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QUANTUM THEORY OF RELAXATION PROCESS

V. M. FAĬN

Radiophysics Institute, Gorkiĭ State University

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We consider relaxation of a system consisting of a dynamic subsystem having a finite number of degrees of freedom and a discrete spectrum and of a dissipative subsystem with an infinite number of degrees of freedom and a continuous spectrum. A kinetic equation for the density matrix, which is diagonal with respect to the continuous indices of the dissipative subsystem and generally speaking nondiagonal with respect to the discrete indices, is derived from quantum theory under the assumption that the interaction energy is small. It is also assumed that the diagonal singularity condition is fulfilled and that two time scales exist.

The equations derived by Van Hove, Bloch, and Wangsness as well as the usual transport equations with Einstein coefficients are deduced from the kinetic equations as particular cases.

1. INTRODUCTION

IN the investigation of relaxation processes of various physical systems we are concerned with the following characteristic situation. Relaxation occurs as a result of the interaction of some dynamic system with a dissipative one. That part of the system which has a finite number of degrees of freedom, discrete energy levels, and is described in principle by simple dynamic equations, will be called the dynamic system (or dynamic subsystem). This dynamic subsystem interacts with a dissipative system that has in the limit an infinite number of degrees of freedom and a continuous energy spectrum. The dissipative system represents the macroscopic body. A simple example of a relaxation process is the spontaneous emission of an atom in free space. Here the atom plays the role of the dynamic system, and the dissipative system is the radiation field in free space. The radiation field in free space has a continuous energy spectrum, whereas the atom has a discrete spectrum.

Relaxation processes are described by kinetic equations. Boltzmann was the first to derive kinetic equations from the equations of classical mechanics. Boltzmann's derivation was based on the assumption of molecular chaos (Stosszahlansatz). This assumption does not follow from the equations of mechanics; hence it is of interest to derive the kinetic equations without assuming molecular chaos. In the classical case this problem was considered by Bogolyubov[1] and by Prigogine and his co-workers.[2]

Quantum-mechanical derivations of the kinetic equations were undertaken by Landau,[3] Pauli,[4] and Bloch.[5] They deduced the transport equation (assuming molecular disorder):

$$\frac{dP_m}{dt} = \sum_n (W_{mn}P_n - W_{nm}P_m). \qquad (1)$$

Here P_m is the probability of finding the system in state m, and W_{mn} is the transition probability per unit time. The derivation of the transport equation without the assumption of molecular disorder was accomplished by Van Hove,[6,7] and by by Sher and Primakoff.[8] Van Hove considered also the case when the perturbation causing the transitions is not small; in this case the relaxation process has a non-Markov character.* Van Hove [6,7] considered the case where the relaxing system has a continuous spectrum. Of interest would be the case in which the spectrum of the system is characterized by both discrete (dynamic part) and continuous indices (dissipative part). Just such a case was also considered in the aforementioned works of Landau, Pauli, and Bloch.

Equation (1) contains only the diagonal elements of the density matrix of the system

$$\rho_{mm} = P_m.$$

Hence this equation does not give the likelihood of determining all the average properties of the physical system. The latter, generally speaking, are

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*The question of the derivation of a quantum kinetic equation for rarefied gases was also considered in the work of Bogolyubov and Gurov [9] and in the work of a number of authors who used their method (see, for example, [10]).

determined by both the diagonal elements of the density matrix and the non-diagonal ones. Bloch and Wangsness [12-14] obtained for a density matrix an equation that was non-diagonal in the discrete indices. In this case it is assumed that the dissipative part of the system, characterized by the continuous indices, is in a state of thermodynamic equilibrium. (On the other hand, Van Hove considers in essence the case of relaxation of a dissipative system.)

In a number of cases, the assumption that the dissipative subsystem is in a state of equilibrium is not fulfilled. In Secs. 2 and 3 of this paper a quantum kinetic equation is derived for a density matrix $\rho_{m\alpha;n\alpha}$, nondiagonal in the discrete indices m, n and diagonal in the continuous indices α.* As particular cases, the equations derived by Van Hove and by Bloch and Wangsness are obtained in Sec. 4. In Sec. 5 the question of the application of the various quantum kinetic equations in quantum radio physics is briefly discussed.

2. DERIVATION OF THE QUANTUM KINETIC EQUATION (IN THE ABSENCE OF EXTERNAL FORCES)

In the case of the absence of external forces the dynamic subsystem, which interacts with the dissipative subsystem, forms together with the latter a closed system. The Hamiltonian of this system we shall write in the form

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

where $\hat{V}$ is the energy of the interaction between the dynamic and dissipative subsystems. Clearly, the operator $\hat{\mathcal{H}}$ is independent of time. In what follows we will make use of the following assumptions:

(a) The interaction energy satisfies the diagonal singularity condition [6] in the continuous indices α, i.e., the matrix element of $\hat{V}\hat{A}\hat{V}$ diagonal in α is singular. Here $\hat{A}$ is assumed to be a matrix diagonal in α;

(b) If λ is a dimensionless constant characterizing the order of smallness of $\hat{V}$, and the probability per unit time found from perturbation theory has the form $\lambda^2\Gamma$ (where Γ does not depend on λ), [15] then it is assumed that the condition

$$\lambda^2\Gamma \ll \delta_1 E/\hbar, \ \delta_2 E/\hbar, \tag{2}$$

holds, where $\delta_1 E$ is a difference in the energy levels of $\mathcal{H}_0$ such that any dependence of the matrix elements of $\hat{V}$ on E can be neglected in the interval $\delta_1 E$, and $\delta_2 E$ is the characteristic difference of the energy levels of the dynamic subsystem.

In the interaction representation the equation for the density matrix has the form

$$\partial\hat{\rho}/\partial t = -i\hbar^{-1}[\hat{V}\hat{\rho}]. \tag{3}$$

Our task will be to obtain the quantum kinetic equation, starting from this equation and using the approximations just mentioned.

We shall be interested in the behavior of the density matrix $\hat{\rho}$, on the basis of a time scale of the order $1/(\lambda^2\Gamma)$. This means that when we later refer to a change in the density matrix in an infinitesimally small time, we shall mean a change in a time much shorter than the accepted time scale $1/(\lambda^2\Gamma)$. But, on the other hand, this small time should be very large compared to the other time scales ($\hbar/\delta_1 E$ and $\hbar/\delta_2 E$). Thus, in considering spontaneous emission from an atom, the time, short in comparison to the time of emission τ_r, should be long relative to the period of the radiation $2\pi/\omega_0$. It should be emphasized that it is possible to neglect changes in the density matrix in times comparable to $\hbar/\delta_1 E$ and $\hbar/\delta_2 E$ only in the interaction representation. The point is that the transformation to the interaction representation really implies freedom from high-frequency dependence. The density matrix $\hat{\rho}$ in the interaction representation represents, roughly speaking, the amplitude of the density matrix in the Schrödinger representation. An essential change in this "amplitude" with time is associated with processes of relaxation and because of the smallness of λ^2 is a relatively slow change.

An increment in the density matrix in a time τ, as we shall see below, can be written in the form

$$\hat{\rho}(t+\tau) - \hat{\rho}(t) = \hat{A}(t)\lambda^2\tau + \hat{B}(t)\lambda + \hat{C}(t)\lambda^2, \tag{4}$$

where τ satisfies the condition

$$1/\lambda^2\Gamma \gg \tau \gg \hbar/\delta_1 E, \quad \hbar/\delta_2 E. \tag{5}$$

Allowing $\lambda \to 0$ and $\lambda^2\tau \to 0$ (the latter implies only smallness in the λ^{-2} scale), and keeping $\lambda^2 t$ finite, we arrive at the differential equation

$$\partial\hat{\rho}/\partial t = \lambda^2\hat{A}. \tag{6}$$

Here, in order to find $\lambda^2\hat{A}$, use is made of Eq. (3) for the density matrix. From this equation we obtain, correct to terms of the order of λ^2,

$$\hat{\rho}(t+\tau) - \hat{\rho}(t) = -\frac{i}{\hbar}\int_0^{\tau}[\hat{V}(t+\tau'), \hat{\rho}(t)]\,d\tau' - \frac{1}{\hbar^2}\int_0^{\tau}d\tau'\int_0^{\tau'}d\tau''[\hat{V}(t+\tau'), [\hat{V}(t+\tau''), \hat{\rho}(t)]]. \tag{7}$$

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*The equations derived below, as well as those of Van Hove, are equations for the density matrix of the entire system. In this they differ from the usual kinetic equations; in the foreign literature they are called "master equations" (see, for example, [11]).

The first term in the right hand member of Eq. (7) can be written in the form

$$(\Delta_1 \rho)_{mn} = -\frac{i}{\hbar}\sum_k \int_0^\tau [V_{mk}(t+\tau')\,\rho_{kn}(t) - \rho_{mk}(t)\,V_{kn}(t+\tau')]\,d\tau'$$

$$= -\frac{i}{\hbar}\sum_k \int_0^\tau \{V_{mk}(t)\,\rho_{kn}\,e^{i\omega_{mk}\tau'} - \rho_{mk}(t)\,V_{kn}(t)\,e^{i\omega_{kn}\tau'}\}\,d\tau', \tag{8}$$

where $\omega_{mk} = (E_m - E_k)/\hbar$, and E_m and E_k are eigenvalues of the Hamiltonian operator $\mathcal{H}_0$. The indices m and k symbolize the complete set of indices characterizing these eigenvalues. A part of these indices is continuous. We shall use Greek letters for the continuous indices and Latin letters for the discrete ones. It should be kept in mind that summations over the Greek indices are to be changed to integrals. In deriving Eq. (8) we have made use of the fact that in the interaction representation

$$V_{mk}(t) = V_{mk}(0)\,e^{i\omega_{mk}t}.$$

Equation (8) can be rewritten in the form

$$(\Delta_1\rho)_{m\alpha;\,n\alpha} = \frac{1}{\hbar}\sum_{k\alpha'} \{V_{m\alpha;\,k\alpha'}(t)\,\rho_{k\alpha';\,n\alpha}(t)\,\zeta_\tau(\omega_{m\alpha;\,k\alpha'})$$

$$-\rho_{m\alpha;\,k\alpha'}(t)\,V_{k\alpha';\,n\alpha}(t)\,\zeta_\tau(\omega_{m\alpha;\,k\alpha'})\}, \tag{9}$$

where

$$\zeta_\tau(x) = -i\int_0^\tau e^{ix\tau'}\,d\tau'.$$

For τ satisfying the condition (5), $\zeta_\tau(x)$ transforms into a singular function $\zeta(x)$ (see, for example, [15]). According to the definition of $\zeta(x)$,[15]

$$\int dx\,\zeta(x)\,F(x) = \int dx\,\frac{F(x)}{x} - i\pi F(0),$$

where the first integral on the right hand side is understood as a principal value. Replacing ζ_τ by ζ and transforming the summation over α' into an integral in the right hand side of Eq. (9), we find that $(\Delta_1\rho)_{m\alpha;n\alpha}$ does not depend on τ and is of order λ. Thus we can neglect $(\Delta_1\rho)_{m\alpha;n\alpha}$ in our approximation.

The second term on the right side of Eq. (7) can be represented in the form

$$(\Delta_2\rho)_{m\alpha;\,n\alpha} = -\frac{1}{\hbar^2}\sum_{k,\,l,\,\alpha',\,\alpha''} \{V_{m\alpha;k\alpha'}(t)$$

$$\times V_{k\alpha';l\alpha''}(t)\,\rho_{l\alpha'';n\alpha}(t)\,\varphi_\tau(\omega_{m\alpha;\,k\alpha'};\ \omega_{m\alpha;\,l\alpha''})$$

$$-V_{m\alpha;\,k\alpha'}(t)\,V_{l\alpha'';\,n\alpha}(t)\,\rho_{k\alpha';\,l\alpha''}$$

$$\times [\varphi_\tau(\omega_{m\alpha;\,k\alpha'};\ \omega_{m\alpha;\,k\alpha'} + \omega_{l\alpha'';\,n\alpha})$$

$$+\varphi_\tau(\omega_{l\alpha'';\,n\alpha};\ \omega_{m\alpha;\,k\alpha'} + \omega_{l\alpha'';\,n\alpha})]$$

$$+V_{k\alpha';\,l\alpha''}(t)\,V_{l\alpha'';\,n\alpha}(t)\,\rho_{m\alpha;\,k\alpha'}(t)\,\varphi_\tau(\omega_{l\alpha'';\,n\alpha};\ \omega_{k\alpha';\,n\alpha})\}, \tag{10}$$

where we have introduced the symbol

$$\varphi_\tau(u;\,u+v) = \int_0^\tau d\tau' \int_0^{\tau'} d\tau' e^{iu\tau'+iv\tau''}$$

$$= \frac{(u+v)\,(e^{iu\tau}-1) - u\,(e^{i(u+v)\tau}-1)}{uv\,(u+v)}.$$

The function $\varphi_\tau(x, y)$ has, for sufficiently large τ satisfying condition (5), the following form:

$$\varphi_\tau(x,\,y) = \begin{cases} \pi\tau\delta(x)\,\delta_{y,\,0}, & \text{if y takes discrete values} \\ -\pi\delta(x)\,\zeta(y), & \text{if y runs over a continuous series of values;} \end{cases}$$

here $\delta(x)$ is the Dirac δ-function, and $\delta_{y,0}$ is the Kronecker symbol.

Using these asymptotic properties of $\varphi_\tau(x, y)$ and the condition of diagonal singularity introduced above, it is possible to find quite simply that terms of the form $\hat{A}^2$ in the right hand member of Eq. (10) equal*

$$(\Delta_2\rho)_{m\alpha;\,n\alpha} = -\frac{\pi\tau}{\hbar^2}\sum_{k,\,l,\,\alpha'} \{V_{m\alpha;\,k\alpha'}V_{k\alpha';\,l\alpha}\rho_{l\alpha;n\alpha}(t)\,\delta(\omega_{m\alpha;\,k\alpha'})\,\delta_{\omega_{ml};\,0}$$

$$-V_{m\alpha;\,k\alpha'}V_{l\alpha';\,n\alpha}\rho_{k\alpha';\,l\alpha'}(t)\,[\delta_{\omega_{mk}+\omega_{ln};\,0}(\delta(\omega_{m\alpha;\,k\alpha'})$$

$$+\delta(\omega_{l\alpha';\,n\alpha}))]$$

$$+V_{k\alpha;\,l\alpha'}V_{l\alpha';\,n\alpha}\rho_{m\alpha;\,k\alpha}(t)\,\delta(\omega_{l\alpha';\,n\alpha})\,\delta_{\omega_{kn};\,0}\}. \tag{11}$$

Here the matrix elements of $\hat{V}$ no longer depend on time. The time dependence has vanished because of the Kronecker symbols.

Using Eq. (6), we finally obtain the sought-for kinetic equation,

$$\frac{\partial\rho_{m\alpha;\,n\alpha}}{\partial t}$$

$$= \frac{\pi}{\hbar}\sum_{k,\,l,\,\alpha'} \{V_{m\alpha;\,k\alpha'}V_{l\alpha';\,n\alpha}\rho_{k\alpha';\,l\alpha'}[\delta(E_m + E_\alpha - E_k - E_{\alpha'})$$

$$+\delta(E_l + E_{\alpha'} - E_n - E_\alpha)]\,\delta_{\omega_{mk}+\omega_{ln};\,0}$$

$$-V_{m\alpha;\,k\alpha'}V_{k\alpha';\,l\alpha}\rho_{l\alpha;n\alpha}\delta(E_m + E_\alpha - E_k - E_{\alpha'})\,\delta_{\omega_{ml};\,0}$$

$$-V_{k\alpha;\,l\alpha'}V_{l\alpha';\,n\alpha}\rho_{m\alpha;\,k\alpha}\delta(E_l + E_{\alpha'} - E_n - E_\alpha)\,\delta_{\omega_{kn};\,0}\}. \tag{12}$$

This equation connects matrix elements of $\hat{\rho}$ that are diagonal in the continuous index with matrix elements that also are diagonal in the continuous index. It is not difficult to see that the various average values belonging to the dynamic subsystem are determined by just such a matrix. In fact, since the continuous index labels the eigenvalues of the dissipative part of the system, the operator of a quantity A belonging to the dynamic subsystem can be represented by the matrix

$$A_{m\alpha;\,n\alpha'} = A_{mn}\delta_{\alpha\alpha'},$$

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*The remaining terms in the right hand member have the form $\hat{C}\lambda^2$ and we shall discard them.

and the average value of this quantity equals

$$\overline{A} = \mathrm{Sp}\,\hat{\rho}\hat{A} = \sum_{n,\,m,\,\alpha',\,\alpha} \rho_{n\alpha';\,m\alpha} A_{m\alpha;\,n\alpha'} = \sum_{n,\,m,\,\alpha} \rho_{n\alpha;\,m\alpha} A_{mn}.$$

3. ACCOUNT OF EXTERNAL FORCES

In the preceding section we considered a relaxation process proceeding in the absence of an external field. In this case it is clear that the Hamiltonian function of the system is independent of time. The Hamiltonian of a system under the influence of an external perturbation is written in the form

$$\mathcal{H} = \mathcal{H}_0 + \hat{V} + \hat{W}(t), \tag{13}$$

where $\hat{W}(t)$ is the interaction between the dynamic system and the external field in time-dependent form. We shall consider for what follows that the perturbation $\hat{W}$ is rather small. This means that w, the order of magnitude of the quantity $\hat{W}(t)$, satisfies the inequality

$$w \ll \delta_2 E. \tag{14}$$

In this assumption, limiting ourselves to terms linear in w, we find

$$\hat{\rho}(t+\tau) - \hat{\rho}(t) = -\frac{i}{\hbar}\int_0^\tau [\hat{W}(t+\tau'),\, \hat{\rho}(t)]\, d\tau' + \Delta_2\hat{\rho}, \tag{15}$$

where $\Delta_2\hat{\rho}$ is given in the preceding section by Eq. (10). Here $\hat{W}(t)$ is an operator in the interaction representation. We now consider the interaction energy to be $\hat{V} + \hat{W}$.

In order to go from the integral equation (15) to a differential equation it is necessary to assume that $\hat{W}$ and $\hat{\rho}$ contain only such frequencies ω that satisfy the condition

$$\omega\tau \ll 1, \tag{16}$$

i.e., $\hat{W}$ and $\hat{\rho}$ should be gradual functions.

In particular, this condition is fulfilled if the Schrödinger operator $\hat{W}(t)$ depends on time in resonance fashion, i.e.,

$$\hat{W} = \hat{W}_0 \cos \omega_1 t$$

and $\omega_1 \approx \omega_0$, where ω_0 is one of the characteristic frequencies of the dynamic system. In this case, after transformation to the interaction representation, the matrix $\hat{W}$ will contain resonant terms with the low frequency $\omega_1 - \omega_0$ and high frequency terms with $\omega_1 + \omega_0$. However, it is not difficult to see that the contribution of these high frequency terms to the density matrix is much less than the contribution of the resonant slow terms. To the approximation that we neglect terms with frequency $\omega_1 + \omega_0$ it can be considered that even in this case the condition (16) is satisfied.*

After these observations, we transform the integral equation (15) into a differential one. As a result we obtain the following kinetic equation:

$$\begin{aligned} &\frac{\partial\rho_{m\alpha;\,n\alpha}}{\partial t} + \frac{i}{\hbar}[\hat{W}(t),\, \hat{\rho}]_{m\alpha;\,n\alpha} \\ &= \frac{\pi}{\hbar}\sum_{k,\,l,\,\alpha'} \{V_{m\alpha;\,k\alpha'} V_{l\alpha';\,n\alpha} \rho_{k\alpha';\,l\alpha'} [\delta(E_m + E_\alpha - E_k - E_{\alpha'}) \\ &+ \delta(E_l + E_{\alpha'} - E_n - E_\alpha)]\delta_{\omega_{mk}+\omega_{ln};\,0} \\ &- V_{m\alpha;\,k\alpha'} V_{k\alpha';\,l\alpha} \rho_{l\alpha;\,n\alpha} \delta(E_m + E_\alpha - E_k - E_{\alpha'})\,\delta_{\omega_{ml};\,0} \\ &- V_{k\alpha;\,l\alpha'} V_{l\alpha';\,n\alpha} \rho_{m\alpha;\,k\alpha} \delta(E_l + E_{\alpha'} - E_n - E_\alpha)\,\delta_{\omega_{kn};\,0}\}. \end{aligned} \tag{17}$$

4. SOME PARTICULAR CASES

We shall now consider some particular cases of the general equation (17). First of all, we shall consider the case when m = n in the left member of Eq. (17) and there is no external field:

$$\begin{aligned} &\frac{\partial\rho_{m\alpha;\,m\alpha}}{\partial t} = \frac{2\pi}{\hbar} \\ &\times \sum_{k,\,l,\,\alpha'} V_{m\alpha;\,k\alpha'} V_{l\alpha';\,m\alpha} \rho_{k\alpha';\,l\alpha'} \delta(E_m + E_\alpha - E_k - E_{\alpha'})\,\delta_{\omega_{lk};\,0} \\ &- \frac{\pi}{\hbar}\sum_{k,\,l,\,\alpha'} V_{m\alpha;\,k\alpha'} V_{k\alpha',\,l\alpha} \rho_{l\alpha;\,m\alpha} \\ &\times \delta(E_m + E_\alpha - E_k - E_{\alpha'})\,\delta_{\omega_{ml};\,0} \\ &- \frac{\pi}{\hbar}\sum_{k,\,l,\,\alpha'} V_{k\alpha;\,l\alpha'} V_{l\alpha';\,m\alpha} \rho_{m\alpha;\,k\alpha} \delta \\ &\times (E_l + E_{\alpha'} - E_m - E_\alpha)\,\delta_{\omega_{km};0}. \end{aligned} \tag{18}$$

As can be seen in Eq. (18), in general the matrix $\hat{\rho}$, which is diagonal in all indices, is connected with nondiagonal matrix elements of $\hat{V}$. This means that in the case considered the transport Eq. (1) is not obtained.

Let us now consider the case in which the energy levels of the dynamic subsystem E_m are nondegenerate. Then it is easy to find from Eq. (18):

$$\begin{aligned} \frac{\partial\rho_{m\alpha;\,m\alpha}}{\partial t} &= \frac{2\pi}{\hbar}\sum_{k\alpha'} |V_{m\alpha;\,k\alpha'}|^2 \rho_{k\alpha';\,k\alpha'} \delta(E_m + E_\alpha - E_k - E_{\alpha'}) \\ &- \frac{2\pi}{\hbar}\rho_{m\alpha;\,m\alpha}\sum_{l\alpha'} |V_{m\alpha;\,l\alpha'}|^2 \delta(E_m + E_\alpha - E_l - E_{\alpha'}). \end{aligned} \tag{19}$$

This equation agrees with the transport equation, since the coefficients of Eq. (19)

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*It should be kept in mind that in the condition (16) we cannot choose τ as small as we desire, since condition (5) must be satisfied at the same time.

$$\frac{2\pi}{\hbar}\,|V_{m\alpha;\,k\alpha'}|^2\,\delta\,(E_m+E_\alpha-E_k-E_{\alpha'})$$

are the transition probabilities per unit time from state $m\alpha$ to state $k\alpha'$. The presence of the δ-function, as usual, guarantees that energy will be conserved in these transitions.

The equations derived by Van Hove[6] are obtained from Eq. (19) if the index m is eliminated, i.e., for the case of relaxation of only the dissipative system. Equations (17) become the equations of Bloch and Wangsness[9] if the following assumption about the form of the density matrix is made:

$$\rho_{m\alpha;\,n\alpha}=\sigma_{mn}P\,(\alpha), \tag{20}$$

which implies a quasi-independence of the motions of the dissipative and dynamic subsystems. In particular, Bloch and Wangsness assumed that

$$P\,(\alpha)=e^{-E(\alpha)/kT}\Big/\sum_\alpha e^{-E(\alpha)/kT}. \tag{21}$$

This assumption means that the dissipative system is at all times in a state of thermodynamic equilibrium at a temperature T. To what extent such an assumption is justifiable can be in principle decided by an analysis of the general equation (17).

In the works by Landau and Bloch quoted in the introduction[3,5] it was considered that the dissipative system (specifically, the radiation field in free space) exists in a vacuum at all times. The equations of Landau and Bloch[3,5] are easily obtained from Eq. (17) if one sets $T = 0$ [and $\hat{W}(t) = 0$] in Eqs. (20) and (21). In particular, we find for the diagonal elements of the density matrix from Eq. (19)

$$\begin{aligned}\frac{\partial\sigma_{mm}}{\partial t}&=\frac{2\pi}{\hbar}\sum_{k>m}\sum_{\alpha}|V_{m\alpha;\,k0}|^2\,\sigma_{kk}\delta\,(E_m-E_k+E_\alpha)\\&-\frac{2\pi}{\hbar}\,\sigma_{mm}\sum_{l<m}\sum_{\alpha'}|V_{m0;\,l\alpha'}|^2\,\delta\,(E_m-E_l-E_{\alpha'}).\end{aligned} \tag{22}$$

Here the index 0 means vacuum, and it is assumed that the larger indices correspond to greater energy. Equation (22) can be rewritten in the more customary way:

$$\frac{\partial\sigma_{mm}}{\partial t}=\sum_{k>m}w_{mk}\sigma_{kk}-\sum_{k<m}w_{km}\sigma_{mm}, \tag{23}$$

where

$$w_{mk}=\frac{2\pi}{\hbar}\sum_\alpha|V_{m\alpha;\,k0}|^2\,\delta\,(E_m-E_k+E_\alpha)$$

is the probability per unit time of a transition from state k to state m.

5. CONCLUSION

One of the important problems of quantum radio physics is the problem of the interaction of a dynamic system with a given external field in the presence of simultaneous relaxation processes. In general, this problem is resolved by an application of the equations derived in the present paper (and in the papers cited above). The problem is greatly simplified if the dissipative system can be considered to be in a state of equilibrium at all times. In particular, if the dynamic system is represented by a spin and the dissipative system by a lattice that is assumed to be in thermodynamic equilibrium, then we have the case of spin-lattice relaxation. In the case of processes of the spin-lattice relaxation type the density matrix σ_{mn} of an individual spin is connected by the kinetic equations to the density matrix of the very same spin. And, in the general case the density matrix depends also on the variables of the dissipative system. Thus, for example, in the case of spin-spin relaxation the spin system can be considered to be the dissipative system, and an individual spin the dynamic system. However in this case it is already impossible to consider that the dissipative system is in a state of equilibrium. Hence, it follows that in the spin-spin relaxation case it is impossible to use simple equations of the Bloch type[16]

$$\frac{d\mathbf{M}}{dt}=\gamma\,[\mathbf{MH}]-\mathbf{i}\,\frac{M_x}{T_2}-\mathbf{j}\,\frac{M_y}{T_2}-\mathbf{k}\,\frac{M_z-M_z^0}{T_1}, \tag{24}^*$$

which are obtained from Eq. (17) in the case of spin-lattice relaxation.† When we speak of spin-lattice and spin-spin relaxation, we certainly do not have in mind the relaxation only of spin systems. The relaxation of an arbitrary system can be divided into two relaxations of this kind. For example, spontaneous radiation in free space has a spin-lattice character. Everything which has been said here about the relaxation of a spin system pertains, in particular, to the relaxation of energetic spins.[17]

We make the following further observations: If the external alternating field has a coherent character, as is usually the case in the radio-frequency region, then the calculation of this field is possible only in the framework of the completely quantum-mechanical formalism, e.g., as was done in Sec. 3. It will be invalid to regard the external field in the transport equations as the source of the probability of an induced transition. The calculation of the ex-

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*$[\mathbf{MH}] = \mathbf{M}\times\mathbf{H}$.

†Very frequently, these equations are used to calculate spin-spin relaxation, and thereby T_2 is called the spin-spin relaxation time. In solving such equations we obtain order-of-magnitude results (if the true value of T_2, the characteristic spin-spin relaxation time, is found). But, of course we cannot consider this an accurate quantitative and qualitative description of the behavior of the system.

ternal field in the framework of the transport equation leads, generally speaking, to invalid qualitative and quantitative results.

Note added in proof (March 5, 1962). The calculation of the external field can be carried through without any assumption about the smallness of $\hat{W}(t)$ (see [14]). The equation obtained in this way has the form

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{1}{\hbar^2}\sum_{r,s} e^{i(\omega_r+\omega_s)t} \times \left[\hat{V}^{(r)}\left[\left(\int_0^\infty e^{-i\hat{F}t'}\hat{V}^{(s)}e^{-i\omega_s t'}e^{i\hat{F}t'}\,dt'\right),\ \hat{\rho}\right]\right],$$

where by $\hat{\rho}$ is understood that part of the density matrix that is diagonal in the continuous indices, and $\hat{V}^{(r)}$ and ω_s are defined by the equalities

$$\hat{S}\hat{V}\hat{S}^{-1} = \sum_r \hat{V}^{(r)}e^{i\omega_r t}, \qquad \dot{\hat{S}} = \frac{i}{\hbar}\hat{S}\hat{E}(t)$$

[$\hat{E}(t)$ is the Hamiltonian operator of the dynamic subsystem, and $\hbar\hat{F}$ is the Hamiltonian operator of the dissipative subsystem]. This equation also differs from Eq. (12) in that: (1) smallness of $\hbar/\delta_2 E$ is not assumed and (2) that part of the function φ_r that corresponds to a shift in the energy levels is regarded as imaginary.

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