# DENSITY MATRIX THEORIES IN QUANTUM PHYSICS

Boris V. Bondarev

# Density Matrix Theories in Quantum Physics

## Authored by

## Boris V. Bondarev

*Moscow Aviation Institute (National Research University),*
*Moscow,*
*Russia*

# Density Matrix Theories in Quantum Physics

need for a court order if at any point you breach any terms of this License Agreement. In no event will any delay or failure by Bentham Science Publishers in enforcing your compliance with this License Agreement constitute a waiver of any of its rights.

3.  You acknowledge that you have read this License Agreement, and agree to be bound by its terms and conditions. To the extent that any other terms and conditions presented on any website of Bentham Science Publishers conflict with, or are inconsistent with, the terms and conditions set out in this License Agreement, you acknowledge that the terms and conditions set out in this License Agreement shall prevail.

# CONTENTS

# PREFACE

In this book, the author opens up new possibilities for the main quantities in quantum physics – the statistical operator $\hat{\varrho}$ and the density matrix_$\varrho_{nm}$. The meaning of the density matrix is that its diagonal elements $\varrho_{nn}$ are equal to the probability $w_n$ that the system in the quantum state n. The point in this book is the Lindblad equation for the statistical operator $\hat{\varrho}$, where the main element of influence on the system of its environment is the dissipative operator $\hat{D}$:

$$ i\,\hbar\,\partial\hat{\varrho}/\partial t = [\,\hat{H}\,\hat{\varrho}\,] + i\,\hbar\,\hat{D}\,. $$

This operator is written in the most General form. In order for the Lindblad equation to be solved, the $\hat{D}$ operator must be specified. The author wrote down the dissipative diffusion and attenuation operators that will allow us to find the $\hat{D}$ operator. Now, this operator depends on the temperature T and describes the effect of the thermostat R on the quantum system S. This new equation is not difficult to write for the particle density matrix in coordinate representation as compared to the Wigner equation, which coincides with the Fokker – Planck equation. This proved the equivalence of quantum physics and classical statistical physics.

The author wrote the Lindblad equation for a harmonic oscillator and inserted a dissipative attenuation operator into it. And without any approximation, he derived the equation of damped oscillations for the average value of the $\bar{x}$(t) coordinate with absolute accuracy.

Bondarev based on the Lindblad equation with another operator $\hat{D}$ developed the theory of the harmonic oscillator, in which he found the density matrix and proved the Heisenberg relation.

He further developed the theories of the light diode and ball lightning. In light diode theory, he used the diffusion and attenuation operators and derived the Fokker – Planck equations for electrons and holes. These equations present the terms that are responsible for radiation.

The theory of ball lightning is based on the assumption that the gas inside the ball is completely ionized and electrons, due to their lightness in comparison with nuclei, evenly fill this ball. The equation for the statistical operator $\hat{\varrho}$ nuclei contains operators of diffusion and damping. This equation is a second-degree equation with respect to the coordinate and momentum operators. The probability of distribution of nuclei over the volume of a ball lightning is found.

Bondarev derived von Neumann equation from the Liouville, which is valid for a non-equilibrium system S and an equilibrium thermostat R, the equations for the density matrix S of a single particle and a system of identical particles. These equations have a remarkable property. When the density matrix has a diagonal form, they get turned into quantum kinetic equations for probabilities, which are obtained in the wave graphical representation.

The book presents new theories of such experimentally discovered phenomena as step kinetics of bimolecular reactions in solids, superconductivity, superfluidity, energy spectrum of an arbitrary atom, laser, spaser and graphene.

Kinetics is called as a stepwise process, in which the reaction suddenly stops at a constant temperature even in the presence of a lot of reagents. But as soon as the temperature is raised, the reaction starts again. The reason for this reaction is the tunnel effect, which is observed only in solids, when there are molecules in the bodies that hold the reagents near them. In liquids, these molecules can move along with the reagents and enter into a reaction that goes all the way while there are reagents. The reaction in liquids always obeys the Arrhenius law. To describe stepwise kinetics, the author came up with a correlation theory.

So, when processing the results of the step kinetics experiment using correlation theory, it was found that the Arrhenius law is also fulfilled here. And there was also an increase in localization volume with increasing temperature, as predicted by the tunnel effect.

Superconductivity can be described by the law of changing the probability $w_k$ of filling the state of electrons with the wave vector k as a function of temperature. This law has long been known. It depends on the energy $\varepsilon_{kk'}$ of the interaction of electrons with the wave vectors k and $k'$. When $\varepsilon_{kk'} = 0$, the probability $w_k$ obeys the Fermi − Dirac law. Our goal was to find the energy $\varepsilon_{kk'}$ of the interaction of electrons.

We denote the matrix elements of the interaction Hamiltonian of two particles as $H_{12,1'2'}$, where 1 is the spin quantum number of the particles. If the particles are bosons, then the matrix elements must be antisymmetric, i.e. then the matrix elements must change the sign when replacing variables 1 and 2, or $1'$ and $2'$. This is possible if the matrix elements represent the sum of two terms of different characters. In the wave representation, the energy ε_(kk^') will also represent two terms of different signs. But in this case, it is very difficult to solve the equation. Therefore, we roughly denote these terms as

$$\varepsilon_{kk'} = I\,\delta_{k+k'} - J\,\delta_{k-k'}\,,$$

where I and J are positive constants, $\delta_k$ is the Kronecker symbol. Now we can substitute this function into the equation and get

$$\ln\left[\,(1-w_k)/w_k\,\right] = \beta\,(\varepsilon_k + I\,w_{-k} - J\,w_k - \mu)\,.$$

This equation has a remarkable property. For some areas of $k$ will this inequality be true

$$w_k \neq w_{-k}\,.$$

The property that is expressed by this inequality is called anisotropy. The appearance of this property here is superconductivity.

Solving this equation, we obtain for T = 0 functions that have five values for one argument value. Since this function describes stationary states, the lowest energy is the value of the function where the electrons remain indefinite. This will be a superconducting state.

In theory, the parameter represents f = $(J - I)/(J + I)$. This parameter divides superconductivity into two kinds. If $0 \leq f \leq 1$, then it is a I-type superconductor, and if $-1 \leq f < 0$, then it is a II-type superconductor. Critical temperature is defined as $T_c = (I + J)/(4\,k_B)$. All the main effects and properties of superconductors are covered by this theory.

In the theory of superfluidity for liquid helium, $He^3$ and $He^4$, all values that express the properties of this mixture are described by functions having multiple values in a certain temperature range. As a consequence, the heat capacity tends to infinity when the temperature approaches the temperature $T_\lambda$ of the lambda transition.

The theory of the energy spectrum of an arbitrary atom begins with determining the energy using statistical operators:

$$E = \int \widehat{H}^{(1)}\,\hat{\varrho}^{(1)}\,dq + 1/2 \int \widehat{H}^{(2)}\,\hat{\varrho}^{(2)}\,dq_1\,dq_2\,,$$

where $\widehat{H}^{(1)}$ is the Hamiltonian of one electron, $\widehat{H}^{(2)}$ is the Hamiltonian of two interacting electrons, $\hat{\varrho}^{(1)}$ and $\hat{\varrho}^{(2)}$ are the statistical operators of one and two electrons. The matrix $H_{\alpha_1\alpha_2,\,\alpha_1'\alpha_2'}$ of the Hamiltonian $\widehat{H}^{(2)}$ must be antisymmetric. To do this, it is taken equal to

$$H_{\alpha_1\alpha_2,\,\alpha_1'\alpha_2'} = \int \Phi^*_{\alpha_1\alpha_2}(q_1,q_2)\,\widehat{H}^{(2)}(q_1,q_2)\,\Phi_{\alpha_1'\alpha_2'}(q_1,q_2)\,dq_1\,dq_2\,,$$

where

$$\Phi_{\alpha_1\alpha_2}(q_1, q_2) = 1/\sqrt{2}\,[\,\varphi_{\alpha_1}(q_1)\,\varphi_{\alpha_2}(q_2) - \varphi_{\alpha_1}(q_2)\,\varphi_{\alpha_2}(q_1)\,]$$

there is an antisymmetric Slater function. The eigenfunctions of electrons in the hydrogen atom are taken as functions $\varphi_\alpha(q)$. After a series of calculations, an equation is obtained from which one can obtain the eigenfunction and energy $\varepsilon_{nml\sigma}$ of electrons of an arbitrary atom.

In the following chapters, new theories of the laser and spaser are constructed, which are similar to each other in the content of the main quantum approaches to describing the phenomena occurring in them. The basis of these theories is the Lindblad equation. The equation for the density matrix will be written in a coordinate form with a known Hamiltonian and an unknown dissipative matrix. To find this matrix, we need to remember that we know the kinetic equation for active atoms, which follows from the equation for the density matrix in the representation where it has a diagonal form. So, a representation needs to be find out where the density matrix has a diagonal form. The closest to this representation is the representation in which the Hamiltonian of active atoms will also have a diagonal form. Thus, the Hamiltonian has two representations. One $\alpha$-representation is a coordinate representation. The other is the $\kappa$-representation, in which the Hamiltonian has a diagonal form. These two Hamiltonians are connected by the unitary matrix $U_{\alpha\kappa}$. The density matrices $\varrho_{\alpha\alpha'}$ and $\tilde{\varrho}_{\kappa\kappa'}$ will also be connected by the same unitary transformation:

$$\varrho_{\alpha\alpha'} = \sum_{\kappa\kappa'} U_{\alpha\kappa}\,\tilde{\varrho}_{\kappa\kappa'} U^*_{\alpha'\kappa'}\ .$$

We find the dissipative matrix in the $\kappa$-representation.

Now we need to create another equation in the α-representation. This is the most important equation in laser theory. This is the equation for the spectral energy density of radiation. To solve it, we will use the density matrix $\varrho_{\alpha\alpha'}$. As a result, we will have the spectral energy density of the radiation from the laser.

Almost free electrons wander along the surface of graphene. For every carbon atom, there is one such electron. To obtain the kinetic equation of these electrons, their Hamiltonian must be reduced to a diagonal form. After these transformations, we will have a system of two equations that are equivalent to the equation obtained in the theory of superconductivity.

## CONSENT FOR PUBLICATION

Not applicable.

## CONFLICT OF INTEREST

The authors confirm that there is no conflict of interest.

## ACKNOWLEDGEMENT

Declared none.

**Boris V. Bondarev**
Moscow Aviation Institute (National Research University)
Moscow
Russia

# INTRODUCTION

## 1. Fundamentals of Quantum Mechanics. Schrödinger Equation

In quantum mechanics, the Schrödinger equation was obtained:

$$i \hbar \, \partial\psi/\partial t = \hat{H}\psi, \tag{1}$$

where the unknown

$$\psi = \psi(t, q) \tag{2}$$

is called the wave function, $\hat{H}$ is the Hamilton operator энергии. Here $q$ is a quantum variable on which the Hamiltonian acts. The physical meaning of the $\psi$ function is that the product

$$w = \psi^* \, \psi \tag{3}$$

is the probability of finding the system in state $q$. The probability satisfies the normalization condition

$$\int w \, (t, q) \, dq \ = 1 \tag{4}$$

The energy operator $\hat{H}$ is by definition, such an action on the wave function $\psi(t, q)$ to obtain the known energy $E(t, q)$ of the system:

$$\hat{H} \, \psi(t, q) = E(t, q) \, \psi(t, q)$$

## 2. Liouville − von Neumann Equation

Soon another function was invented, it is called the density matrix:

$$\varrho = \varrho(\, t, q, q') \tag{5}$$

At first, this function was equal to the product

$$\varrho(\, t, q, q') = \psi^*(t, q) \, (t, q') \tag{6}$$

In this case, the state of the quantum system is called **pure**. This function satisfies the equation that can be easily deduced from the Schrödinger equation:

$$\mathrm{i}\,\hbar\,\partial\varrho/\partial t = [\,\hat{H}\,\varrho\,] \tag{7}$$

then there was invented the density matrix

$$\varrho_{nn'}(t) = \int \psi_n^*(t,q)\,\hat{\varrho}\,\psi_{n'}(t,q)\,\mathrm{d}q \tag{8}$$

Here $\psi_n(t,q)$ is a set of wave functions, and $\hat{\varrho}$ is called the statistical operator.

The state described by the density matrix (8) is called **mixed**.

The physical meaning of the density matrix is that its elements

$$\varrho_{nn} = w_n \tag{9}$$

are probabilities to find a quantum system in states n. The probability is such that

$$\sum_n w = 1 \tag{10}$$

The equation for the mixed state density matrix:

$$\mathrm{i}\,\hbar\,\partial\varrho_{nn'}/\partial t = \sum_m (\,H_{nm}\,\varrho_{mn'} - \varrho_{nm}\,H_{mn'}\,) \tag{11}$$

It can be shown that the statistical operator $\hat{\varrho}$ satisfies the equation

$$\mathrm{i}\,\hbar\,\partial\hat{\varrho}/\partial t = [\,\hat{H}\,\hat{\varrho}\,] \tag{12}$$

The equations (11) and (12) are called Liouville − von Neumann equations. Both of these equations follow from the Schrödinger equation.

## 3. Lindblad Equation

The Schrödinger equation includes only the operator $\hat{H}$ of the quantum system energy. The equation for the statistical operator was first supplemented by Lindblad [1]:

$$\mathrm{i}\,\hbar\,\partial\hat{\varrho}/\partial t = [\,\hat{H}\,\hat{\varrho}\,] + \mathrm{i}\,\hbar\,\hat{D}\,, \tag{13}$$

where the operator $\widehat{D}$ can be called a dissipative operator. According to Lindblad, this operator is

$$\widehat{D} = \sum_{jk} C_{jk} \{ 2 \, \hat{a}_j \, \hat{\varrho} \, \hat{a}_k^+ - \hat{a}_k^+ \hat{a}_j \, \hat{\varrho} - \hat{\varrho} \, \hat{a}_k^+ \hat{a}_j \}, \tag{14}$$

$C_{jk}$ are some numbers, $\hat{a}_j$ is an arbitrary operator. The operator $\widehat{D}$ can be written as follows:

$$\widehat{D} = \sum_{jk} C_{jk} \{ [ \hat{a}_j \, \hat{\varrho} \, , \hat{a}_k^+ ] + [\hat{a}_j \, , \hat{\varrho} \, \hat{a}_k^+ ] \}$$

Operators $\hat{a}_j$ are still to be found.

## 4. Equation for the Density Matrix

The Liouville − von Neumann equation (11) is applied to the composite system $R$ + $S$, where $R$ is a thermostat and $S$ is an arbitrary system that is much smaller than the thermostat. The author of this work has derived from equation (11) the equation for the density matrix of the system $S$ [2]:

$$i \, \hbar \, \partial \varrho_{nn'}/\partial t = \sum_m \left( H_{nm} \varrho_{mn'} - \varrho_{nm} H_{mn'} \right) + i \, \hbar \, D_{nn'}, \tag{15}$$

where $D_{nn'}$ is a **dissipative** matrix that equals to

$$D_{nn'} = \sum_{m \, m'} \gamma_{nm,m'n'} \, \varrho_{mm'} - 1/2 \sum_m \left( \gamma_{nm} \, \varrho_{mn'} + \varrho_{nm} \, \gamma_{mn'} \right), \tag{16}$$

$\gamma_{nm,m'n'}$ − a matrix,

$$\gamma_{nn'} = \sum_m \gamma_{mn',nm} \tag{17}$$

## 5. Quantum Kinetic Equation

At the moment of time when the density matrix $\varrho_{nm}$ is diagonal:

$$\varrho_{nm} = w_n \, \delta_{nm}, \tag{18}$$

where $\delta_{nm}$ is the Kronecker symbol. Then from equation (16) follows the kinetic equation

$$\partial w_n / \partial t = \sum_m (p_{nm} \, w_m - p_{mn} \, w_n), \qquad \textbf{(19)}$$

where

$$p_{nm} = \gamma_{nm,mn} = (2\pi/\hbar) \sum_N \sum_M |v_{nN,mM}|^2 W_M \delta(\varepsilon_n - \varepsilon_m + E_N - E_M) \qquad \textbf{(20)}$$

is the probability of transition of the system $S$ from the state $m$ to the state $n$ per unit of time,

$$W_N = \nu \exp(-\beta \, E_N)$$

is a probability that the system $R$ is in a state $N$ with energy $E_N$, $\nu$ is the normalization factor,

$$\beta = 1/(k_{\mathrm{B}} T)$$

is the inverse temperature of the thermostat; $v_{nN,mM}$ is the matrix element of the energy of interaction of the system $S$ with thermostat $R$. Formula (20) is the **Fermi Golden rule**. Equations (13) and (15) are used in the articles included in this book.

## 6. Connection Dissipative Matrix and Dissipative Operator

Equations (14) and (16) are connected by the ratio

$$\gamma_{nm,m'n'} = 2 \sum_{jk} C_{jk} \, a_{nm,j} \, a^+_{m'n',k}, \qquad \textbf{(21)}$$

where $a_{nm,j}$ — matrix elements of operators $\hat{a}_j$.

## 7. Probability of Transition and Relaxation

Rule (20), together with the Boltzmann principle, allows to record the probability of transition in the form of

$$p_{nm} = p^{(o)}_{nm} \exp[-\beta(\varepsilon_n - \varepsilon_m)/2],$$

where

$$p^{(o)}_{nm} = p^{(o)}_{mn}.$$

*z*

Let's use formula (20):

$$p_{nm} = \gamma_{nm,mn} \,.$$

We express the matrices $\gamma_{nm,m'n'}$ and $\gamma_{nn'}$ by the transition probability $p_{nm}$. We will have

$$\gamma_{nm,m'n'} = \sqrt{p_{nm}\, p_{n'm'}}\,, \qquad \gamma_{nn'} = \sum_m \sqrt{p_{mn'}\, p_{mn}}$$

Substituting these matrices into formula (6.2), we obtain the dissipative matrix in the form

$$D_{nn'} = \sum_{mm'} \{ \sqrt{p_{nm}\, p_{n'm'}}\; \varrho_{mm'} - $$
$$- 1/2\, ( \sqrt{p_{m'm}\, p_{m'n}}\; \varrho_{mn'} + \varrho_{nm} \sqrt{p_{m'n'}\, p_{m'm}}\; ) \}$$

If we put the density matrix $\varrho_{nn'} = w_n\, \delta_{nn'}$ and $n = n'$ in this formula, we get the dissipative matrix

$$D_{nn} = \sum_m ( p_{nm}\, w_m - p_{mn}\, w_n )$$

If the matrix $p_{nm}$ is such that

$$\pi_{nm} = \gamma_n\, \delta_{nm},$$

then

$$\gamma_{nm,m'n'} = \sqrt{\gamma_n\, \gamma_{n'}}\; \delta_{nm}\, \delta_{n'm'},$$

Here with

$$\gamma_{nn'} = \gamma_n\, \delta_{nn'},$$

the dissipative matrix will be equal to

$$D^{(r)}_{nn'} = - \Gamma_{nn'}\, \varrho_{nn'},$$

where

$$\Gamma_{nn'} = 1/2\,(\,\gamma_n + \gamma_{n'}) - \sqrt{\gamma_n\,\gamma_{n'}} \geq 0$$

The value

$$\Gamma_{nn} = 0.$$

The matrix $D_{nn'}^{(r)}$ describes the relaxation of the system $S$, which is the pursuit of zero non-diagonal elements of the density matrix.

## 8. Heisenberg Uncertainty Relation

The seventh chapter discusses two dissipative matrices that are used for the quantum oscillator. First, in a dissipative operator, we put the operator

$$\hat{a} = (\,\mathrm{i}\,\hat{p}/\sqrt{m} + \sqrt{\kappa}\,\hat{x}\,)/\sqrt{2\,\hbar\,\omega}\,,$$

which is used to describe the harmonic oscillator. Equations for density matrix in different representations are written. An equilibrium density matrix is found from these equations. The equation for the Wigner function is written. The equilibrium solution of these equations is found and with the help of this function, the Heisenberg uncertainty relation for the quantum harmonic oscillator is found:

$$\overline{x^2}\cdot\overline{p^2} = \hbar^2/4\left[\left(e^{\beta\,\hbar\,\omega} + 1\right)/\left(e^{\beta\,\hbar\,\omega} - 1\right)\right]^2$$

In the future articles, the dissipative operator using the operator

$$\hat{a} = \hat{x} + \mathrm{i}\,\hbar\,\beta\,\hat{p}/(4\,m)\,,$$

is applied to describe the motion of the damped oscillator. It has been proved that from the Lindblad equation with such a dissipative operator, the Newton equation for the mean value of $\bar{x}(t)$ follows exactly, which describes the damped oscillations of the pendulum.

# REFERENCES

[1]     G. Lindblad, "On the generators of quantum dynamical semigroups," Commun. Math. Phys., vol. 48, pp. 119-130, 1976.

[2]     B.V. Bondarev, "Derivation of the quantum kinetic equation from the equation Liouville – von Neumann", Theor. Math. Phys., vol. 100, pp. 33-43, 1994.

**1**

**CHAPTER 1**

# New Theory of Step Kinetics

## 1. STEP KINETICS OF REACTIONS IN SOLIDS CORRELATION THEORY

### 1.1. Introduction

One of the most characteristic features of the kinetics of low-temperature reactions occurring in the condensed phase is the kinetic stop of the reaction. The phenomenon of kinetic stopping is observed in the recombination of radicals (radical R is a particle with an unpaired electron), in the interaction of radicals with oxygen, *etc*. The particles entering these reactions appear due to the irradiation of a solid at a low temperature by ionizing radiation. After irradiation of the solid body, the reaction is not observed. If the temperature is increased to a certain level and kept constant, the reaction begins to proceed and then stops. If the temperature is increased once again by some value, the reaction resumes. The kinetics of this reaction is called stepwise.

In this paper, the theory of solid-phase reactions is presented, the essence of which is that the reactivity of particles is characterized not only by one constant of velocity, but during the reaction the correlation function is determined by the mutual arrangement of particles changes [1]. Consider two particles A and B, which appear in a solid under the action of ionizing radiation, when the temperature of the solid body is not very high. These particles might react, but for some reason, they do not react. If the temperature is not much increased, then the reaction will proceed. But after a while, it will stop again. This is called step kinetics of a bimolecular reaction.

In solids, there are various kinds of heterogeneities. When new particles appear in a solid, they are localized in the vicinity of these inhomogeneities. Fig. (**1**) shows particles A and B, arising at a constant temperature in the body under irradiation. Black dots represent the heterogeneity of the solid body. Particles A and B are localized in some volumes in the vicinity of these inhomogeneities. The particles are moving all the time inside these volumes of localization, making the "tunnel" transitions at the node of the crystal lattice. In Fig. (**1**), it can be observed that particles A and B can not meet and react, since the volumes of their localization are

**Boris V. Bondarev**

small. In the next article, it will be shown that, according to the laws of quantum mechanics, the volume of localization increases with the increase in temperature.
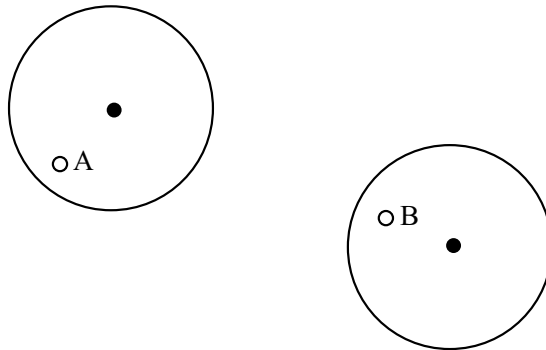


**Fig. (1).** The volumes of localization of particles **A** and **B** at constant temperature are small. Therefore, the particles cannot meet and react.

If the temperature is increased to a certain level, the volume of localization will increase, particles A and B will meet and react (see Fig. **2**).
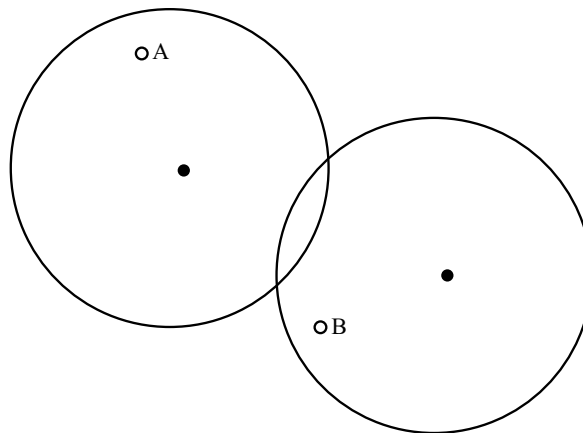


**Fig. (2).** The volume of localization of particles with increasing temperature expanding and after a while particles **A** and **B** meet and react.

This paper presents the theory of kinetics of solid-phase reactions, taking into account the correlation of the distributions of reacting particles. Kinetic equations are derived. Their solution for the homogeneous case is given. The obtained solution explains the basic laws of "step" kinetics.

## 1.2. Kinetic Theory of Solid-Phase Reactions

Let the particles A and B stabilize in some matrix, which can react as follows:

$$A + B \longrightarrow AB .$$
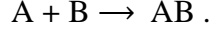
Each of these particles is localized around some center, which will be called the stabilization center and the particles move through diffusion in the microregions surrounding the center. The area in which the microdiffusion of the particle occurs increases with temperature. At a certain temperature, the size of this area becomes so large that the particle can be considered almost "free". In this case, the particle movement in the matrix volume is determined by the macrodiffusion process.

$$n_A = n_A(\boldsymbol{r}_A, t) \qquad \text{and} \qquad n_B = n_B(\boldsymbol{r}_B, t)$$

denote concentrations of the centers of particle stabilization A and B, respectively.

By definition

$$\int n_A \, dV_A = N_A , \quad \int n_B \, dV_B = N_B \tag{1.1.1}$$

where $N_A$ and $N_B$ are the numbers of particles A and B stabilized in volume $V$ of the matrix. Let the probability be given as:

$$F_{AB} = F_{AB}(\boldsymbol{r}_A, \boldsymbol{r}_B, t)$$

where $F_{AB}$ is formation per unit time of a composite particle AB from two arbitrarily selected particles A and B, whose stabilization centers are at points $\boldsymbol{r}_A$ and $\boldsymbol{r}_B$. The function $F_{AB}$ satisfies the following relations:

$$\int F_{AB} \, dV_A = \int F_{AB} \, dV_B = k , \tag{1.1.2}$$

where $k$ is the reaction rate constant given as:

$$k = 4 \pi r_0 \, D \, p \, e^{-E/(k_B T)} \, ( 1 + r_0/\sqrt{\pi D t} \,) \tag{1.1.3}$$

where $r_0$ is the distance between the particles at which their active interaction begins; $D$ is the microdiffusion coefficient, $p$ is the steric factor, and $E$ is the activation energy of the reaction.

# Density Matrix

## 2.1. EQUATION FOR DENSITY MATRIX DERIVATION OF QUANTUM MARKOV KINETIC EQUATION FROM THE LIOUVILE − VON NEUMANN EQUATION

In the framework of the second-order kinetic perturbation theory, the quantum Markov kinetic equation is derived from the Liouville − von Neumann equation [1]. This equation holds when the density matrix is diagonal. An arbitrary representation of the resulting equation is called the equation for the density matrix. The last equation written in the operator form is called the Lindblad equation [2].

### 2.1.1. Introduction

From a practical point of view of the problems of statistical physics, the kinetics of a stochastic system interacting with its environment is crucial. One of the main goals of the experimental or theoretical study of an open system, which was initially in some arbitrary nonequilibrium state, is the study of relaxation processes that lead this system to an equilibrium state. The basis of kinetic studies of the open system is the equation that controls the evolution of its States in time. The derivation of this equation, which is called a generalized kinetic equation, is generally a very complex problem.

A mathematically rigorous theory can not raise doubts about its validity only if it is built on the first principles. In the quantum theory of nonequilibrium processes, the first principle is expressed by the Liouville − von Neumann equation for the density matrix. Therefore, various methods for obtaining a generalized kinetic equation from the Liouville − von Neumann equation are of interest. The simplest form of the generalized kinetic equation takes when it describes a random Markov process.

The kinetic theory of an open system is usually formulated on the basis of the "system − reservoir" model, when the "small" system $S$ interacts with the "large" system $R$, which is considered as an infinitely capacious heat reservoir. It is assumed that the composite system $S + R$ is closed and the evolution of its States is described in the framework of quantum theory by the Liouville − von Neumann equation for the statistical operator $\hat{\rho}(t) = \hat{\rho}_{S+R}(t)$:

$$i\hbar\,\dot{\hat{\rho}} = [\,\hat{\mathcal{H}}\hat{\rho}\,]\,, \tag{2.1.1}$$

where the complete Hamiltonian

$$\hat{\mathcal{H}} \equiv \hat{\mathcal{H}}_{S+R} = \hat{H}_S + \hat{H}_R + \hat{V} \tag{2.1.2}$$

consists of Hamiltonian $\hat{H}_S$ and $\hat{H}_R$ of system $S$ and reservoir $R$, respectively, and Hamiltonian of their interaction $\hat{V}$.

Statistical operator

$$\hat{\varrho}_S = \hat{\varrho}(t)$$

of system $S$ is determined by the ratio

$$\hat{\varrho}(t) = \mathrm{Tr}_R\,\hat{\rho}(t)\,. \tag{2.1.3}$$

The main task is to obtain an equation for the operator (3). There are two ways to solve this problem: 1) the generalized kinetic equation can be derived from the Liouville − von Neumann equation and 2) the quantum Markov kinetic equation can be obtained phenomenologically taking into account the basic properties of the statistical operator, such as Hermitian, positive certainty, and normalization. The first way attracts the rigor and sequence of actions that lead to the desired equation. But this path is very difficult. Mathematically correct and practically useful results can be obtained in this way only in extreme cases. It is usually assumed that the interaction of the system with its environment is "weak", and at a certain stage of calculations make a thermodynamic limit transition. In addition, you have to make others strong and well-educated guesses. As for the second way, it should be noted that the phenomenologically obtained quantum Markov kinetic equation makes it possible to explain successfully many qualitative and quantitative regularities of kinetic phenomena in quantum open systems. It is therefore interesting to compare these two approaches and derive the quantum Markov kinetic equation directly from the Liouville − von Neumann equation.

Formally, the general solution of equation (2.1.1) can be represented as

$$\hat{\rho}(t) = \exp\left[-i/\hbar \int_0^t \hat{\mathcal{H}}(t')\,\mathrm{d}t'\right]\hat{\rho}(0)\exp\left[i/\hbar \int_0^t \hat{\mathcal{H}}(t')\,\mathrm{d}t'\right]. \tag{2.1.4}$$

It is usually assumed that at the initial time $t = 0$, the states of the system and the reservoir are statistically independent, and the latter is in a state of statistical equilibrium. This assumption corresponds to the equality

$$\hat{\rho}(0) = \hat{\varrho}_S(0)\, \hat{\varrho}_R^{(\text{eq})} \,, \tag{2.1.5}$$

where $\hat{\varrho}_S(0)$ is an arbitrary statistical operator describing the initial state of the system;

$$\hat{\varrho}_R^{(\text{eq})} = \nu \exp(-\beta\, \hat{H}_R) \tag{2.1.6}$$

is the statistical operator of the equilibrium state of the reservoir, $\nu$ is the normalizing multiplier,

$$\beta = 1/(k_{\text{B}}\, T)$$

is return temperature. Using formulas $(2.1.3) - (2.1.6)$, it is not difficult to obtain a relation linking the statistical operators $\hat{\varrho}_S(0)$ and $\hat{\varrho}_S(t)$. Unfortunately, this formal solution to the problem is almost useless because of its complexity.

As it is known, the density matrix $\varrho_{nn'}$ of the system $S$ must be self-adjoint, normalized, and positive definite at any time $t$. The quantum Markov kinetic equation, which guarantees the preservation of these properties of the density matrix, in the most general case has the form

$$i\, \hbar\, \dot{\varrho}_{nn'} = \sum_m ( h_{nm}\, \varrho_{mn'} - \varrho_{nm}\, h_{mn'} ) + i\, \hbar\, [\, \sum_{mm'} \gamma_{nm,\, m'n'}\, \varrho_{mm'} - 1/2 \sum_m ( \gamma_{nm}\, \varrho_{mn'} + \varrho_{nm}\, \gamma_{mn'} )\, ] \,, \tag{2.1.7}$$

where $h_{nm}$ are matrix elements of the effective Hamiltonian of the system, variables $n, m,...$ the essence of the quantum numbers that characterize its state,

$$\gamma_{nm,\, m'n'} = \sum_j a_{nm,j}\, a_{n'm',j}^* \,, \tag{2.1.8}$$

$a_{nm,j}$ are a system of arbitrary linearly independent matrices, $\gamma_{nm} = \sum_l \gamma_{lm,nl}$ .

The purpose of this paper is to derive the quantum Markov kinetic equation (7) from the Liouville $-$ von Neumann equation and to obtain calculation formulas for

# New Theory of Superconductivity

## 3.1. HISTORY OF SUPERCONDUCTIVITY

### 3.1.1. Discovery of Superconductivity

Kamerlingh Onnes discovered the phenomenon of superconductivity at the Leiden Laboratory, Holland, in 1991 [1]. While studying the dependence of Hg resistance on temperature, he found out that when the material is cooled down to the temperature of about 4K the resistance drops abruptly to zero. This phenomenon was called **superconductivity**. Soon after that, other elements with similar properties were discovered. Fig. (**3.1.1**) demonstrates the scheme of measurement of superconductor resistance.
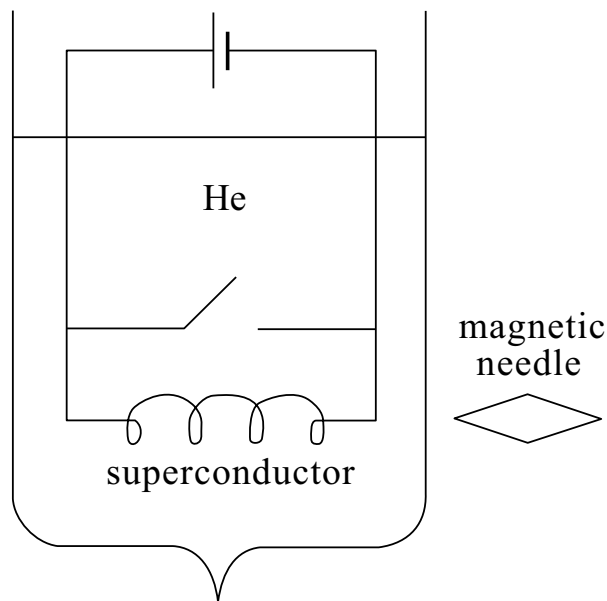


**Fig. (3.1.1).** The magnetic needle detects a supercurrent-induced magnetic field.

A superconductor is immersed in liquid helium. Initially, a weak current is supplied from a battery, then temperature is reduced. When the temperature falls below a certain value, the superconductor circuit is shortened. The current in the superconductor circuit can be sustained for a long time. A magnetic needle provided as a detector indicates the magnetic field produced by the current in the solenoid.

Fig. (**3.1.2**) shows the dependence of resistivity $\rho$ on temperature $T$ in a superconductor. Temperature $T_c$ is called **critical** temperature. This means that we cannot measure the resistance of the superconductor at $T < T_c$ . At the same time, we cannot say that the resistivity $\rho$ is equal to zero. The superconductor has a property that makes it impossible to measure the resistivity.

### 3.1.2. Meissner – Ochsenfeld Effect Silsbee Effect

It was discovered that superconductivity disappears when a test piece is placed in a relatively weak magnetic field. This phenomenon was discovered by Meissner and Ochsenfeld [2]. Value $H_m$ of the magnetic field strength in which superconductivity is disrupted is called a **critical** field. The temperature dependence of the critical field is described by the following empirical formula:

$$H_m(T) = H_m(0) \left[ 1 - (T/T_c)^2 \right] ,$$

**(3.1.1)**

where $H_m(0)$ is a critical field produced at absolute zero of temperature energy gap $T = 0$. Dependence (1.1) is shown in Fig. (**3.1.3**). Plane ($H$, $T$) represents a phase diagram of the superconductive state. The substance in the superconductive state $S$ is shown below the curve (3.1.1) and this substance in the normal state $N$ is above the curve. The superconductor that demonstrates such states is called the type-I superconductor. Superconductivity is disrupted when the current in the substance exceeds a certain critical value (The Silsbee effect).
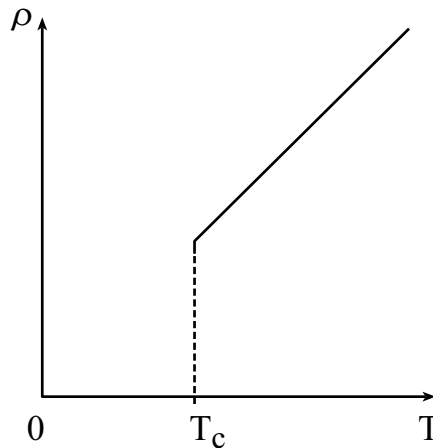


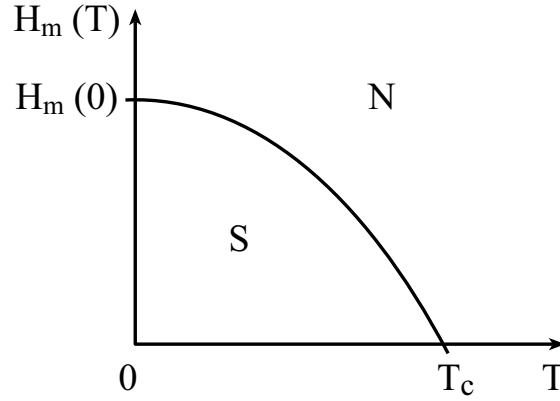**Fig. (3.1.2).** The dependence of the resistivity on temperature.

**Fig. (3.1.3).** Phase diagram of the type-I superconductive state at coordinates $(H, T)$.

There are two magnetic fields in the superconductor. One magnetic field is created by the supercurrent and another external field is induced from other sources. The compass needle shown in Fig. (**3.1.3**) responds to the supercurrent-induced field. Let us denote such strength of field by parameter $\boldsymbol{H}^{(super)}$ and name this field the superconductor self-generated magnetic field. We shall denote the strength of other magnetic fields by parameter $\boldsymbol{H}^{(exter)}$. This is an external magnetic field. Let the strength of the external magnetic field on the surface of the superconductor be equal to $H^{(exter)} = H_o$ . The Meissner − Ochsenfeld effect can be expressed by the following inequality. Superconductivity is generated in metal when its temperature $T$ drops down below the critical temperature $T_c$:

$$T < T_c ,$$

**(3.1.2)**

where the strength of the external magnetic field at the surface of the superconductor is less than that of the critical field:

$$H_o < H_m (T) .$$

**(3.1.3)**

In other cases, the superconductor will show ordinary metal properties.

There are superconductors of type II, for which the phase diagram has the form shown in Fig. (**3.1.4**). The state of the superconductor, which lies between the normal state $N$ and superconducting state $S$ is called **mixed**.

<div style="text-align:right">

**CHAPTER 4**

</div>

# New Theory of Superfluidity

## 4.1. NEW THEORY OF SUPER-FLUIDITY EQUILIBRIUM DENSITY MATRIX METHOD

### 4.1.1. Liquid Helium

Gaseous helium at atmospheric pressure becomes liquid when its temperature reaches a value of 4.44 K. Solid helium can only exist at a pressure of at least 25 atm. At lower pressures, helium remains liquid down to zero absolute temperature.

There are two isotopes of helium: $He^3$ and $He^4$. In the liquid $He^4$, a phase transition occurs at a temperature $T_\lambda = 2,18$ K, *i.e.* two helium phases are distinguished, which denote He I and He II. At temperature $T < T_\lambda$, helium $He^4$ is in a phase He II. In this case, helium behaves so, as if it is a mixture of two liquids, which are called normal and superfluid components. Distinctive features of the latter are 1) its zero entropy and 2) the lack of friction of this component with the normal component and the walls of the vessel.

The phenomenon of superfluidity of helium He II was discovered in 1937 by the Soviet physicist, Peter Leonidovich Kapitsa. In 1978, he received the Nobel prize for this discovery.

As the temperature decreases, the density $\rho_N$ of the normal component decreases, and the density $\rho_S$ of the superfluid increases. The density of He II is:

$$\rho = \rho_N + \rho_S.$$

Temperature dependence of the relationship $\rho_N/\rho$ is set experimentally. The dependence presented in this graph is satisfactorily described by the empirical formula as,

$$\rho_N/\rho = \begin{cases} (T/T_\lambda)^{5,6} & \text{at} \quad T < T_\lambda, \\ 1 & \text{at} \quad T \geq T_\lambda. \end{cases}$$

Experimental dependence of $C = C(T)$ helium heat capacity on temperature it resembles the letter $\lambda$. Therefore, this phase transition is called $\lambda$-transition. At the point $T = T_\lambda$ the function $C = C(T)$ becomes infinitely large.
Atoms $He^3$ are fermions, and atoms $He^4$ -- bosons. It is therefore natural to assume that the $\lambda$-transition in $He^4$ is somehow related to the possible Bose condensation of helium atoms.

Today, the question of Bose condensation has aroused quite a keen interest in the study of the nature of this phenomenon and the thermodynamic properties of multifrequency systems. The most general statistical formulation of a multifrequency system in quantum mechanics is obtained by applying a density matrix. To describe the density matrix of the boson equilibrium system, the variational principle [1] is used in this paper.

### 4.1.2. Uniform Distribution of Particles in Space

For analysis of equilibrium states of quantum gas consisting of angular momentum zero-spin particles, we apply a variational density matrix method. We assume that $N$ of the above particles finds itself within a certain space area with the volume equal to $V$. If the particles have their mean uniform distribution, a single-particle density matrix, which in coordinate representation depends on radius vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$, will obtain the form as follows:

$$\varrho_{\boldsymbol{r}\boldsymbol{r}'} = 1/V \sum_{\boldsymbol{k}} p_{\boldsymbol{k}}\, e^{i\,\boldsymbol{k}\,(\boldsymbol{r} - \boldsymbol{r}')}\,, \tag{4.1.1}$$

where $p_{\boldsymbol{k}}$ is the probability that an arbitrarily accepted particle is in the state defined by wave vector $\boldsymbol{k}$. Particle momentum

$$\boldsymbol{p} = \hbar\,\boldsymbol{k}.$$

Probability $p_{\boldsymbol{k}}$ meets its normalizing condition,

$$\sum_{\boldsymbol{k}} p_{\boldsymbol{k}} = 1\,. \tag{4.1.2}$$

As formula (4.1.1) indicates, the momentum representation density matrix is diagonal, *i.e.*

$$\varrho_{\boldsymbol{k}\boldsymbol{k}'} = p_{\boldsymbol{k}}\,\delta_{\boldsymbol{k}\boldsymbol{k}'}\,,$$

and transition from momentum representation to the nodal one is affected by a unitary matrix

$$u_{rk} = 1/\sqrt{V} \, e^{i \, k \, r} , \tag{4.1.3}$$

which is subject to the condition as follows:

$$\int u_{rk} \, u^*_{rk'} \, dr = \delta_{kk'} \quad \text{or} \quad 1/V \int e^{i(k-k')r} \, dr = \delta_{kk'} .$$

## 4.1.3. Kinetic Energy of Particle

Particle kinetic energy operator $\widehat{H}^{(1)}$ takes the form as follows:

$$\widehat{H}^{(1)} = -\hbar^2 \nabla^2/(2 \, m) , \tag{4.1.4}$$

where $m$ – particle mass.

Applying formula:

$$H_{kk'} = \int u^*_{rk} \, \widehat{H}^{(1)} u_{rk'} \, dr$$

we can find elements of operator $\widehat{H}^{(1)}$ in momentum representation:

$$H_{kk'} = \varepsilon_k \, \delta_{kk'} . \tag{4.1.5}$$

where $\varepsilon_k$ is the particle kinetic energy with pulse $p = \hbar \, k$:

$$\varepsilon_k = \hbar^2 k^2/(2 \, m) . \tag{4.1.6}$$

## 4.1.4. Particle Interaction Energy

We assume that $U_{rr'} = U_{r-r'}$ is potential two particle interaction energy. In virtue of translation invariance, the potential energy depends on vectors difference $r_1 - r_2$ only and it is represented by its symmetrical function:

$$U_{rr'} = U_{r'r}.$$

In this case, interaction Hamiltonian matrix elements shall be formulated by the following method:

# New Theory of Arbitrary Atom

## 5.1. METHOD OF DENSITY MATRIX NEW CALCULATION OF ENERGY LEVEL OF ELECTRONS IN ATOM

In this chapter, we apply a stationary Shrödinger equation, the solution of which allows us to find the energy levels of electrons in an arbitrary atom. This approach is based on the density matrix method. The density matrix was used to find the average electron energy in the atom. **The main idea of this paper is that all two-electron matrices must be antisymmetric.** To ensure that the two-electron Hamiltonian is anti-symmetric we use the Slater two-particle wave function.

### 5.1.1. Introduction

The density matrix is the most general description of the system in quantum mechanics. The state of the system, which is described by the density matrix, is called mixed. In a particular case, the density matrix can be proportional to the product of two wave functions. In this case, the state of the system is called pure.

At first, the concept of density matrix was defined [1, 2]. The method of calculation of energies in the spectrum of an arbitrary atom, which is called the **Hartree – Fock** method, is used. Based on the variational principle, this method applies different combinations of single-electron wave functions that take into account their anti-symmetry. This makes electrons to be fermions.

Here, the density matrix method is used to derive the average energy of electrons in an atom. The Slater wave function is used to obtain an anti-symmetric two-electron Hamiltonian. The stationary Schrödinger equation for the wave function is written. The solution of this equation makes it possible to find the energy levels of electrons in an atom.

### 5.1.2. Statistical Operator

The system of identical particles in quantum mechanics is characterized by a hierarchical sequence of statistical operators as given below:

$$\hat{\varrho}^{(1)}, \hat{\varrho}^{(2)}, \hat{\varrho}^{(3)}, \ldots$$

**Boris V. Bondarev**

We need only the first two operators from this sequence: $\hat{\varrho}^{(1)}$ and $\hat{\varrho}^{(2)}$. Let $q_1$ and $q_2$ be quantum coordinates that determine the States of two particles of the system. The first of these operators $\hat{\varrho}^{(1)}$ depends only on one of these numbers:

$$\hat{\varrho}^{(1)} = \hat{\varrho}^{(1)}(q) \,. \tag{5.1.2.1}$$

The statistical operator $\hat{\varrho}^{(2)}$ depends on these two numbers:

$$\hat{\varrho}^{(2)} = \hat{\varrho}^{(2)}(q_1, q_2) \,. \tag{5.1.2.2}$$

Electrons are identical particles. The consequence of the indistinguishability of two electrons is the symmetry of the operator $\hat{\varrho}^{(2)}$, *i.e.*

$$\hat{\varrho}^{(2)}(q_1, q_2) = \hat{\varrho}^{(2)}(q_2, q_1) \,. \tag{5.1.2.3}$$

By definition, we will use equality

$$\mathrm{Tr}_q \, \hat{\varrho}^{(1)}(q) = N \,, \tag{5.1.2.4}$$

where $N$ is the number of particles in the system;

$$\mathrm{Tr}_{q_1 q_2} \, \hat{\varrho}^{(2)}(q_1, q_2) = N(N-1) \,, \dots \tag{5.1.2.5}$$

## 5.1.3. Density Matrix

The density matrix of any system in quantum mechanics is of the form $\varrho_{\alpha\alpha'}$, where $\alpha$ and $\alpha'$ are quantum numbers that determine the States of one particle. The density matrix corresponds to the statistical operator $\hat{\varrho}^{(1)}$. This correspondence is determined by the following formula:

$$\varrho_{\alpha\alpha'} = \int \varphi_\alpha^*(q) \, \hat{\varrho}^{(1)}(q) \, \varphi_{\alpha'}(q) \, \mathrm{d}q \,, \tag{5.1.3.1}$$

where $\varphi_\alpha(q)$ is some wave function satisfying the ortho-normalization condition:

$$\int \varphi_\alpha^*(q) \, \varphi_{\alpha'}(q) \, \mathrm{d}q = \delta_{\alpha\alpha'} \,. \tag{5.1.3.2}$$

where $\delta_{\alpha\alpha'}$ – Kronecker symbol.

The meaning of the density matrix is that the diagonal elements $\varrho_{\alpha\alpha'}$ of this matrix are equal to the probability

$$w_\alpha = \varrho_{\alpha\alpha}$$

detecting the system in the state $\alpha$. Probability $w_\alpha$, according to (5.1.2.4), satisfies the normalization condition as follows:

$$\sum_\alpha w_\alpha = N, \tag{5.1.3.3}$$

The two-part operator $\hat{\varrho}^{(2)}$ corresponds to the density matrix $\varrho^{(2)}$:

$$\varrho^{(2)} = \varrho_{\alpha_1\alpha_2,\alpha_1'\alpha_2'}. \tag{5.1.3.4}$$

Density matrix in abbreviated form can be written in any coordinate as follows:

$$\varrho^{(1)} = \varrho_{11'}, \qquad \varrho^{(2)} = \varrho_{12,1'2'}.$$

Since electrons are fermions, their two-electron density matrix must be anti-symmetric. This means that the ratios are fair:

$$\varrho_{12,1'2'} = -\varrho_{21,1'2'} = -\varrho_{12,2'1'} = \varrho_{21,2'1'}. \tag{5.1.3.5}$$

The anti-symmetry ratio can be approximately satisfied if the two-electron density matrix is approximately equal to

$$\varrho_{12,1'2'} \simeq \varrho_{11'}\,\varrho_{22'} - \varrho_{12'}\,\varrho_{21'}. \tag{5.1.3.6}$$

Exactly two-electron density matrix will satisfy the ratio (5.1.3.5), if it has the form
$$\varrho_{12,1'2'} = \varrho_{11'}\,\varrho_{22'} - \varrho_{12'}\,\varrho_{21'} + \xi_{12,1'2'}.$$

Here, the correlation function $\xi_{12,1'2'}$ is symmetric:

$$\xi_{12,1'2'} = \xi_{21,1'2'} = \xi_{12,2'1'} = \xi_{21,2'1'}.$$

One-electron density matrix is related to the two-electron matrix by the ratio

$$\sum_{\alpha_2} \varrho_{12,1'2} = (N-1)\,\varrho_{11'}. \tag{5.1.3.7}$$

# New Theory of Laser

## 6.1. DENSITY MATRIX METHOD IN TWO-LEVEL LASER THEORY

In his earlier work, the author obtained the quantum kinetic equation for the density matrix. The equation contains two summands in the right part. The first one is the same as in Liouville − von Neumann equation. The second one describes the dissipative members. This quantum equation can be written in any representation. We show that in perturbation theory, this equation has the order associated with the order parameter. The order parameter expansion leads to two equations, which determine the zero and the first approximation of the density matrix. Because of the presence of time-dependent perturbations in the Hamiltonian, even the zero representation of the density matrix suggests that the states of quantum systems are mixed, *i.e*., the density matrix will not be equal to the product of the wave functions.

In this chapter, we use the method of density matrix in the theory of lasers with two energy levels [1]. Written for the atom, the equation of the density matrix of zero approximation is very simple and widely known. In the second approximation, the quantum kinetic equation for the density matrix becomes the classical kinetic equation, if the density matrix has a diagonal form. The resulting Hamiltonian also has a diagonal form. In quantum mechanics, this form can be obtained using a unitary matrix. The elements of the diagonal Hamiltonian in this representation are the eigenvalues of the atom energy. We found the density matrix in this representation. We obtained the dissipative matrices, which characterize the operations of pumping and damping. In the representation where the Hamiltonian is diagonal, we wrote the equations that describe the work of the laser.

### 6.1.1. Introduction

In 1964, N. G. Basov, A. M. Prokhorov and C. H. Townes won the Nobel Prize. They were awarded this prize for their fundamental research in quantum electronics. These studies have led to the development of masers and lasers [2, 3].

Let us consider the principle of operation of the quantum generator, laser. The basic element of the quantum generator is the active environment, *i.e.* the substance that creates the inverse population of levels. The active medium typically has the shape of a long cylinder (see Fig. **1**). At the ends of this cylinder, there are two plane-

parallel mirrors, one at each end, perpendicular to its axis. The purpose of these mirrors is to increase the length of the path where increased radiation occurs, by means of the multiple passages of the beam through the active medium. The mirrors form a so-called resonator. Between them appears a standing electro-magnetic wave. One of the mirrors is half-translucent. Through this mirror, the electromagnetic radiation comes out of the resonator in the form of a narrow, almost non-divergent beam. The process, in which the energy is transferred in some way to the active medium and the inversion of the population of levels is created, is called pumping (see Fig. **6.1.1**).
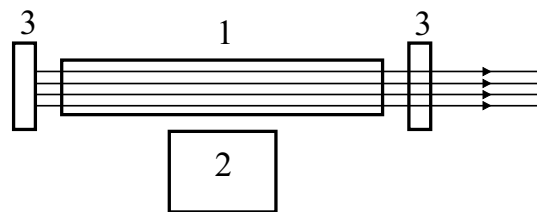


**Fig. (6.1.1).** The scheme of the quantum generator: 1 − active substance; 2 − pumping; 3 – mirrors.

The process in which energy is transferred to the active medium in some way creating a population inversion of the levels is called pumping. Pump energy may be in the form of light, electric current, energy, chemical or nuclear reactions, thermal or mechanical energy.

Various methods have been proposed to create a population inversion of energy levels. The method of two levels proposed by Basov and Prokhorov in 1955 is the most convenient and common. The atoms or molecules of the active substance are greatly influenced in some way, so that the electrons in them move from the ground state $\varphi_1(r)$ with energy $\varepsilon_1$, into the excited state $\varphi_2(r)$ with energy $\varepsilon_2$ (see Fig. **6.1.2**).
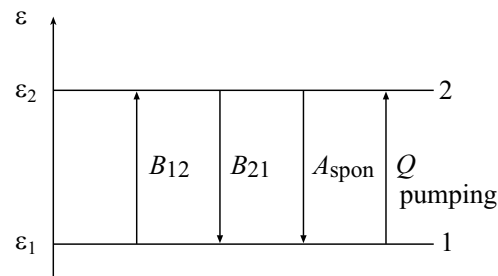


**Fig. (6.1.2).** The two-level scheme of the interaction of atom and radiation.

Due to the intense pumping, the saturation is reached, in which the number of electrons $N_2$ in the state $\varphi_2(r)$ becomes equal to the number $N_1$ of electrons in the ground state $\varphi_1(r)$. At the same time for a pair of levels $\varepsilon_1$ and $\varepsilon_2$, there is population inversion ($N_2 > N_1$). Only a small part of the energy given to the active medium during the pumping is converted into the energy of the generated radiation. Most of this energy is converted into heat. The active medium becomes very hot and sometimes it requires intense cooling.

### 6.1.2. Kinetics of Quantum Transitions

Consider a system of non-interacting atoms in which valence electron can make the quantum jump from one stationary state to another. The community of atoms in the state $\varphi_1$ with energy $\varepsilon_1$ can pass into the state $\varphi_2$ with bigger energy $\varepsilon_2$ during the absorption of photons by atoms. The number $dN_{12}^{(\text{absor})}$ of transitions made by electrons from the state $\varphi_1$ into the state $\varphi_2$ during the time from $t$ to $t + dt$ of the absorption of a photon by the atom, is proportional to the number $N_1(t)$ of atoms in the state $\varphi_1$, time dt and the number of photons $W(\omega)$ with frequency $\omega$, flying into atoms:

$$dN_{12}^{(\text{absor})} = B_{12} W(\omega)\, N_1(t)\, dt, \qquad\qquad \textbf{(6.1.2.1)}$$

where $B_{12}$ is the coefficient of proportionality, the frequency $\omega$ of these photons is determined by the formula,

$$\omega = (\varepsilon_2 - \varepsilon_1)/\hbar, \qquad\qquad \textbf{(6.1.2.2)}$$

Where the spectral energy density $W(\omega)$ is equal to the energy of electromagnetic radiation, which falls per unit volume $dV = 1$ and the unit of frequency $d\omega = 1$:

$$W(\omega)\, dV\, d\omega. \qquad\qquad \textbf{(6.1.2.3)}$$

Let at time $t$ this system have the number $N_2(t)$ of atoms in which the electron is in the state $\varphi_2$ with energy $\varepsilon_2$. The number $dN_{21}^{(\text{spon})}$ of spontaneous transitions made by electrons from the state $\varphi_2$ to the state $\varphi_1$ with smaller energy $\varepsilon_1$ with the emission of a photon during the time from the moment $t$ to the moment $t + dt$, is proportional to the number $N_2(t)$ of atoms and the time interval $dt$:

$$dN_{21}^{(\text{spon})} = A^{(\text{spon})} N_2(t)\, dt, \qquad\qquad \textbf{(6.1.2.4)}$$

# Dissipative Operator

## 7.1. LINDBLAD EQUATION FOR HARMONIC OSCILLATOR UNCERTAINTY RELATION DEPENDING ON TEMPERATURE

Specific nonequilibrium states of the quantum harmonic oscillator described by the Lindblad equation have been hereby suggested. This equation makes it possible to determine time-varying effects produced by the statistical operator or statistical matrix. Thus, respective representation-varied equilibrium statistical matrixes and specific mean value equations have been found, and their equilibrium solutions have been obtained.

### 7.1.1. Lindblad Equation

Statistical operator $\hat{\varrho}$ or density matrix is basically applied as the quantum mechanics; any information of the nonequilibrium process proceeding within the tested system may be gained from the study [1]. When the process concerned proceeds within the system which fails to interact with its environment, statistical operator $\hat{\varrho}$ will satisfy the Liouville-von Neumann equation as follows:

$$i\,\hbar\,\dot{\hat{\varrho}} = [\,\widehat{H}\hat{\varrho}\,]$$

$$(7.1.1.1)$$

With provision for the fact that the system interacts with any environment, a new equation shall be produced [1]. Lindblad is the first one who offered the equation describing the interaction of the system with a thermostat. This work is devoted to the Markovian equation [4], which hereby describes nonequilibrium quantum harmonic oscillator performance.

We will write the kinetic equation for a quantum harmonic oscillator as follows:

$$i\,\hbar\,\dot{\hat{\varrho}} = [\,\widehat{H}\,\hat{\varrho}\,] + i\,\hbar\,A\,(\,[\,\hat{a}\,\hat{\varrho},\hat{a}^{+}\,] + [\,\hat{a},\hat{\varrho}\,\hat{a}^{+}\,]\,) + i\,\hbar\,B\,(\,[\,\hat{a}^{+}\hat{\varrho},\hat{a}\,] + [\,\hat{a}^{+},\hat{\varrho}\,\hat{a}\,]\,)\,,$$

$$(7.1.1.2)$$

where

$$\widehat{H} = \hbar\,\omega\,(\,\hat{a}^+\hat{a} + 1/2\,)\,,$$

**(7.1.1.3)**

*A* and *B* are constants. Operator $\hat{a}$ is formulated as follows:

$$\hat{a} = (\,\mathrm{i}\,\hat{p}/\sqrt{m} + \sqrt{\kappa}\,\hat{x}\,)/\sqrt{2\,\hbar\,\omega}\,,$$

**(7.1.1.4)**

where

$$\omega = \sqrt{\kappa/m}\,.$$

Equation (7.1.1.2) is very precise to describe the time-varying state of the thermostat-interacted quantum harmonic oscillator and its equilibrium state.

## 7.1.2. Energy Representation

Now, we will define the wave functions, describing specific energy state $\varphi_n(x)$ which will satisfy the equation as follows:

$$\widehat{H}\varphi_n(x) = E_n\,\varphi_n(x),$$

**(7.1.2.1)**

where

$$E_n = \hbar\,\omega\,(\,n + 1/2\,)\,,$$

**(7.1.2.2)**

$$n = 0,\,1,\,2,\,...$$

As referred to energy representation, the matrix elements of statistical operator $\hat{\varrho}$ will be formulated by the equation as follows:

$$\varrho_{nn'} = \int \varphi_n^*(x)\,\hat{\varrho}\,\varphi_{n'}(x)\,\mathrm{d}x\,.$$

<div align="right">**(7.1.2.3)**</div>

Wave functions satisfy the following equations:

$$\hat{a}\, \varphi_n = \sqrt{n}\, \varphi_{n-1}, \qquad\qquad \hat{a}^+ \varphi_n = \sqrt{n+1}\, \varphi_{n+1}.$$

<div align="right">**(7.1.2.4)**</div>

With provision for the above formulas, the following matrix-formed Equation (1.2) is derived as:

$$\dot{\varrho}_{nn'} = -\,i\,\omega\,(n - n')\,\varrho_{nn'} + A\,[\,2\sqrt{(n+1)(n'+1)}\,\varrho_{n+1,n'+1} - (n+n')\,\varrho_{nn'}]$$
$$+\ B\,[\,2\sqrt{n\,n'}\,\varrho_{n-1,n'-1} - (n+n'+2)\,\varrho_{nn'}].$$

<div align="right">**(7.1.2.5)**</div>

Now, we will write the equation for diagonal elements of the density matrix $\varrho_{nn} = w_n$, where $w_n$ is the probability referred to oscillator state $\varphi_n$. The equation produced has the form as follows:

$$\dot{w}_n = 2\,A\,[\,(n+1)\,w_{n+1} - nw_n\,] + 2\,B\,[n\,w_{n-1} - (n+1)\,w_n].$$

<div align="right">**(7.1.2.6)**</div>

This kinetic equation describes particular harmonic oscillator state transitions. In this case, there may be gained coefficients $A$ and $B$ as follows:

$$A = 1/2\,P\exp\,(\beta\,\hbar\,\omega/2), \qquad B = 1/2\,P\exp\,(-\,\beta\,\hbar\,\omega/2),$$

<div align="right">**(7.1.2.7)**</div>

where $P$ is probability of transition per unit time; $\beta = 1/(k_B T)$ is reciprocal temperature.

Equation (7.1.2.6) has specific oscillator state equilibrium distribution, which satisfies the following equation:

$$A\,[\,(n+1)\,w_{n+1} - n\,w_n] + B\,[\,n\,w_{n-1} - (n+1)\,w_n] = 0.$$

<div align="right">**(7.1.2.8)**</div>

# The Beginning of Theoretical Nanophysics

## 8.1. EQUATION FOR DENSITY MATRIX SYSTEMS OF IDENTICAL PARTICLES

The equations for the statistical operator and the density matrix are considered here for a single particle and a system of identical particles when dissipative forces act on them. From the equation for the density matrix, a kinetic equation can be obtained when the density matrix is diagonal. These equations are the basis for the study of the simplest models of nanophysics [1].

### 8.1.1. Introduction

In quantum mechanics, the most general description of the system is the statistical operator $\hat{\varrho}$. The statistical operator must be normalized at any time

$$\mathrm{Tr}\,\hat{\varrho} = 1 \,, \tag{8.1.1.1}$$

self-adjoint

$$\hat{\varrho}^* = \hat{\varrho} \tag{8.1.1.2}$$

and positively definite. A correct equation describing the evolution of a statistical operator must ensure that these properties are preserved over time.

For the first time the equation for the statistical operator

$$\hat{\varrho} = \hat{\varrho}\,(t,\,q), \tag{8.1.1.3}$$

where $q$ is the quantum coordinate of the system, which was obtained by Lindblad [1]. This equation has the form

$$i\,\hbar\,\dot{\hat{\varrho}} = [\,\hat{H}\,\hat{\varrho}\,] + i\,\hbar\,\widehat{D}, \tag{8.1.1.4}$$

where $\hat{H}$ is the Hamiltonian of the system,

$$\widehat{D} = \sum_{jk}\,C_{jk}\{\,[\,\hat{a}_j\,\hat{\varrho}\,,\,\hat{a}_k^+] + [\,\hat{a}_j\,,\,\hat{\varrho}\,\hat{a}_k^+]\,\}, \tag{8.1.1.5}$$

$C_{jk}$ are some numbers, and $\hat{a}_j$ is an arbitrary operator. The operator $\hat{D}$ is called the dissipative operator. This statement can be written as

$$\hat{D} = \sum\nolimits_{jk} C_{jk} \{ 2 \hat{a}_j \hat{\varrho} \hat{a}_k^+ - \hat{a}_k^+ \hat{a}_j \hat{\varrho} - \hat{\varrho} \hat{a}_k^+ \hat{a}_j \}. \tag{8.1.1.6}$$

### 8.1.2. Equation for the Density Matrix of One Particle

The density matrix is related to the operator $\hat{\varrho} \, (t, q)$ formula

$$\varrho_{nn'} (t) = \int \varphi_n^*(t, q) \, \hat{\varrho} \, (t, q) \, \varphi_{n'}(t, q) \, \mathrm{d}q. \tag{8.1.2.1}$$

This formula specifies the density matrix $\varrho_{nn'} (t)$ in the $n$-representation. Wave function $\varphi_n(t, q)$ can be found from the Schrödinger equation

$$i \, \hbar \, \dot{\varphi}_n = \hat{H} \, \varphi_n . \tag{8.1.2.2}$$

The equation for the density matrix was derived from the Liouville - von Neumann equation. This equation is analogous to the Lindblad equation and has the form

$$i \, \hbar \, \dot{\varrho}_{nn'} = \sum\nolimits_m ( H_{nm} \, \varrho_{mn'} - \varrho_{nm} \, H_{mn'} ) + i \, \hbar \, \{ \sum\nolimits_{mm'} \gamma_{nm,m'n'} \, \varrho_{mm'} - 1/2 \sum\nolimits_m ( \gamma_{nm} \, \varrho_{mn'} + \varrho_{nm} \, \gamma_{mn'} ) \} , \tag{8.1.2.3}$$

where $H_{nm}$ are the matrix elements of the Hamiltonian $\hat{H}$ system, $\gamma_{nm,m'n'}$ is some matrix,

$$\gamma_{nn'} = \sum\nolimits_m \gamma_{mn'nm}. \tag{8.1.2.4}$$

The equation (8.1.2.3) can be written as

$$i \, \hbar \, \dot{\varrho}_{nn'} = \sum\nolimits_m ( H_{nm} \, \varrho_{mn'} - \varrho_{nm} \, H_{mn'} ) + i \, \hbar \, D_{nn'},$$

$$\tag{8.1.2.5}$$

where $D_{nn'}$ is a dissipative matrix, which will now be equal to

$$D_{nn'} = \sum\nolimits_{mm'} \gamma_{nm,m'n'} \, \varrho_{mm'} - 1/2 \sum\nolimits_m ( \gamma_{nm} \, \varrho_{mn'} + \varrho_{nm} \, \gamma_{mn'} ).$$

$$\tag{8.1.2.6}$$

Compare this formula with the formula (8.1.1.6), we establish that

$$\gamma_{nm,m'n'} = 2 \sum_{jk} C_{jk}\, a_{nm,j}\, a^{+}_{m'n',k}, \tag{8.1.2.7}$$

where $a_{nm,j}$ are matrix elements of the operator $\hat{a}_j$.

The diagonal element $\varrho_{nn'}$ is the probability $w_n$ that the system is in the state $n$. This value satisfies the normalization condition

$$\sum_n \varrho_{nn} = 1. \tag{8.1.2.8}$$

This formula is similar to formula (8.1.1.1).

In addition, the density matrix $\varrho_{nm}$ satisfies the following condition

$$\varrho^{*}_{nm} = \varrho_{mn}\,. \tag{8.1.2.9}$$

The same condition is subject to Hamiltonian:

$$H^{*}_{nm} = H_{mn}\,. \tag{8.1.2.10}$$

Consider the system where the density matrix $\varrho_{nm}$ at an arbitrary time $t$ is in the diagonal state:

$$\varrho_{nm} = w_n\, \delta_{nm}\,, \tag{8.1.2.11}$$

where $\delta_{nm}$ is the Kronecker symbol. Then from equation (3.3), we obtain

$$\dot{w}_n = \sum_m ( p_{nm}\, w_m - p_{mn}\, w_n), \tag{8.1.2.12}$$

where

$$p_{nm} = \gamma_{nm,mn} = 2\,\pi/\hbar \sum_{NM} |\, v_{nN,mM}\,|^2\, W_M\, \delta(\varepsilon_n - \varepsilon_m + E_N - E_M), \tag{8.1.2.13}$$

there is a probability of transition of the system in a unit of time from the state $m$ to the state $n$,

$$W_N = v \exp ( - \beta\, E_N)$$

there is a possibility that the environment is in an equilibrium state with quantum numbers $N$, and $E_N$ is its energy in this state, $v$ is the normalization factor, $\beta = 1/(k_B\, T)$ is the inverse temperature; $v_{nN,mM}$ are the matrix elements of the system interaction with its environment. Formula (2.13) is the **Golden rule of Fermi**.

# Perspective of Quantum Physics

## 9.1. THE LOOK INTO FUTURE OF QUANTUM PHYSICS

Quantum mechanics was based on the Schrödinger equation. Soon a statistical operator and a density matrix were invented, for which the Liouville – von Neumann equations were written. But it was impossible to find a statistical operator from this equation. About fifty years passed when the equation for the statistical operator, in which the dissipative operator was present, was phenomenologically written by Lindblad. Two decades later, the author of this article derived the equation for the density matrix. This equation contains a dissipative matrix, knowledge of which makes it possible to find the density matrix. Subsequently the author found the equation for the density matrix of the particle, which is in the system of identical particles [1].

### 9.1.1. Introduction

The statistical operator and density matrix in quantum physics are the most informative and most accurate tools. They were named after **J**. **von Neumann** shortly after the quantum theory was constructed [1]. But for a relatively long time, there was no equation that allowed us to find these values. Although many attempts have been made to find this equation, this article is devoted to the history and further development of quantum physics.

### 9.1.2. Schrödinger Equation

The basis of quantum mechanics is considered to be the **Schrödinger equation**. In this equation, the unknown is the so-called wave function

$$\psi = \psi(\, q, t \,) \,, \tag{9.1.2.1}$$

where $t$ is time and $q$ is a quantum variable that determine the state of the system.

The meaning of the wave function is the product of

$$\psi^*(\, q, t \,)\, \psi(\, q, t \,) = w(\, q, t \,) \tag{9.1.2.2}$$

it is possible to detect the system in the state $q$ at time $t$. The probability must satisfy the normalization condition:

$$\int \psi^*(q,t)\,\psi(q,t)\,\mathrm{d}q = 1 . \tag{9.1.2.3}$$

The Schrödinger equation itself can be written as follows

$$\mathrm{i}\,\hbar\,\partial\psi/\partial t = \widehat{H}\,\psi , \tag{9.1.2.4}$$

where $\widehat{H} = \widehat{H}(q,t)$ is the energy operator of the system. This operator explains what to do with the wave function $\psi(q,t)$ so that it gives us the average energy $E(t)$ of the system at time $t$:

$$E(t) = \int \psi^*(q,t)\,\widehat{H}(q,t)\,\psi(q,t)\,\mathrm{d}q . \tag{9.1.2.5}$$

### 9.1.3. Statistical Operator and Density Matrix

But soon **J. von Neumann** came up with the statistical operator

$$\widehat{\varrho} = \widehat{\varrho}(q,t) . \tag{9.1.3.1}$$

The statistical operator is related to the density matrix $\varrho_{nn'}(t)$ by the formula

$$\varrho_{nn'}(t) = \int \varphi_n^*(q,t)\,\widehat{\varrho}(q,t)\,\varphi_{n'}(q,t)\,\mathrm{d}q . \tag{9.1.3.2}$$

where functions $\varphi_n(q,t)$ can be found from the Schrödinger equation. The formula (3.2) specifies the density matrix $\varrho_{nn'}(t)$ in the n-representation. The diagonal element $\varrho_{nn}$ of the density matrix is the probability $w_n = w_n(t)$ that the system is in the state $n$:

$$\varrho_{nn}(t) = w_n(t) . \tag{9.1.3.3}$$

If the statistical operator is

$$\widehat{\varrho}(q) = \delta(q - q_\mathrm{o}) , \tag{9.1.3.4}$$

where $\delta(q - q_\mathrm{o})$ is Delta function, $q_\mathrm{o}$ – constant, then the state of the system is called **pure**. Formula (9.1.3.2) gives

$$\varrho_{nn'}(t) = \varphi_n^*(q_o, t)\,\varphi_{n'}(q_o, t)\,. \tag{9.1.3.5}$$

Otherwise, the system state is called **mixed**.

The equation for the statistical operator was derived

$$i\,\hbar\,\partial\hat{\varrho}/\partial t = [\,\hat{H}\,\hat{\varrho}\,]\,, \tag{9.1.3.6}$$

which is called the **Liouville – von Neumann equation**. This equation was derived from the Schrödinger equation. But it turned out that it was impossible **to find a statistical operator from the Liouville – von Neumann equation**. Prove it.

### 9.1.4. Something is Missing from Liouville – von Neumann Equation

For the density matrix, equation (9.1.3.6) will look like this

$$i\,\hbar\,\partial\varrho_{nn'}/\partial t = \sum_m\,(\,H_{nm}\,\varrho_{mn'} - \varrho_{nm}\,H_{mn'}\,), \tag{9.1.4.1}$$

where $H_{nn'}$ are the matrix elements of the Hamiltonian $\hat{H}$ of the system. By analogy with the formula (9.1.3.2), we write

$$H_{nn'}(t) = \int \varphi_n^*(q, t)\,\hat{H}(q, t)\,\varphi_{n'}(q, t)\,\mathrm{d}q\,. \tag{9.1.4.2}$$

If it turns out that the matrix elements $H_{nn'}$ are diagonal, *i.e.* have the form

$$H_{nn'}(t) = \varepsilon_n(t)\,\delta_{nn'}, \tag{9.1.4.3}$$

where $\varepsilon_n$ – energy eigenvalues of the system, $\delta_{nn'}$ – symbols of Kronecker, then the equation (4.1) takes the form

$$i\,\hbar\,\partial\varrho_{nn'}/\partial t = \{\varepsilon_n(t) - \varepsilon_{n'}(t)\,\}\,\varrho_{nn'}\,. \tag{9.1.4.4}$$

For $n = n'$ we obtain

$$\partial\varrho_{nn}/\partial t = 0 \quad \text{or} \quad \partial w_n/\partial t = 0\,. \tag{9.1.4.5}$$

According to this equation, the probability of $w_n$ to find a system in the state $n$ is always constant, which was to be proved.

# SUBJECT INDEX

## A

Absolute 18, 40, 238, 298, 334, 353
   accuracy 238
   error 18
   temperature 40, 298, 334, 353
Absorption bands of stabilized electrons 16
Anisotropic distribution 70, 74, 80, 82, 106, 107, 123
   electrons 82, 107
   of Electrons 74
   pattern 80
   stable 123
Anisotropic energy distribution of conduction electrons 77
Anisotropy 69, 70, 93, 101
   electron state distribution 101
   function 70
Atomic nucleus density matrix 282
Atoms 152, 180, 184, 246
   acceptor 246
   arbitrary equilibrium 180
   helium 152
   non-interacting 184
Atom's energy 308

## B

Bimolecular reactions 1, 4, 6, 8, 16, 18, 19, 23, 24
   kinetics of 4, 16
Boltzmann 284, 300, 307, 342
   principle 284, 307, 342
   rule 300
Bose condensation temperature 158
Bose gas 163, 164, 165, 167
   condensation 164
   heat capacity 164, 165
Bravais lattices 321, 322, 323

## C

Carbon atoms 321, 322
   isolated 322
   neighboring 321, 322
Charge 67, 175, 246, 247, 331
   distributed 247
   elementary electric 331
   fixed 247
   negative 247
Coefficients 3, 13, 15, 28, 34, 184, 185, 208, 209, 213, 222, 236, 258, 283, 318, 319
   attenuation 258, 283
   friction 236
   microdiffusion 3
   stiffness 15
   transitions 34
Coherent radiation 303, 318
Condition 9, 41, 42, 73, 87, 91, 92, 118, 125, 137, 138, 139, 152, 159, 167, 171, 187, 190, 194, 209, 297, 317, 341, 347
   anisotropic 73, 87
   boundary 209
   heating 9
   normalizing 118, 125, 152, 159
   ortho-normalization 171
Conduction band 83, 84, 93, 107, 244
   bottom of 83
Conduction electrons 68, 75, 77, 84, 85, 86, 88, 122, 123, 128, 129
   macro-state 88
   wave-vector 122
Conductivity 239, 321
   high electrical 321
   thermal 321
Conductor 132, 140, 143
   border 132
   passing 143
   surface 140
Constant 3, 8, 17, 24, 229
   bimolecular rate 24
   power 229
   reaction rate 3, 8, 17

# W

## Boris V. Bondarev

After graduation from Moscow Institute of Physics and Technology in 1965, he worked at Lebedev Institute of Physics. In 1968, he started his work in Moscow Aviation Institute. Since then, his scientific and teaching activities are connected to MAI. His PhD thesis (1974) was dedicated to general relativity theory. Soon after that, he developed the theory of capillary discharge in plasma. He also developed the theory of step kinetics of solid-phase reactions based on correlation function of reagents. He showed that the Arrhenius Law works at low temperatures. He constructed the statistics theory of solid-phase biomolecular reactions, and developed the probability theory of biomolecular reactions. He also built the statistics theory of kinetics of ordered binary alloys. From Liouville-von Neumann equation, he derived the quantum kinetic equation for density matrix, taking into account the behaviour of quantum system of interaction with a thermostat. He received the equation for a many-particle system that was true for one-particle density matrix and described the behaviour of quantum system with thermostat. He developed the variational method for one- and two-particle density matrices. He wrote the Lindblad equation for quantum harmonic oscillator and derived the relation of indefiniteness in dependence on temperature.