$	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
$5p$	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
$6p$	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
$7p$						

	f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}
$4f$ *Lanthanides	58 **Ce** $5d^0 4f^2$	59 **Pr** $5d^0 4f^3$	60 **Nd** $5d^0 4f^4$	61 **Pm** $5d^0 4f^5$	62 **Sm** $5d^0 4f^6$	63 **Eu** $5d^0 4f^7$	64 **Gd** $5d^0 4f^7$	65 **Tb** $5d^0 4f^9$	66 **Dy** $5d^0 4f^{10}$	67 **Ho** $5d^0 4f^{11}$	68 **Er** $5d^0 4f^{12}$	69 **Tm** $5d^0 4f^{13}$	70 **Yb** $5d^0 4f^{14}$	71 **Lu** $5d^0 4f^{14}$
$5f$ **Actinides	90 **Th** $6d^2 5f^0$	91 **Pa** $6d^1 5f^2$	92 **U** $6d^1 5f^3$	93 **Np** $6d^1 5f^4$	94 **Pu** $6d^1 5f^5$	95 **Am** $6d^1 5f^6$	96 **Cm** $6d^1 5f^7$	97 **Bk** $6d^1 5f^8$	98 **Cf** $6d^0 5f^{10}$	99 **Es** $6d^0 5f^{11}$	100 **Fm** $6d^0 5f^{12}$	101 **Md** $6d^0 5f^{13}$	102 **No** $6d^0 5f^{14}$	103 **Lr** $6d^1 5f^{14}$

Figure 19.4. The periodic table of elements.

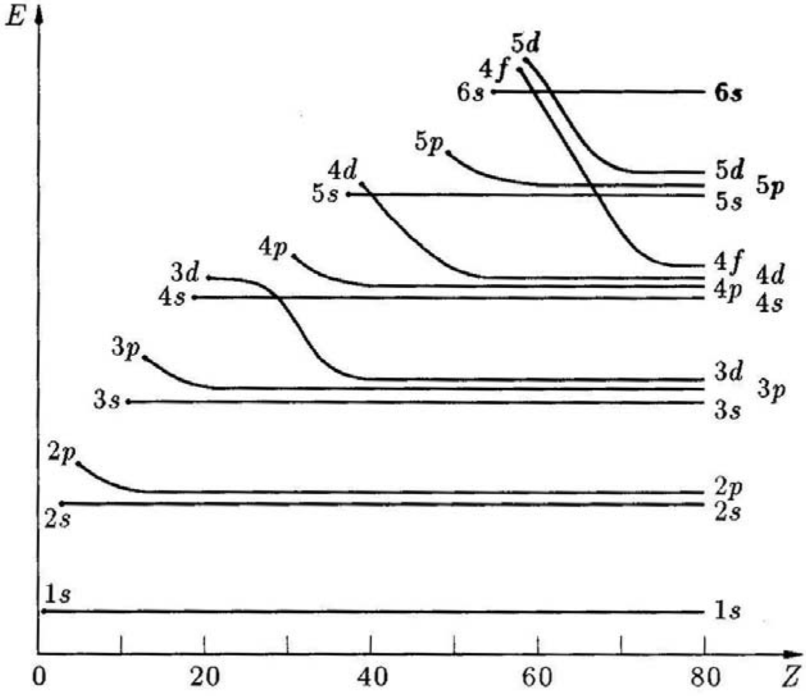


Figure 19-5. Relative energy of the subshells of the multielectron atoms as a function of the atomic number Z. Each curve starts at the value of Z for which the corresponding subshell begins to be occupied. When *d*- and *f*-subshell are outer the order of the subshells is shown on the left (real scheme); when *d*- and *f*-subshell are inner, it is shown on the right (ideal scheme).

The first exception occurs at the fourth row, which begins with $^{19}\mathrm{K}$. There is nothing exceptional about its configuration (there is no label below $^{19}\mathrm{K}$). Then, listing in order of the lowest energy subshell, i.e. applying the real scheme (19.17), we obtain the configuration:

$$^{19}\mathrm{K}:\quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1.$$

In $^{20}\mathrm{Ca}$ one electron is added to the 4*s*-subshell. The 4*s* is now full. The closed subshell with the next highest energy is the 3*d* subshell. Adding 1, 2 or 3 electrons we consecutively obtain $^{21}\mathrm{Sc}$, $^{22}\mathrm{Ti}$ or $^{23}\mathrm{V}$. These configurations obey the real scheme and the configuration for $^{23}\mathrm{V}$ is

$$^{23}\mathrm{V}:\quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3.$$

Adding one more electron, we expect that it will be in the next element in the $3d$ subshell, retaining the configuration of the remaining subshell. But the next element ${}^{24}\mathrm{Cr}$ is with a label $4s^1 3d^5$ below the chemical symbol, which means that the configuration of this atom does not end as would be expected, but instead is:

$${}^{24}\mathrm{Cr}:\ \ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5.$$

For the next elements the subshell $3d$ is filled with the level $4s$ remaining with one electron only (for example, ${}^{29}\mathrm{Cu}:\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$). Here the real scheme is violated. From ${}^{24}\mathrm{Cr}$ the energy of the $3d$ subshell is lower than the energy of the $4s$ subshell (Fig. 19-5). Since the real scheme is valid for every s- and p-subshell and none of the configurations is exceptional for elements in the first two columns and in the first three rows of the last six columns, it is accepted to ascribe to the configuration the real order (see above example with ${}^{29}\mathrm{Cu}$); nevertheless, the energy of the $3d$ subshell is lower than the energy of the $4s$ subshell and $3d$ is positioned after $4s$. The reader can find an excellent explanation of the configurations of other elements in [1], Section 9-7.

19.4 HUND'S RULE

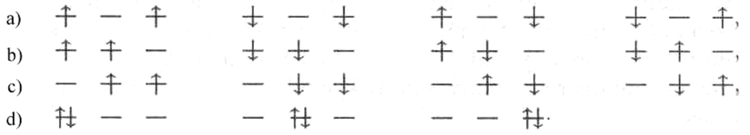
Knowing how the subshells are ordered, consider the states of the electrons inside them. Let us take two subshells, s and p. Three different states are possible in the s-subshell - two with one electron, but with different orientations of the spin and one with two electrons with opposite oriented spins:

$$\begin{array}{ccc} \uparrow & \downarrow & \uparrow\downarrow \\ (n,0,0,1/2) & (n,0,0,-1/2) & (n,0,0,0). \end{array} \tag{19.20}$$

Four quantum numbers are written for each states - n, L, m_L and m_S (L, m_L and m_S are the quantum numbers of the atom: the orbital, the magnetic and the magnetic spin numbers; for the separate electrons they are correspondingly, n, l, $m_l \equiv m$ and m_s). The first two states are energetically equivalent - they differ only by the orientation of the spin; the third state is with two electrons which according to the Pauli's principle have opposite spins.

The arrangement of the electrons in an s-subshell does not create problems as it has only one state. In some sense it is trivial. Not the case for p-subshell - there are three states in it. We shall begin the analysis of a p-subshell with two electrons in it. Some physical considerations will help us to reach the rules of the arrangements of electrons in a subshell. The first such subshell ($2p$) in the periodic system is in the atom of $^{6}\mathrm{C}$, which has the configuration $1s^{2}2s^{2}2p^{2}$. So, our analysis relates also to the distribution of both valence electrons in the atom of $^{6}\mathrm{C}$.

The number of possible states of the two electrons in the subshell is 15:



(19.21)

Which one of these states has the lowest energy? We ask this question while neglecting the spin-orbit interaction. It is equivalent to the question: does the choice of the spin states influence the electrostatic energy of the electron system? The reply is: yes, via the Pauli's principle. The choice of the spin states influences indirectly the distribution of the electron states inside the subshell and different distributions have different electrostatic interaction energy.

Indeed, two electrons with the same spins $(\uparrow\uparrow \text{ or } \downarrow\downarrow)$ according to the Pauli's exclusion principle cannot be found in one state, i.e. cannot have equal quantum numbers n, l and m. But this means that they cannot be found in one and the same place in space. At the same time if they are in a state with antiparallel spins - they can be found at the same place. The electrostatic repulsion force between two close electrons is greater than between two distant electrons. In the case of antiparallel spins larger positive term is added to the negative electrostatic energy of the interaction of the electrons with the nucleus than in the case of parallel spins. Therefore *the states with parallel spins are with lower energy, i.e. they are energetically more advantageous*. These are the states in the first column of (19.21); the states in the second column have the same energies - the difference is only in the orientation of the spins. In Fig. 19-6 are represented the states with the

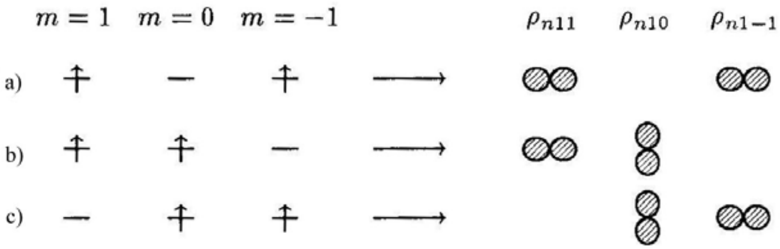


Figure 19-6. States with parallel spins of two p-electrons (only the positively oriented electrons are shown) and their corresponding electron clouds ρ_{nlm}.

parallel spins together with their electron clouds. In the state a) the electron clouds coincide and the repulsion is greater than in the states b) and c).

Hence the states b) and c) have the lowest energy among the possible 15 states of the 2 electrons in the *p*-subshell (19.21). These two states differ from one another only by orientation of the total orbital momenta: in b) it is positive and in c) negative.

Let's see what the total spin and orbital angular momenta are of both electrons in the energetically most advantageous states. According to the rule of summation of angular momenta, the total spin can have a spin number $S = 0, 1$. In the energetically most advantageous states the spin number *S* of the atom is maximal: $S = 1$. Two electrons with orbital numbers $l_1 = l_2 = 1$ (we consider a *p*-subshell) can have total orbital number $L = 0, 1, 2$. But in the state with lower energy (parallel spins) Pauli's principle does not permit both electrons to have the same magnetic numbers *m*, which is equivalent to prohibition of the state $L = 2$. The state in which $L = 0$ (in Fig. 19-6 this is case a)) was rejected above as the electron clouds in it coincide. From three possible cases the energetically most advantageous state is that with $L = 1$. From Fig. 19-6b and Fig. 19-6c it is seen that *the state with the maximal orbital angular momentum has the lowest energy* (among the electron levels allowed by the Pauli's principle).

So, we reached the first Hund's rule: *in a given subshell the minimal energy belongs to the state with maximal spin, and for equal spins - the state with the maximal orbital angular momentum.*

From the above qualitative discussion and the Hund's rule *it is clear that in the atom only one of the possibilities with regard to the total spin and the total orbital angular momentum is realized. This is so because additional conditions - the Pauli's principle and the requirement for lower energy - are added to the general rule of summation of angular momenta* (*see Section* 16.2). *These additional conditions reduce the general rule to a simpler rule.* Let us try to establish the rule for determining the orbital and the spin numbers of the atom.

The vector interpretations of the three states of Fig. 19-6 are plotted in Fig. 19-7.

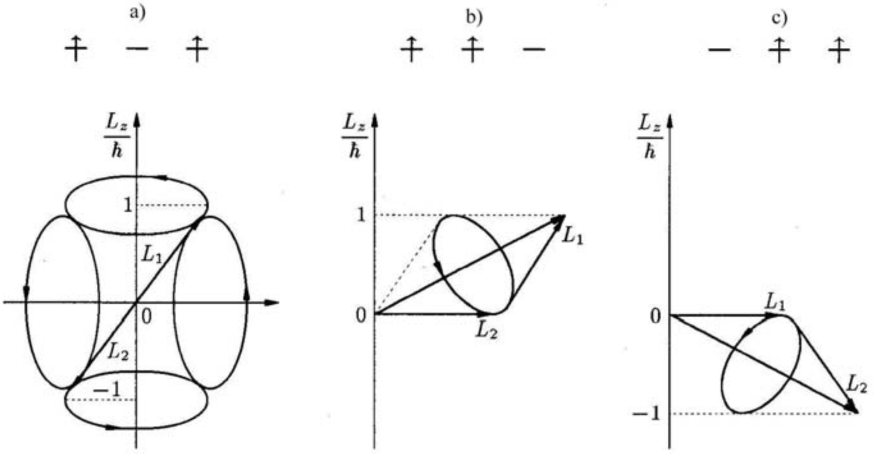
After summation of the orbital angular momenta $\mathbf{L}_1$ and $\mathbf{L}_2$ of both electrons with orbital numbers $l_1 = l_2 = 1$ and magnetic numbers $m_{li} = -1, 0, 1$ $(i = 1, 2)$, we obtain the orbital angular momentum $\mathbf{L}_a$ of the atom with an orbital quantum number *L*:

$$\mathbf{L}_a = \mathbf{L}_1 + \mathbf{L}_2, \quad L_a = \hbar\sqrt{L(L+1)}\,. \tag{19.22}$$

From the considered examples it is clear that the orbital quantum number of the atom is determined not by the general rule of summation of angular momenta (Section 16.2) but by the following rule:

$$L = \left| \sum_k m_k \right| . \tag{19.23}$$

The orbital quantum number of the atom is equal to the absolute value of the sum of the magnetic numbers of the separate electrons.



$m_1 = 1,\ m_2 = -1,$
$l_1 = l_2 = 1,$
$L = 0,\ L_a = 0,$
$m_L = 0,\ L_{az} = 0,$
$L = \left|\sum_k m_k\right| = 0$

$m_1 = 1,\ m_2 = 0,$
$l_1 = l_2 = 1,$
$L = 1,\ L_a = \hbar\sqrt{2},$
$m_L = 1,\ L_{az} = \hbar,$
$L = \left|\sum_k m_k\right| = 1$

$m_1 = 0,\ m_2 = -1,$
$l_1 = l_2 = 1,$
$L = 1,\ L_a = \hbar\sqrt{2},$
$m_L = -1,\ L_{az} = -\hbar,$
$L = \left|\sum_k m_k\right| = 1$

Figure 19-7. Total orbital angular momenta of the states with parallel spins.

Summing up the spin angular momenta $\mathbf{S}_1$ and $\mathbf{S}_2$ of both electrons with spin numbers $s_1 = s_2 = 1/2$ and magnetic spin numbers $m_{s_1} = m_{s_2} = 1/2$, we obtain the spin $\mathbf{S}_a$ of the atom with a spin quantum number *S*:

$$\mathbf{S}_a = \mathbf{S}_1 + \mathbf{S}_2, \quad S_a = \hbar\sqrt{S(S+1)} . \tag{19.24}$$

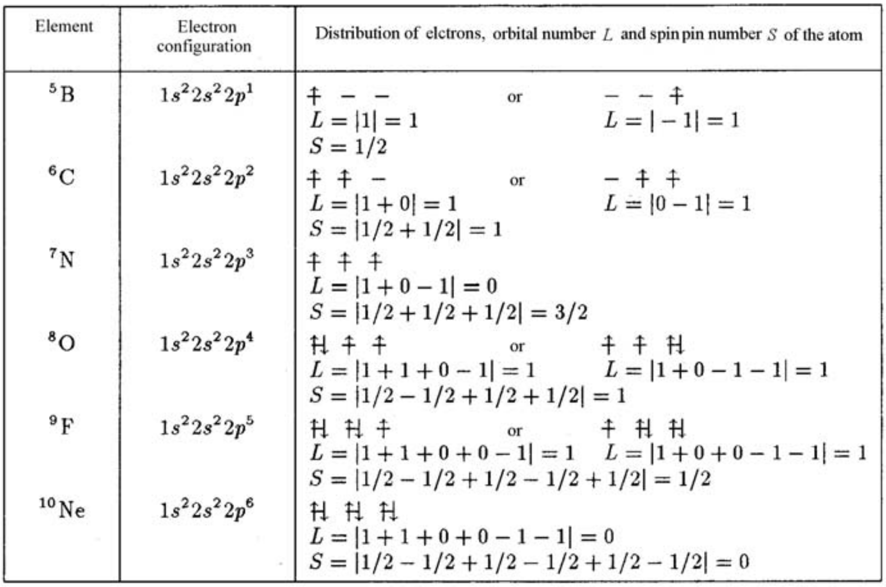
The spin quantum number of the atom is determined not by the general rule of summation of angular momenta but by the reduced rule through the magnetic spin numbers m_{s_k} :

$$S = \left| \sum_k m_{s_k} \right| . \tag{19.25}$$

The spin number of the atom is determined by the reduced rule as the absolute value of the sum of the magnetic spin numbers m_{s_k} *of the separate electrons.*

The arrangements of the electrons which fill the *p*-subshell of the elements in the second period of the periodical system, B, C, N, O, F and Ne, are shown in Table 19-4. As it can be seen from the example with Ne, for a completely filled subshell all angular momenta of the atom (orbital L_a, spin S_a and total J_a) are equal to zero. The filled subshells do not change the atomic angular momenta - the last are determined only by the valence electrons. Therefore, usually only the configuration and the distribution of the valence electrons are given.

Table 19-4. The electron configuration and the arrangement in the *p*-subshell of the second period of the periodic table



Element	Electron configuration	Distribution of elctrons, orbital number L and spinpin number S of the atom
^{5}B	$1s^2 2s^2 2p^1$	$\uparrow$ – – or – – $\uparrow$ $L = \|1\| = 1$ $L = \|-1\| = 1$ $S = 1/2$
^{6}C	$1s^2 2s^2 2p^2$	$\uparrow$ $\uparrow$ – or – $\uparrow$ $\uparrow$ $L = \|1+0\| = 1$ $L = \|0-1\| = 1$ $S = \|1/2+1/2\| = 1$
^{7}N	$1s^2 2s^2 2p^3$	$\uparrow$ $\uparrow$ $\uparrow$ $L = \|1+0-1\| = 0$ $S = \|1/2+1/2+1/2\| = 3/2$
^{8}O	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$ $\uparrow$ $\uparrow$ or $\uparrow$ $\uparrow$ $\uparrow\downarrow$ $L = \|1+1+0-1\| = 1$ $L = \|1+0-1-1\| = 1$ $S = \|1/2-1/2+1/2+1/2\| = 1$
^{9}F	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ or $\uparrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $L = \|1+1+0+0-1\| = 1$ $L = \|1+0+0-1-1\| = 1$ $S = \|1/2-1/2+1/2-1/2+1/2\| = 1/2$
^{10}Ne	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $L = \|1+1+0+0-1-1\| = 0$ $S = \|1/2-1/2+1/2-1/2+1/2-1/2\| = 0$

The same distributions, but with negative spins, are energetically completely equivalent to the shown ones. I leave the justification of these distributions on the basis of Hund's rule to the reader.

19.5 FINE STRUCTURE OF THE MULTIELECTRON ATOMS

In the previous section we considered the states with different L and S which belong to one and the same electron configuration. They have different energy due to the different electrostatic interactions between electrons in different states. The energy differences between the states of one configuration are usually substantially smaller than the energy differences between the states of two different configurations. The order of the states in increasing energy is determined by the Madelung rule. The presence of the spin-orbit interaction of the electrons leads to additional splitting of the energetic levels. As a result of this interaction the levels of one and the same configuration and of one and of the same values of L and S split in a row of levels with different values of the total quantum number J of the atom.

Let us consider the state ${}^3P$ of the C atom, which was analyzed in Section 19.4. According to (19.23) and (19.25) the orbital and spin angular momenta are

$$L_a = \hbar\sqrt{L(L+1)} = \hbar\sqrt{2}, \quad S_a = \hbar\sqrt{S(S+1)} = \hbar\sqrt{2}\,. \qquad (19.26)$$

The total angular momentum of the atom, $\mathbf{J}_a$ is a sum of the spin and orbital angular momenta

$$\mathbf{J}_a = \mathbf{L}_a + \mathbf{S}_a, \quad J_a = \hbar\sqrt{J(J+1)}\,. \qquad (19.27)$$

The quantum number of the atom (often called internal) according to the rule of a summation of angular momenta (Section 16.2) takes the following values:

$$J = |L-S|, |L-S|+1, ..., L+S\text{-}1, L+S\,. \qquad (19.28)$$

The number of states with different total angular momenta is defined by the smaller of the two quantum numbers L and S:

$$\begin{aligned} &\text{a) } 2S+1 \text{ when } S<L:\ J = L-S,\ L-S+1,\ ...,\ L+S\text{-}1, L+S,\\ &\text{b) } 2L+1 \text{ when } S>L:\ J = S-L,\ S-L+1,\ ...,\ S+L\text{-}1, S+L. \end{aligned} \qquad (19.29)$$

In case a) there is a physically fixed direction by the strongest angular momentum (the orbital) and the number $2S+1$ shows the number of the possible orientations of the spin with respect to the orbital angular momentum (also with respect to the total angular momentum). In case b) there are $2L+1$ orientations of the orbital angular momentum with respect to the spin angular momentum. The internal number can take the values $J=0,1,2$ and the level 2*p* splits in the three close levels ${}^3P_0, {}^3P_1$ and ${}^3P_2$. This set of split levels forms a multiplet, which is called fine structure of level ${}^3P$.

For the additional energy of splitting we can use formula (17.21), which we write in the form

$$\Delta U = A_{LS}\mathbf{L}_a\mathbf{S}_a, \tag{19.30}$$

where A_{LS} is a constant which depends on *L* and *S* but not on *J*. As the vector **J** is a sum of the vectors **L** and **S,** which we can write according to elementary geometry

$$\mathbf{L}_a\mathbf{S}_a = \frac{1}{2}\left(\mathbf{J}_a^2 - \mathbf{L}_a^2 - \mathbf{S}_a^2\right), \tag{19.31}$$

and consequently for the energy ΔU we obtain

$$\Delta U = \frac{\hbar^2}{2}A_{LS}\left[J(J+1) - L(L+1) - S(S+1)\right]. \tag{19.32}$$

It is clear from this expression that the distance Δ between two adjacent levels (e.g. between *J*th and (*J*-1)th levels) depends only of the coefficient A_{LS} and the internal number *J*:

$$\Delta = \Delta U_J - \Delta U_{J-1} = \hbar^2 A_{LS} J. \tag{19.33}$$

This dependence is known as the Lande rule of the intervals.

Two configurations of the equivalent electrons which are mutually supplementing to make a full subshell, have a state ${}^{2S+1}L_J$ of one and the same type. For example, such are the configurations of ${}^6\mathrm{C}$ and ${}^8\mathrm{O}$. Actually, the configurations of the outer subshells of ${}^6\mathrm{C}\text{-}2p^2$ and of ${}^8\mathrm{O}\text{-}2p^4$ are supplementing to make a full *p*-subshell with 6 electrons. The constant A_{LS} can be: a) positive - then the state with the minimum value of $J=|L-S|$ has lower energy and the multiplet is called normal; b) negative - then the state with the maximum value of $J=L+S$ has lower energy and the multiplet is called reversed. It is found empirically that when a subshell is filled less than a half, $A_{LS} > 0$ and a normal multiplet arises, but when the subshell is filled more than a half $A_{LS} < 0$ and a reversed multiplet arises. (We note that when a subshell is half-full $L = 0$ and there are no multiplets!) This is the content of the second Hund's rule, which defines the order of the fine-structure level:

In the fine-structure levels a lower energy belongs to: a) the level with minimal internal number $J_{\min} = |L - S|$, *if the subshell is filled less than a half and b) the level with maximal internal number* $J_{\max} = L + S$, *if the subshell is filled more than in a half.*

In the example with C and O the electrons are 2 and 4 out of 6 possible. In the C atom the subshell is completed less than half and the ground state is with $J_{\min}$, i.e. with the term ${}^3P_0$ (Fig.19-9a). In the O atom the subshell is completed more than half and the level with $J_{\max}$ has lower energy. From Fig. 19-8b it is clear that according to (19.23) and (19.25) in O $L = 1$ and $S = 1$. Hence, the possible values of the internal number are $J = 0, 1, 2$ and $J_{\max} = 2$. The ordering of the levels of O is shown in Fig.19-8b.

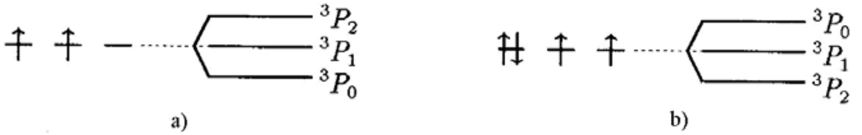


Figure 19-8. Energy levels of the fine structure of the atom of: a) ^{6}C - a normal triplet; b) ^{8}O a reversed triplet. The distance between the levels is determined by the Lande rule of the interval.

For the heavier elements the position of the levels predicted by the *LS* coupling starts to deviate from the experimental results and the *LS* coupling becomes inadequate. The reason for this lies in the fact that the energy of the electrostatic interaction is proportional to *Z* (more accurately to *Z*(r) (19.8)), but the energy of the spin-orbit interaction increases as Z^4. For the light elements the spin-orbit interaction can be neglected. But with increasing *Z* the spin-orbit interaction plays a greater role. For the heavy elements it becomes stronger than the electrostatic interaction.

For this reason, the *JJ* coupling in such cases replaces the *LS* coupling. For the *JJ* coupling the states of the separate electrons are described by the quantum numbers n, l, j, m_j, the total number having two values $j = j_{1,2} \equiv l \pm 1/2$ (compare with the quantum number n, l, m, m_s of the electron at *LS* coupling). Because of the spin-orbit interaction the energy of the state j_+ differs so much from the energy of the state j_- that the energetic levels of the electrons are defined not by $n,\ l$ as in *LS* coupling, but by *n, l, j*. The levels are ordered in a totally different way. This problem is out of scope of this book and won't be analyzed in details.

We shall only note that when one of the magnetic interactions plays an important role we must also take into account other interactions mentioned in the discussion of helium in Section 18.3 (see (18.19) and the comments about this formula). From the magnetic interaction - a spin-other's-orbit interaction, an orbit-orbit interaction, a spin-spin interaction - the only one which does not cause splitting but only a shift is the last one. For correct and adequate description of it, it is necessary to take into account also relativistic effects. Experiments show that the beginning and the middle of the periodic system are well described by the *LS* coupling and the end - by the *JJ* coupling. Passing from the middle toward the heavier elements the energy levels take values intermediate to the predicted by *LS* and *JJ* coupling.

SUMMARY

One of the most widely used methods for solving the Schroedinger equation of multielectron atoms is the approximation of Hartree-Fock, or the self-consisting field. This method allows describing the atom instead by a many particle wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_N)$, with a single particle wave function $\psi_{n_1}(\mathbf{r}_1),\psi_{n_2}(\mathbf{r}_2),\psi_{n_3}(\mathbf{r}_3)\,...\,\psi_{n_N}(\mathbf{r}_N)$ of each electron. This provides a possibility to describe the atomic state by the quantum numbers n,l,m and m_s of the separate electrons. The interaction between the electrons is accounted both in the equations and in the Hamiltonians.

The results of the Hartre-Fock theory show that the energy of he multyelectron atom is defined by the principal quantum number *n* and orbital quantum number *l*. Electrons of the same energy approximately are the same distance from the nucleus. The atom has layered structure - the electrons are placed in shells and subshells. The inner shells with small *n* have small radius because they experience a strong attraction by the positively charged nucleus. With increasing *n,* the radius of the outer shell (of the atom) increases very slowly and for the heaviest elements is only three times greater than that of hydrogen.

For the construction of the periodic system the following empirical rules are used:

1. The structure of atoms is defined by the atomic number *Z*, i.e. by the charge of the nucleus.

2. With increasing atom number, i.e. with increasing number of electrons in the atom, the electrons gradually fill the states with minimal possible energy.
3. The energetic order of the subshells follows the Madelung rule:
   $1s,2s,2p,3s,3p,4s,3d,4p,5s,4d,5p,6s,4f,5d,6p,7s,5f,6d$
4. While filling the energetic levels, the number of electrons is limited by the Pauli's exclusion principle.
5. The electrons in the subshells are arranged according to the first Hund's rule.
6. The order of states in the approximation of the fine structure follows the second Hund's rule.
7. The energetic levels of the fine structure are nonequidistant and the space between them is determined by the Lande rule of the intervals.

QUESTIONS

1. What is the essence of the self-consistent method?
2. How are the electron states in an atom described?
3. On which quantum numbers does the energy depend?
4. Why do atoms have layered structure?
5. How many electrons has one subshell or one shell?
6. Which is the ideal order of filling of the atomic states?
7. For which subshells is the ideal order violated and how can this be explained?
8. How can we approximately estimate the range of the electron cloud?
9. Why do the *d*- and *f*-subshells contract?
10. Which subshells are inner and which outer?
11. What defines the periods (the rows) of the Mendeleev system?
12. What is called an electron configuration?
13. How do spins influence the electrostatic energy of interaction between electrons?
14. Which states of an atom - with parallel or with antiparallel spins are more stable?
15. Explain physically which of the states with parallel spins of two electrons in a *p*-subshell have lower energy?
16. What do the Hund's rules state?
17. How are the orbital and spin numbers of an atom described?
18. Why the rules for additions of orbital and spin angular momenta of the electrons in an atom differ from the general rule of addition of angular momenta?
19. Why does the *JJ* coupling occur in the heavy elements?

PROBLEMS

1. Prove that the average probability density of a system of degenerate states corresponding to the energy E_2 does not depend on the angles θ and φ.
2. Using formulae for rough estimate, determine the average radii of the K-shell and the outer shell of the atom ${}^{82}\mathrm{Pb}$.
3. Estimate approximately the energy of an electron in: a) the inner shell and b) the outer shell of ${}^{49}\mathrm{In}$.
4. Using the first and the second Hund's rules obtain the arrangements of the electrons and the term order in the atom of ${}^{22}\mathrm{Ti}$.
5. Determine the possible values of the total angular momentum in the state ${}^{5}\mathrm{D}$.
6. Using the Hund's rules determine the term of the ground state of the element with a configuration of unfilled subshell: a) nd^3; b) nd^6.
7. Find the ratio of spaces between the term of ${}^{6}\mathrm{C}$.
8. For the atom of ${}^{55}\mathrm{Cs}$ find: a) the electron configuration; b) the order of states; c) S, S_a, m_S and S_z, and construct the vector diagram of the $\mathbf{S}_a$; d) L, L_a, m_L and L_{az}, and construct the vector diagram of the $\mathbf{L}_a$; e) J, J_a, m_J and J_{az}, and construct the vector diagram of the $\mathbf{J}_a$; f) the possible vector interpretation of $\mathbf{J}_a = \mathbf{L_a} + \mathbf{S}_a$; g) the terms; h) the fine structure; i) the splitting of levels in a strong magnetic field; j) the splitting of levels in a weak magnetic field.

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Theoretical mechanics

1. **Alonco, M., E. J. Finm,** Fundamental University Physics, 1. Mechanics, Addison-Wesley Publishing Co., 1988.

It is written by a good pedagogue and is well illustrated. A systematic and complete course. The level is a little lower compared to the present manual.

2. **Fetter, A. L., J. D. Walecka**, Theoretical Mechanics of Particles and Continua, McGraw-Hill Book Co., 1980.

This is a fundamental book at a high and rigorous level with very wide and detailed exposition. It is very worthwhile book for the modern state of theoretical mechanics.

3. **Goldstein, H**., Classical Mechanics, Addison-Wesley Publishing Co., 3rd ed., 2002.

This book is a masterpiece with many examples which are selected very carefully. Even though it is a book for physicists, I recommend it to the reader of this course.

4. **Kibble, T. W**., Classical mechanics, McGraw-Hill Book Co., 2nd ed., 1988.

Very appropriate combination between physics and mathematics. Many mathematical categories (e.g. vectors, differential equations etc.) are used from the start in the text itself. I recommend chapters 1÷5, 7, 11÷13 to the chemistry students.

5. **Kittel, Ch., W. D. Nayt, M. Ruderman**, Mechanics, Berkeley Physics Course, vol. I, McGraw-Hill Book Co., 2nd ed., 1973.

A nice complement to the theoretical-mechanics courses in the list. This is an excellent manual.

6. **Landau, L. D. and E. M. Lifshitz**, Mechanics, Pergamon Press, 2nd ed., 1969.

This is the basic book for the course. The exposition is compact (in some places synoptically), consecutive and rigorous. This is the most accessible book of the series of superb books covering all of theoretical physics.

7. **Savelev, I. V.,** Fundamental of Theoretical Physics, Mir Publishing House, 1982.

Part I is comparable with the level of theoretical mechanics of this course with detailed mathematical explanations.

8. **Spolsky, E. V.,** Atomic Physics, Vol. 1, Mir Publishing House 1963.

The material necessary for this course is exposed completely and accessibly on a very good pedagogical level.

9. **Whittaker, E. T.,** A Treatise on the Analytical Dynamics of Particles and Rigid Bodies, 4th ed., Cambridge University Press, 1937; Dover Publications, 1944.

This is a well-known book giving the a complete exposition of theoretical mechanics with an old point of view. I included the book in this list only because many special problems are explained very well in it, which could be hardly found in other sources.

Quantum mechanics

10. **Arya, A.**, Elementary modern physics, Addison-Wesley Publishing Co., 1976.

This is a good manual with a good physical interpretation, which is accessible and comprehensible. The level is lower than this book, for first reading.

11. **Atkins, P. M.,** Molecular Quantum Mechanics, Oxford University Press, 2nd ed., 1983.

This is an irreplaceable book for a chemist. It consists of four parts: I. Elementary Quantum Theory, II. Formal Aspects of the Quantum Theory, III. Atom and Molecular Spectra, IV. Electrical and Magnetic Properties of Molecules.

12. **Beiser, A.**, Perspectives of Modern Physics, McGraw-Hill Book Co., 1972.

This is an accessible book, nice manual at a lower level, comparable to the present book. The book is extremely useful for chemistry students with the consideration of chemical objects and a successful combination of popular explanations with high scientific level.

13. **Bethe, H. A. and R. W. Jackiw**, Intermediate Quantum Mechanics, W. Benjamin, 2nd ed., 1968.

I include in the references this book, because much of the material in it is not to be found in any other textbook. There are detailed discussions of calculation methods in the photoelectric effect, atomic structure, atomic collisions and the multiplet splitting. It is an advanced book.

14. **Blokhintsev, D. I.**, Principles of Quantum Mechanics, Allyn and Bacon, 1964.

It is a basic book for this course and its level is comparable to this one. It is a university manual (difficult one).

15. **Born M.**, Atomic Physics, London-Glasgow, Blackie and Son Limited, 1963.

The book is useful for a number of here discussed questions, it is a nice manual.

16. **Brasden, B. H., C. J. Joahain**, Introduction to Quantum Mechanics, John Wiley & Sons, 1989.

This is a detailed and wide version of quantum mechanics. The book is clear and easily readable with a lot of examples. It is ta book for first reading and there are more topics than in this course.

17. **Davidov, A. S.** Quantum Mechanics, Addison-Wesley Publishing Co., 1965.

This is an advanced book. It emphasizes the treatment of many physical systems which are not considered in this course.

18. **Dicke, R. H. and J. P. Wittke**, Introduction to Quantum Mechanics, Addison-Wesley Publishing Co., 1973.

This well-known manual of Princeton University for physicists is on a level with the present book (maybe a little higher). The explanations are compact and physical and the problems are nice.

19. **Eisberg, R. and R. Resnic**, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, John Wiley & Sons, 1974.

I enjoy this book very much. The main merit of the book is the excellent physical explanation of the problems. The book interprets very many topics, which are not in this course. The explanations are very detailed ones and the volume is large. The difficult mathematical problems are taken out of the text into appendices.

20. **Fano, U., L. Fano,** Physics of Atoms and Molecules, an Introduction to the Structure of Matter, University of Chicago Press, 1972.

As a manner of education it is not a standard course of quantum mechanics. Traditionally classical mechanics is studied in the first year and the theoretical mechanics is left for the subsequent yeas. The authors propose two levels of quantum-mechanical education. This book is the first level. The book is some kind of a transition from atomic physics to the standard formal apparatus of quantum mechanics.

21. **Feynman, R. P., R. B. Leithon, M. Sands**, The Feynman Lectures on Physics, vol. 1, Addison-Wesley Publishing Co., 1965.

This part of the famous Feynman lectures is for the first reading. It is not enough for the level of this course.

22.**Garcia, N. and A. Damask**, Physics for Computer Science Students with Emphasis on Atomic and Semiconductor Physics, John Wiley & Sons, 1986.

This is not really a textbook on quantum mechanics, but Chapters 18-24 are devoted to the basic of quantum mechanics. Subsequently and successfully, the problems of the microword are exposed with more physics than mathematics, for the first reading.

23. **Gasiorowicz, S.**, Quantum Physics, John-Wiley & Sons, 3rd ed., 2003.

This university course for physicists is a good manual which covers more topics that the present book. The book should be understandable to the student who has gone through the material of this book.

24. **W. Greiner**, Quantum Mechanics, An Introduction, Vol. 1, Springer-Verlag, 1989.

This is a fundamental book. It is widely used and is one of the best modern manuals for physicists and the level is higher than here.

25. **Landau, L. D. and E. M. Lifchitz**, Quantum Mechanics, Non-Relativistic Theory, Addison-Wesley Publishing Co., 2nd ed., 1965.

The book is one of the well-known series (see [R5]) for theoretical physics. It is a fundamental and advanced book, which discusses a number of advanced topics in some details. A student who has reached the advanced level will find much that is useful in this book.

26. **Levy-Leblond, J.-M, F. Balere**, Quantics, Rudiment of Quantum Physics, North Holland, 1990 (*Quant*um Phys*ics*).

There is only a few books, which introduce quantum-mechanical formalism intuitively and in this way give to the reader a sense of how quantum mechanics manifests itself in Nature. A number of fascinating examples are discussed with a minimum of formal apparatus. The book is not for first reading.

27. **Liboff R. L**., Introductory Quantum Mechanics, Holden-Day Inc., 4th ed., 2003.

This is a very good manual, with illustrative figures and comprehensible discussion on high physical level about both the fundamental of quantum mechanics and its applications in simple systems (mainly one-dimensional). There is a review of the concepts of classical mechanics which relate directly to quantum mechanics The students, who have reached the advanced level are encouraged to look it up, since it is always useful to see the same basic material presented from a different point of view.

28. **Mandl, F.**, Quantum Mechanics, John Wiley & Sons, 1992.

The level is comparable with the present book. There are many problems and this is a book for first reading.

29. **Messiah, A.**, Quantum Mechanics (Physics), Dover Publications, 2000.

This is a fundamental book at a high level with large volume and detailed and thorough exposition. It covers quantum theory completely, including the elements of relativistic quantum mechanics. This is an advanced book and it requires a mathematical sophistication.

30. **Ral, A. I. M.**, Quantum Mechanics, Adam Hilger, 2nd ed., 1986.

The foundations of quantum mechanics are exposed compactly and subsequently at a good pedagogical level. The book is useful for students because it is written relying only on physical and mathematical concepts usually taught in the first year of an undergraduate course.

31. **Shankar R.**, Principles of Quantum Mechanics, Kluwer Academic/Plenum Publishers, 2nd ed., 1994.

This is an advanced book that develops the subject from its postulates. The level is high, but the language is clear and comprehensible. It is written for physicists and is for starting graduate students.

32. **Shiff, L. I.,** Quantum Mechanics, McGraw-Hill Book Co., 1968.

This was one of the most popular books in the past with at a very high pedagogical level of physics. The book is compact and the calculations are left to the reader.

33. **Sommerfeld, A.**, Atomic Structure and Spectral lines, E. P. Dutton, 1934.

Most popular monograph in the past. The best and complete exposition of the old quantum mechanics. The physical interpretation and the clearness of the explanations are simple also today.

34. **Spolsky, E. V.**, Atomic Physics, Vol. 1, 2, Mir Publishing House, 1963.

It is the a basic book for this course. Despite that it is relatively old, it is a nice manual with a lot of pedagogical finds.

35. **Wichmann, E. H.**, Quantum Physics, Berkeley Physics Course, vol. IV, McGraw-Hill Book Co., 2nd. ed., 1973.

The book is for references about the physical essence of the problems.

36. **Willett, E.**, The Basics of Quantum Physics: Understanding the Photoelectric Effect and Line Spectra, Rosen Pub. Group, 2005.

I recommend this book students to read before this course. It gives a good starting knowledge of quantum mechanics.

37. **Zare, R. W.** Angular Momentum (Understanding Spatial Aspects in Chemistry and Physics, John Wiley & Sons, 1988.

It is not a book on quantum mechanics, but a good superstructure in treatment of angular momentum in many applications in atomic physics. The book is very useful for chemists.

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