

PRINCIPLE OF ENTROPY INCREASE AND QUANTUM THEORY OF RELAXATION

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1. INTRODUCTION

THE transition of a system from a non-equilibrium to equilibrium state—relaxation—is accompanied by a change in the entropy. The entropy usually increases. This circumstance connects naturally the two problems indicated in the title of the present review.

The question of motivating the principle of entropy increase has a rather long history. One can refer, for example, to the detailed review of ter Haar^[1]. However, several original papers devoted to the theory of relaxation processes appeared after the publication of this review. We present a more or less detailed analysis of these papers later. Here we note merely that equations describing irreversible relaxation processes are derived in these papers from dynamic equations. These include the papers of Van Hove^[2-4], the series of papers by Prigogine and his co-workers^[5,6] (see also the collection of papers^[7]), as well as a paper by Bogolyubov^[8], which is earlier but not indicated in^[1], and several other papers (see below).

An analysis of the premises that have formed the basis of the derivation of the equations that describe relaxation enables us to establish the limits of applicability of the principle of entropy increase. This is indeed one of the purposes of the present review. Another purpose is to describe several specific applications of the quantum theory of relaxation processes.

In many parts of the review we deal with a closed system. We assume that such an idealization is always possible, in other words, that we can always choose a system so large that the influence of the

remaining part of the universe can be neglected in the analysis of the given processes.

For a closed system one can introduce a quantity $\sigma = -k \int f^{(N)} \ln f^{(N)} d\tau$ [where $f^{(N)}$ is the distribution function of all the coordinates and momenta of the N particles that make up the system and $d\tau$ is a volume element of phase space]. The quantity σ might naturally be regarded as the total entropy of the system, but it is easy to show, by using the Liouville theorem, that σ is independent of the time. An analogous situation obtains in quantum theory. This raises the question of how to define entropy (that is, how to define entropy such that it can increase). In the paper by P. and T. Ehrenfest^[9] and in many other papers (see^[1,10]) the point of view assumed is that whereas the fine-grained entropy is conserved, the coarse-grained entropy increases. We cannot agree with such a point of view and we shall discuss this question below (Sec. 6). (The definition of entropy given in Sec. 2 pertains to the coarse-grained density matrix.) We point out here that we are defining the entropy everywhere in the sense of Gibbs, that is, we refer to an ensemble and not to an individual state*. This means that a monotonic increase of such an entropy does not contradict the possibility of fluctuations, since the very concept of entropy in the sense of Gibbs has a probabilistic meaning. Section 2 contains in addition to a definition of the entropy some general laws governing the behavior of a closed system. It turns out, however,

*On the other hand, the Boltzmann definition pertains to an individual member of the ensemble, so that the Boltzmann entropy is a random quantity.

that these general laws are insufficient for an investigation of the region of applicability of the principle of entropy increase. It is necessary to analyze the solutions of the dynamic equations (the Neumann equation for the density matrix, the Liouville equation) in one approximation or another. Such solutions (or approximate equations) were indeed obtained for systems with infinitely many degrees of freedom in the previously cited papers^[2-6] and elsewhere. In Secs. 3-5 we analyze the assumptions and the conditions for the derivation of irreversible equations that describe the behavior of the corresponding statistical ensembles.

In Sec. 6 the limits of applicability of the principle of entropy increase are obtained on the basis of this analysis. If the statistical ensemble under consideration is in a non-equilibrium state at a given instant of time t_0 , then, by using the equations of Secs. 3-5, we are in a position to indicate, generally speaking, the further behavior of the ensemble. However, the entropy increases in this case only for definite classes of initial conditions. At the macroscopic level of information concerning the state of the system we can, in general, make only some a priori statistical predictions concerning the initial state. In Sec. 6 we consider precisely the statistical assumptions and initial conditions that give rise to an increase in the entropy.

In Sec. 7 we give a generalization of the balance equation of the entire system to include the case when one part of the system has a discrete spectrum and another part has a continuous spectrum. We call the former part of the system the dynamic subsystem and the latter the dissipative one. The introduced equation describes the behavior of a system consisting of these subsystems, which interact with each other, in the presence of an external field acting on the dynamic subsystem. In Secs. 8-11 this equation is used to investigate several processes (under the assumption that the time variation of the state of the dissipative system can be neglected). In the Appendix we give some information concerning the description of quantum systems with the aid of the density matrix.

2. ENTROPY AND INFORMATION. GENERAL THEOREMS

In thermodynamics the entropy of an equilibrium system is usually defined with the aid of the equation

$$\Delta S = \frac{\Delta Q}{T},$$

where ΔS is the increment in the entropy of a system that has a temperature T and receives an amount of heat ΔQ . The thermodynamic definition of entropy can be related to the statistical definition

of entropy with the aid of the Boltzmann principle*

$$S = k \ln \Delta\Gamma, \tag{1}$$

where k is Boltzmann's constant and $\Delta\Gamma$ is the thermodynamic probability or the statistical weight of the macroscopic state of the system^[32,33]. We shall be henceforth interested in the behavior of non-equilibrium systems, to which the foregoing relations cannot be applied directly. It is therefore necessary to give a more general definition of the entropy, valid for all systems. Such a general definition of entropy is used, in particular, in information theory^[34].

Let a probability distribution characterizing a certain statistical ensemble \dagger be given. The entropy of the ensemble characterizes the statistical spread or the randomness of the probability distribution in the ensemble. By definition, the entropy satisfies the following requirements: It is a functional of the probability distribution function and has a maximum value in the most "random" ensemble, in which all the states (members of the ensemble) are encountered with equal probability. The entropy has a minimum value (equal to zero) when the system is with certainty in the specified state. Finally, the entropy should have an additivity property wherein the entropy of a system consisting of two statistically independent subsystems is equal to the sum of the entropies of each of the subsystems. All these requirements are satisfied (apart from a constant factor) by the quantity

$$\mathcal{E} = - \sum_i p_i \ln p_i, \tag{1'}$$

where p_i is the probability with which the i -th term of the statistical ensemble is represented ($\sum_i p_i = 1$). The index i denotes the aggregates of indices characterizing a given state. The indices i , in particular, can vary continuously. In this case it is necessary to change over from summation to integration. In thermodynamics and in statistical physics one uses also the dimensional entropy

$$S = k\mathcal{E} = -k \sum_i p_i \ln p_i. \tag{1''}$$

This formula leads to the Boltzmann principle (1) for equilibrium distributions. In a microcanonical ensemble all $\Delta\Gamma$ states in the energy interval ΔE are equally probable and the entropy (1'') is

$$S = -k \sum_1^{\Delta\Gamma} \frac{1}{\Delta\Gamma} \ln \frac{1}{\Delta\Gamma} = k \ln \Delta\Gamma.$$

*As is well known^[32], Boltzmann himself did not write down such a formula. The term "the Boltzmann principle" was introduced by Einstein, who also used the inverted form of the Boltzmann principle $\Delta\Gamma = \exp(S/k)$ for investigations of fluctuations.

†See the Appendix.

For a canonical ensemble, the statistical weight $\Delta\Gamma$ can be defined as^[8]

$$\Delta\Gamma p(\bar{E}) = 1,$$

where $p(E)$ is the probability distribution in the canonical ensemble. Using (1'') we get

$$S = -k \sum_E p(E) \ln p(E) = -k \overline{\ln p(E)} = k \ln \Delta\Gamma.$$

The last equation follows from the fact that in a canonical distribution $\ln p(E)$ depends linearly on the energy E .

Along with the entropy we can introduce a quantity characterizing the "orderliness" of the given probability distribution. This quantity is called information and is equal to^[9]*

$$I = \sum_i p_i \ln p_i = -\mathcal{E}. \quad (2)$$

Let this system be in a quantum state (generally speaking, mixed) described by a density matrix ρ . Let us consider the connection between the entropy or information and the density matrix of the system. This question, generally speaking, has no unambiguous solution. The point is that specification of a quantum state, described by a density matrix $\hat{\rho}$, does not mean as yet specification of a definite statistical ensemble †. In order to specify the ensemble it is necessary to spell out the measurements that have to be made on the system which is in the state $\hat{\rho}$. Assume that we perform on the system measurements of a quantity described by an operator \hat{A} , the eigenvalues of which are numbered by an index n . Then the probability distribution in such an ensemble is specified by the diagonal element of the density matrix $\rho_{nn}^{(A)}$, and the entropy of the ensemble is ‡

$$\mathcal{E}_A = - \sum_n \rho_{nn}^{(A)} \ln \rho_{nn}^{(A)}. \quad (3)$$

(The matrix elements $\hat{\rho}$ are taken here in a representation in which the operator \hat{A} is diagonal.) Measurements of another quantity \hat{B} , which does not commute with \hat{A} , lead to a different ensemble with an accordingly different value of the entropy

$$\mathcal{E}_B = - \sum_k \rho_{kk}^{(B)} \ln \rho_{kk}^{(B)} \neq \mathcal{E}_A, \quad (3')$$

*We shall henceforth use Wiener's definition of information. This measure of information differs from that introduced by Shannon. (For more details see [12]).

†The quantum state, the density matrix, and similar problems are discussed in the Appendix.

‡Of course, the density matrix is characterized not only by the indices n but also by other indices. Obviously, it is necessary to sum over these indices, too, that is,

$$\mathcal{E}_A = - \sum_{n,l} \rho_{nl}^{(A)} \ln \rho_{nl}^{(A)}.$$

where the matrix elements $\hat{\rho}$ are taken in a representation in which the operator \hat{B} is diagonal. Among all the ensembles corresponding to the given state there are some special ones, arising in the course of measurements of a set of quantities $\hat{L}, \hat{M}, \hat{N}, \dots$ and characterized by the fact that in the representation diagonal in these quantities the density matrix is also diagonal. We call such ensembles "complete," and call the corresponding measurements complete. The entropy of a complete ensemble is

$$\mathcal{E} = - \sum_i \rho_{ii} \ln \rho_{ii} = - \text{Sp } \hat{\rho} \ln \hat{\rho}, \quad (4)$$

and the last equation (where Sp stands for the operation of summing the diagonal elements) enables us to determine the entropy of a complete ensemble if the density matrix is specified in an arbitrary representation. Equation (4) enables us to characterize the quantum states described by the density matrix $\hat{\rho}$, defined by entropy or information

$$\mathcal{E}_m = -I_m = - \text{Sp } \hat{\rho} \ln \hat{\rho}. \quad (5)$$

It must be borne in mind, however, that this entropy (information) does not characterize all the ensembles that arise during the measurements in a given state, but only the complete ensemble. The following statement can be made. The information defined by (5) is the maximum information possessed by the state $\hat{\rho}$. In other words, the information $I_m = \text{Sp } \hat{\rho} \ln \hat{\rho}$ is larger than the information of any ensemble that is realized in the case of an incomplete measurement

$$I_m > I_A \text{ or } I_B.$$

This statement follows from the fact that

$$\text{Sp } \hat{\rho} \ln \hat{\rho} \geq \sum_n \rho_{nn} \ln \rho_{nn}, \quad (6)$$

where the equality holds if the nondiagonal elements $\rho_{nm} = 0$. Formula (6) is an expression of the so-called Klein lemma^[13]. The proof of this lemma follows from the properties of the unitary transformation relating the matrix elements ρ_{nn} with the matrix element $\hat{\rho}$ in the arbitrary representation. Elsasser^[14] has called the quantity

$$I_m = \text{Sp } \hat{\rho} \ln \hat{\rho}$$

the mixture index. This designation derives from the fact that this quantity allows us to determine whether the system is in a pure or in a mixed state. In fact, in the pure state and in a representation in which the density matrix is diagonal, the density matrix has, as can be readily visualized, only one non-zero matrix element, equal to unity. Therefore in the pure state we have

$$I_m = \text{Sp } \hat{\rho} \ln \hat{\rho} = 0.$$

In any mixed state $I_m < 0$. We shall henceforth call

the quantity I_m (or respectively \mathcal{E}_m) the information of the state, to distinguish it from the information I (the entropy \mathcal{E}) characterizing the ensemble. The index m denotes that I_m is the maximum information (which is realized in a complete measurement)*.

We now proceed to investigate the evolution of closed systems, and consider in the present section only exact consequences of quantum theory.

From the invariance of the trace under unitary transformations (and the evolution of the density matrix in time can be regarded as a unitary transformation) it follows that the entropy of the state (the information of the state) of a closed dynamic system does not depend on the time

$$I_m = -\mathcal{E}_m = \text{const.}$$

This means that the state of the system varies in such a way, that the information (or entropy) does not change in an ensemble arising during complete measurements. Thus, if the entire system is initially in a pure state, it continues to remain in this state during all the time.†

Assume that a complete measurement of the system is made at some instant of time t_0 , and let the distribution of the probabilities be a diagonalized density matrix

$$q_{mn}(t_0) = q_{nn}(t_0) \delta_{mn}.$$

The entropy of this ensemble is

$$\mathcal{E}(t_0) = -\sum_n q_{nn}(t_0) \ln q_{nn}(t_0) = -\text{Sp } \hat{q}(t_0) \ln \hat{q}(t_0).$$

Assume that at an instant of time $t > t_0$ a measurement is made of the same quantities as at the instant t_0 , that is, we are considering the evolution of the ensemble in time. This ensemble (which initially was complete) is now, generally speaking, not complete, since a complete measurement realizes at each instant of time a different ensemble, corresponding to a different set of quantities‡. At the instant t the entropy of the initially chosen ensemble (which was complete at the instant t_0) has a value

*It must be emphasized that we are dealing here with the maximum of information (or with the minimum of entropy) with respect to other ensembles, produced by measurements in a given state at a definite instant of time. The question of the time variation of the entropy will be considered later.

†We assume throughout, as is customary, that we have an aggregate of identical systems, and that if a measurement is made at some instant of time on some representatives of the ensemble, then these are subsequently disregarded, since the measurement has changed them into a different state.

‡A complete ensemble arises in the measurement of a set of quantities $\hat{L}, \hat{M}, \hat{N}, \dots$, such that in the representation diagonal in these quantities the density matrix is diagonal. This property of the quantities $\hat{L}, \hat{M}, \hat{N}, \dots$ (and of the ensemble of measurements of these quantities) is not, generally speaking, conserved in time. At the instant $t > t_0$ the density matrix $\hat{\rho}$ is no longer diagonal in the $\hat{L}, \hat{M}, \hat{N}, \dots$ representation.

$$\mathcal{E}(t) = -\sum_n q_{nn}(t) \ln q_{nn}(t) \geq \mathcal{E}(t_0) = -\text{Sp } \hat{q} \ln \hat{q}, \quad (7)$$

where the inequality sign follows from Klein's lemma, since the matrix ρ_{nm} is generally speaking diagonal at the instant t . Of course, inequality (7) is not the expression for the entropy increase in its ordinary thermodynamic formulation, since it does not follow from (7) that $\mathcal{E}(t_1) = -\sum_n \rho_{nn}(t_1) \ln \rho_{nn}(t_1)$ must be larger than $\mathcal{E}(t_0)$ at an instant $t_1 > t$. It can only be stated that $\mathcal{E}(t_1) \geq \mathcal{E}(t_0)$. The instant t_0 is special because the density matrix is diagonal at that instant. We shall see below (Sec. 6) that in general we cannot prove that the entropy increases monotonically. The question of when the entropy actually increases can be solved in investigations of specific solutions of the equations of a closed dynamic system (see below).

We note that everything stated above can be readily translated into classical language. The role of the complete ensemble is assumed by the ensemble of measurements of all the coordinates and momenta of the system. This ensemble is characterized by a probability distribution $W(x_i, p_i)$. The entropy of this ensemble, as can be readily shown with the aid of the Liouville theorem, does not depend on the time. On the other hand, the entropy of any incomplete ensemble, for example the ensemble characterized by a distribution of the momenta only with arbitrary values of the coordinates, can depend on the time. The increase of such an entropy can be gauged by solving the equations of classical dynamics for a closed system (Sec. 6).

We now continue the general investigation of the behavior of closed systems. We shall show (see also^[15]) that if $\langle A(t) \rangle$ is the mean value of some quantity A at the instant of time t , then in a finite closed dynamic system $\langle A(t) \rangle$ has a limit as $t \rightarrow \infty$ only if $\langle A(t) \rangle$ does not depend on t . On the other hand, in an infinite closed system, the energy levels of which form a continuous spectrum, $\langle A(t) \rangle$ tends to a limit as $t \rightarrow \infty$ under sufficiently general assumptions. The mean value of the quantity A at the instant t is equal to

$$\langle A(t) \rangle = \text{Sp } (\hat{q}(t) \hat{A}), \quad (8)$$

where $\hat{\rho}$ obeys the Neumann equation^[16]

$$i\hbar \frac{\partial \hat{q}}{\partial t} = \hat{H} \hat{q} - \hat{q} \hat{H}. \quad (9)$$

Recognizing that the general solution of (9) can be written in the form

$$\hat{q}(t) = e^{-i\hat{H}t/\hbar} \hat{q}(0) e^{i\hat{H}t/\hbar},$$

we obtain the value of $\langle A(t) \rangle$ in the form

$$\langle A(t) \rangle = \sum_{nm} q_{nu; mu'}(0) A_{mu'; nu} e^{-i\omega_{nm}t} = \int_{-\infty}^{\infty} g(\omega) e^{-i\omega t} d\omega, \quad (10)$$

where n and m are indices that number the energy

levels; u, u' are other quantum numbers; the quantity $g(\omega)$, as can be readily verified, is defined by the equation

$$g(\omega) = \sum_{uu'nm} Q_{nu; nu'}(0) A_{mu'; nu} \delta\left(\frac{E_n - E_m}{\hbar} - \omega\right). \quad (11)$$

If the system has a discrete spectrum of energies, then $g(\omega)$ is a discontinuous function and $\langle A(t) \rangle$ is equal to a discrete sum of harmonic functions and has no limit as $t \rightarrow \infty$. After a finite time the system will come arbitrarily close to the initial state^[17]. In order for a limit to exist as $t \rightarrow \infty$ for an infinite system with a continuous spectrum, it is sufficient that the function $g(\omega)$ have the form

$$g(\omega) = G\delta(\omega) + h(\omega),$$

where $h(\omega)$ does not have any delta-like singularities and is absolutely integrable in the interval $[-\infty, +\infty]$. Then we get on the basis of the Lebesgue-Riemann theorem

$$\lim_{t \rightarrow \infty} \langle A(t) \rangle = \lim_{t \rightarrow \infty} \left\{ G + \int_{-\infty}^{\infty} h(\omega) e^{-i\omega t} d\omega \right\} = G. \quad (12)$$

Using further Eqs. (10) and (11) we find for the asymptotic value $\langle A(\infty) \rangle$

$$\langle A(\infty) \rangle = \sum_{n, u, u'} Q_{nu; nu'}(0) A_{nu'; nu}. \quad (13)$$

It must be emphasized that the proof given here is based essentially on the assumption that $g(\omega)$ does not contain any delta functions when $\omega \neq 0$. As can be seen from (11), this assumption pertains both to the density matrix $\hat{\rho}$ and to the operator \hat{A} of interest to us. In principle we can visualize idealized situations when $g(\omega)$ contains delta functions when $\omega \neq 0$. Thus, if the matrix elements of \hat{A} differ from zero only when $(E_n - E_m)/\hbar = \omega_0$,* then, as can be readily seen from (11),

$$g(\omega) = h_1 \delta(\omega - \omega_0) + h_2 \delta(\omega + \omega_0)$$

and consequently

$$\langle A \rangle = h_1 e^{-i\omega_0 t} + h_2 e^{i\omega_0 t}$$

has no limit as $t \rightarrow \infty$.

We note that the deduced presence of a definite limit for the average values as $t \rightarrow \infty$ is not at all connected with the averaging of the density matrix over the coordinates and over the time of observation. This means that the system can have an irre-

versible behavior, one characteristic of which is the presence of a limit $\langle A(\infty) \rangle$, even if we deal with a so-called fine-grained density matrix. Frequently a different point of view is assumed, according to which the irreversible behavior is connected precisely with averaging and with the introduction of a fine-grained density matrix^[1,9,10]. We shall return to this question later on when we discuss the principle of entropy increase (Sec. 6).

3. QUANTUM BALANCE EQUATION IN Γ SPACE

In this section and in the two that follow we analyze the assumptions used to derive the kinetic equations that describe the time variation of the corresponding ensemble. We begin with the derivation of the equations in the Γ space, that is, in the complete phase space of the system. These equations, under certain assumptions which will be made more precise below, reduce to equations that describe transitions in accordance with a Markov-chain scheme. We know that Markov chains play an important role in the analysis of many physical problems (see, for example,^[18] and also^[19], which contains a detailed bibliography).

The notion that the processes occurring in a gas can be regarded as processes that follow a Markov-chain scheme was first used by the Ehrenfests. Leontovich^[20] has shown that the actual subject matter of kinetic theory can be developed with the aid of a statistical scheme of Markov chains. Later papers by Kac^[21] are devoted to the same question. A Markov process is described by a balance equation

$$\frac{dP_\alpha}{dt} = \sum_{\beta} (W_{\beta\alpha} P_\beta - W_{\alpha\beta} P_\alpha), \quad (14)$$

where P_α are the probabilities of observing the system in states α , while $W_{\alpha\beta}$ is the probability per unit time of the transition from α into the state β . Equation (14) is frequently called (in the foreign literature) the master equation. It was first introduced in Γ space by Pauli^[22]. However, he used in the derivation the assumption that molecular chaos sets in every sufficiently small time interval Δt . The balance equation was derived under analogous assumptions by Landau^[13] and Bloch^[24] for a small part of a large closed system* (see also the paper by Vonsovskii^[25], who considered the question of the requirements that must be satisfied by a quantum-mechanical ensemble in order for the balance equation to hold). It is obvious that the derivation of the balance equation in^[22-24] is not satisfactory, since the assumption of molecular chaos, which must be made at every instant of time, is a very strong statistical assumption which does not follow from the dynamic Schrödinger equation.

The derivation of the balance equations from the

*It might seem that matrix elements of the coordinate (or momentum) of a harmonic oscillator satisfy this condition. One must not forget, however, that the Hamiltonian \hat{H} (by virtue of the assumption that the spectrum of the system is continuous) differs from the Hamiltonian of a harmonic oscillator, and consequently the matrix elements of the coordinate of a harmonic oscillator do not generally speaking satisfy the foregoing condition in a representation in which \hat{H} is diagonal.

*For details about these equations see Sec. 8.

Schrödinger equation for a definite class of initial conditions was first made by Van Hove^[2,3,7]. We discuss now in greater detail the premises used to base the derivation^[2,3] [we do not cite the derivation itself; in Sec. 7 we derive an equation which in a particular case goes over into (14)].

The balance equations (14) are derived in Van Hove's papers for a quantum-mechanical system with an infinitely large number of degrees of freedom. Such a system is obtained as a result of going to the limit from a system having a finite number of degrees of freedom (finite volume) and accordingly a discrete spectrum. If the number of degrees of freedom N and the volume Ω tend to infinity (such that N/Ω remains finite), the spectrum of the system becomes continuous. The Hamiltonian of the system can be written in the form

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \quad (15)$$

where the resolution into an unperturbed Hamiltonian \hat{H}_0 and an interaction Hamiltonian $\lambda \hat{V}$ is to a considerable degree arbitrary and is determined by the ensemble whose time behavior is of interest to us. Let the density matrix have in the representation in which \hat{H}_0 is diagonal a form $\rho_{\alpha\alpha'}$ (the indices α run through a continuous series of values). Then $P_\alpha = \rho_{\alpha\alpha}$ determines the probability distribution in the ensemble of interest to us, and P_α obeys the balance equation upon satisfaction of a series of conditions, which we shall now consider.

1) The matrix elements of the operator V , taken with the aid of the eigenfunctions of the operator \hat{H}_0 , satisfy the condition of diagonal singularity, which consists in the fact that the diagonal elements of the matrix $\langle \alpha | \hat{V} \hat{A} | \alpha' \rangle$ (where \hat{A} is a diagonal matrix) is at least N times larger than the nondiagonal element of the same matrix. This condition is satisfied for all known energies of interactions that lead to dissipation. An example for the case of an electromagnetic field interacting with matter is given in Sec. 7. The condition of diagonal singularity reduces essentially to the fact that the transition probability per unit time differs from zero. It is easy to verify that matrix elements $\hat{V} \hat{A}_1 \hat{V} \hat{A}_2 \hat{V} \dots \hat{A}_n \hat{V}$ and $\hat{A}_1 \hat{V} \hat{A}_2 \dots \hat{V} \hat{A}_n$ (where \hat{A}_i are diagonal matrices) also have diagonal singularity.

2) The second condition concerns the smallness of the interaction energy. In order to write down this condition, it is necessary to introduce a correlation time τ_c . This time is determined in the following manner (see also footnote on page 300):

$$\tau_c = \frac{\hbar}{\delta_0 E} = \frac{1}{\omega^*}, \quad (16)$$

where $\delta_0 E$ is the energy difference (difference between the eigenvalues of the unperturbed Hamiltonian \hat{H}_0), which determines the characteristic energy scale of the matrix elements of the operators, which

are functions of the interaction energy \hat{V} . This means that if $f(E)$ is such a matrix element, then when $\Delta E \ll \delta_0 E$ the function $f(E)$ does not differ from $f(E + \Delta E)$, and when $\Delta E > \delta_0 E$ there is an appreciable difference between $f(E)$ and $f(E + \Delta E)$.

Let T_0 be the characteristic relaxation time, and then the condition that the interaction energy be small can be written in the implicit form

$$T_0 \gg \tau_c.$$

If this condition is satisfied, we can write $T_0 = \lambda^{-2} \Gamma$ (where Γ does not depend on λ)*. Thus, the condition for the smallness of the interaction energy is written in the form

$$\lambda^2 \Gamma^{-1} \ll \omega^* = \frac{1}{\tau_c}. \quad (17)$$

3) The third condition pertains to the choice of the initial conditions. We shall characterize the initial state of the density matrix $\rho_{\alpha\alpha'}(0)$. Such a description enables us to consider both pure and mixed states in a single manner. Let

$$\hat{U} = e^{-\frac{i}{\hbar}(\hat{H}_0 + \lambda \hat{V})t}$$

be a unitary operator, describing the evolution of the system in time. The solution of the Neumann equation (9) can be written in the form

$$\hat{\rho}(t) = \hat{U} \hat{\rho}(0) \hat{U}^*.$$

It follows therefore that the quantity P_α of interest to us, namely the probability of the state $|\alpha\rangle$, is written in the form

$$P_\alpha = \rho_{\alpha\alpha}(t) = \sum_{\alpha'} \sum_{\alpha''} U_{\alpha\alpha'} Q_{\alpha''\alpha'}(0) U_{\alpha''\alpha}^*. \quad (18)$$

The diagonal-singularity condition indicated above leads to the diagonal singularity of $U \hat{U}^*$, and the latter means that $P_\alpha(t)$ can be broken up into two parts:

$$P_\alpha(t) = \sum_{\alpha'} U_{\alpha\alpha'} Q_{\alpha'\alpha'}(0) U_{\alpha'\alpha}^* + \sum_{\alpha' \neq \alpha''} \sum_{\alpha''} U_{\alpha\alpha'} Q_{\alpha''\alpha'}(0) U_{\alpha''\alpha}^*, \quad (19)$$

the single sum having the same order of magnitude in N as the double sum. In^[2] the first sum of (19) is investigated in approximation 2). This sum is expanded in powers of $\lambda \hat{V}$ and only the terms of order $\lambda^{2n} t^n$ are retained [the remaining terms are of order $\lambda^{2n+k} t^n$ and are assumed to vanish when $k > 0$ by virtue of the condition (17)]. A result of such an investigation is the fact that the first sum in (19)

$$P_\alpha = \sum_{\alpha'} U_{\alpha\alpha'} Q_{\alpha'\alpha'}(0) U_{\alpha'\alpha}^* \quad (20)$$

satisfies the balance equation (14). Thus, the equa-

*The fact that T_0 has the form $\lambda^{-2} \Gamma$ follows from the balance equation (14), in which $W_{\alpha\beta}$ are the probabilities per unit time, calculated by perturbation theory; consequently, $W_{\alpha\beta} \sim \lambda^2$ and $T_0 \sim W_{\alpha\beta}^{-1} \sim \lambda^{-2}$.

tion turns out to be applicable under such initial conditions which cause the vanishing of the expression

$$\sum_{\alpha' \neq \alpha} U_{\alpha\alpha'} Q_{\alpha'\alpha'}(0) U_{\alpha'\alpha}^* \quad (21)$$

This expression vanishes, first, if the system has been initially in a mixed state with diagonal density matrix

$$Q_{\alpha'\alpha'}(0) = Q_{\alpha'\alpha'}(0) \delta_{\alpha'\alpha'};$$

second, if the system has been initially in a state with definite α , that is, $\psi(0) = |\alpha\rangle$, or in a state which would be approximately stationary after a relaxation time $T_0 = \Gamma\lambda^{-2}$, provided the perturbation $\lambda\hat{V}$ were not effective. More accurately, if

$$\psi(0) = \sum_{\alpha} C_{\alpha} |\alpha\rangle, \quad (22)$$

then the energy interval δE characterizing this wave packet should satisfy the inequality

$$\delta E \ll \frac{\hbar}{T_0}. \quad (23)$$

Third, it can be shown that (21) tends to zero as $\lambda \rightarrow 0$ ($\lambda^2 t$ finite) if the initial state is the wave packet (22) and if δE satisfies the inequality*

$$\delta E \gg \frac{\hbar}{T_0}. \quad (24)$$

We have thus proved the balance equation for two classes of pure initial conditions, represented by packets (23) or (24), or else for mixed initial states with a diagonal density matrix. In^[3] (see also^[7]) it is shown that if we do not assume λ to be small, the balance equation is incorrect. We cannot, for example, calculate the probability per unit time in higher-order approximations and use the same balance equation (14). An investigation carried out in^[3] by the resolvent method yields for the quantity (20) an integro-differential equation that describes a non-Markov process. When λ is small this equation goes over into (14). Unlike (14), the equation of^[3] with finite λ is valid only for initial conditions (23) and for mixed initial states with diagonal density matrix.

The derivation of the Van Hove integro-differential equation, made in^[3] without assuming λ small, is rather complicated. This equation is derived in much simpler fashion in the paper by Zwanzig^[26]. We present this derivation. In order not to give a separate derivation for the classical case, we write (9) in the form

$$i \frac{\partial \rho}{\partial t} = \hat{L} \rho, \quad (25)$$

where

$$\hat{L} \rho = \begin{cases} -i \{ \mathcal{H} \rho \} = -i \sum_{\alpha} \left(\frac{\partial \mathcal{H}}{\partial p_{\alpha}} \frac{\partial \rho}{\partial q_{\alpha}} - \frac{\partial \mathcal{H}}{\partial q_{\alpha}} \frac{\partial \rho}{\partial p_{\alpha}} \right) & \text{in the classical theory,} \\ \frac{1}{\hbar} [\hat{\mathcal{H}}, \rho] = \frac{1}{\hbar} (\hat{\mathcal{H}} \rho - \rho \hat{\mathcal{H}}) & \text{in quantum theory.} \end{cases}$$

In the classical case (25) is the Liouville equation and ρ denotes the distribution function of all the coordinates q_{α} and momenta p_{α} of the system. The formal solution of (25) has the form

$$\rho(t) = e^{-it\hat{L}} \rho(0).$$

In quantum theory this equation is equivalent to

$$\rho(t) = e^{-it\hat{\mathcal{H}}/\hbar} \rho(0) e^{it\hat{\mathcal{H}}/\hbar}.$$

We shall not distinguish between the quantum and classical cases from now on. We are usually interested in the time behavior of a definite ensemble, which is characterized by a certain "projection" of the density matrix (or distribution function). We therefore write ρ in the form

$$\rho = \hat{P} \rho + (1 - \hat{P}) \rho \equiv \rho_1 + \rho_2, \quad (26)$$

where ρ_1 is the density matrix projection of interest to us. Thus, formula (18) separates the diagonal part of the density matrix, and in this case (26) is written in the form

We note that in this case the characteristic correlation frequency ω^ coincides with $\delta E/\hbar$ if $\delta E < \delta_0 E$ (but if $\delta_0 E < \delta E$ then $\omega^* = \delta_0 E/\hbar$).

$$Q_{\alpha\alpha'} = Q_{\alpha\alpha'} \delta_{\alpha\alpha'} + (1 - \delta_{\alpha\alpha'}) Q_{\alpha\alpha'}. \quad (26')$$

Another example of subdivision of (26) will be given later on in the derivation of the classical balance equation. We assume henceforth that \hat{P} is an operator that is linear and independent of the time, so that \hat{P} and $\partial/\partial t$ commute. Equation (25) can in this case be rewritten in the form

$$i \frac{\partial \rho_1}{\partial t} = \hat{P} \hat{L} (\rho_1 + \rho_2), \quad (27a)$$

$$i \frac{\partial \rho_2}{\partial t} = (1 - \hat{P}) \hat{L} (\rho_1 + \rho_2). \quad (27b)$$

The formal solution of (27b) is written in the form

$$\rho_2(t) = \exp[-it(1 - \hat{P})\hat{L}] \rho_2(0) - i \int_0^t ds \exp[-is(1 - \hat{P})\hat{L}] (1 - \hat{P}) \hat{L} \rho_1(t-s) \quad (28)$$

[it is possible to verify by direct substitution that this solution satisfies (27b)]. We then substitute (28) in (27a) and obtain the sought equation

$$i \frac{\partial \rho_1}{\partial t} = \hat{P} \hat{L} \exp[-it(1 - \hat{P})\hat{L}] \rho_2(0) + \hat{P} \hat{L} \rho_1 - i \int_0^t ds \hat{P} \hat{L} \exp[-is(1 - \hat{P})\hat{L}] (1 - \hat{P}) \hat{L} \rho_1(t-s). \quad (29)$$

This equation is a generalization of the Van Hove equations and goes over into the latter after separation of the Hamiltonian given by formula (15), when the operator \hat{P} separates only the diagonal matrix elements ρ in the representation of the unperturbed Hamiltonian \hat{H}_0 . The initial conditions indicated above correspond to

$$\hat{P}Q(0) = Q(0), \quad Q_2(0) = 0.$$

In this case (29) does not contain ρ_2 at all. The choice of initial conditions and the irreversibility of (29) [with $\rho_2(0) = 0$] will be discussed in greater detail in Sec. 6 below. Equation (29) goes over into the balance equation (14) as $\lambda \rightarrow 0$ ($\lambda^2 t$ finite). We do not derive the balance equation now, but proceed to derive^[20] its classical analog.

4. DERIVATION OF CLASSICAL BALANCE EQUATIONS IN Γ SPACE

The classical balance equations in Γ space were derived in the paper by Brout and Prigogine^[5]. Different generalizations and applications of these equations are the subject of several papers by Prigogine and his co-workers^[6]. The derivation of the classical balance equation given in^[5] corresponds fully to the Van Hove derivation^[2]. We therefore do not stop to discuss the premises on which this derivation is based. We merely note that a condition of the type of diagonal singularity of the perturbation energy is used here, too. Now, however, this condition is imposed not on the matrix elements V , but on the corresponding Fourier components of the perturbation energy. It is known^[27] that the matrix elements go over into the Fourier components in the quasiclassical approximation.

We now proceed to derive^[26] the classical balance equations. We consider a classical system of N particles in a volume Ω . The Hamiltonian of such a system has the form

$$\mathcal{H} = \sum_{\mathbf{j}}^N \frac{P_{\mathbf{j}}^2}{2m} + \frac{1}{2} \lambda \sum_{\mathbf{j} \neq \mathbf{k}}^N \sum U(r_{\mathbf{j}\mathbf{k}}), \quad (30)$$

where the \mathbf{j} -th particle has a momentum $p_{\mathbf{j}}$, a coordinate $r_{\mathbf{j}}$, and a mass m ; $U(r_{\mathbf{j}\mathbf{k}})$ is the energy of interaction between the \mathbf{j} -th and \mathbf{k} -th particles. The corresponding Liouville operator has the form*

$$\hat{L} = \hat{L}_0 + \lambda \hat{L}_1, \quad (31)$$

$$\hat{L}_0 = -i \sum_{\mathbf{j}=1}^N \frac{p_{\mathbf{j}}}{m} \frac{\partial}{\partial r_{\mathbf{j}}},$$

$$\hat{L}_1 = -\frac{i}{2} \sum_{\mathbf{j} \neq \mathbf{u}}^N \sum F_{\mathbf{j}\mathbf{k}} \left[\left(\frac{\partial}{\partial p_{\mathbf{j}}} \right) - \left(\frac{\partial}{\partial p_{\mathbf{k}}} \right) \right], \quad (32)$$

where $\lambda F_{\mathbf{j}\mathbf{k}} = -\lambda [\partial U(r_{\mathbf{j}\mathbf{k}}) / \partial r_{\mathbf{j}}]$.

*We recall that in classical mechanics the Liouville operator is defined by Eq. (25).

The Liouville equation (25) describes the evolution of the distribution function $\rho(r_{\mathbf{j}}, p_{\mathbf{j}}, t)$ in time. The balance equation which we derive pertains to the distribution function of the momenta only; then

$$\hat{P} = (V^N)^{-1} \int d^{3N} r \quad (33)$$

and

$$\hat{P}Q(r, p, t) = Q_1(p, t). \quad (34)$$

We assume that the distribution is homogeneous at the initial instant of time, that is, $\rho_2(0) = 0$. It is easy to show further that^[26]

$$\hat{P}\hat{L}Q_1 = 0. \quad (35)$$

In this case (29) simplifies to

$$\frac{\partial Q_1}{\partial t} = - \int_0^t ds \hat{P}\hat{L} \exp[-is(1-\hat{P})\hat{L}] \hat{L}Q_1(t-s). \quad (36)$$

We furthermore use the fact that

$$\hat{L}Q_1 = \lambda \hat{L}_1 Q_1 \text{ and } \hat{P}\hat{L}f = \lambda \hat{P}\hat{L}_1 f, \quad (37)$$

where the first equality follows from the fact that $\hat{L}_0 \rho_1 = 0$ and the second follows from the fact that the operator \hat{P} annihilates any function $\hat{L}_0 f$.

Using these equations, we obtain ultimately

$$\frac{\partial Q_1}{\partial t} = \lambda^2 \int_0^t ds \hat{k}(s; \lambda) Q_1(t-s), \quad (38)$$

where $\hat{k}(s; \lambda)$ is an operator in momentum space:

$$\hat{k}(s; \lambda) = -\hat{P}\hat{L}_1 \exp[-is(1-\hat{P})\hat{L}] \hat{L}_1. \quad (39)$$

Equation (38) is exact. This equation describes a non-Markov process of approaching the equilibrium state. It can be simplified in case of small λ . In this case we introduce a new time scale

$$\tau = \lambda^2 t. \quad (40)$$

Equation (38) is written in the form

$$\frac{\partial \tilde{Q}_1(\tau)}{\partial \tau} = \int_0^{\tau/\lambda^2} ds \hat{k}(s; \lambda) \tilde{Q}_1(\tau - \lambda^2 s).$$

We assume further that the kernel \hat{k} is finite in the interval $0 < s < \tau_c$:

$$\hat{k}(s; \lambda) \cong 0, \quad \text{if } s > \tau_c.$$

Here τ_c is the characteristic correlation time; it is, in particular, equal to the collision time (whereas the relaxation time is of the order of the time between collisions; see also Sec. 3). We now go to the limit as $\lambda \rightarrow 0$ for fixed $\tau > 0$. As a result we obtain

$$\frac{\partial Q_1(t)}{\partial t} = \lambda^2 \int_0^{\infty} ds \hat{k}(s; 0) Q_1(\tau) \quad (41)$$

which is an equation describing a Markov process. Using (37) we find

$$\hat{k}(s; 0) = -\hat{P}\hat{L}_1 \exp(-is\hat{L}_0)\hat{L}_1. \quad (42)$$

Equations (41) and (42) coincide with those derived by Brout and Prigogine^[5].

5. KINETIC EQUATIONS IN μ SPACE

So far we have dealt with equations in Γ space. For the case of sufficiently rarefied gases it becomes possible to write closed equations in μ space, that is, in the space of the individual particle. The μ space is characterized in general by the coordinates x , y , and z and momenta p_x , p_y , p_z of the individual particle. The first to write the kinetic equations in μ space was Boltzmann^[28]. These equations, however, were not derived from dynamic equations, inasmuch as the statistical assumption of molecular chaos (Stosszahlansatz) was made for each instant of time t .

From the balance equations we can obtain directly the following equations for the occupation numbers n_k in μ space (see, for example, ^[29,30]):

$$\begin{aligned} \frac{d\langle n_k \rangle}{dt} &= \frac{1}{2} \sum_{ijl} [A_{ij}^{kl} \langle n_i n_j (1 + \theta n_i) (1 + \theta n_l) \rangle \\ &\quad - A_{kl}^{ij} \langle n_k n_l (1 + \theta n_i) (1 + \theta n_j) \rangle], \end{aligned} \quad (43)$$

where A_{ij}^{kl} are constant coefficients characterizing the transition probability per unit time, while the angle brackets $\langle \dots \rangle$ denote averaging with the aid of the probability distribution function $P(n_1, n_2, \dots, n_k, \dots, t)$ in Γ space. Thus, for example,

$$\langle n_k \rangle = \sum_{n_1} \sum_{n_2} \dots \sum_{n_k} \dots \sum_{n_j} n_k P(n_1 \dots n_k \dots t).$$

$\theta = 0, 1$, and -1 , respectively, for particles obeying classical, Bose-Einstein, and Fermi-Dirac statistics.

Equation (43) is essentially not in μ space and differs from the Uehling-Uhlenbeck equation used in kinetic theory of gases^[31] in that the right half of (43) contains the average of particle products $\langle n_i n_j \rangle$, $\langle n_i n_j n_k \rangle$, etc. in place of products of averages. It is essentially necessary to make an assumption which is equivalent to Stosszahlansatz:

$$\langle n_i n_j (1 + \theta n_i) (1 + \theta n_l) \rangle = \langle n_i \rangle \langle n_j \rangle (1 + \theta \langle n_k \rangle) (1 + \theta \langle n_l \rangle), \quad (44)$$

in order to go over to the ordinary kinetic equations used in theory of gases*.

The question of the derivation of the kinetic equations in μ space from the balance equations in Γ space was considered in^[20,21]. Several papers are

also devoted to the derivation of kinetic equations in μ space directly on the basis of the Liouville equation or the Schrödinger equation for the density matrix. Foremost among these is the work of Bogolyubov^[8]. Let us dwell briefly on the assumption that serves as the basis for the derivation of the kinetic equation in that paper.

From the Liouville equation (25), (30) we can derive a hierarchy of equations for the s -particle distribution functions

$$\begin{aligned} F_s(t, x_1, \dots, x_s) \\ = \Omega^s \int \dots \int \rho(t, x_1, x_2, \dots, x_N) dx_{s+1} dx_{s+2} \dots dx_N, \end{aligned} \quad (45)$$

where $x_i \equiv q_i, p_i$ stands for the coordinates and the momentum of the i -th particle and Ω is the volume of the gas. When Ω and N tend to infinity in such a way that $v = \Omega/N$ remains finite, the system of coupled equations for the functions F_s has the form (see also^[32,33])

$$-\frac{\partial F_s}{\partial t} = \{H_s; F_s\} + \frac{1}{v} \int \left\{ \sum_{1 \leq i \leq s} \lambda U(|q_i - q_{s+1}|); F_{s+1} \right\} dx_{s+1}, \quad (46)$$

where H_s is the Hamiltonian of the system of s particles, and the braces denote Poisson brackets. This is an exact system of equations, equivalent to the initial Liouville equation. To go over to the ordinary kinetic equations [which are equations for the function $F_1(x_1)$], the following assumptions are made:

1. For a broad class of initial conditions for the function ρ , F_s depends on the time only through F_1 : after a time that is large compared with the collision time (i. e., τ_c)

$$F_s(x_1 \dots x_s; t) \rightarrow F_s(x_1 \dots x_s | F_1).$$

2. The decrease in correlation is assumed to have the form

$$[S_{-\tau}^{O(s)} F_s(0, x_1 \dots x_s)$$

$$- \prod_{1 \leq i \leq s} F_1(0, x_i)] \rightarrow 0 \text{ as } \tau \rightarrow \infty, \quad s = 2, 3, \dots,$$

where $S_{-\tau}^{O(s)}$ denotes an operator corresponding to uniform straight-line motion of the system of s material particles with momenta p_s . This condition expresses the fact that the particles were statistically independent prior to "turning on" the interaction. If τ is made to approach $-\infty$ in the condition for the weakening correlation (which denotes that F_s is expressed as a product of functions F_1 as $t \rightarrow \infty$), then the collision integral in the kinetic equation will have the opposite sign^[34] and in this case it will not describe the approach to the state of equilibrium with increasing entropy.

Using the indicated assumptions and expanding in powers of $1/v$, we can obtain an equation for F_1 in closed form. We shall not dwell in greater detail on^[8] and other papers devoted to the derivation of

*Equation (43) and the equation obtained from it under condition (44) describe the relaxation of a homogeneous gas in the absence of external forces, that is, the right half of (43)-(44) yields the collision integral.

the kinetic equation from the Liouville equation. A detailed review and a critical analysis of these papers can be found in the articles^[35,36] (see also^[7,30,37-39]). We point out only the paper by Bogolyubov and Gurov^[40], where a quantum generalization is made of Bogolyubov's paper (to a case when the potential energy can be regarded as a small perturbation). The Bogolyubov method was used in many papers (for a detailed bibliography see^[41]) to derive kinetic equations in different physical situations.

6. PRINCIPLE OF ENTROPY INCREASE

In Secs. 3–5 we have considered the connection between the kinetic equations that determine the time variation of the statistical ensembles and the dynamic equations that determine the time variation of the state of the entire system. Since such a connection has been established, we can proceed to discuss the statistical justification of the entropy increase principle.

We now present the customary proof of the principle of increase of entropy from the balance equation. According to formula (4), the entropy of an ensemble, characterized by diagonal elements of the density matrix ρ , is equal to

$$\mathcal{G} = - \sum_{\alpha} Q_{\alpha\alpha} \ln Q_{\alpha\alpha} = - \sum P_{\alpha} \ln P_{\alpha}.$$

Differentiating this equation and using the balance equations (14), we get

$$\begin{aligned} \dot{\mathcal{G}} &= - \sum_{\alpha} (P_{\alpha} \ln \dot{P}_{\alpha} + \dot{P}_{\alpha}) = - \sum_{\alpha\beta} (W_{\beta\alpha} P_{\beta} - W_{\alpha\beta} P_{\alpha}) \ln P_{\alpha} \\ &= - \sum_{\alpha\beta} W_{\alpha\beta} (P_{\beta} - P_{\alpha}) \ln P_{\alpha}. \end{aligned} \quad (47)$$

In going over from the second equation to the third we have used the fact that the sum $\sum_{\alpha} P_{\alpha}$ does not depend on the time, and in going over to the last equation we used the property of 'microscopic reversibility'

$$W_{\alpha\beta} = W_{\beta\alpha}, \quad (48)$$

which follows from the fact that the perturbation-energy operator \hat{V} is Hermitian. Let us interchange the indices α and β in (47) (which of course, does not change the sum) and add the resultant expression to (47). Dividing by two, we obtain

$$\mathcal{G} = - \frac{1}{2} \sum_{\alpha\beta} W_{\alpha\beta} (P_{\beta} - P_{\alpha}) \ln \frac{P_{\alpha}}{P_{\beta}}. \quad (49)$$

It is easy to see that the expression in the right half of (49) is always positive, i. e., the entropy increases, except for the case

$$P_{\beta} = P_{\alpha}, \quad (50)$$

when the right half of (49) vanishes. This case

corresponds to the state of equilibrium. If we take account of the fact that in the balance equation $W_{\alpha\beta}$ denotes the probability of transition between states with identical energy, then the equilibrium state (50) is described by a microcanonical distribution, in which all states with given energy are encountered with an identical probability

$$P_{\beta} = P_{\alpha} = \frac{1}{\Delta\Gamma(E)}, \quad (50')$$

where $\Delta\Gamma(E)$ is the number of states with a specified energy. It is easy to see that the state (50') has the maximum entropy.

Thus, the balance equations lead to the principle of increase of energy, and the maximum value of the entropy is realized for a microcanonical ensemble. We note that unlike^[22,10], the derivation presented here for the principle of entropy increase does not call for separating the density matrix into fine-grained and coarse-grained components. On the other hand, one cannot agree with the statements made in^[10,1] that the increase in the entropy of a fine-grained ensemble, which we have just proved, is purely a quantum effect and is connected with the measurement process. An analogous statement is made by Davydov^[42]. Let us dwell on this question in somewhat greater detail. The usual reasoning that leads to the need for introducing a coarse-grained density matrix is as follows. The entropy, defined with the aid of the density matrix (or distribution function, in the classical case) of the entire system in the Γ space, does not depend on the time (see Sec. 2). It is concluded therefore that if we define the entropy with the aid of a coarse-grained density matrix, such an entropy will increase. The coarse-grained density matrix is introduced in the following manner^[10,1]. The stationary states of the system are subdivided into groups such that the differences between different groups, but not within the groups, can be established with the aid of accessible measurement methods. Then the coarse-grained density matrix has in the chosen representation the form

$$P_{kl} = \delta_{kl} \sum_j \frac{Q_{ij}}{S_i},$$

where the summation is over all the S_i -states of the i -th group and the energy level E_k belongs to the i -th group. The entropy is defined with the aid of this density matrix as

$$\Sigma = - \sum_k P_{kk} \ln P_{kk} = - \sum Q_{kk} \ln P_{kk}.$$

Of course, the entropy so defined should no longer remain constant, and it is usually concluded (without proof) that Σ increases. On the other hand, the fine-grained quantity

$$\mathcal{G} = - \sum Q_{kk} \ln Q_{kk}$$

should likewise not be constant and both quantities, by virtue of the Klein lemma, should be larger than

$$\mathcal{E}_m = -\text{Sp} \hat{\rho} \ln \hat{\rho}.$$

Tolman^[10] thus concludes that there are two reasons for the increase in Σ . The first is in the difference between the coarse- and fine-grained quantities P and ρ ; the second reason for the change in Σ is the increase in $\mathcal{E} = -\Sigma \rho_{kk} \ln \rho_{kk}$ (this increase is likewise not proved). The second cause of the change in Σ is called by Tolman the quantum-mechanical variation of the fine-grained probability and, according to him, has no classical analog. We cannot agree with such a point of view, and, as we have already seen, the principle of entropy increase and the approaches to the state of equilibrium can be described without resorting to the concept of the coarse-grained density matrix.

The situation can be described in the following fashion. The entropy of the state \mathcal{E}_m in γ space does not depend on the time. In order to check this statement experimentally, it is necessary to carry out at each instant of time a complete measurement on the system and to separate an ensemble (which in general is different at each instant of time) corresponding to this complete measurement. On the other hand, if we are interested in the behavior of the same ensemble, specified by the same measurements, then the entropy of such an ensemble, as has been shown above, increases monotonically. This is true also for the same assumptions under which the balance equation (14) has been derived. We can say more generally the following: we are usually interested not in the entire density matrix $\hat{\rho}$, which contains all the information concerning the system, but in part of the density matrix, its projection $\hat{\rho}_1 = \hat{P} \hat{\rho}$, for which we establish the corresponding kinetic equation that leads in turn to the entropy increase principle. Thus, in the case analyzed the operator \hat{P} separated the diagonal elements of the density matrix of the entire system in terms of the eigenfunctions of the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$, and the corresponding ensemble was determined by the same token. In Sec. 4 the operator \hat{P} separated the classical ensemble corresponding to the measurement of all the momenta of the system:

$$\rho_1(p_1, p_2, \dots) = \hat{P} \rho(r_1, r_2, \dots, p_1, p_2, \dots).$$

In the case of gases, the entropy increase principle can be established for the ensemble corresponding to measurement in μ space, i. e., in the space of momenta and velocities of one particle. In this case the operator \hat{P} projects ρ on the μ space. We thus see that the situation is the same here for both the classical and quantum cases, and what Tolman calls the quantum-mechanical change in the fine-grained probability is none other than the change in the entropy of the corresponding ensemble, which does not coincide with the complete ensemble and is characterized by specification of the type of measure-

ments.* We can say also the following. We are usually interested not in the complete information I_m , but only in the part of the information contained in the density matrix $\hat{P} \hat{\rho}$. For this part we obtain the law of decrease of information (entropy increase). The information contained in $\hat{P} \hat{\rho}$ is transferred to the remaining part $(1 - \hat{P}) \hat{\rho}$, so that the total information remains unchanged. Davydov^[42] has actually suggested that the change in entropy $\mathcal{E} = -\Sigma \alpha P_\alpha \ln P_\alpha$ is due to the repeated measurements. As is obvious from the foregoing, the change in \mathcal{E} follows from the Schrödinger equation, in which the effect of the measurement is not taken into account.

The principle of entropy increase and the micro-canonical distribution in the state of equilibrium were derived above from the balance equation. The latter was derived from the Schrödinger equation with the aid of several assumptions. These assumptions concern, on the one hand, the properties of the perturbation energy and are the necessary conditions for the existence of a dissipative process. On the other hand, these conditions are not sufficient, since the satisfaction of a definite class of initial conditions is required. It is precisely here that the statistical assumptions should be contained. Were it possible to prove the balance equations (or the corresponding kinetic equations) for arbitrary initial conditions, then we could prove by the same token the entropy increase principle in a statistical form[†] and the ergodic theorem. However, it is impossible to obtain such a proof, as will be seen from the examples given below.

Let us turn now to discuss in somewhat greater detail the initial conditions. As was noted in Sec. 3, the balance equations can be derived if at the initial instant the density matrix is diagonal in the indices α which characterize the states of the unperturbed

*To single out a corresponding ensemble by the type of measurement performed may seem somewhat artificial in the classical case. However, the kinetic equation (both classical and quantum) determines the time variation of the projection $\hat{P} \rho$ of the complete distribution function, and this projection always gives the probability distribution only for a definite class of measurements on the system. On the other hand, the ensemble and accordingly the projection $\hat{P} \rho$ are determined in natural fashion by the class of physical quantities whose averages are of interest to us. Thus, for example, the average values of physical quantities, which depend only on the momenta p_i of systems, are determined by the projection of the distribution function

$$\rho_1(r_1, \dots, p_N) = \hat{P} \rho(q_1, \dots, p_N; p_1, \dots, p_N).$$

Analogously, single-particle physical quantities (such as volume or gas pressure) are determined by the distribution function in μ space.

[†]Inasmuch as we are using the Gibbs definition of entropy (see Sec. 2), a monotonic increase in this quantity does not contradict the existence of fluctuations in the equilibrium ensembles and by the same token the increase in the Boltzmann entropy (see, for example, [43]).

Hamiltonian \mathcal{H}_0 . [In addition, the balance equation can be derived if in the initial instant the system is in a pure state, satisfying condition (24).] If the density matrix is diagonal at the initial instant (in the chosen representation) then, without confining ourselves to small values of the parameter λ , we can show^[2,3] that as $t \rightarrow \infty$ the system is characterized by a microcanonical distribution. (However, for an initial distribution corresponding to condition (24), such a statement has not been proved for finite λ .) The question arises whether the initial ensemble can have a representation (at $t = 0$) with a diagonal density matrix. Were it possible to prove such a representation at the initial instant (i. e., prove that such an ensemble can be used to obtain correctly all the mean values of the physical quantities), then we could prove by the same token the principle of entropy increase in its statistical form. Let us examine the degree to which such an ensemble can be regarded as representative. In the macroscopic experiment, the initial state is characterized by specifying a series of averages

$$\text{Sp} \hat{\rho}(0) \hat{A}_1 = a_1, \quad \text{Sp} \hat{\rho}(0) \hat{A}_2 = a_2, \quad \dots, \quad \text{Sp} \hat{\rho}(0) = 1. \quad (51)$$

The last equality is the normalization condition (the average value of the unit operator is always equal to 1). However, equations (51) still do not determine the density matrix. In order to determine the density matrix we must advance the postulate that the state $\hat{\rho}(0)$ is the most chaotic of all the states that are compatible with conditions (51)^[16,14,10] (see also^[44,45,1]). Analytically this is expressed by the condition of maximum entropy (or minimum information) of the state

$$\delta \mathcal{E}_m = -\delta \text{Sp} \hat{\rho}(0) \ln \hat{\rho}(0) = 0 \quad (52)$$

with supplementary conditions (51). In particular, the requirement that the mean value of the energy and of the unit operator be definite leads to a canonical distribution. We can generalize this principle by assuming that the distribution is specified in the initial ensemble, i. e., that the diagonal elements of the density matrix are specified

$$Q_{\alpha\alpha} = P_\alpha, \quad \sum P_\alpha = 1, \quad (53)$$

and that in all other respects the state is the most chaotic, i. e., it has a minimum of information

$$\delta \text{Sp} \hat{\rho}(0) \ln \hat{\rho}(0) = 0 \quad (54)$$

subject to condition (53). It is obvious that the solution of this extremal problem is given in accordance with the Klein lemma by the diagonal matrix $\rho_{\alpha\alpha}(0)$ ($\rho_{\alpha\alpha'} = 0$ when $\alpha \neq \alpha'$). Thus, an initial state with diagonal density matrix (for which the irreversible equations are derived) is the most probable of all the possible initial states compatible with the specified probability distribution (53). It has maximum entropy (maximum lack of information)

subject to conditions (53). One must not think, however, that the extremal principle considered here is an unavoidable consequence of quantum theory. Although such a notion can result from the previously cited papers (see also^[46]), this is nevertheless not so. We now proceed to an examination of cases when this principle is not satisfied. From the paper of Van Hove^[2] (see also^[47,48]) it follows that for negative t an analogous balance equation is valid, which leads to a microcanonical distribution as $t \rightarrow -\infty$. The behavior of the entropy is shown schematically in Fig. 1. When $t = 0$ the entropy has the smallest value [for initial conditions (53)–(54)*].

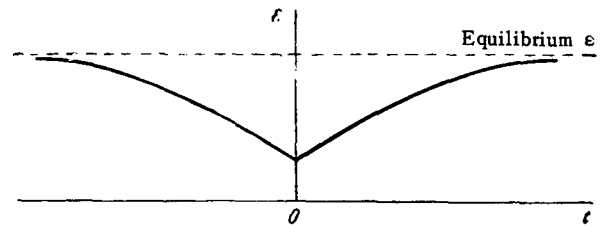


FIG. 1

At an instant of time $t \neq 0$ the density matrix is no longer diagonal, and if we choose such an instant of time as the initial one, then, depending on the values of the non-diagonal matrix elements $\rho_{\alpha\alpha'}$, the entropy will increase or decrease (the latter will be realized if the matrix elements correspond to the instant of time $t < 0$). As a rule, however, in a macroscopic experiment we do not know all the details of the initial state and choose a priori the most probable one, i. e., in fact the state (53)–(54); and in this case we obtain the balance equation. On the other hand, if as a result of the experiment we observe that the behavior of the system is such that the entropy decreases, we ascribe such a behavior to a low-probability fluctuation.

However, cases are possible when we can predict that the entropy will decrease after a certain time interval. Such a case occurs in the spin-echo experiment^[49] (see also^[50], in which the statistical aspect of this experiment is discussed). This experiment can be described roughly and schematically in the following fashion. The system of spins is in an inhomogeneous magnetic field, and at the initial instant of time all the spins are aligned with the x axis, which is perpendicular to the direction of the magnetic field (the z axis). The spins in the magnetic field precess with a frequency $\omega = \gamma H$, which is different for each spin. Let the frequencies ω be symmetrically distributed with respect to the

*To avoid a misunderstanding we note that at the initial instant of time the entropy is the largest of all those possible at that instant [subject to conditions (51)], but it has a smallest value compared with the entropy for $|t| > 0$.

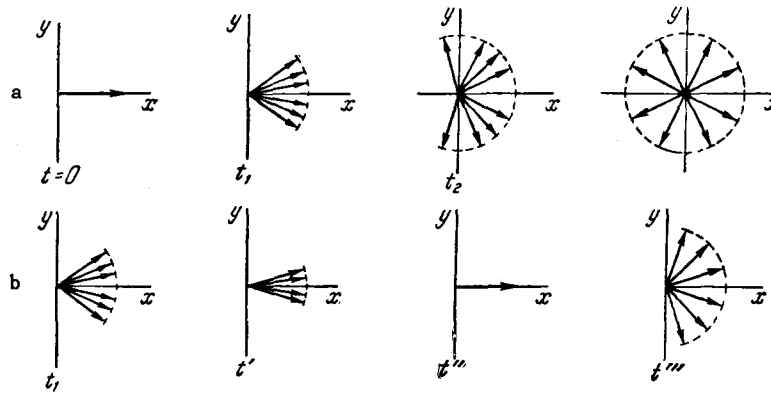


FIG. 2

frequency ω_0 . We proceed to a system rotating with frequency ω_0 . Then, if $g(\omega)$ (the distribution function of the frequencies in this system) is a delta-function

$$g(\omega) = \delta(\omega),$$

the total spin of the system will be aligned at all times with the x axis (in the rotating system of coordinates). In the general case, when $g(\omega)$ is not a delta-function, the summary spin along the x axis is proportional to

$$\int_{-\infty}^{\infty} g(\omega) e^{i\omega t} d\omega$$

and, in accordance with the Lebesgue-Riemann theorem, it tends to zero as $t \rightarrow -\infty$. The behavior of the spins at different instants of time is shown schematically in Fig. 2a, from which it is seen that the entropy of the spin distribution increases monotonically (the state t_1 is more chaotic than $t = 0$). However, if we reverse the magnetic field at the instant t_1 , the signs of the frequencies are reversed [$g(\omega)$ does not change], and the process proceeds in the opposite direction (Fig. 2b). The entropy then first decreases, reaches a minimum at $t = t''$, and then increases again and the system goes into the equilibrium state.

Let us summarize the contents of the present section. If an initial non-equilibrium state is specified in a macroscopic experiment, when we do not know all the details of the states, then the a priori most probable state will be one with a diagonal density matrix, and consequently an entropy increase will be observed in further experiments in the same ensemble. However, cases are probable in which the entropy decreases. In all the analyzed examples, whether the entropy behaves monotonically or not, the system goes over into an equilibrium state characterized by a microcanonical ensemble. This suggests that it is possible to prove the ergodic theorem for a much more general class of initial conditions than given in the paper of Van Hove^[4].

7. QUANTUM THEORY OF RELAXATION PROCESSES

In the investigation of relaxation processes of different physical systems we usually deal with the following characteristic situation. Relaxation occurs as a result of the interaction between some dynamic system and a dissipative system. We define as dynamic that part of a system (or subsystem) which has a finite number of degrees of freedom and discrete energy levels, and which is described in principle by simple dynamic equations. This dynamic subsystem interacts with the dissipative system, which has an infinite number of degrees of freedom and a continuous spectrum. A simple example of a relaxation process is the spontaneous radiation of an atom in free space. The role of the dynamic system is played here by the atom, while the dissipative system is the radiation field in free space. The radiation field in free space has a continuous spectrum, while the atom has a discrete spectrum. The probability of spontaneous radiation in a quantum transition from excited state a into state b is equal to^[5]

$$W_{ab} = \frac{2\pi}{\hbar} \sum_{\lambda} |V_{a0; b1\lambda}|^2 \delta(E_{a0} - E_{b1\lambda}) t \\ = \frac{2\pi}{\hbar} \sum_{\lambda} V_{a0; b1\lambda} V_{b1\lambda; a0} \delta(E_{a0} - E_{b1\lambda}) t \equiv \omega_{ab} t. \quad (55)$$

The singularities of spontaneous radiation, which follow in particular from expression (55) and which are of interest to us, are:

1. The interaction between the atom and the radiation field leads to an "accumulation" effect—the transition probability is proportional to the time.

2. Expression (55) is valid if the following condition is satisfied

$$\tau_c \ll t \ll \tau_0 = \frac{1}{\omega_{ab}}, \quad (56)$$

where $\tau_c = 2\pi/\omega_0$ is the period of the spontaneous radiation and $1/\omega_{ab}$ is the average lifetime of the

excited state^[51]. Thus, in order for a transition probability to exist in a unit time, it is necessary to have

$$\tau_0 = \frac{1}{\omega_{ab}} \gg \tau_c = \frac{2\pi}{\omega_0}. \quad (57)$$

It is easy to see that the latter condition is analogous to condition (17), which we encountered in the investigation of the applicability of the balance equation.

3. It follows from (55) that to have a non-zero transition probability per unit time it is necessary to satisfy the diagonal singularity condition. In fact, the matrix elements of the energy \hat{V} of interaction with the radiation field are inversely proportional to $\sqrt{L^3}$, (where L is the dimension of the cube in which the radiation field is contained). For free space $L \rightarrow \infty$, and consequently the matrix elements are infinitesimally small. On the other hand, the expression

$$\sum_{\lambda} V_{a0; b1\lambda} V_{b1\lambda; a0} = (\hat{V}^2)_{a0; a0} \quad (58)$$

is finite, since it is necessary to change over from summation to integration, and the state density is proportional to L^3 . [Expression (55) contains the sum

$$\sum_{\lambda} V_{a0; b1\lambda} V_{b1\lambda; a0},$$

which is taken on the constant-energy surface

$$E_{a0} = E_{b1\lambda}.$$

However, it is easy to see that this sum is also finite, and corresponds to a diagonal singularity of the matrix $\hat{V}\hat{A}\hat{V}$.

The foregoing singularities of the spontaneous radiation are inherent also in other relaxation processes. An account of these singularities makes it possible to derive the balance equation (see Sec. 3). The balance equation (14) derived by Van Hove^[2] characterizes essentially the relaxation of a dissipative system (the dynamic system is not introduced at all). In order to be able to determine the different averages pertaining to the dynamic subsystem it is necessary to derive the kinetic equation for a density matrix which is diagonal in the indices α of the dissipative subsystem and is, generally speaking, nondiagonal in the discrete indices m and n of the dynamic subsystem. In fact, the average value of some operator \hat{A} pertaining to the dynamic subsystem is equal to

$$\langle A \rangle = \text{Sp} \hat{\rho} \hat{A} = \sum_{nm\alpha\alpha'} \rho_{n\alpha'; m\alpha} A_{m\alpha; n\alpha'} = \sum_{m, n, \alpha} \rho_{n\alpha; m\alpha} A_{m\alpha}. \quad (59)$$

The last equality follows from the fact that the matrix A is diagonal in the indices α in the represen-

tation with a diagonal Hamiltonian operator for a system consisting of non-interacting dynamic and dissipative subsystems.

We now proceed to derive the equation for the matrix $\rho_{m\alpha; n\alpha}$ ^[52].

The Hamiltonian of a system consisting of a dynamic and dissipative subsystem that interact with each other has the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hbar\hat{V}, \quad \hat{\mathcal{H}}_0 = \hbar\hat{F} + \hbar\hat{E}, \quad (60)$$

where $\hbar\hat{F}$ is the Hamiltonian operator of the dissipative subsystem, $\hbar\hat{E}$ is the Hamiltonian operator of the dynamic subsystem, and $\hbar\hat{V}$ is the interaction energy. In order to take into account the external forces acting on the dynamic subsystem, we assume that \hat{E} can depend explicitly on the time in an arbitrary fashion. Equation (9) for the density matrix assumes the form

$$i \frac{\partial \hat{\rho}}{\partial t} = [\hat{F} + \hat{E} + \hat{V}, \hat{\rho}]. \quad (61)$$

Let us change over to the interaction representation. For this purpose it is necessary to carry out a unitary transformation on all the operators

$$\hat{A} \rightarrow e^{i\hat{F}t} \hat{S} \hat{A} \hat{S}^{-1} e^{-i\hat{F}t}, \quad (62)$$

where the matrix \hat{S} satisfies the equations

$$\frac{d\hat{S}}{dt} = i\hat{S}\hat{E}, \quad \frac{d\hat{S}^{-1}}{dt} = -i\hat{E}\hat{S}^{-1}, \quad \hat{S}^{\pm 1}(0) = 1. \quad (63)$$

In this representation Eq. (61) assumes the form

$$i \frac{\partial \hat{\rho}}{\partial t} = [\hat{V}\hat{\rho}]. \quad (64)$$

Here \hat{V} and $\hat{\rho}$ are operators in the interaction representation. Our problem consists of deriving the kinetic equation for the density matrix $\rho_{m\alpha; n\alpha}$ by starting from this equation and using the above-considered assumptions concerning the smallness of v (v characterizes the order of magnitude of the operator \hat{V}) and the condition of diagonal singularity in the index α . We are interested in the behavior of the density matrix $\hat{\rho}$, using for the scale a time on the order of the relaxation time $\tau_0 = \Gamma/v^2$ (where Γ does not depend on v). This means that when we refer later on to the variation of the density matrix over an infinitesimally short time, we shall have in mind variation over a time much shorter than τ_0 . On the other hand, however, this short time should be very long compared with another time scale, of the order of $\tau_c = \hbar/\delta_0 E$, where $\delta_0 E$ is the already-introduced energy difference [see formula (16) of Sec. 3], characterizing the dissipative subsystem. The increment in the density matrix* over a time τ satisfying the condition

$$\tau_c \ll \tau \ll \tau_0, \quad (65)$$

*We refer throughout to a matrix with elements $\rho_{m\alpha; n\alpha}$.

can be reduced, as will be shown below, to the form

$$\hat{q}(t+\tau) - \hat{q}(t) = \hat{A}(t)v^2\tau + \hat{B}(t)v + \hat{C}(t)v^2. \quad (66)$$

We denote by \tilde{t} the time in the v^{-2} scale, $\tilde{t} = v^2t$. Equation (66) assumes the form

$$\hat{q}(\tilde{t} + \tilde{\tau}) - \hat{q}(\tilde{t}) = \hat{A}(\tilde{t})\tilde{\tau} + \hat{B}(\tilde{t})v + \hat{C}(\tilde{t})v^2. \quad (66')$$

Letting now $v \rightarrow 0$ and $\tilde{\tau} \rightarrow 0$ (the latter denotes smallness only in the scale v^{-2}), we arrive at the differential equation

$$\frac{\partial \hat{q}}{\partial \tilde{t}} = \hat{A}$$

or, going over to the old time scale t , we obtain

$$\frac{\partial \hat{q}}{\partial t} = v^2 \hat{A}. \quad (67)$$

This indeed will be the sought-for differential equation. We note that only in the interaction representation can we assume that the density matrix varies slowly and neglect its variation over a time of the order of τ_C . The point is that the transition to the interaction representation denotes precisely the elimination of the high-frequency dependence. The density matrix $\hat{\rho}$ in the interaction representation represents, roughly speaking, the amplitude of the probability matrix in the Schrödinger representation. The principal variation of this "amplitude" with time is connected with the relaxation processes and, by virtue of the smallness of v^2 , is relatively slow. We note also that the approximation consisting in the changeover from (66) to (67) corresponds to the approximation used by Van Hove^[2] ($\lambda \rightarrow 0$, $\lambda^2 t$ finite).

In order to find $v^2 \hat{A}$ in (67), we use Eq. (64). From this equation we obtain, accurate to terms of order v^2

$$\begin{aligned} \hat{q}(t+\tau) - \hat{q}(t) = & -i \int_0^\tau [\hat{V}(t+\tau'), \hat{q}(t)] d\tau' \\ & - \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' [\hat{V}(t+\tau'), [\hat{V}(t+\tau''), \hat{q}(t)]] \end{aligned} \quad (68)$$

It is easy to see that without loss of generality we can expand an arbitrary operator \hat{A} in the interaction representation in a series of harmonic functions of the time:

$$\hat{A} = \sum_r \hat{A}^r(t) e^{i\omega_r t}, \quad \hat{A}^r(t) = e^{i\hat{F}t} \hat{A}^r e^{-i\hat{F}t}, \quad (69)$$

where the time-independent operators \hat{A}^r and the frequencies ω are determined by the transformation $\hat{S}(t)$

$$\hat{S} \hat{A} \hat{S}^{-1} = \sum_r \hat{A}^r e^{i\omega_r t} \quad (70)$$

Using (69) and (70), we can write the first term of (68) in the form

$$\begin{aligned} \Delta_1 \hat{q}_{\alpha\alpha} = & \sum_{r\alpha'} [\zeta_r(\omega_r + \omega_{\alpha\alpha'}) \hat{V}_{\alpha\alpha'}^r(t) \hat{q}_{\alpha\alpha'} \\ & - \zeta_r(\omega_r + \omega_{\alpha\alpha'}) \hat{q}_{\alpha\alpha'} \hat{V}_{\alpha\alpha'}^r(t)] \exp(i\omega_r t), \end{aligned} \quad (71)$$

where $\hat{\rho}_{\alpha\alpha'}$ is an operator matrix acting on the variables of the dynamic subsystem, and in the representation $|m\alpha\rangle$ its matrix elements are $\rho_{m\alpha; n\alpha'}$;

the function $\zeta_r(x) = i \int_0^\tau \exp(ix\tau') d\tau'$ goes over

when $\tau \gg \hbar/\delta_0 E$ into the singular function^[5]

$\zeta(x) = P/x - i\delta(x)$. Since α' varies continuously by assumption, it is necessary to change over from summation over α' in (71) to integration. This integral, subject to condition (65), does not depend on the time τ and is of the order of v , that is, it has a structure $\hat{B}(t)v$. We discard such terms. We note that the dependence on the time τ could appear were the matrix $\hat{V}_{\alpha\alpha'}$ to have a singularity, that is, were the contribution made to the sum by the individual term of the sum different from zero. Each individual term of the sum can yield a proportionality to τ . However, we assume later on that the matrix \hat{V} is not singular. This means that as the number of degrees of freedom N tends to infinity, the matrix element $\hat{V}_{\alpha\alpha'}$ tends to zero.

Let us proceed now to examine the second term in the right half of (68). It can be written in the form

$$\begin{aligned} \Delta_2 \hat{q}_{\alpha\alpha} = & - \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' [\hat{V}(t+\tau'), [\hat{V}(t+\tau''), \hat{q}]_{\alpha\alpha}] \\ = & - \sum_{rs} \sum_{\alpha'\alpha''} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \{ \hat{V}_{\alpha\alpha'}^r(t) \\ & \times \hat{V}_{\alpha'\alpha''}^s(t) \hat{q}_{\alpha''\alpha} e^{i(\omega_r + \omega_{\alpha\alpha'})\tau' + i(\omega_s + \omega_{\alpha'\alpha''})\tau''} \\ & - \hat{V}_{\alpha\alpha'}^r(t) \hat{q}_{\alpha'\alpha''} \hat{V}_{\alpha''\alpha}^s(t) e^{i(\omega_r + \omega_{\alpha\alpha'})\tau' + i(\omega_s + \omega_{\alpha'\alpha''})\tau''} \\ & - \hat{V}_{\alpha\alpha'}^s(t) \hat{q}_{\alpha'\alpha''} \hat{V}_{\alpha''\alpha}^r(t) e^{i(\omega_r + \omega_{\alpha\alpha'})\tau' + i(\omega_s + \omega_{\alpha'\alpha''})\tau''} \\ & + \hat{q}_{\alpha\alpha'} \hat{V}_{\alpha'\alpha''}^s(t) \hat{V}_{\alpha''\alpha}^r(t) e^{i(\omega_r + \omega_{\alpha\alpha'})\tau' + i(\omega_s + \omega_{\alpha'\alpha''})\tau''} \} e^{i(\omega_r + \omega_s)t}. \end{aligned} \quad (72)$$

Just as in the case of $\Delta_1 \hat{\rho}_{\alpha\alpha}$, when τ satisfies the condition (65) the double sum (double integral) with respect to α and α' does not depend on the time and has a structure $c(t)v^2$; we neglect such terms. However, there is now the condition of diagonal singularity, which separates from the double sum only the sum over α' . Before we calculate this single sum, let us carry out the following auxiliary computation. The sum analogous to that obtained from (72) after leaving out the diagonal-singular terms, has for fixed r and s the form

$$I = \sum_{\substack{u, v \\ u+v=\text{const}}} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' e^{i\omega_r \tau' + i\omega_s \tau''} f(u, v). \quad (73)$$

Changing integration variables we have

$$I = \int_0^\tau d\tau_1 \left\{ \frac{e^{i(u+v)\tau} - e^{i(u+v)\tau_1}}{i(u+v)\tau} \right\} \tau F(\tau_1), \quad (73')$$

where the function

$$F(\tau_1) = \sum_{\substack{u, v \\ u+v=\text{const}}} e^{-i v \tau_1} f(u, v) \quad (73a)$$

is essentially different from zero when $\tau_1 \lesssim \tau_c$, and τ_c is determined by the interval δv of the variation of $f(\text{const} - v, v)$; $\tau_c = 1/\delta v$. Let $\tau \gg \tau_c$ and then for $(u + v)\tau \gg 1$ the curly bracket in (73') is small, and when $(u + v)\tau \lesssim 1$ we can replace $\exp[i(u + v)\tau_1]$ by unity. Thus, discarding small terms with $(u + v)\tau \gg 1$, we have

$$I = \sum_{\substack{u, v \\ u+v=\text{const} \ll \frac{1}{\tau_c}}} \int_0^\tau dt' e^{i(u+v)t'} \int_0^\infty dt_1 e^{-i v \tau_1} f(u, v) \quad (73'')$$

[we have also replaced the limits of integration in (73') by infinity, by virtue of the properties of $F(\tau_1)$]. Now, using (73) and the diagonal-singularity condition, and going in the sense indicated above to the limit as $\tau \rightarrow 0$, we obtain the sought-for kinetic equation in the form

$$\frac{\partial \hat{Q}}{\partial t} = - \sum_{r, s} e^{i(\omega_r + \omega_s)t} [\hat{V}^r [\hat{V}^s \hat{Q}]] \Delta(\omega_r + \omega_s), \quad (74)$$

where \hat{p} is the part of the matrix \hat{p} diagonal in the indices α :

$$\hat{V}^s = \int_0^\infty e^{-i \hat{p} t'} \hat{V}^s e^{-i \omega_s t'} e^{i \hat{p} t'} dt'$$

and

$$\begin{aligned} \hat{V}_{\alpha\alpha'}^s &= \int_0^\infty e^{-i(\omega_s + \omega_{\alpha\alpha'})t'} dt' \hat{V}_{\alpha\alpha'}^s = -i \hat{V}_{\alpha\alpha'}^s \zeta^*(\omega_s + \omega_{\alpha\alpha'}) \\ &\equiv i \hat{V}_{\alpha\alpha'}^s \left[\frac{P}{\omega_s + \omega_{\alpha\alpha'}} + i\pi \delta(\omega_s + \omega_{\alpha\alpha'}) \right], \end{aligned} \quad (75)$$

$\Delta(x)$ denoting the function

$$\Delta(x) = \begin{cases} 1 & \text{when } x \ll \omega^* = \frac{1}{\tau_c}, \\ 0 & \text{otherwise.} \end{cases}$$

Equation (74) can be rewritten in a somewhat different form, which is more convenient for applications. If we expand the commutators in (74), use relation (75) as well as the fact that $\omega_r + \omega_s \ll \omega^*$, we can obtain the kinetic equation (74) in the form*

$$\frac{\partial \hat{Q}}{\partial t} = -i [\hat{N}, \hat{Q}] + \hat{R}(\hat{Q}), \quad (76)$$

where

$$\hat{N}_{\alpha\alpha} = - \sum_{r, s, \alpha'} e^{i(\omega_r + \omega_s)t} \frac{\hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s}{\omega_s + \omega_{\alpha'\alpha}} \Delta(\omega_r + \omega_s), \quad (77)$$

$$\begin{aligned} \hat{R}_{\alpha\alpha}(\hat{Q}) &= \pi \sum_{r\alpha'} e^{i(\omega_r + \omega_s)t} \delta(\omega_s + \omega_{\alpha'\alpha}) \{ 2 \hat{V}_{\alpha\alpha'}^r \hat{Q}_{\alpha'\alpha} \hat{V}_{\alpha'\alpha}^s \\ &\quad - \hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s \hat{Q}_{\alpha\alpha} - \hat{Q}_{\alpha\alpha} \hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s \} \Delta(\omega_r + \omega_s). \end{aligned} \quad (78)$$

It is assumed here that we are dealing with the case described by formula (24), when $\delta E/\hbar \geq \omega^$ (δE characterizes the energy scale of the inhomogeneity of the density matrix).

We now change over to a second representation:

$$\hat{Q} \rightarrow \hat{S}^{-1} \hat{Q} \hat{S}, \quad \hat{V}^r = \hat{S}^{-1} \hat{V}^r \hat{S}. \quad (79)$$

It is easy to see that in this representation Eqs. (76)–(78) assume the form

$$\frac{\partial \hat{Q}}{\partial t} + i [\hat{E} + \hat{N}, \hat{Q}] = \hat{R}(\hat{Q}), \quad (76')$$

where

$$\begin{aligned} \hat{N}_{\alpha\alpha} &= \hat{S}^{-1} \hat{N}_{\alpha\alpha} \hat{S} = - \sum_{r, \alpha'} e^{i(\omega_r + \omega_s)t} \frac{\hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s}{\omega_s + \omega_{\alpha'\alpha}} \Delta(\omega_s + \omega_r), \\ \hat{R}_{\alpha\alpha} &= \pi \sum_{r, \alpha'} e^{i(\omega_r + \omega_s)t} \delta(\omega_s + \omega_{\alpha'\alpha}) \{ 2 \hat{V}_{\alpha\alpha'}^r \hat{Q}_{\alpha'\alpha} \hat{V}_{\alpha'\alpha}^s - \hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s \hat{Q}_{\alpha\alpha} \\ &\quad - \hat{Q}_{\alpha\alpha} \hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s \} \Delta(\omega_r + \omega_s). \end{aligned} \quad (78')$$

Let us consider the particular case where the Hamiltonian of the dynamic subsystem consists of a large constant part $\hbar \hat{E}_0$ and a small addition $\hbar \hat{W}(t)$:

$$\hat{E} = \hat{E}_0 + \hat{W}(t), \quad (80)$$

The smallness of \hat{W} signifies that the matrix elements W_{nm} are much smaller than $\delta_1 E$ (the difference between the terms of the dynamic subsystem) and are much smaller than ω^* :

$$W_{nm} \ll (\delta_1 E, \omega^*). \quad (81)$$

In this case we can put approximately

$$\hat{S}^{\pm 1} \approx e^{\pm i \hat{E}_0 t}, \quad \hat{V}_{n\alpha; m\alpha'}^r = V_{n\alpha; m\alpha'} \delta_{\omega_r; \omega_{nm}} e^{-i \omega_{nm} t}, \quad (82)$$

and Eqs. (76)–(78) assume the form

$$\frac{\partial \hat{Q}}{\partial t} + i [\hat{E}_0 + \hat{W} + \hat{N}, \hat{Q}] = \hat{R}(\hat{Q}), \quad (76'')$$

where

$$\tilde{N}_{m\alpha; n\alpha} = - \sum_{k\alpha'} \frac{V_{m\alpha; k\alpha'} V_{k\alpha'; n\alpha}}{E_k - E_n + F_{\alpha'} - F_\alpha} \Delta(\omega_{nm}), \quad (77'')$$

$$\begin{aligned} \tilde{R}_{m\alpha; n\alpha} &= \pi \sum_{k\alpha'} \{ 2 V_{m\alpha; k\alpha'} V_{k\alpha'; n\alpha} Q_{k\alpha'} \delta(E_k - E_n + F_{\alpha'} - F_\alpha) \\ &\quad \times \Delta(\omega_{kn} + \omega_{mk}) \\ &\quad - V_{m\alpha; k\alpha'} V_{k\alpha'; n\alpha} Q_{n\alpha} \delta(E_k - E_l + F_{\alpha'} - F_\alpha) \Delta(\omega_{ml}) \\ &\quad - V_{k\alpha; l\alpha'} V_{l\alpha'; n\alpha} Q_{m\alpha; k\alpha} \delta(E_l - E_n + F_{\alpha'} - F_\alpha) \Delta(\omega_{lk}) \}. \end{aligned} \quad (78'')$$

Let us consider now the question of the conditions under which we obtain from (76)–(78) the balance equation (14). For this purpose we put $\hat{W} = 0$ and take the diagonal part of (76)

$$\begin{aligned} \frac{\partial Q_{n\alpha; n\alpha}}{\partial t} + i \sum_k (\tilde{N}_{n\alpha; k\alpha} Q_{k\alpha; n\alpha} - Q_{n\alpha; k\alpha} \tilde{N}_{k\alpha; n\alpha}) \\ = \pi \sum_{kl} \{ 2 V_{n\alpha; k\alpha'} V_{l\alpha'; n\alpha} Q_{k\alpha'} \delta(E_l - E_n + F_{\alpha'} - F_\alpha) \Delta(\omega_{lk}) \\ - V_{n\alpha; k\alpha'} V_{k\alpha'; l\alpha} Q_{l\alpha; n\alpha} \delta(E_k - E_l + F_{\alpha'} - F_\alpha) \Delta(\omega_{nl}) \\ - V_{k\alpha; l\alpha'} V_{l\alpha'; n\alpha} Q_{n\alpha; k\alpha} \delta(E_l - E_n + F_{\alpha'} - F_\alpha) \Delta(\omega_{nk}) \}. \end{aligned}$$

As can be seen from this equation, in the general case, the part of the matrix $\hat{\rho}$ which is diagonal in all the indices is connected with the nondiagonal elements of $\hat{\rho}$. This means that in order to obtain the balance equations it is necessary to introduce additional conditions, namely, it is necessary first that there exist no term differences ω_{nm} different from zero and much smaller than ω^* and, second, that the levels of the dynamic subsystem be nondegenerate. Then, as can be readily seen, (76) assumes the form

$$\frac{\partial Q_{n\alpha; n\alpha}}{\partial t} = \sum_{k\alpha'} 2\pi |V_{n\alpha; k\alpha'}|^2 \delta(E_n - E_k + F_\alpha - F_{\alpha'}) \times [Q_{k\alpha'; k\alpha'} - Q_{n\alpha; n\alpha}], \quad (83)$$

which coincides with the balance equation, and

$$2\pi |V_{n\alpha; k\alpha'}|^2 \delta(E_n - E_k + F_\alpha - F_{\alpha'})$$

are the transition probabilities per unit time. The equations derived by Van Hove^[2] are obtained from (83) by removing the index n , that is, in the case when there is no dynamic subsystem. Then these equations describe the relaxation of the dissipative subsystem. We note that the term containing \hat{N} has dropped out in the transition to the balance equations. The point is that this term, as can be seen from its structure, yields the correction to the energy levels of the unperturbed system and does not lead by itself to relaxation.

The relaxation of the entire system (dissipative + dynamic) has in our approximation a Markov character (we are dealing with a case when the balance equations are valid). This cannot be said, generally speaking, about the relaxation of the dynamic subsystem itself. The density matrix σ_{nm} of only the dynamic part of the system does not obey a first-order equation in the general case, and accordingly σ_{nm} does not obey the balance equations.

In fact, since

$$\sigma_{mn} = \sum_{\alpha} Q_{m\alpha; n\alpha},$$

it follows from (76) that

$$\frac{\partial \sigma_{mn}}{\partial t} + i[\hat{E}, \hat{\sigma}]_{mn} + i \sum_{\alpha} (\tilde{N}_{m\alpha; k\alpha} Q_{k\alpha; n\alpha} - Q_{m\alpha; k\alpha} \tilde{N}_{k\alpha; n\alpha}) = \sum_{\alpha} \tilde{R}_{m\alpha; n\alpha}. \quad (84)$$

It is obvious that the sum in the left half and the right half of this equation do not reduce in general to functions of σ only. However, such a reduction is possible under the assumption that the dissipative system is much larger than the dynamic system and is all the time in a specified state, so that the influence of the dynamic system on it can be neglected. In other words, this assumption means that all the average quantities pertaining to the dissipative sub-

system do not depend on the time (or vary very slowly). Let us consider in this approximation, for example, the first sum in the left half of (84)

$$\sum_{\alpha} \tilde{N}_{m\alpha; k\alpha} Q_{k\alpha; n\alpha} = \tilde{N}_{m\bar{\alpha}; k\bar{\alpha}} \sum_{\alpha} Q_{k\alpha; n\alpha} = \tilde{N}_{m\bar{\alpha}; k\bar{\alpha}} \sigma_{kn}(t),$$

where $\tilde{N}_{m\bar{\alpha}; k\bar{\alpha}}$ is some average value of $\tilde{N}_{m\alpha; k\alpha}$. Our assumption is that this average should not depend on the time. We therefore calculate it for the instant of time $t = t_0$ when the interaction between the dynamic dissipated subsystems is turned on, assuming that at that instant of time the density matrix of the entire system can be represented by

$$Q_{m\alpha; n\alpha}(t_0) = \sigma_{mn}(t_0) P_{\alpha}(t_0).$$

Thus,

$$\begin{aligned} \tilde{N}_{m\bar{\alpha}; k\bar{\alpha}} &\equiv \frac{\sum_{\alpha} \tilde{N}_{m\alpha; k\alpha} Q_{k\alpha; n\alpha}}{\sum_{\alpha} Q_{k\alpha; n\alpha}} \approx \frac{\sum_{\alpha} \tilde{N}_{m\alpha; k\alpha} P_{\alpha}(t_0) \sigma_{kn}(t_0)}{\sigma_{kn}(t_0)} \\ &= \sum_{\alpha} \tilde{N}_{m\alpha; k\alpha} P_{\alpha}. \end{aligned}$$

We shall henceforth leave out the argument t_0 in the function P_{α} , since by assumption the variation of the state of the dissipative circuit can be neglected. In this assumption the kinetic equation defining the behavior of the dynamic system assumes the form

$$\frac{\partial \sigma_{mn}}{\partial t} + i[\hat{E} + \hat{\Gamma}, \sigma]_{mn} = \sum_{kl} (2\Gamma_{mkl} \sigma_{kl} - \Gamma_{klm} \sigma_{ln} - \Gamma_{lnk} \sigma_{mk}), \quad (85)$$

where

$$\hat{\Gamma} = - \sum_{r, s\alpha\alpha'} e^{i(\omega_r + \omega_s)t} P_{\alpha} \frac{\hat{V}_{\alpha\alpha'}^r \hat{V}_{\alpha'\alpha}^s}{\omega_s + \omega_{\alpha'}} \Delta(\omega_r + \omega_s), \quad (86)$$

$$\Gamma_{mk} = \sum_{\alpha} \tilde{N}_{m\alpha; k\alpha} P_{\alpha}$$

$$= - \sum_{l, r, s\alpha\alpha'} e^{i(\omega_r + \omega_s)t} P_{\alpha} \frac{\tilde{V}_{m\alpha; l\alpha'}^r \tilde{V}_{l\alpha'; k\alpha}^s}{\omega_s + \omega_{\alpha'}} \Delta(\omega_r + \omega_s),$$

$$\Gamma_{mkl} = \pi \sum_{\alpha\alpha'\alpha''} e^{i(\omega_r + \omega_s)t} \delta(\omega_s + \omega_{\alpha'}) \tilde{V}_{m\alpha; k\alpha'}^r P_{\alpha'} \tilde{V}_{l\alpha'; n\alpha''}^s \Delta(\omega_r + \omega_s). \quad (87)$$

In the particular case when we can use (82) (the external force is small), the coefficients Γ do not depend on the time and assume the form

$$\begin{aligned} \hat{\Gamma} &= - \sum_{r, s} \frac{\tilde{V}_{\alpha\alpha'}^r \tilde{V}_{\alpha'\alpha}^s P_{\alpha}}{\omega_s + \omega_{\alpha'}} \Delta(\omega_r + \omega_s), \\ \Gamma_{mk} &= - \sum_{lrs\alpha\alpha'} \frac{V_{m\alpha; l\alpha'}^r V_{l\alpha'; k\alpha}^s}{\omega_s + \omega_{\alpha'}} P_{\alpha} \Delta(\omega_r + \omega_s) \\ &= - \sum_{l\alpha\alpha'} P_{\alpha} \frac{V_{m\alpha; l\alpha'} V_{l\alpha'; k\alpha}}{E_l - E_k + F_{\alpha'} - F_{\alpha}} \Delta(\omega_{mk}), \quad (86') \end{aligned}$$

$$\begin{aligned}\Gamma_{mkl_n} &= \pi \sum_{\alpha\alpha'} \Delta(\omega_r + \omega_s) V_{m\alpha; k\alpha'}^r P_{\alpha'} V_{l\alpha'}^s; n\alpha \delta(\omega_s + \omega_{\alpha'}) \\ &= \pi \sum_{\alpha\alpha'} V_{m\alpha; k\alpha'} P_{\alpha'} V_{l\alpha'}; n\alpha \delta(E_l - E_n + F_{\alpha'} - F_{\alpha}) \Delta(\omega_{mk} + \omega_{ln}).\end{aligned}\quad (87')$$

If the dissipative subsystem is in the state of thermodynamic equilibrium characterized by a temperature T , then a connection exists between the different coefficients Γ . In order to derive this connection, it is necessary to change over from summation to integration over the energies:

$$\sum_{\alpha} \rightarrow \sum_{\alpha} \int dF_{\alpha} \eta_{\alpha}(F_{\alpha}),$$

where $\eta_{\alpha}(F_{\alpha})$ is the density of the number of states with specified quantum number α in the energy interval dF_{α} . It is further necessary to take into account the fact that if the dissipative system is in an equilibrium state, then

$$P_{\alpha} = P(F_{\alpha}) = \frac{e^{-\hbar F_{\alpha}/kT}}{\sum_{\alpha'} e^{-\hbar F_{\alpha'}/kT}}.$$

As a result we get

$$\begin{aligned}\Gamma_{lnmk} &= \pi \sum_{uu'rs} e^{i(\omega_r + \omega_s)t} \Delta(\omega_r + \omega_s) \int dF_{\alpha} \eta_{\alpha}(F_{\alpha}) \eta(F_{\alpha} + \omega_s) \\ &\quad \times \langle m, F_{\alpha} + \omega_s, u' | \hat{V}^r | k, F_{\alpha}, u \rangle P(F_{\alpha}) \\ &\quad \times \langle l, F_{\alpha}, u | \hat{V}^s | n, F_{\alpha} + \omega_s, u' \rangle e^{-\hbar\omega_s/kT} \\ &= \Gamma_{mkl_n} e^{-\hbar\omega_s/kT} \approx \Gamma_{mkl_n}^{\hbar\omega_s/kT}.\end{aligned}\quad (88)$$

If it is possible to employ formulas (87'), then (88) assumes the form *

$$\Gamma_{mkl_n} = \Gamma_{lnmk} e^{\hbar(E_l - E_n)/kT} \approx \Gamma_{lnmk} e^{-\hbar(E_m - E_k)/kT}. \quad (88')$$

It follows from the last formulas that in the absence of external forces Eq. (85) has a stationary solution

$$\sigma_{hl}^0 = \delta_{hl} \frac{e^{-\hbar E_k/kT}}{\sum_s e^{-\hbar E_s/kT}},$$

that is, the dynamic subsystem enters into equilibrium with the dissipative subsystem. In the absence of external forces, for nondegenerate levels of the dynamic system under the condition that Δ goes over into the Kronecker symbol (that is, that there exist no nonvanishing $\omega_{nk} \ll \omega^*$), we can obtain from (85) the balance equation

$$\dot{\sigma}_{mm} = \sum_k (\omega_{mk} \sigma_{kk} - \omega_{km} \sigma_{mm}), \quad (89)$$

where the probabilities per unit time are

$$\omega_{km} = 2\Gamma_{mkk_m},$$

Formulas (88) and (88') hold true if $\omega_r + \omega_s \ll kT/\hbar$. This condition follows from the condition $\omega_r + \omega_s \ll \omega^$ only if equality (24) is satisfied (where the role of δE is played by kT). If $kT < \delta_0 E$, then ω^* plays a role; on the other hand, if $\delta_0 E > kT$, then $kT/\hbar > \omega^*$.

and if the dissipative system is in an equilibrium state, then it follows from (88') that

$$\omega_{km} = \omega_{mk} e^{-\hbar(E_m - E_k)/kT}. \quad (90)$$

The corrections to the eigenvalues of the energy of the dynamic subsystem can be obtained from (86')

$$\Delta E_m = \Gamma_{mm} = - \sum_{\alpha, \alpha', k} \frac{|V_{m\alpha; k\alpha'}|^2 P_{\alpha}}{E_k - E_m + F_{\alpha'} - F_{\alpha}}. \quad (91)$$

It is sometimes convenient to use not the kinetic equation (85), but equations that follow from it for the mean values of the operators pertaining to the dynamic system. To obtain such equations we represent the operator \hat{V}^r in the form of a sum of products of operators \hat{v}_i^r and \hat{W}_i^r acting on the dynamic subsystem and on the dissipative systems, respectively:

$$\hat{V}^r = \sum_i \hat{W}_i^r \hat{v}_i^r. \quad (92)$$

In this case the coefficients (86) and (87) can be rewritten in the form

$$\left. \begin{aligned}\hat{\Gamma} &= \sum_{r, s, i, i'} \Phi_{ii'}^{rs} \hat{v}_i^r \hat{v}_{i'}^s, \\ \Gamma_{mkl_n} &= \sum_{r, s, i, i'} \Phi_{ii'}^{rs} \langle m | \hat{v}_i^r | k \rangle \langle l | \hat{v}_{i'}^s | n \rangle,\end{aligned}\right\} \quad (93)$$

where

$$\left. \begin{aligned}\Phi_{ii'}^{rs} &= - \sum_{\alpha\alpha'} e^{i(\omega_r + \omega_s)t} \frac{\langle \alpha | W_i^r | \alpha' \rangle \langle \alpha' | W_{i'}^s | \alpha \rangle}{\omega_s + \omega_{\alpha'}} P_{\alpha} \Delta(\omega_r + \omega_s), \\ \Phi_{ii'}^{rs} &= \pi \sum_{\alpha\alpha'} e^{i(\omega_r + \omega_s)t} \delta(\omega_s + \omega_{\alpha'}) \langle \alpha | W_i^r | \alpha' \rangle \langle \alpha' | W_{i'}^s | \alpha \rangle \\ &\quad \times P_{\alpha} \Delta(\omega_r + \omega_s).\end{aligned}\right\} \quad (94)$$

We can establish a connection between the coefficients Φ analogous to (88) (if the dissipative system is in a state of equilibrium):

$$\Phi_{ii'}^{rs} = \Phi_{i'i}^{sr} e^{\hbar\omega_s/kT}. \quad (95)$$

We are now in a position to find the equations for the mean value of some operator \hat{Q}

$$\langle \dot{Q} \rangle = \text{Sp} \hat{\sigma} \hat{Q}.$$

Simple transformations lead to the formulas

$$\frac{d\langle Q \rangle}{dt} = i \langle [\hat{E} + \hat{\Gamma}, \hat{Q}] \rangle + \sum_{r, s, i, i'} \Phi_{ii'}^{rs} \langle \hat{v}_i^r [\hat{Q}, \hat{v}_{i'}^s] + [\hat{v}_i^r, \hat{Q}] \hat{v}_{i'}^s \rangle. \quad (96)$$

We shall present below different applications of the formulas obtained here.

We now consider the connection between the results reported here and those in other papers. As was already noted, Van Hove^[2] derived Eq. (83) without discrete indices (see also^[53]). This is called the master equation, since it pertains to the behavior of the entire system. The general kinetic equation (74) and (76) is essentially a generalization of

the master equation to include the presence of external forces acting on the dynamic subsystem. Another departure from the usual master equation is that the density matrix is generally speaking non-diagonal in the indices of the dynamic subsystem. Equation (76) (in the presence of a weak external field and disregarding \tilde{N}) was derived in [52]. The same equation (without the external force) was derived in [54] by the Van Hove method. Equation (85) and the following equations were derived in the main in the papers of Bloch and Wangsness [55-57] for the case when the dissipative subsystem is in an equilibrium state (see also [58]).

8. RELAXATION DUE TO INTERACTION WITH THE RADIATION FIELD

We have already mentioned that the radiation field in free space has a continuous spectrum and can play the role of a dissipative system. The Hamiltonian operator of a complete system consisting of charged particles (which play the role of the dynamic subsystem) interacting with the radiation field can be written in the form (60)

$$\hat{\mathcal{H}} = \hbar \hat{E} + \hbar \hat{F} + \hbar \hat{V},$$

where \hat{E} is the Hamiltonian of the dynamic subsystem,

$$\hat{F} = \frac{1}{2\hbar} \sum (\hat{P}_\nu^2 + \omega_\nu^2 Q_\nu^2)$$

is the Hamiltonian of the radiation field, and

$$\hat{V} = \sum \hat{B}_\nu \hat{Q}_\nu, \quad \hat{B}_\nu = - \sum_{s=1}^n \frac{e_s}{\hbar m_s c} (\hat{\mathbf{P}}_s \mathbf{A}_\nu(s)) \quad (97)$$

is the Hamiltonian of the interaction with the radiation field*, while e_s , m_s , and $\hat{\mathbf{P}}_s$ are the charge, mass, and momentum of the s -th particle of the dynamic subsystem, $\hat{\mathbf{A}}_\nu(s)$ is the vector potential of the ν -th normal oscillation of the free space at the location of the s -th particle.

The complete vector potential is equal to

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \sum \mathbf{A}_\nu(\mathbf{r}) Q_\nu.$$

It is easy to see that the non-zero matrix elements of \hat{V} have the form

$$\langle m; n_1 n_2 \dots n_\nu, n_{\nu+1} \dots | V | k; n_1 n_2 \dots n_\nu \pm 1, n_{\nu+1} \dots \rangle = \sqrt{\frac{\hbar}{2\omega_\nu}} B_{\nu mk} \left\{ \sqrt{\frac{n_\nu+1}{n_\nu}} \right\}. \quad (98)$$

We now proceed to calculate the relaxation coefficients. For simplicity we use formulas (86') and (87'), which are valid for a sufficiently weak external field \hat{W} :

*We have assumed here, as is customary, that the omitted term in the interaction energy, which is proportional to the square of the charge, can be neglected.

$$\Gamma_{mkln} = \pi \sum_{\{n_\nu\} \{n'_\nu\}} V_{m\{n_\nu\}; k\{n'_\nu\}} P(\{n'_\nu\}) V_{l\{n'_\nu\}; n\{n_\nu\}} \times \delta(E_l - E_n + F_{\{n'_\nu\}} - F_{\{n_\nu\}}) \Delta(\omega_{mk} + \omega_{ln}),$$

where $\{n_\nu\}$ denotes the totality of the quantum numbers $n_1 n_2 \dots n_\nu \dots$. Using formula (98) and the fact that $P(\{n'_\nu\})$ is the distribution of the probabilities of $\{n'_\nu\}$, we obtain

$$\Gamma_{mkln} = \pi \sum_\nu B_{\nu mk} B_{\nu ln} \Delta(\omega_{mk} + \omega_{ln}) \times \frac{\hbar}{2\omega_\nu} [(\bar{n}_\nu + 1) \delta(E_m - E_k + \omega_\nu) + \bar{n}_\nu \delta(E_m - E_k - \omega_\nu)]. \quad (99)$$

Analogously we obtain

$$\Gamma_{mk} = - \sum_{l\nu} \Delta(\omega_{mk}) \frac{B_{\nu ml} B_{\nu lk}}{E_l - E_k + \omega_\nu} \frac{(\bar{n}_\nu + 1) \hbar}{2\omega_\nu} - \sum_{l\nu} \Delta(\omega_{mk}) \frac{B_{\nu ml} B_{\nu lk}}{E_l - E_k + \omega_\nu} \frac{\bar{n}_\nu \hbar}{2\omega_\nu}. \quad (100)$$

In these formulas \bar{n}_ν denotes the mean value of the number of photons in the state characterized by the index ν . In particular, if the radiation field is in equilibrium, then

$$\bar{n}_\nu = \frac{1}{e^{\hbar\omega_\nu/kT} - 1}.$$

Equations (85), (99), and (100) describe the relaxation of a dynamic system due to interaction with the radiation field. We now consider some particular cases of these equations. If the conditions of transition to the balance equation (89) are satisfied, then the probabilities per unit of time have the form

$$\omega_{mk} = \begin{cases} 2\pi \sum_\nu |B_{\nu mk}|^2 \frac{(\bar{n}_\nu + 1) \hbar}{2\omega_\nu} \delta(E_m - E_k + \omega_\nu), & E_k > E_m, \\ 2\pi \sum_\nu |B_{\nu mk}|^2 \frac{\bar{n}_\nu \hbar}{2\omega_\nu} \delta(E_m - E_k - \omega_\nu), & E_m > E_k. \end{cases} \quad (101)$$

It is interesting to see that these expressions coincide with those obtained when Einstein's coefficients are used for spontaneous and induced emission ($E_k > E_m$) and absorption ($E_k < E_m$).

In order to relate (101) with the Einstein coefficients, it is necessary to change over from summation over ν to integration over the frequencies and propagation directions. As a result we obtain

$$\omega_{km} = \begin{cases} \sum_{s=1}^2 \int d\Omega (a_{ms}^k + \rho_s(\omega_{km}, \Omega) b_{ms}^k), & E_k > E_m, \\ \sum_{s=1}^2 \int d\Omega \rho_s(\omega_{km}, \Omega) b_{ms}^m, & E_k < E_m, \end{cases} \quad (101')$$

where a_{ms}^k and $b_{ms}^k = b_{ks}^m$ are the Einstein coefficients for spontaneous emission, induced emission, and absorption,

$$\rho_s(\omega_\nu, \Omega) d\omega_\nu d\Omega = \frac{\omega_\nu^3}{2\pi\hbar c^3} \frac{d\omega_\nu d\Omega}{\hbar\omega_\nu}$$

is the radiation density in the frequency interval $d\omega_\nu$ and in the interval of solid angles $d\Omega$ with polarization s . In particular, for dipole radiation of one particle (generally speaking, bound) we obtain the usual expressions

$$a_n^m = \frac{\omega^3}{2\pi\hbar c^3} |d_{mn}|^2 \cos^2\theta_s, \quad b_{ns}^m = \frac{4\pi}{\hbar^2} |d_{mn}|^2 \cos^2\theta_s = b_{ms}^n,$$

where d_{mn} is the dipole moment matrix element and θ_s is the angle between the direction of the dipole moment and the direction of the polarization vector e_s .

We note that to find different averages pertaining to the dynamic subsystem it is necessary to know not only the density-matrix diagonal elements σ_{nn} entering into the balance equation, but also the nondiagonal elements σ_{nm} of the density matrix. The equations for these quantities are (85), (99), and (100).

It is seen from (85), (99), and (100) that in general the relaxation of the separate parts of the dynamic subsystem does not occur independently. The point is that there is always a coupling through the radiation field (although, if we disregard the interaction through the radiation field, the individual parts of the system can behave perfectly independently). Let us dwell on this question in somewhat greater detail.

Let the dynamic system represent an aggregate of non-interacting objects (for the sake of being definite—molecules). If the levels of the molecules are not equidistant, then in many problems connected with the radiation it becomes possible to take into account only two energy levels (which we shall henceforth regard as nondegenerate). It is therefore convenient to introduce an idealization of a molecule with two levels*. All the operators pertaining to the two-level molecule are represented by two-by-two matrices. If we further stipulate that they be Hermitian, these matrices can be represented in the form of a linear combination of spin operators \hat{r}_i and a unit operator

$$\hat{Q} = a\hat{I} + b\hat{r}_1 + c\hat{r}_2 + d\hat{r}_3,$$

where $a, b, c,$ and d are constant coefficients and the \hat{r}_i have the following form in the representation in which r_3 is diagonal:

$$\hat{r}_1 = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{r}_2 = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{r}_3 = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

It must be emphasized that the \hat{r}_i , generally speaking, do not coincide with the usual spin 1/2 which represents the angular momentum. In^[59] this spin was called energy spin to distinguish it from the

*It should be borne in mind that the possibility of introducing such an idealization is, generally speaking, connected with the quantum properties of the system. In fact, quasiclassical systems have quasi-equidistant spectra (see, for example, [27]).

ordinary spin. In particular, it can be shown that the energy of interaction between one molecule and the radiation field has in the dipole approximation the form

$$\hat{V}_j = -\hat{A}(j)(e_1\hat{r}_{1j} + e_2\hat{r}_{2j}) = \hat{r}_j^+ \hat{F}_j + \hat{r}_j^- \hat{F}_j^+,$$

with the constants

$$e^\pm = e_1 \pm ie_2 = \left\{ \begin{array}{l} 2i\omega_0 d_{21}/\hbar c, \\ -2i\omega_0 d_{12}/\hbar c, \end{array} \right\},$$

d_{12} is the molecule matrix element, dipole moment

$$\hat{r}_j^\pm = \hat{r}_{1j} \pm i\hat{r}_{2j}$$

and

$$F_j^\pm = -\frac{1}{2} \hat{A}(j) e^\pm.$$

It is easy to see that the energy of the j -th molecule can be expressed as

$$\hbar\hat{E}_j = \hbar\omega_0 \hat{r}_{3j}.$$

We shall henceforth assume that all the molecules have the same energy-level difference, equal to $\hbar\omega_0$. The Hamiltonian of the dynamic subsystem consisting of molecules that do not interact with one another can be written in the form

$$\hbar\hat{E} = \hbar\omega_0 \sum_j \hat{r}_{3j} \equiv \hbar\omega_0 \hat{R}_3.$$

The energy of interaction between the system of two-level molecules and the radiation field has the form

$$\hat{V} = \sum_j \hat{V}_j = \sum_j \hat{r}_j^+ \hat{F}_j + \hat{r}_j^- \hat{F}_j^+.$$

We proceed now to derive equations for the mean values $\langle r_{ij}^\pm \rangle$ and $\langle r_{3j} \rangle$. For this purpose we use formulas (96), where the role of the operators \hat{v}_j^{\pm} is played by the operators \hat{r}_j^\pm . As a result we obtain for the derivative of the mean value of some operator \hat{Q}

$$\begin{aligned} \frac{d\langle Q \rangle}{dt} &= i\langle [E + \hat{V}, Q] \rangle + \sum_{i,i'} \Phi_{ii'}^{+-} \langle \hat{r}_i^- [Q, r_i^+] + [\hat{r}_i^-, \hat{Q}] \hat{r}_i^+ \rangle \\ &+ \sum_{ii'} \Phi_{ii'}^{-+} \langle \hat{r}_i^+ [\hat{Q}, \hat{r}_i^-] + [\hat{r}_i^+, \hat{Q}] \hat{r}_i^- \rangle, \end{aligned} \quad (102)$$

where

$$\left. \begin{aligned} \Phi_{ii'}^{+-} &= \frac{\pi}{8} \sum_\nu (A_\nu(i) e^-) (A_\nu(i') e^+) \frac{\bar{n}_\nu \hbar}{\omega_0} \delta(\omega_0 - \omega_\nu), \\ \Phi_{ii'}^{-+} &= \frac{\pi}{8} \sum_\nu (A_\nu(i') e^+) (A_\nu(i) e^-) \frac{(\bar{n}_\nu + 1) \hbar}{\omega_0} \delta(\omega_0 - \omega_\nu), \\ \hat{\Gamma} &= \sum_{i,i'} \Phi_{ii'}^{+-} \hat{r}_i^+ \hat{r}_i^- + \Phi_{ii'}^{-+} \hat{r}_i^- \hat{r}_i^+ * \end{aligned} \right\} \quad (103)$$

If the radiation field is in the state of thermodynamic equilibrium, then

$$\Phi_{ii'}^{+-} = e^{-\hbar\omega_0/kT} \Phi_{ii'}^{-+}.$$

The coefficients Φ characterize the relaxation of

*We do not write out the coefficients φ here. The calculation is analogous to the calculation of the coefficients Φ .

the dynamic subsystem. Let us calculate these coefficients. We assume that the molecules have linearly polarized dipole moments perpendicular to the line joining their centers of gravity. The average occupation numbers \bar{n}_ν are assumed to depend only on the frequency $\omega_\nu = \omega_0$ (as is the case, in particular, for thermodynamic equilibrium).

Then

$$\begin{aligned} \Phi_{ii'}^+ &= \bar{n}_\nu \frac{\gamma_{ii'}}{2}, & \Phi_{ii'}^- &= (\bar{n}_\nu + 1) \frac{\gamma_{ii'}}{2}, \\ \gamma_{ii'} &= \gamma_{i'i} = \frac{\pi}{2} \frac{\omega_0}{\hbar^2 c^2} \sum_{\nu} (\mathbf{A}_\nu(i') \mathbf{d}_{12}) (\mathbf{A}_\nu(i) \mathbf{d}_{21}) \delta(\omega_0 - \omega_\nu) \\ &= \frac{\omega_0^3 d^2}{\pi c^3 \hbar} \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \sin^3 \theta \cos(ka \sin \theta \cos \varphi). \end{aligned} \quad (104)$$

We ultimately obtain

$$\gamma_{ii'} = \gamma_0 \frac{3}{2} \left\{ \frac{\sin ka}{ka} + \frac{\cos ka}{(ka)^2} - \frac{\sin ka}{(ka)^3} \right\}. \quad (105)$$

Here $k = \omega_0/c$; a is the distance between the i -th and i' -th molecules, d is the value of the molecule dipole moment matrix element ($|\mathbf{d}_{12}|$), and γ_0 is the natural line width of the isolated molecule^[5†]

$$\gamma_0 = \frac{4}{3} \omega_0^3 \frac{d^2}{c^3 \hbar}.$$

From (102) and (104) we get*

$$\begin{aligned} \frac{d\langle r_{3i} \rangle}{dt} &= -2\bar{n}_\nu \gamma_0 \langle r_{3i} \rangle - \sum_{i'} \frac{1}{2} \gamma_{ii'} \langle \hat{r}_i^+ \hat{r}_{i'}^- + \hat{r}_i^- \hat{r}_{i'}^+ \rangle \\ &= -\gamma_0 (2\bar{n}_\nu + 1) (\langle r_{3i} \rangle + \frac{1}{2} \frac{1}{2\bar{n}_\nu + 1}) \\ &\quad - \sum_{i'(\neq i)} \frac{\gamma_{ii'}}{2} \langle \hat{r}_i^+ \hat{r}_{i'}^- + \hat{r}_i^- \hat{r}_{i'}^+ \rangle, \end{aligned} \quad (106)$$

$$\frac{d\langle r_i^+ \rangle}{dt} = i\omega_0 \langle r_i^+ \rangle - \left(\bar{n}_\nu + \frac{1}{2} \right) \gamma_0 \langle r_i^+ \rangle + \sum_{i'(\neq i)} \gamma_{ii'} \langle \hat{r}_i^+ \hat{r}_{i'}^- \rangle, \quad (107)$$

$$\frac{d\langle r_i^- \rangle}{dt} = -i\omega_0 \langle r_i^- \rangle - \left(\bar{n}_\nu + \frac{1}{2} \right) \gamma_0 \langle r_i^- \rangle + \sum_{i'(\neq i)} \gamma_{ii'} \langle \hat{r}_i^- \hat{r}_{i'}^+ \rangle. \quad (108)$$

(We have used here the commutation relations for the energy spin, which coincide with the commutators for the ordinary spin, $\hat{\mathbf{r}} \times \hat{\mathbf{r}} = i\mathbf{r}$; in addition, we used relations that are valid for spin 1/2, namely

$$\hat{r}_2 \hat{r}_3 = \frac{i}{2} \hat{r}_1, \quad \hat{r}_3 \hat{r}_1 = \frac{i}{2} \hat{r}_2, \quad \hat{r}_1 \hat{r}_2 + \hat{r}_2 \hat{r}_1 = 0, \quad \hat{r}_i^2 = \frac{1}{4}$$

etc.). It is seen from (106)–(108) that the relaxation of the i -th molecule (which is described by the operators \hat{r}_i^\pm and \hat{r}_{3i}) is connected with the relaxations of the other molecules. This connection is the result of the fact that each molecule is in the radiation field of the remaining molecules.

Let us consider some consequences of equations (106)–(108). Assume that at some instant of time the states of the molecules are statistically independent and the mean values are $\langle \hat{r}_i^\pm \rangle = 0^*$. The intensity of the spontaneous emission of the i -th molecule at that instant is equal to

$$-\frac{d\langle \hat{r}_{3i} \rangle}{dt} \hbar \omega_0 = \gamma_0 \hbar \omega_0 \left(\frac{1}{2} + \langle \hat{r}_3 \rangle \right) = n_+ \gamma \hbar \omega_0 = n_+ I_0$$

and does not depend on the spontaneous radiation of the remaining molecules. The total intensity of spontaneous radiation of the entire system is equal in this case to the sum of the radiation intensities of the isolated molecules. As time goes on, the correlations $\langle \hat{r}_i^+ \hat{r}_{i'}^- + \hat{r}_i^- \hat{r}_{i'}^+ \rangle$ ($i' \neq i$) differ from zero and the intensity of the spontaneous radiation is no longer equal to the sum of the intensities of the isolated molecules. The width and the shape of the spontaneous-radiation lines always differ from the width and shape of the line of the individual isolated molecule. The point is that the width and shape of the radiation line are characteristics of the radiation process not at an individual instant of time, but over a sufficiently long time. Therefore, even if the molecules are statistically independent at the initial instant, in the course of time a connection arises between them (characterized by the value of the correlation $\langle \hat{r}_i^+ \hat{r}_{i'}^- + \hat{r}_i^- \hat{r}_{i'}^+ \rangle$, $\langle \hat{r}_{3i} \hat{r}_{i'} \rangle$, $\langle \hat{r}_i^+ \hat{r}_{3i} \rangle$ for $i' \neq i$).

Let us illustrate these considerations using as an example the spontaneous emission of a system of molecules, the dimensions of which are much smaller than the wavelength^[60–64, 59]. In this case ($ka \rightarrow 0$) $\gamma_{ii'} = \gamma_0$ for any pair of molecules i and i' . The total intensity of spontaneous emission is equal to†

$$\begin{aligned} -\hbar \omega_0 \sum_i \frac{d\langle \hat{r}_{3i} \rangle}{dt} &= \hbar \omega_0 \gamma_0 \sum_{i, i'} \frac{1}{2} \langle \hat{r}_i^+ \hat{r}_{i'}^- + \hat{r}_i^- \hat{r}_{i'}^+ \rangle \\ &= \hbar \omega_0 \gamma_0 \langle \hat{R}^+ \hat{R}^- \rangle = I_0 \langle \hat{R}_1^2 + \hat{R}_2^2 + \hat{R}_3^2 \rangle = I_0 \langle \hat{R}^2 - \hat{R}_3^2 + \hat{R}_3^2 \rangle \end{aligned} \quad (109)$$

and, generally speaking, it is not equal to the sum of intensities of the individual molecules. The sum of

*We recall the meaning of the components of the energy spin $\hat{\mathbf{r}}$ (see, for example, [59]). We express the molecule dipole moment as a function of the time through $\hat{\mathbf{r}}^+$ and $\hat{\mathbf{r}}^-$:

$$\frac{1}{c} \frac{d\mathbf{d}}{dt} = e^+ \hat{\mathbf{r}}^- + e^- \hat{\mathbf{r}}^+.$$

The mean value of the component r_3 is connected with the difference of the populations n_+ and n_- of the upper and lower levels of the molecule:

$$\langle \hat{r}_3 \rangle = \frac{1}{2} (n_+ - n_-), \quad n_+ + n_- = 1, \quad \frac{1}{2} + \langle \hat{r}_3 \rangle = n_+.$$

The mean value is $\langle \hat{r}_i^+ \rangle = 0$, in particular, for the state in which the molecule energy has a definite value (or the density matrix of the molecule is diagonal in the energy representation).

†Here $\hat{\mathbf{R}} = \sum_i \hat{\mathbf{r}}_i$.

*In order not to complicate the discussion, we disregard the shift of the frequency ω_0 due to the presence of the operator $\hat{\Gamma}$ in the right half of (102).

the correlations can be expressed in terms of R in the form

$$\sum_{i \neq i'} \frac{1}{2} \langle \hat{r}_i^{\pm} \hat{r}_i^{\pm} + \hat{r}_{i'}^{\pm} \hat{r}_{i'}^{\pm} \rangle = \langle \hat{R}_1^2 + \hat{R}_2^2 \rangle - \frac{n}{2} = \langle \hat{R}^2 - \hat{R}_3^2 \rangle - \frac{n}{2}, \tag{110}$$

where n is the total number of molecules. The process of spontaneous emission proceeds in this case with conservation of \hat{R}^2 and with decrease of R_3 (that is, the energy of the dynamic system decreases). Consequently, if the correlation (110) is equal to zero at the initial instant (in which case the radiation intensity is equal to $nn_+ \hbar \omega_0 \gamma_0$), then it will subsequently increase, as can be seen from (110). This causes the radiation line width of the entire system to be of the order of $n \gamma_0$ (in place of γ_0 for the isolated molecule), and the line shape differs from Lorentzian^[60,62]. Along with the broadening of the line, the center of the radiation line is displaced (in analogy to the Lamb shift). This shift is also determined for the entire system of molecules^[64]. The system (106)–(108) is nonlinear. It is incomplete, since the mean values of \hat{r}_i are expressed in it in terms of the correlations. The equations for the latter can be obtained from (102). We can thus obtain a system of equations that are coupled with one another. However, for states that are weakly excited relative to the equilibrium position, the system (107)–(108) can be linearized. Let us consider the case $n_{\nu} = 0$ (spontaneous emission). In the equilibrium state $r_{3i} = -1/2$; substituting this value into the right hand half (107)–(108), we obtain

$$\frac{d}{dt} \langle r_i^{\pm} \rangle = \pm i \omega_0 \langle r_i^{\pm} \rangle - \sum_{i'} \frac{1}{2} \gamma_{ii'} \langle r_{i'}^{\pm} \rangle. \tag{111}$$

We note that we obtain precisely the same system of equations for the mean values of the annihilation and creation operators $\langle a_i \rangle$ and $\langle a_i^{\dagger} \rangle$ of a system of oscillators. At the same time, the equations for the mean values of the coordinates of the harmonic oscillators coincide (the Ehrenfest theorem) with the classical equations. Thus, (111) is essentially a classical system of equations. Let us consider the case of two molecules

$$\left. \begin{aligned} \langle \dot{r}_1^{\pm} \rangle &= \pm i \omega_0 \langle r_1^{\pm} \rangle - \frac{1}{2} \gamma_0 \langle r_1^{\pm} \rangle - \frac{1}{2} \gamma_{12} \langle r_2^{\pm} \rangle, \\ \langle \dot{r}_2^{\pm} \rangle &= \pm i \omega_0 \langle r_2^{\pm} \rangle - \frac{1}{2} \gamma_0 \langle r_2^{\pm} \rangle - \frac{1}{2} \gamma_{12} \langle r_1^{\pm} \rangle. \end{aligned} \right\} \tag{111'}$$

The solution of this system has the form

$$\langle r_{1,2}^{\pm} \rangle = A_{1,2}^{\pm} e^{\pm i \omega_0 t - \frac{1}{2} \gamma_1 t} + B_{1,2}^{\pm} e^{\pm i \omega_0 t - \frac{1}{2} \gamma_2 t}, \tag{112}$$

where

$$\gamma_{1,2} = \gamma_0 \pm \gamma_{12} = \gamma_0 \left\{ 1 \pm \frac{3}{2} \frac{\sin ka}{ka} \pm \frac{3}{2} \frac{\cos ka}{(ka)^2} \mp \frac{3}{2} \frac{\sin ka}{(ka)^3} \right\}.$$

The problem of the radiation from an excited classical oscillator in the presence of similar unexcited oscillators was solved in^[65,66] under the assumption

*More accurately, of the order of $R \gamma_0$ (where $R = \sqrt{\langle \hat{R}^2 \rangle}$).

that $ka \gg 1$. * Formulas (112) go over in this case into the corresponding formulas of^[65] (for the case of two oscillators, the variation of the radiation frequencies was also taken into account^[65]). It is seen from (112) that the relaxation process is not exponential (sum of exponentials), resulting in a non-Lorentzian line shape.

To conclude this section we note that the problem of relaxation due to interaction with the radiation field becomes particularly significant (in the optical range) in connection with the invention of lasers. In this case both the spontaneous emission ($\bar{n}_{\nu} = 0$) and the induced emission ($\bar{n}_{\nu} \neq 0$) are of interest. The induced emission is due here to two causes. First, when $T \neq 0$ the average numbers of the photons $\bar{n}_{\nu}(T)$ differ from zero, and second, $\bar{n}_{\nu} \neq 0$ owing to the pumping field, which has a continuous spectrum, like thermal radiation. The results of the present section enable us to take account of relaxation due to interaction with radiation in systems of the laser type.

9. RELAXATION OF FIELD IN REAL RESONATORS

As a result of interaction between the electromagnetic field and the electrons of the resonator walls, the field relaxes to an equilibrium state. The atoms and electrons of the resonator walls play the role of the dissipative subsystem, while the field in the resonator now plays the role of the dynamic subsystem.

In a resonator of finite dimensions, the field has a discrete spectrum (unlike the field in free space). The questions of quantum theory of attenuation of a field in a resonator were considered in many papers^[50,67,68]. We apply here the results of quantum theory of relaxation (Sec. 7) to an investigation of the attenuation of the field in a resonator.

The Hamiltonian of the system comprising the resonator field and the resonator-wall electrons can be written in the form

$$\begin{aligned} \mathcal{H} = & \frac{1}{2} \sum_{\nu} (\hat{P}_{\nu}^2 + \omega_{\nu}^2 \hat{Q}_{\nu}^2) + \sum_k \frac{\hat{P}_k^2}{2m_k} + \frac{1}{2} \sum_{i \neq k} \frac{e_i e_k}{r_{ik}} \\ & - \sum_{\nu} \hat{Q}_{\nu} \sum_k \frac{e_k}{m_k c} (\mathbf{P}_k \mathbf{A}(k)). \end{aligned}$$

Here the first sum represents the energy of the radiation field, the second and third sums represent the nonrelativistic energy of the particles comprising the resonator, and the last sum is the energy of interaction between the field and the particles of the

*In these papers, the system of oscillators is the model of a system of nuclei that emit γ quanta under conditions when the Mössbauer effect takes place and the interaction via the radiation field can be observed in principle, in spite of the smallness of this interaction.

resonator walls. Introducing the annihilation and creation operators \hat{a}_ν and \hat{a}_ν^+ , we can rewrite the interaction Hamiltonian in the form

$$\hat{V} = - \sum_{\nu} (\hat{a}_\nu + \hat{a}_\nu^+) \hat{F}_\nu, \quad \hat{F}_\nu = \sqrt{\frac{\hbar}{2\omega_\nu}} \sum_k \frac{e\hbar}{\hbar m_k c} (\mathbf{P}_k \mathbf{A}(k)). \quad (113)$$

We can now use formulas (93)–(96), where the role of \hat{v}_r is taken by $\hat{a}_\nu(\omega_r = -\omega_\nu)$ and $\hat{a}_\nu^+(\omega_r = \omega_\nu)$, since in the interaction representation we have $a_\nu \sim \exp[i\omega_\nu t]$ and $a_\nu^+ \sim \exp[-i\omega_\nu t]$. From (96) we obtain for the derivative of the mean value of some operator \hat{Q}

$$\begin{aligned} \frac{d}{dt} \langle \hat{Q} \rangle &= i \langle [\hat{E} + \hat{\Gamma}, \hat{Q}] \rangle + \sum_{\nu\nu'} \Phi_{\nu\nu'}^+ \langle \hat{a}_{\nu'} [\hat{Q}, \hat{a}_\nu^+] + [\hat{a}_{\nu'}, \hat{Q}] \hat{a}_\nu \rangle \\ &+ \sum_{\nu\nu'} \Phi_{\nu\nu'}^- \langle \hat{a}_\nu^+ [\hat{Q}, \hat{a}_\nu] + [\hat{a}_\nu^+, \hat{Q}] \hat{a}_\nu \rangle, \end{aligned} \quad (114)$$

where

$$\Phi_{\nu\nu'}^\pm = \pi \sum_{\alpha\alpha'} \delta(\mp\omega_\nu + \omega_{\alpha'\alpha}) \langle \alpha | F_{\nu'} | \alpha' \rangle \langle \alpha' | F_\nu | \alpha \rangle P_{\alpha'\alpha} \Delta(\omega_\nu - \omega_{\nu'}), \quad (115)$$

and if the resonator walls are in a state of thermodynamic equilibrium, then, according to (95)

$$\Phi_{\nu\nu'}^+ = \Phi_{\nu\nu'}^- e^{-\hbar\omega_\nu/kT}. \quad (116)$$

From expressions (114) we can, in particular, obtain equations for the quantities $\langle a_\nu \rangle$ and $\langle a_\nu^+ \rangle$ themselves* (in the absence of external forces)

$$\left. \begin{aligned} \frac{d}{dt} \langle a_\nu \rangle &= -i\omega_\nu \langle a_\nu \rangle - \sum_{\nu'} \gamma_{\nu\nu'} \langle a_{\nu'} \rangle, \\ \frac{d}{dt} \langle a_\nu^+ \rangle &= i\omega_\nu \langle a_\nu^+ \rangle - \sum_{\nu'} \gamma_{\nu\nu'} \langle a_{\nu'}^+ \rangle, \end{aligned} \right\} \quad (117)$$

where

$$\gamma_{\nu\nu'} = \Phi_{\nu\nu'}^- - \Phi_{\nu\nu'}^+ = \Phi_{\nu\nu'}^- (1 - e^{-\hbar\omega_\nu/kT}). \quad (118)$$

It is assumed in (117) that the frequencies ω_ν are sufficiently large and therefore the frequency shift connected with the operator $\hat{\Gamma}$ is disregarded. It must be borne in mind, however, that such a shift does take place, generally speaking. Thus an account of the interaction with the dissipative system leads not only to relaxation, but also to a shift of the natural frequencies of the system. It is seen from (117) that an account of dissipation leads to coupling, due to the presence of attenuation, between field oscillators that are not coupled with one another in the absence of attenuation. However, this coupling occurs only at sufficiently high frequencies. This is

*We recall that

$$\hat{Q}_\nu = \sqrt{\hbar/2\omega_\nu} (\hat{a}_\nu + \hat{a}_\nu^+), \quad \hat{P}_\nu = \hat{Q}_\nu = i \sqrt{\hbar\omega_\nu/2} (\hat{a}_\nu^+ - \hat{a}_\nu);$$

the energy of the ν -th natural oscillation is $\hat{H}_\nu = \frac{1}{2} \hbar\omega_\nu (\hat{a}_\nu^+ \hat{a}_\nu + \hat{a}_\nu \hat{a}_\nu^+)$ and the permutations differing from zero are $[\hat{a}_\nu, \hat{a}_\nu^+] = 1$.

seen from (116). Here the $\Phi_{\nu\nu'}^\pm$ differ essentially from zero if

$$\omega_\nu - \omega_{\nu'} \ll \frac{1}{\tau_c} = \omega^*, \quad (119)$$

where τ_c is the correlation time of the system of particles comprising the resonator walls. The inequality (119) holds in particular, for degenerate frequencies of the resonator. In resonator theory the coefficient $\gamma_{\nu\nu'}$ is usually denoted by $(1/2)\omega_\nu/Q$, where Q is the figure of merit of the resonator for the specified mode. As can be seen from the foregoing analysis, the attenuation in a resonator is determined, generally speaking, not only by its Q but also by the coefficients $\gamma_{\nu\nu'} (\nu \neq \nu')$.* We have encountered an essentially analogous situation in the preceding section, where it is shown that the attenuation of a system of molecules proceeds in a mutually-dependent manner and is in general not proportional to the number of particles.

Using (114), we can determine the energy damping of the ν -th oscillator

$$\langle H_\nu \rangle = \hbar\omega_\nu \left(\langle n_\nu \rangle + \frac{1}{2} \right),$$

where

$$\hat{n}_\nu = \hat{a}_\nu^+ \hat{a}_\nu.$$

From (114) we get

$$\begin{aligned} \frac{d}{dt} \langle \hat{a}_\nu^+ \hat{a}_\nu \rangle &= - \sum_{\nu'} \gamma_{\nu\nu'} \left(\langle \hat{a}_\nu^+ \hat{a}_{\nu'} \rangle - \frac{\delta_{\nu\nu'}}{e^{\hbar\omega_\nu/kT} - 1} \right) \\ &- \sum_{\nu'} \gamma_{\nu\nu'} \left(\langle \hat{a}_\nu^+ \hat{a}_\nu \rangle - \frac{\delta_{\nu\nu'}}{e^{\hbar\omega_\nu/kT} - 1} \right). \end{aligned}$$

As can be seen from this expression, we do not obtain, generally speaking, a closed system of equations for the occupation numbers (this corresponds to the fact that in the presence of degeneracy the balance equation does not hold true). In the same case, when

$$\gamma_{\nu\nu'} = \gamma_{\nu\nu} \delta_{\nu\nu'},$$

we obtain

$$\frac{d \langle n_\nu \rangle}{dt} = -2\gamma_{\nu\nu} (\langle n_\nu \rangle - n_\nu^0),$$

where

$$n_\nu^0 = \frac{1}{e^{\hbar\omega_\nu/kT} - 1}$$

is the equilibrium value of $\langle \hat{n}_\nu \rangle$, corresponding to the temperature of the dissipative system. Thus, the energy of the natural mode is damped in accordance with

$$\begin{aligned} \langle H_\nu \rangle &= \hbar\omega_\nu \left(\langle n_\nu \rangle + \frac{1}{2} \right) = \hbar\omega_\nu \left(n_\nu^0 + \frac{1}{2} \right) \\ &+ \hbar\omega_\nu (\langle n_\nu(0) \rangle - n_\nu^0) e^{-2\gamma_{\nu\nu} t}, \end{aligned}$$

*The latter are connected with the mutual impedance of the resonator (see, for example [69]).

where $\langle \hat{n}_\nu(0) \rangle$ is the mean value of $\langle \hat{n}_\nu \rangle$ at the instant $t = 0$.

To conclude this section we note that the foregoing examination of the attenuation of a system of oscillators is sufficiently general and is applicable not only to fields in resonators, but to any system of oscillators whose energy of interaction with the dissipative subsystem has the form (113).

10. SPIN-LATTICE RELAXATION. BLOCH'S EQUATIONS

The results of the general theory, developed in Sec. 7, can be used to study the relaxation of the spins of nuclei interacting with a crystal lattice (or, generally speaking, with molecules of matter). Such an analysis was made in^[55], in which the previously-derived Bloch's phenomenological equations^[76] were proved.

The lattice (or the molecular environment) is a dynamic subsystem, while the nuclear spins are a dynamic subsystem. This is called spin-lattice relaxation to distinguish it from spin-spin relaxation, in which energy is exchanged between the spins (and not between the spins and the lattice). We do not repeat here the entire analysis of^[55], but derive Bloch's equations for the case of a spin-1/2 system interacting with the lattice. The character of the assumptions made in^[55] will be made clear by this derivation.

The Hamiltonian of the system of nuclei interacting with the lattice has the form

$$\hat{\mathcal{H}} = -\gamma \hbar \mathbf{H} \sum_i \hat{\mathbf{I}}_i + \hbar \hat{F} - \gamma \hbar \sum_i (h_z(i) \hat{I}_{zi} + h^-(i) \hat{I}_i^- + h^+(i) \hat{I}_i^+), \quad (120)$$

where the external magnetic field is

$$\mathbf{H} = \mathbf{k}H_0 + \mathbf{H}_1(t) \quad (H_1(t) \ll H_0),$$

$\hat{\mathbf{I}}_i$ is the spin operator of the i -th nucleus, $\hat{I}_i^\pm = I_{ix} \pm I_{iy}$, and $\hbar \hat{F}$ is the lattice energy; the last term in (120) represents the energy of interaction between the nuclei and the lattice, $\mathbf{h}(i)$ is the magnetic field of the lattice at the location of the i -th nucleus ($h^\pm = h_x \pm ih_y$), and γ is the gyromagnetic ratio. We note that for spin 1/2 (140) is the most general expression for the interaction energy. As we have already noted in Sec. 8, any linear Hermitian operator can be expanded in a series of spin-1/2 operators; the interaction energy (120) represents precisely this type of expansion [where $\mathbf{h}(i)$ is some effective magnetic field]. The operators \hat{I}_{zi} and \hat{I}_i^\pm can be identified with the operators \hat{v}_i^r introduced in Sec. 7 [see (92)], the operator \hat{I}_{zi} corresponds to the frequency $\omega_r = 0$, while the operators \hat{I}_i^\pm corresponds to frequencies $\pm \omega_0 = \pm \gamma H_0$. From formulas (93)–(96) we obtain the equations of motion for the mean value of the spin operator $\langle \hat{Q} \rangle^*$

*For simplicity we do not consider the level shifts connected with Γ in (96).

$$\begin{aligned} \frac{d\langle Q \rangle}{dt} &= -i\gamma \sum_i \langle (\mathbf{H}\mathbf{I}_i, \hat{Q}) \rangle \\ &+ \sum_{r, s, i, i'} \Phi_{ii'}^{rs} (\hat{I}_{ii'}^s [\hat{Q}, \hat{I}_i^r] + [\hat{I}_i^s, \hat{Q}] \hat{I}_i^r); \end{aligned} \quad (121)$$

r and f assume here the values $+$, $-$, and 0 ($\hat{I}_z \equiv \hat{I}^0$),

$$\begin{aligned} \Phi_{ii'}^+ &= \pi\gamma^2 \sum_{\alpha\alpha'} \delta(\omega_0 + \omega_{\alpha'\alpha}) \langle \alpha | h^-(i) | \alpha' \rangle \langle \alpha' | h^+(i') | \alpha \rangle P_{\alpha'} \\ &= \Phi_{i'i}^+ e^{\hbar\omega_0/kT}, \end{aligned} \quad (122)$$

$$\Phi_{ii'}^0 = \pi\gamma^2 \sum_{\alpha\alpha'} \delta(\omega_{\alpha'\alpha}) \langle \alpha | h_z(i) | \alpha' \rangle \langle \alpha' | h_z(i') | \alpha \rangle P_{\alpha'}, \quad (123)$$

$$\begin{aligned} \Phi_{ii'}^{\pm} &= \pi\gamma^2 \sum_{\alpha\alpha'} \delta(\pm\omega_0 + \omega_{\alpha'\alpha}) \langle \alpha | h^\pm(i) | \alpha' \rangle \\ &\times \langle \alpha' | h^\pm(i') | \alpha \rangle P_{\alpha'} \Delta(2\omega_0), \end{aligned} \quad (124)$$

$$\begin{aligned} \Phi_{ii'}^{0\pm} &= \pi\gamma^2 \sum_{\alpha\alpha'} \delta(\pm\omega_0 + \omega_{\alpha'\alpha}) \langle \alpha | h_z(i) | \alpha' \rangle \langle \alpha' | h^\pm(i') | \alpha \rangle P_{\alpha'} \Delta(\omega_0) \\ &= \Phi_{i'i}^{0\pm} e^{\pm \frac{\hbar\omega_0}{kT}}. \end{aligned} \quad (125)$$

If we substitute in (121) the operators \hat{I}_i^r in place of \hat{Q} , then it is easy to see that the resultant equations relate the spin of the i -th nucleus with the spin of the other nuclei (with index i'). Thus, the relaxation of the individual spins does not occur, generally speaking, in an independent fashion, and a certain coherence takes place. As can be seen from (122)–(125), this coherence is connected with the correlation between the effective field of the lattice at different points i and i' . If we neglect these correlations, as can be done, obviously, for a sufficiently rarefied gas, we obtain a closed system of equations for the spin of the i -th nucleus. If we furthermore assume that the inequality

$$\omega_0 \ll \omega^* \quad (126)$$

is satisfied, then the coefficients of (124) and (125) can be neglected. In this approximation we can readily obtain Bloch's equations

$$\frac{d}{dt} \langle \mathbf{I} \rangle = \gamma \langle \mathbf{I} \times \mathbf{H} \rangle - i \frac{I_x}{T_2} - j \frac{I_y}{T_2} - k \frac{I_z - I_0}{T_1}, \quad (127)$$

where

$$\left. \begin{aligned} T_1^{-1} &= 2(\Phi_{ii}^- + \Phi_{ii}^+) = \Phi_{ii}^- (1 + e^{\hbar\omega_0/kT}), \\ T_2^{-1} &= \frac{1}{2} T_1^{-1} + \Phi_{ii}^0; \quad I_0 = \frac{1}{2} \tanh \frac{\hbar\omega_0}{2kT}. \end{aligned} \right\} \quad (128)$$

Bloch's equations (127), as can be seen from their derivation are valid for not very strong external alternating fields

$$H_1(t) \ll H_0 \text{ and } \gamma_1 H_1(t) \ll \omega^*.$$

In the case of sufficiently strong external fields, it is necessary to take into account the dependence of

This follows from the dependence of $P(E_\alpha)$ on F_α in the state of thermodynamic equilibrium. In general, however, we can state $kT/h \geq \omega^$ (see also^[56]).

the relaxation coefficients $\Gamma_{mkl n}$ (and consequently also of T_1 and T_2) on the field amplitude H_1 . Such a dependence follows from the general formulas of Sec. 7. An analysis of the nonlinear effects that arise in this connection is given in^[71-73, 57, 58].

11. RELAXATION IN FERROMAGNETS AND ANTI-FERROMAGNETS

In experiments on ferromagnetic resonance we are usually interested in the relaxation of the uniform precession of magnetization, or generally speaking, in the behavior of the uniform precession in the presence of an external alternating field. The relaxation of uniform precession can be due to many reasons. One of the mechanisms of relaxation is the interaction between the uniform precession of magnetization (spin wave with wave vector $\mathbf{k} = 0$) and spin waves with $\mathbf{k} \neq 0$ (see the review^[74]). Another possible mechanism is interaction with phonons^[74]. To be specific, we consider now the relaxation connected with the interaction between spin waves. Such an interaction is the result of the fact that spin-wave amplitudes are the normal coordinates of the system only if they are infinitesimally small. The account of the finite nature of the amplitude of the spin waves leads to their interaction. The Hamiltonian of a system of interacting spin waves situated in an alternating transverse magnetic field H_x , H_y (and in a constant magnetic field H_0 directed along the z axis) can be written in the form

$$\begin{aligned} \hat{\mathcal{H}} = & \hbar\omega_0 a_0^* a - \frac{1}{2} (h^- \hat{a}_0^* + h^+ \hat{a}_0) + \sum_{\mathbf{k} \neq 0} \hbar\omega(\mathbf{k}) \hat{a}_{\mathbf{k}}^* \hat{a}_{\mathbf{k}} \\ & + \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} [\Phi_{12,3} \hat{a}_1^* \hat{a}_2^* \hat{a}_3 \delta_{\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3} + \text{conj.}] \\ & + \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} [\Phi_{12,34} \hat{a}_1^* \hat{a}_2^* \hat{a}_3^* \hat{a}_4 \delta_{\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_3 + \mathbf{k}_4} \\ & + \Phi_{1,234} \hat{a}_1^* \hat{a}_2^* \hat{a}_3^* \hat{a}_4 \delta_{\mathbf{k}_1, \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4} + \text{conj.}], \end{aligned} \quad (129)$$

where $\omega(\mathbf{k})$ is the frequency of the spin wave with wave vector \mathbf{k} , $h^\pm = (H_x \pm iH_y) \sqrt{2\mu M_0 V}$, μ is the Bohr magneton, $M_0 V$ is the saturation magnetic moment, and \hat{a} and \hat{a}^+ are the magnon annihilation and creation operators; the coefficients Φ are given in^[74]. The annihilation and creation operators of magnons with $\mathbf{k} = 0$ are connected with the transverse components of the total magnetic moment by the relations

$$\begin{cases} \hat{M}_x + i\hat{M}_y = \sqrt{2\mu M_0 V} \hat{a}^* \\ \hat{M}_x - i\hat{M}_y = \sqrt{2\mu M_0 V} \hat{a} \end{cases} \quad (130)$$

We assume further that all the spin waves ($\mathbf{k} \neq 0$) are in the state of equilibrium and represent a dissipative subsystem, while the role of the dynamic subsystem is played by the uniform precession. The

first two terms in (129) represent the Hamiltonian of the dynamic subsystem, where the third term represents the Hamiltonian of the dissipative subsystem. The energy of interaction between the dynamic and dissipative subsystems is obtained from the interaction Hamiltonian of (129) by separating the terms proportional to \hat{a}_0 and \hat{a}_0^+ :

$$V = \hat{a}_0 \sum_{\mathbf{s}} \hat{F}_{\mathbf{s}}^* + \hat{a}_0^* \sum_{\mathbf{s}} \hat{F}_{\mathbf{s}}. \quad (131)$$

We do not give here all the operators $\hat{F}_{\mathbf{s}}^*$, but indicate only, using an example, the methods for their derivation. Thus, in the first sum, the terms proportional to \hat{a}_0 have the form

$$\left. \begin{aligned} \hat{F}_1^* &= \sum_{\mathbf{k}_1, \mathbf{k}_2} \Phi_{12,0} \hat{a}_1^* \hat{a}_2^* \delta_{\mathbf{k}_1, -\mathbf{k}_2} \\ \hat{F}_2^* &= \sum_{\mathbf{k}_2, \mathbf{k}_3} \Phi_{02,3} \hat{a}_2^* \hat{a}_3^* \delta_{\mathbf{k}_2, \mathbf{k}_3} \\ \hat{F}_3^* &= \sum_{\mathbf{k}_1, \mathbf{k}_3} \Phi_{10,3} \hat{a}_1^* \hat{a}_3^* \delta_{\mathbf{k}_1, \mathbf{k}_3} \end{aligned} \right\} \quad (132)$$

The last two terms can be combined into

$$F_2^* = \sum_{\mathbf{k}} (\Phi_{0\mathbf{k}, \mathbf{k}}^* + \Phi_{\mathbf{k}0, \mathbf{k}}^*) \hat{a}_{\mathbf{k}}^* \hat{a}_{\mathbf{k}}^*.$$

We analogously obtain the remaining $F_{\mathbf{s}}^*$. In addition to the terms (131), the interaction energy includes terms describing the interaction of spin waves with $\mathbf{k} \neq 0$. We disregard these terms, since we assume that the spin waves ($\mathbf{k} \neq 0$) are in equilibrium. Using (93)–(96) we obtain from the Hamiltonian (129) and (131) the equations of motion for the mean values $\langle a_0^+ \rangle$ and $\langle a_0 \rangle \equiv \langle a_0^- \rangle$

$$\frac{d \langle a^\pm \rangle}{dt} = \pm i\omega_0 \langle a^\pm \rangle \mp \frac{i}{2\hbar} h^\pm - \frac{1}{T} \langle a^\pm \rangle, \quad (133)$$

where

$$T^{-1} = \Phi^{-+} (1 - e^{-\hbar\omega_0/hT}) \quad (134)$$

and

$$\Phi^{-+} = \frac{\pi}{\hbar} \sum_{\alpha\alpha'} \delta(\omega_0 + \omega_{\alpha'\alpha}) \langle \alpha | F_{\mathbf{s}}^* | \alpha' \rangle \langle \alpha' | F_{\mathbf{s}}^- | \alpha \rangle P_{\alpha'}. \quad (135)$$

The coefficients Φ^{-+} are calculated in analogy with the calculation of the relaxation coefficients in the case of interaction with the radiation field (Sec. 8). Let us write down in explicit form, for example, the contribution to Φ^{-+} connected with F_1^+ (132):

$$\begin{aligned} \Phi_{(1)}^+ &= \frac{\pi}{\hbar} \sum_{\mathbf{k}} \delta(\omega_0 - \omega_{\mathbf{k}} - \omega_{-\mathbf{k}}) \langle \bar{n}_{\mathbf{k}} \bar{n}_{-\mathbf{k}} | \Phi_{12,0} \hat{a}_1^* \hat{a}_2^* | \bar{n}_{\mathbf{k}} - 1; \bar{n}_{-\mathbf{k}} + 1 \rangle \\ &\quad \times \langle \bar{n}_{\mathbf{k}} - 1; \bar{n}_{-\mathbf{k}} + 1 | \Phi_{12,0}^* \hat{a}_1 \hat{a}_2 | \bar{n}_{\mathbf{k}}; \bar{n}_{-\mathbf{k}} \rangle, \end{aligned}$$

Where $\bar{n}_{\mathbf{k}}$ are the mean values of the occupation numbers in the equilibrium state

$$\bar{n}_{\mathbf{k}} = \frac{1}{e^{\hbar\omega(\mathbf{k})/hT} - 1}.$$

An explicit calculation of the relaxation coefficients was made in^[54]. Equations (133) are the sought equa-

tions of motion for uniform precession or, according to (130), for the transverse magnetic moment M_x , M_y in the presence of a transverse magnetic field. It must be noted that such equations can be used at sufficiently small values of M_x and M_y , and accordingly in not too strong fields $H_{x,y}$. For a certain critical value of the field $H_{x,y}$, the occupation numbers n_k of the spin waves begin to increase exponentially, and this upsets the equilibrium and the spin-waves [75-77].

Relaxation in an antiferromagnet is analyzed in similar fashion [78, 79]. Now, however, the presence of two sublattices leads to the need for including in the dynamic system two kinds of annihilation and creation operators for the spin waves. In particular, the interaction energy assumes the form

$$\hat{V} = \sum_{i=1,2} \hat{a}_i \sum_s \hat{F}_{si}^+ + \sum_{i=1,2} \hat{a}_i \sum_s \hat{F}_{si}.$$

An account of the spin-wave interaction, similar to that considered above, leads to independent relaxations $\langle a_1^\pm \rangle$ and $\langle a_2^\pm \rangle$. A connection appears between the relaxations $\langle a_{1,2}^\pm \rangle$ if account is taken of the "linear" mechanism of spin-wave interaction—the interaction of the spin waves due to the presence of random inhomogeneities in a crystal structure of the antiferromagnet [79]. Calculations for such an interaction were made in [80] for the case of a ferroelectric.

APPENDIX

DENSITY MATRIX AND DESCRIPTION OF A QUANTUM STATE

Quantum theory is principally a statistical theory. The predictions of quantum theory have usually a probabilistic character. But probability and statistics have a definite meaning if one singles out the aggregate of elements to which the statistics apply. This circumstance was emphasized in particular by Mandel'shtam [81]. Using his terminology, we shall call an aggregate of elements on which the statistical processing is being carried out a statistical ensemble.

An important question is how to separate the corresponding statistical ensemble in quantum theory. In quantum theory the statistical ensemble is an aggregate of identical experiments (measurements) carried out on an object which is in a specified quantum state. The measurement or experiment, generally speaking, changes the state of the object. It is therefore necessary (in order to stay within the framework of the given ensemble), to return the object after each measurement to the initial quantum state. In this case the measurement is carried once on each object. In the ensemble thus produced it is possible to introduce the probability distribution of one measurement result or another. Thus, in order

to separate the ensemble in quantum theory it is necessary, first, to specify the type of measurement which must be carried out on the object, and second, to specify the state of the object.

In quantum theory states are classified as "pure" and "mixed" or "mixtures." The pure state is described by a wave function. The probability distribution of a certain quantity q in an ensemble resulting from the measurement of this quantity is specified by the square of the modulus of the wave function $\Psi(q)$ in the q -representation. Thus, for example, the distribution of the probabilities of the coordinates of an electron in a state with wave function $\Psi(x)$ (in the ensemble resulting from the measurement of the coordinate x) is given by $|\Psi(x)|^2$. In order to obtain the momentum distribution (in the ensemble resulting from the measurement of the momentum of an electron in the same state) it is necessary to change over to the p -representation, by expanding $\Psi(x)$ in a series of eigenfunctions of the momentum operator \hat{p}

$$\Psi(x) = \sum_p \Phi(p) \Psi_p(x).$$

The aggregate of the coefficient $\Phi(p)$ is indeed the wave function in the p -representation, while $|\Phi(p)|^2$ gives the momentum probability distribution. It must be borne in mind that in an individual measurement the electron goes over from the state $\Psi(x)$ into a state with a definite value of the coordinate $\delta(x - x_0)$ [or with a definite value of the momentum $\Psi_p(x)$]. (Therefore, in order to investigate the ensemble of the given state it becomes necessary to carry out measurements over a series of identical objects, all in the same state, or somehow return the system to the initial state after each measurement.) In the general case the transition from one representation to the other is realized with the aid of the corresponding unitary transformation

$$\Psi(q) = \hat{U}\Phi(Q). \tag{I}$$

Thus the presence of a definite wave function causes the probability distributions in the different ensembles that result from different measurements in a given pure state to be related through the unitary transformation

$$|\Psi(q)|^2 = |\hat{U}\Phi(Q)|^2, \quad |\Phi(Q)|^2 = |\hat{U}^{-1}\Psi(q)|^2.$$

No such connection exists for mixed states, which are not described by a wave function. The fact that a state is not always describable by a wave function can be understood by considering a subsystem A of some system A + B. Let the system A + B be described by a wave function

$$\Psi = \Psi(x_A, x_B),$$

where x_A and x_B are the coordinates of the subsystems A and B, respectively. This function, generally speaking, can not be factored into a product of the

wave functions

$$\Psi = \Psi_A \Psi_B \quad (\text{II})$$

even when the systems A and B do not interact*. This means that neither A nor B are described by wave functions. (For more details see^[3,4].)

How does one describe the state of a quantum system when there is no wave function? Such a description was found by von Neumann^[1,6]. Mixed states (like pure ones) can be described uniquely by a density matrix. We first introduce the density matrix for the pure state. Let the wave function of this state be $\Psi(q, t)$. Then, as is well known, the mean value of some quantity described by the operator F is equal to †

$$\bar{F} = \int \Psi^*(q, t) \hat{F} \Psi(q, t) dq. \quad (\text{III})$$

Let us change over to a second representation, characterized, for the sake of being specific, by a discrete index n :

$$\Psi(q, t) = \sum_n a_n \Psi_n(q); \quad (\text{IV})$$

here $\Psi_n(q)$ are the eigenfunctions of some Hermitian operator \hat{A} , describing a certain physical quantity; a_n is the wave function in the representation of this operator. Substituting (IV) in (III), we obtain an expression for the mean value \bar{F} in the A-representation

$$\bar{F} = \sum_{n'n} \sigma_{n'n} F_{nn'} = \text{Sp}(\hat{\sigma} \hat{F}) = \text{Sp}(\hat{F} \hat{\sigma}), \quad (\text{V})$$

where $\sigma_{n'n} = a_n^* a_{n'}$, and Sp stands for the sum of the diagonal elements (trace) of the matrix:

$$(\sigma F)_{n'n} = \sum_n \sigma_{n'n} F_{nn'},$$

$F_{nn'}$ denotes the matrix elements of the operator \hat{F}

$$F_{nn'} = \int \Psi_n^* \hat{F} \Psi_{n'} dq.$$

The matrix $\hat{\sigma}$ is called a density matrix. It is obvious that a density matrix yields the same information as the wave function (if the latter exists). From formula (V) we can obtain different mean values, and

*It is easy to show, for example, that the wave function of the system A + B can differ from (II) if an interaction (collision) has taken place between these systems, although they do not interact at the present instant of time t .

†One may ask in which ensemble the mean value of \hat{F} is taken, since \hat{F} can, in particular, be a function of the noncommuting operators \hat{q} and \hat{p} . It is obvious that this cannot be the ensemble of the measurement of \hat{p} (or \hat{q}). In fact, this ensemble is determined by measurements of \hat{F} or, more accurately, the eigenvalues f of this operator, that is,

$$\bar{F} = \sum w(f) f,$$

where $w(f)$ is the probability that a single measurement will cause the system to go over into a state with a definite value of f .

the diagonal elements of the density matrix give, as can be readily seen, the probability distribution of \hat{A} . From this, in particular, follow the normalization condition

$$\sum_n \sigma_{nn} = \text{Sp} \hat{\sigma} = 1.$$

We can describe mixtures, too, with the aid of the density matrix. Let \hat{F} be an operator pertaining to the subsystem A of the system A + B. Then the matrix elements of \hat{F} , taken with the aid of the eigenfunctions $\Psi_{nu} = \Psi_n(x_A) \Psi_u(x_B)$, have the form

$$F_{nu; n'u'} = F_{nn'} \delta_{uu'}, \quad (\text{VI})$$

where $\Psi_n(x_A)$ are the eigenfunctions of the operator \hat{A} pertaining to the subsystem A, while $\Psi_u(x_B)$ are the eigenfunctions of the operator \hat{B} of the subsystem B. We note that the use of eigenfunctions Ψ_{nu} in the form of products of eigenfunctions does not mean at all that the subsystems A and B are statistically independent. In fact, an arbitrary wave function can be expanded in a series in Ψ_{nu} and this series, generally speaking, cannot be represented in the form of a product $\Psi_A \Psi_B$. Substituting (VI) in (V) (this can be done, since the entire system A + B is in a pure state), we obtain

$$\bar{F} = \sum_{nn'} \sigma_{n'u; nu} F_{nn'} = \sum_{nn'} \rho_{nn'} F_{nn'} = \text{Sp}(\hat{\rho} \hat{F}), \quad (\text{V}')$$

where $\rho_{n'n} = \sum_{u'} \sigma_{n'u}; nu$ is by definition the density matrix of the subsystem A. It is easy to see that with the aid of a density matrix we can obtain all the mean values and the probability distributions in the subsystem A. Thus, mixed states can be described by the density matrix $\rho_{nn'}$. The density matrix has the following properties (see, for example, ^[4,5]):

a) the density matrix is Hermitian;

$$\rho_{n'n} = \rho_{nn'}^*,$$

b) it is normalized to unity:

$$\text{Sp} \hat{\rho} = 1;$$

c) for the diagonal elements of the density matrix, which have the meaning of the probabilities of the states $|n\rangle$, we have

$$\rho_{nn} \geq 0;$$

d) $\text{Sp} \hat{\rho}^2 \leq 1$, where the equal sign holds for the pure state. It is also easy to show that in the pure state $\hat{\rho}^2 = \hat{\rho}$. From the invariance of (V')

$$\bar{F} = \text{Sp} \hat{\rho} \hat{F}$$

[see (V')] under the unitary transformation \hat{U} , it follows for an arbitrary operator \hat{F} that under such a transformation

$$\hat{\rho} \rightarrow \hat{U} \hat{\rho} \hat{U}^{-1} \quad (\text{VII})$$

(whereas $\hat{F} \rightarrow \hat{U} \hat{F} \hat{U}^{-1}$).

Making use of tensor terminology, $\hat{\rho}$ and \hat{F} can be called second rank tensors and the wave function can be called a vector (the roles of the different coordinate systems are assumed by the different representations). The mean values of a quantity are invariants of the transformation or scalars. It is therefore clear that in the general case the states should be represented by a second-rank tensor $\hat{\rho}$, since the operators \hat{F} are second-rank tensors, and the invariants can consequently be obtained by contracting these tensors with tensors of the same dimensionality. Only in particular cases can $\hat{\rho}$ be represented by a product of two vectors ($\rho_{n'n} = a_n a_n^*$).

It follows from (VII) that the probability distributions in the different ensembles that arise upon measurement of different quantities are connected by the relations

$$\rho'_{hk} = \sum_n U_{kn} \rho_{nn'} (U^{-1})_{n'h}, \quad \rho_{nn} = \sum_{h,h'} (U^{-1})_{nh} \rho_{hh'} U_{h'n}, \quad \text{(VIII)}$$

which replace relations (I), since the latter are valid only for pure states.

If the system is in a pure state, then the measurement of the total assembly of the quantities characterizing the wave function of the state leads with assurance to the initial state, that is, the probability distribution in such an ensemble consists of two terms, 0 and 1. In a mixed state, in analogy to the complete assembly of quantities, we can introduce the commuting operators \hat{L} , \hat{M} , and \hat{N} , which are characterized by the fact that the density matrix is diagonal in the representation that is diagonal in these quantities. A measurement of these quantities leads to an ensemble in which the probability distribution defines completely the density matrix (since there are no nondiagonal elements)*. We shall call such a measurement a complete measurement and the corresponding ensemble a complete ensemble. It can be seen that the complete measurement goes over in the particular case of a pure state into a measurement of a complete assembly of quantities. (In this case $\rho_{nn}^2 = \rho_{nn}$ since $\hat{\rho}^2 = \hat{\rho}$.) It can be said that a pure state differs from a mixed state in the sense that in a pure state there is always an ensemble in which the probability distribution consists of two terms, 0 and 1.

Let us consider now the time variation of the density matrix. If a closed system has been at some instant of time in a pure state, it remains in the pure state all the time, and the time variation of the wave function is described by the Schrödinger equation. It is easy to verify that the density matrix of such a pure state obeys the equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \hat{\mathcal{H}} \hat{\rho} - \hat{\rho} \hat{\mathcal{H}} \equiv [\hat{\mathcal{H}}, \hat{\rho}],$$

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

We shall show that in a closed system the density matrix of the mixed state also obeys this equation. For this purpose it is sufficient to assume that there is a more general system A + B, including the subsystem A as a part (the subsystems A and B do not interact), and that this system A + B is in a pure state. Then

$$i\hbar \frac{\partial \hat{\rho}_{A+B}}{\partial t} = [\hat{\mathcal{H}}_A + \hat{\mathcal{H}}_B, \hat{\rho}_{A+B}].$$

Taking the trace of the right and left halves of the equation over the indices B, we obtain without difficulty

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{\mathcal{H}}, \hat{\rho}], \quad \text{(IX)}$$

where $\hat{\rho} = \text{Sp}_B \hat{\rho}_{A+B}$ is the density matrix of the system A and the subscript of \mathcal{H}_A has been left out. We shall call equation (IX) the Neumann equation (see [16]).

In describing the variation of the quantum states with the aid of (IX) it is assumed that the operators of the physical quantities do not depend on the time, and the entire time dependence is contained in the density matrix. Such a description or representation is called a Schrödinger description. The time dependence of the density matrix can be written in this representation in the form

$$\hat{\rho}(t) = e^{-i\hbar^{-1} \hat{\mathcal{H}} t} \hat{\rho}(0) e^{i\hbar^{-1} \hat{\mathcal{H}} t}. \quad \text{(X)}$$

The forms (IX) and (X) are equivalent. Another possible representation is the Heisenberg representation. In this representation the entire time dependence is transferred to the operators

$$\hat{F}(t) = e^{i\hbar^{-1} \hat{\mathcal{H}} t} \hat{F}(0) e^{-i\hbar^{-1} \hat{\mathcal{H}} t}, \quad \text{(XI)}$$

and the density matrix does not depend on the time. There exists a representation "intermediate" between the Schrödinger and Heisenberg representations, namely the interaction representation. Let the Hamiltonian of the system $\hat{\mathcal{H}}$ be divisible into two parts *

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V}.$$

In the interaction representation the operators depend on the time-like Heisenberg operators with Hamiltonian $\hat{\mathcal{H}}_0$

$$\hat{F}_{\text{int}} = e^{i\hbar^{-1} \hat{\mathcal{H}}_0 t} \hat{F}(0) e^{-i\hbar^{-1} \hat{\mathcal{H}}_0 t},$$

and the density matrix depends on the time, as in a Schrödinger representation with Hamiltonian \hat{V}_{int} :

*In the general case the distribution of probabilities in one ensemble does not make it possible to determine the density matrix (or the wave function).

*Of course, such a subdivision is arbitrary and is determined every time by the character of the problem.

$$i\hbar \frac{\partial \hat{Q}_{\text{int}}}{\partial t} = [\hat{V}_{\text{int}}, Q_{\text{int}}]. \quad (\text{XII})$$

Of course, the question of which representation should be used in each specific case is solved exclusively by considerations of convenience and simplicity. In all other respects the three representations are perfectly equivalent.

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