CERTAIN MODEL PROBLEMS OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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Submitted December 4, 1970

Zh. Eksp. Teor. Fiz. 60, 1913–1926 (May, 1971)

A regular method for deriving the macroscopic equations of motion from the exact microscopic equations, first suggested in[1], is developed further. The analysis is based on a consideration of three model problems in the thermodynamics of irreversible processes, namely the problem of Brownian motion of a quantum oscillator, the problem of motion of an N-level system in a random quantum external field, and the problem of motion of a particle in quantized and random external fields. In these three problems it is possible to assign a small parameter which is the product of the interaction energy and the correlation time of the external field. The method is free of a number of restrictions that must be imposed as a rule in solving similar problems.

1. INTRODUCTION

IN[1], in connection with the particular problem of deriving the macroscopic equations of a transverse electromagnetic field, a method of expansion in terms of semi-invariants was proposed.

The present paper is devoted to further development of this method using as an example three model problems of statistical physics: 1) the classical problem of Brownian motion of a quantum oscillator[2], 2) the problem of the motion of an N-level system in a random external field, and 3) the problem of motion of a particle in quantizing and random external fields. All three problems belong to the same class as the problem considered in[1]. Namely, in all cases it is possible to separate a light-weight system (transverse electromagnetic field, quantum oscillator, N-level system, particle in quantizing field) and a heavy system—the source of the random external field. Interest attaches to the characteristics of the light system.

In problems of statistical physics, the observation (measurement) lasts as a rule so long that even a weak interaction between the light and heavy systems leads to a noticeable change in the state of the light system. Formally this leads to the appearance of secular terms and thereby excluding the applicability of traditional methods of perturbation theory. In the proposed method, on the other hand, an infinite number of terms of the perturbation-theory series is summed; but since the summation of all the terms (i.e., the exact solution of the problem) is hardly ever possible, the main difficulty lies in the selection of the "principal diagrams." This procedure is feasible in practice only in those cases when a small parameter exists.

For the reasons just considered, it is incorrect to regard the interaction energy as the small parameter. In the problems discussed here the small parameter will in essence turn out to be the correlation time of the heavy system, i.e., the time during which the correlation functions (semi-invariants) of the heavy system differ noticeably from zero, and the idea of the method consists in the following.

An estimate of the terms of the perturbation-theory series for the mean value of the physical quantity of interest allows us to write down this mean value in the form

$$\sum_{n,\,m=0}^{\infty} c_{nm}(t)\,(\mu T_c)^m (\mu t)^n,$$

where c(t) are bounded functions of t, μ is a formal small parameter of the interaction energy (its dimension is $\sec^{-1}$), and T_c is the correlation time. This series can also be rewritten in the form

$$\sum_{n=0}^{\infty} c_n(t, \mu T_c)\,(\mu t)^n.$$

If the last series converges in a certain region of variation of the dimensionless parameter μT_c, then the problem reduces to an approximate calculation of its coefficients.

We shall not stop to analyze the convergence of the series, and will be satisfied by the fact that the results are physically reasonable.

2. BROWNIAN MOTION OF A QUANTUM OSCILLATOR

By quantum oscillator, following Schwinger, we shall mean a quantum system whose unperturbed Hamiltonian can be written in the form

$$\mathscr{H}_0 = \hbar\omega_0 y^+ y, \tag{1}$$

and the Hamiltonian of the interaction with the heavy system in the form

$$\mathscr{H}_{\text{int}} = \hbar(Q^+(t)y(t) + Q(t)y^+(t)) \equiv \sum_{\sigma=1,\,-1} \hbar Q(\sigma, t)\, y(\sigma, t), \tag{2}$$

where Q and Q^+ are the operators of the heavy system, $y(1, t) \equiv y(t)$, $y(-1, t) \equiv y^+(t)$, $Q(1, t) \equiv Q^+(t)$, $Q(-1, t) \equiv Q(t)$.

Following the procedure described in[1], we write down the equation of motion of the Heisenberg operator $y_H(t)$:

$$y_H(0) = y(0) + G_0(0,1)Q(1) + \sum_{n=2}^{\infty} G_0(0,1)Q(1,2,\ldots,n)\,y_r(n)\ldots y_H(2). \tag{3}$$

Here

$$G_0(0,1) = -i\theta(t_0 - t_1)[y(0), y(1)], \tag{4}$$

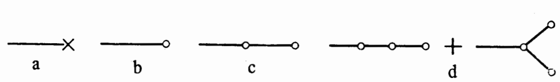
$$Q(0,1,\dots n) = (-i)^n\theta(t_0 - t_1)\theta(t_1 - t_2)\dots\theta(t_{n-1} - t_n)\cdot \times[\dots[[Q(0), Q(1)]Q(2)]\dots Q(n)]. \tag{5}$$

We proceed to write down Eqs. (3) in graphic form, letting a solid line with a cross on the end stand for the operator y, a solid line not terminating in a cross for the function G_0, and points for the operators Q.

We average the perturbation-theory series obtained in this manner and write down a graphic series for the mean values, expanding the mean values of the products of the operators over the semi-invariance in the manner used in[1].

However, unlike in[1], we shall not assume here that the instant t* tends to $-\infty$, we shall not require adiabatic turning on of the interaction, and we shall not impose the condition that the averaging of the operators of the heavy system and of the operators of the light system, taken at the instant of time t*, to be independent. Instead, we shall impose the condition that the semi-invariants be finite and require that the correlation time of the heavy system be small.

We now separate the diagrams in such a way that the separation lines cross only the continuous lines of the diagram and can be closed outside the diagram, and the separation lines crossing the input ends of the section do not cross its output ends. After performing this procedure, sections of diagrams within the same boundaries may turn out to be not interconnected. We shall call such sections compact. It is easy to see that a compact section differs from zero only if the temporal arguments of its ends are separated by $\lesssim T_c$. If there are no

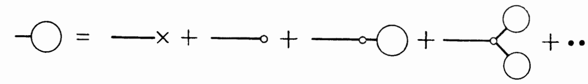


crosses inside a compact section and this section has n ends (both input and output), then the integration generated by these ends leads to the appearance of a factor $(\mu T_c)^{n-1}\mu T$, and in addition the internal integrations can also increase the degree of μT_c. On the other hand, if the compact section contains crosses and furthermore m output ends begin immediately at these crosses, then there appears a factor $(\mu T_c)^{n-m}$, and the degree of μt is equal to zero.

The foregoing estimates enable us to choose the main sequence of the diagrams. Let us consider, by way of an example, the equation for $\langle y\rangle$. The term proportional to $(\mu T)^0$ and containing no factor μT_c is generated only by the diagram a. The term proportional to $(\mu t)(\mu T_c)^0$ is generated by the diagram b. It is easy to see that there are no diagrams proportional to $(\mu t)^2(\mu T_c)^0$. The minimum degree of the factor μT_c corresponding to $(\mu t)^2$ is unity. The corresponding term is generated by the diagram c. Diagrams contributing to the term proportional to $(\mu t)^3$ are shown in Fig. d. Both lead to the appearance of the factor $(\mu T_d)^2$.

Continuing this reasoning, we can verify that the minimal degree of μT_c, corresponding to $(\mu t)^n$, is $n-1$.

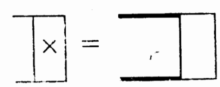
The selection and summation of the corresponding diagrams are carried out in elementary fashion and lead to Eq. (6) without the first term in the right-hand side.

 (6)

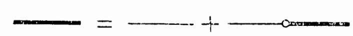
The meaning of this equation is obvious. Since we neglect terms of the type of Fig. a, it determines the forced motion of the system in the nonlinear approximation, with allowance for the damping.

The selection and summation of diagrams proportional to equal powers of μT_c and μt lead to Eq. (6) with allowance for the first term in the right-hand side of the equation. In this approximation, account is taken of the initial conditions, i.e., of the free oscillations of the system.

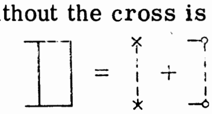
If the coherent component of the external field is equal to zero, then after a certain time (the relaxation time) the solution of Eq. (6) is damped. In this case interest attaches to the correlation function $S_2(y(2), y(1))$. Here, too, the selection of the principal diagrams entails no difficulty and leads to the expression

 (7)

where the thick line satisfies the equation

 (8)

and the block without the cross is defined by the sum

 (9)

Far from t* the contribution of the first term of this block attenuates, so that we can retain only the second term.

Physical considerations show that if the heavy system is in the state of thermodynamic equilibrium, then the light system, after relaxing, should reach a state of thermodynamic equilibrium. We shall show that this indeed follows from the obtained equations.

We rewrite to this end the equations in analytic form. We have

$$G(t_1 - t_2) = G_0(t_1 - t_2) + \int dt_3\,dt_4\,G_0(t_1 - t_3)A(t_3 - t_4)G(t_4 - t_2), \tag{10}$$

where

$$G_0(t_1 - t_2) = -i\theta(t_1 - t_2)[y(t_1), y^+(t_2)],$$
$$A(t_1 - t_2) = -i\theta(t_1 - t_2)\langle[Q(t_1), Q^+(t_2)]\rangle.$$

For the Fourier transform of the function $R(t_1, t_2) \equiv S_2(y_\Gamma^+(t_2), y_\Gamma(t_1))$ we have

$$\tilde{R}(\omega) = (2\pi)^2\tilde{G}(\omega)\tilde{G}^*(\omega)J(\omega)e^{-\beta\omega}, \tag{11}$$

where

$$J(\omega) = \frac{1}{2\pi}\int dt\langle Q(t_1 + t)Q^+(t_1)\rangle e^{i\omega t},$$

and by virtue of (10)

$$\tilde{G}^{-1}(\omega) = \tilde{G}_0^{-1}(\omega) - (2\pi)^2\tilde{A}(\omega). \tag{12}$$

Since certain known spectral relations must be satisfied between the Fourier transforms of the correlation functions in the state of thermodynamic equilibrium[3], we have

$$\tilde{A}(\omega) = -\frac{1}{2\pi}\int d\omega'\frac{J(\omega')}{\omega' - \omega - i\varepsilon}(1 - e^{-\beta\omega'})$$
$$= -\frac{1}{2\pi}\fint d\omega'\frac{J(\omega')}{\omega' - \omega}(1 - e^{-\beta\omega'}) - \frac{i}{2}J(\omega)(1 - e^{-\beta\omega}). \tag{13}$$

Expanding (11), we obtain with account taken of (12) and (13)

$$\bar{R}(\omega)=\frac{i}{e^{\beta\omega}-1}(\bar{G}(\omega)-\bar{G}^{*}(\omega)),$$

i.e., precisely the sought spectral relation, but of course under the condition that

$$G(t_1-t_2)=-i\theta(t_1-t_2)\langle[y_{\mathrm{H}}(t_1),\ y_{\mathrm{H}}^{+}(t_2)]\rangle. \tag{14}$$

Let us verify that condition (14) is indeed satisfied, at least in the assumed approximation.

Indeed, for the difference

$$S_2(y_{\mathrm{H}}(t_1),\ y_{\mathrm{H}}^{+}(t_2))-S_2(y^{+}(t_2),\ y(t_1))\equiv iK(t_1-t_2)$$

we have the following expression:

$$iK(t_1-t_2)=\int dt_3\,dt_4\,G(t_1-t_3)G^{*}(t_2-t_4)\langle[Q(t_3),Q^{+}(t_4)]\rangle$$

or

$$K(t_1-t_2)=\int dt_3\,dt_4\,G(t_1-t_3)G^{*}(t_2-t_4)\{A(t_3-t_4)-A^{*}(t_4-t_3)\}.$$

The difference in the curly brackets can be transformed by adding to it the difference

$$G_0^{*-1}(t_4-t_3)-G_0^{-1}(t_3-t_4)$$

which has zero value. We then obtain

$$K(t_1-t_2)=G(t_1-t_2)-G^{*}(t_2-t_1).$$

Multiplying the last relation by $\theta(t_1-t_2)$ or $\theta(t_2-t_1)$, we finally verify that $G(t_1-t_2)$ is a retarded Green's function and $G^{*}(t_1-t_2)$ is an advanced Green's function.

3. N-LEVEL SYSTEM IN A RANDOM EXTERNAL FIELD

Let the only coordinate of a certain quantum-mechanical system be capable of assuming only a finite number (say N) of values. We call this an N-level system. It is perfectly obvious that the operator of such a system can be represented in the form of an $N\times N$ matrix, and there exist N^2 linearly-independent operators. It is quite easy to show (we omit the proof for the sake of brevity) that it is always possible to choose the basis in such a way that it contains a unit matrix and all the remaining matrices are Hermitian and have a zero trace.

We denote the basis operators by $\gamma(\sigma,\ t)$ ($\sigma = 1,\ 2,\ \ldots,\ N^2$). Obviously, the following relations are satisfied

$$\gamma(\sigma_1,t)\gamma(\sigma_2,t)=\sum_{\sigma_3}b(\sigma_1,\sigma_2,\sigma_3)\gamma(\sigma_3,t),$$
$$[\gamma(\sigma_1,t),\gamma(\sigma_2,t)]=i\sum_{\sigma_3}c(\sigma_1,\sigma_2,\sigma_3)\gamma(\sigma_3,t), \tag{15}$$

with

$$ic(\sigma_1,\sigma_2,\sigma_3)=b(\sigma_1,\sigma_2,\sigma_3)-b(\sigma_2,\sigma_1,\sigma_3).$$

In the most general case the interaction Hamiltonian can be represented in the form

$$\mathcal{H}_{\mathrm{int}}=\hbar\sum_{\sigma}Q(\sigma,t)\gamma(\sigma,t), \tag{16}$$

and the unperturbed Hamiltonian can be set equal to zero. It will be convenient in what follows, however, to separate from (16) the part regular in the external field, and include it in the unperturbed Hamiltonian, which consequently is written in the form

$$\mathcal{H}_0=\hbar\sum_{\sigma}\langle Q(\sigma,t)\rangle\gamma(\sigma,t),$$

and we obtain in place of (16)

$$\mathcal{H}_{\mathrm{int}}=\hbar\sum_{\sigma}Q'(\sigma,t)\gamma(\sigma,t), \tag{17}$$

where

$$Q'(\sigma,\ t)=Q(\sigma,\ t)-\langle Q(\sigma,\ t)\rangle.$$

The operators $\gamma(\sigma,\ t)$ in the interaction representation satisfy the system of equations

$$\frac{\partial\gamma(\sigma,t)}{\partial t}=\sum_{\sigma_1,\sigma_2}c(\sigma,\sigma_1,\sigma_2)\langle Q(\sigma_1,t)\rangle\gamma(\sigma_2,t), \tag{18}$$

the solution which at $t > t_1$ (where t_1 is any instant of time) can be written in the form

$$\gamma(\sigma,t)=\sum_{\sigma_1}G_0(\sigma,t;\ \sigma_1,t_1)\gamma(\sigma_1,t_1).$$

The function G_0 satisfies the equation

$$\frac{\partial G_0(\sigma,t;\ \sigma_1,t_1)}{\partial t}-\sum_{\sigma_2,\sigma_3}c(\sigma,\sigma_2,\sigma_3)\langle Q(\sigma_2,t)\rangle G_0(\sigma_3,t;\ \sigma_1,t_1)=\delta(\sigma,\sigma_1)\delta(t-t_1). \tag{19}$$

This makes it possible to obtain for $\gamma_{\mathrm{H}}(\sigma,\ t)$ the following system of nonlinear operator equations

$$\gamma_{\mathrm{H}}(0)=\gamma(0)+G_0(0,1)c(1,2,3)Q'(2)\gamma_{\mathrm{H}}(3)$$
$$+\sum_{n=4}^{\infty}G_0(0,1)c(1,2,3)Q(2,4\ldots n)\gamma_{\mathrm{H}}(n)\ldots\gamma_{\mathrm{H}}(3), \tag{20}$$

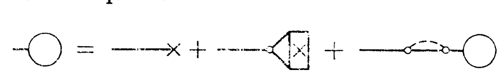
where

$$Q(0,1,\ldots,n)=(-i)^{n}\theta(t_0-t_1)\theta(t_1-t_2)\ldots\theta(t_{n-1}-t_n)$$
$$\cdot[\ldots[[Q(0),\ Q(1)]Q(2)]\ldots Q(n)].$$

An estimate of the compact sections shows that if a compact section does not contain the operators $\gamma(t^{*})$ and has 2n output and input ends, then it generates the factor $(\mu T_c)^{n-1}\mu t$. On the other hand, the compact section containing the operators $\gamma(t^{*})$ does not increase the degree of μt.

We obtain an equation for $\langle\gamma(\sigma,\ t)\rangle$ in the lowest order in μT_c, i.e., retaining only diagrams containing equal powers of μT_c and μt. We note in this connection that separation of the regular part of the interaction Hamiltonian in the main Hamiltonian excludes the appearance of compact section generating the factor $(\mu T_c)^n(\mu t)^m$ with $n < m$.

The summation of the diagrams of the main sequence leads to the equation

 (21)

In this equation the block with two output ends is $\langle\gamma_{\mathrm{H}}(2)\gamma_{\mathrm{H}}(1)\rangle$. Since this block is directly closed on a compact section, it suffices to know its value only at $t_1 - t_2 \sim T_c$, and this makes it possible to express it only in terms of $\langle\gamma_{\mathrm{H}}(2)\rangle$. To this end it suffices, putting $t^{*} = t_2$ and expanding $\langle\gamma_{\mathrm{H}}(2)\gamma_{\mathrm{H}}(1)\rangle$ in an iteration series, to retain only its first term. As a result we obtain

$$\langle\gamma_{\mathrm{H}}(0)\rangle=\langle\gamma(0)\rangle+G_0(0,\ 1)A(1,\ 2)\langle\gamma_{\mathrm{H}}(2)\rangle, \tag{22}$$

where

$$A(1,2)=c(1,3,4)G_0(4,6)\langle Q(3,5)\rangle b(5,6,2)+c(1,3,4)G_0(4,6)S_2(Q(3),\ Q(5))c(6,5,2).$$

For the unit operator, this system of equations gives an obvious solution. As to the remaining operators, it is probably meaningful to assume that none of them commute with the total Hamiltonian. It is clear from physical considerations that the system should forget it prior history. For this reason, it may be convenient to change over from the system of integral equations (22) to a system of integro-differential equations that no longer contain $\langle\gamma(0)\rangle$. This transition is very easily effected if it is recognized that $\langle\gamma\rangle$ and G_0 satisfy Eqs. (18) and (19), which can be written symbolically as $L\gamma = 0$ and $LG_0 = 1$. From this we obtain

$$(L-A)\langle\gamma_H\rangle=0. \tag{23}$$

It is meaningful to consider two particular cases when the integro-differential equations reduce simply to differential equations.

1. $\langle Q\rangle$ can be represented in the form of a sum of a large time-constant term Q_0 and a small time-dependent term q.

2. T_c is much smaller than the characteristic time scale of the unperturbed system.

In both cases we assume that the correlation functions of the external field depend only on the time differences, and confine ourselves for simplicity to two-level systems only.

As the basis we choose the unit operator $\gamma_0 = 1$ and three operators γ_i (i = 1, 2, 3) satisfying the relations

$$\gamma_i\gamma_0=\gamma_0\gamma_i=\gamma_i,\qquad \gamma_i\gamma_k=ie_{ikl}\gamma_l,\quad [\gamma_i,\gamma_k]=2ie_{ikl}\gamma_l. \tag{24}$$

Calculating the kernel of the integral operator in (23), or more accurately the function G_0 contained in it, we replace in (19) approximately $\langle Q_i\rangle$ by $\delta_{i3}Q_0$. We obtain

$$G_{0ik}(t)=\theta(t)\left\{(\delta_{ik}-\delta_{i3}\delta_{k3})\cos\omega_0 t+e_{i3k}\frac{Q_0}{|Q_0|}\sin\omega_0 t+\delta_{i3}\delta_{k3}\right\} \tag{25}$$

where

$$\omega_0=2|Q_0|,$$

and with this value of G_0 the following equation for $\langle\gamma_H\rangle$ (we omit the symbol for the Heisenberg operator)

$$\frac{\partial\langle\gamma_i(t)\rangle}{\partial t}=2e_{ikl}\langle Q_k(t)\rangle\langle\gamma_l(t)\rangle+\int dt_1\,A_{ik}(t-t_1)\langle\gamma_k(t_1)\rangle+B_i, \tag{26}$$

where

$$A_{ik}(t-t_1)=-{}^2/_3\theta(t-t_1)\{(\delta_{ik}-\delta_{i3}\delta_{k3})(1+\cos\omega_0(t-t_1))+2\delta_{i3}\delta_{k3}\cos\omega_0(t-t_1)+e_{i3k}(Q_0/|Q_0|)\sin\omega_0(t-t_1)\}\times\langle\{Q_p'(t),\ Q_p'(t_1)\}\rangle,$$

$$B_i=-\frac{4i}{3}\delta_{i3}\int dt_1\langle[Q_p(t),Q_p(t_1)]\rangle\theta(t-t_1)\sin\omega_0(t-t_1).$$

The same equation can be written also in a different form, by expressing B_i in terms of the equilibrium value $\langle\gamma\rangle$ in the external field Q_0. Putting in (26) $\partial\langle\gamma\rangle/\partial t = 0$ and $\langle Q\rangle = Q_0$, we solve the resultant equation with respect to $\langle\gamma\rangle$. In particular, in the state of thermodynamic equilibrium we obtain for the only non-zero component

$$\langle\gamma_3\rangle=-\frac{1-e^{-\beta\hbar\omega_0}}{1+e^{-\beta\hbar\omega_0}}. \tag{27}$$

We now subtract from (26) the equation for the determination of the stationary $\langle\gamma\rangle$. We have

$$\frac{\partial\langle\gamma_i(t)\rangle}{\partial t}=2e_{ikl}\langle Q_k(t)\rangle\langle\gamma_l(t)\rangle+\int dt_1\,A_{ik}(t-t_1)\left(\langle\gamma_k(t_1)\rangle-\gamma_k^{eq}\right). \tag{28}$$

Here γ_k^{eq} denotes the equilibrium value of $\langle\gamma_k(t)\rangle$.

If the damping is small and the alternating external field is weak, then the solutions of the system (28) for $\langle\gamma_1\rangle$ and $\langle\gamma_2\rangle$ constitute a signal with low-frequency modulation and with a carrier frequency ω_0, while $\langle\gamma_3\rangle$ represents simply a slowly varying quantity. It is therefore meaningful to replace the integral kernel by its Fourier component. As a result we obtain the following equations:

$$\frac{\partial\langle\gamma_3(t)\rangle}{\partial t}=2e_{3kl}\langle Q_k(t)\rangle\langle\gamma_l(t)\rangle-\frac{1}{T_1}\left(\langle\gamma_3(t)\rangle-\gamma_3^{eq}\right), \tag{29}$$

and for i = 1, 2

$$\frac{\partial\langle\gamma_i(t)\rangle}{\partial t}=2e_{ikl}\langle Q_k(t)\rangle\langle\gamma_l(t)\rangle-\frac{1}{T_2}\langle\gamma_i(t)\rangle-\frac{\Omega_1}{\omega_0}\frac{\partial\langle\gamma_i(t)\rangle}{\partial t}-e_{i3k}\frac{Q_0}{|Q_0|}\left(\Omega_2\langle\gamma_k(t)\rangle-\frac{\Omega_3}{\omega_0}\frac{\partial\langle\gamma_k(t)\rangle}{\partial t}\right), \tag{30}$$

where

$$\frac{1}{T_1}=4\pi J(\omega_0)\left(1+e^{-\beta\hbar\omega_0}\right), \tag{31}$$

$$\frac{1}{T_2}=2\pi J(0)+2\pi J(\omega_0)(1+e^{-\beta\hbar\omega_0})+\pi J(2\omega_0)(1+e^{-2\beta\hbar\omega_0}), \tag{32}$$

$$\Omega_1=\int dE\frac{J(E)(1+e^{-\beta E})}{E-2\hbar\omega_0}+2\int dE\frac{J(E)(1+e^{-\beta E})}{E-\hbar\omega_0}, \tag{33}$$

$$\Omega_2=-\int dE\frac{J(E)(1+e^{-\beta E})}{E-2\hbar\omega_0}, \tag{34}$$

$$\Omega_3=2\pi J(0)-\pi J(2\omega_0)(1+e^{-2\beta\hbar\omega_0}), \tag{35}$$

J(E) is the spectral function of the component Q_p with respect to one of the axes.

The physical assumptions made in the derivation of Eqs. (29) and (30) are such that they are expected to lead to the Bloch equations. Indeed, Eq. (29) coincides fully with the Bloch equation for the longitudinal component of the magnetic moment. On the other hand, Eqs. (30) differ from the Bloch equations for the transverse component in the presence of additional terms proportional to Ω_1, Ω_2, and Ω_3. These terms are small only in the case when the product $J(E)(1 + e^{-\beta E})$ changes little in the interval $0 < E < 2\hbar\omega_0$. The smallness of this variation signifies, in turn, that $T_1 = T_2$, as can be seen from a comparison of (31) and (32). But it is precisely in this case that it is possible to obtain approximate equations in which it is not required that the alternating field be small compared with the constant field.

The slowness of the variation of J(E) denotes smallness of T_c compared with $1/\omega_0$. Therefore, in calculating the integral kernel of (22), we can put approximately

$$G_{0ik}(t_1,\ t_2)=\delta_{ik}\theta(t_1-t_2)+2e_{ilk}\langle Q_l(t_1)\rangle(t_1-t_2)\theta(t_1-t_2).$$

We then obtain the following system of equations

$$\frac{\partial\langle\gamma_i(t)\rangle}{\partial t}=2e_{ikl}\langle Q_k(t)\rangle\langle\gamma_l(t)\rangle-\frac{1}{T}\left(\langle\gamma_i(t)\rangle-\chi_0\langle Q_i(t)\rangle\right), \tag{36}$$

where $1/T = 8\pi J(0)$, $\chi_0 = -h\beta$.

This system of equations coincides, apart from the notation, with the system proposed in[4].

4. PARTICLE IN A QUANTIZING OR IN A RANDOM EXTERNAL FIELD

This problem is similar in many respects to the two preceding ones, but differs from the first one in the form of the interaction Hamiltonian, which conserves the number of particles, and from the second in the infinite number of states of the unperturbed system.

The Hamiltonian of the unperturbed system—particle in a quantizing field—is

$$\mathscr{H}_0 = \sum_\sigma \hbar\omega(\sigma)\psi^+(\sigma)\psi(\sigma),$$

and the Hamiltonian of interaction with the random field is

$$\mathscr{H}_{\text{int}} = \hbar \sum_{\sigma,\sigma'} \psi^+(\sigma,t)Q(\sigma,\sigma',t)\psi(\sigma',t).$$

The equation of motion of the Heisenberg operator ψ_H is

$$\psi_H(0) = \psi(0) + G_0(0,1)Q(1,2)\psi_H(2)$$

$$+ G_0(0,1)\sum_{n=2}^{\infty}\psi_H^+(3)\ldots\psi_H^+(2n-1)\,(1,2;3,4;\ldots;2n-1,2n)\psi_H(2n)\ldots\psi_H(2), \tag{37}$$

where

$$G_0(0,1) = -i\theta(t_0 - t_1)\,[\psi(0),\ \psi^+(1)]_\pm,$$

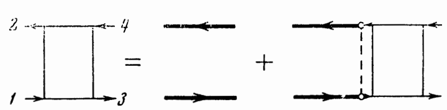
$$(1,2;3,4;\ldots,2n-1,2n) = (-i)^n\theta(t_1-t_3)\theta(t_3-t_5)\ldots\theta(t_{2n-3}-t_{2n-1})\cdot$$
$$\times[\ldots[Q(1,2),\,Q(3,4)]\ldots Q(2n-1,2n)].$$

The operator equations (37) make it possible to obtain equations for the mean values at an arbitrary number of particles and for a relatively arbitrary character of the random external field. We shall dwell below only on the case of motion of one particle in a field at thermodynamic equilibrium. For simplicity we assume that the $\omega(\sigma)$ with different σ are different from one another and confine ourselves to the same approximation as in the two preceding problems.

One of the quantities that may be of interest is $\langle\psi_H^+(2)\psi_H(1)\rangle$. It is connected with the similar quantity specified at $t_1 = t_2 = t^*$ by the relation

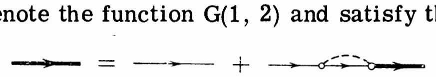
$$\langle\psi_H^+(2)\psi_H(1)\rangle = \Theta(1,2;3,4)\langle\psi_H^+(4)\psi_H(3)\rangle|_{t_3=t_4=t^*}. \tag{38}$$

The quantity Θ, on the other hand, satisfies the equation



(39)

in which the thick lines with the arrows from left to right denote the function G(1, 2) and satisfy the equation



(40)

and the lines with the arrows in the opposite direction denote the complex conjugate equation.

Equation (40), after changing over to the Fourier representation, assumes the analytic form

$$\tilde{G}(\sigma_1,\sigma_2|\omega) = \frac{1}{2\pi}\frac{\delta_{\sigma_1\sigma_2}}{\omega-\omega(\sigma_1)+i\varepsilon}$$
$$+\frac{2\pi}{\omega-\omega(\sigma_1)+i\varepsilon}\sum_{\sigma_3}\tilde{M}(\sigma_1,\sigma_3|\omega)\tilde{G}(\sigma_3,\sigma_2|\omega), \tag{41}$$

where

$$\tilde{M}(\sigma_1,\sigma_3|\omega) = \frac{1}{2\pi}\sum_{\sigma_4}\int\frac{J(\sigma_1\sigma_4;\,\sigma_4,\sigma_3|\omega-\omega')\,d\omega'}{\omega'-\omega(\sigma_4)+i\varepsilon},$$

$$J(\sigma_1,\sigma_2;\,\sigma_3,\sigma_4|\omega) = \frac{1}{2\pi}\int\langle Q(\sigma_1,\sigma_2,t)Q(\sigma_3,\sigma_4,t')\rangle e^{i\omega(t-t')}dt.$$

When solving (41) it must be understood that at sufficiently small μT_c the turning on of the interaction can lead only to a shift of the pole of the function G_0 by an amount on the order of $o(\mu T_c)$ or smaller, and to an increment of the same order.

On this basis, we take into account only the pole part in the vicinity of $\omega = \omega(\sigma)$. As a result we obtain

$$\tilde{G}(\sigma_1,\sigma_2|\omega) = \frac{1}{2\pi}\frac{\delta_{\sigma_1\sigma_2}}{\omega-\omega(\sigma_1)-2\pi\tilde{M}(\sigma_1,\sigma_1|\omega(\sigma_1))}$$
$$\equiv\frac{1}{2\pi}\frac{\delta_{\sigma_1\sigma_2}}{\omega-\omega(\sigma_1)-\Delta(\sigma_1)+i\gamma(\sigma_1)}.$$

We note that

$$\gamma(\sigma_1) = \pi\sum_{\sigma'}J(\sigma_1,\sigma';\,\sigma',\sigma_1|\omega(\sigma_1)-\omega(\sigma')) > 0.$$

Proceeding to the solution of Eq. (39), we note that in the assumed approximation we have for $t_1 > t_2$

$$\Theta(\sigma_1,t_1;\,\sigma_2,t_2;\,3,4) = i\sum_{\sigma_1'}G(\sigma_1,t_1;\,\sigma_1',t_2)\Theta(\sigma_1',t_2;\,\sigma_2,t_2;\,3,4)$$

(without integration with respect to t_2), and for $t_1 < t_2$

$$\Theta(\sigma_1,t_1;\,\sigma_2,t_2;\,3,4) = -i\sum_{\sigma_2'}G^*(\sigma_2,t_2;\,\sigma_2',t_1)\Theta(\sigma_1,t_1;\,\sigma_2',t_1;\,3,4).$$

In addition, if $|t_1 - t_2| \ll 1/\gamma$, then the functions G can be replaced by G_0. Similar relations can be written down also for the ends 3 and 4 of the function Θ, and for the function Θ_0—the first term of the right-hand side of (39).

Taking this into consideration, we transform the equation for $\Theta(1, 2; 3, 4)$ into an equation for the quantity

$$\Theta(\sigma_1,t_1;\,\sigma_2,t_1|\sigma_3,t_3;\,\sigma_4,t_3) \equiv \Theta(\sigma_1,\sigma_2;\,\sigma_3,\sigma_4|t_1-t_3).$$

We obtain

$$\Theta(\sigma_1,\sigma_2;\,\sigma_3,\sigma_4|t_1-t_3) = \Theta_0(\sigma_1,\sigma_2;\,\sigma_3,\sigma_4|t_1-t_3)$$
$$+\sum_{\substack{\sigma_5,\sigma_6\\\sigma_7,\sigma_8}}\int dt'\,dt''\,\Theta_0(\sigma_1,\sigma_2;\,\sigma_5,\sigma_6|t_1-t')A(\sigma_5,\sigma_6;\,\sigma_7,\sigma_8|t'-t'')\cdot$$
$$\times\Theta(\sigma_7,\sigma_8;\,\sigma_3,\sigma_4|t''-t_3), \tag{42}$$

where

$$A(\sigma_5,\,\sigma_6;\,\sigma_7,\,\sigma_8|t'-t'')$$
$$= G_0(\sigma_5|t'-t'')\langle Q(\sigma_8,\sigma_6,t')Q(\sigma_5,\sigma_7,t'')\rangle G_0^*(\sigma_8|t'-t'')$$
$$+ G_0^*(\sigma_6|t'-t'')\langle Q(\sigma_8,\sigma_6,t'')Q(\sigma_5,\sigma_7,t')\rangle G_0(\sigma_7|t'-t'').$$

It is obvious that

$$\tilde{A}(\sigma_5,\sigma_6;\,\sigma_7,\sigma_8|\omega) = \frac{i}{2\pi}\int d\omega'\left\{\frac{J(\sigma_8,\sigma_6;\,\sigma_5,\sigma_7|\omega-\omega')}{\omega'-(\omega(\sigma_5)-\omega(\sigma_8))+i\varepsilon}\right.$$
$$\left.+\frac{J(\sigma_8,\sigma_6;\,\sigma_5,\sigma_7|-\omega+\omega')}{\omega'+(\omega(\sigma_6)-\omega(\sigma_7))+i\varepsilon}\right\}$$

$$\text{Re}\,\tilde{A}(\sigma_5,\,\sigma_6;\,\sigma_7,\,\sigma_8|\omega) = {}^1\!/_2\{J(\sigma_8,\sigma_6;\,\sigma_5,\sigma_7|\omega-\omega(\sigma_5)+\omega(\sigma_8))$$
$$+J(\sigma_8,\sigma_6;\,\sigma_5,\sigma_7|-\omega-\omega(\sigma_6)+\omega(\sigma_7))\}.$$

We consider the Fourier transform of the function $\Theta_0(\sigma_1,\,\sigma_2;\,\sigma_3,\,\sigma_4|t_1-t_3)$. It has poles in the vicinity of the order of μT_c points $\omega(\sigma_1)-\omega(\sigma_3)$. Thus, in the vicinity of the same point there are poles of the function $\tilde{\Theta}_0$ with different values of σ_1 and σ_3. Therefore, unlike G, the turning on of the interaction with a random field leads not only to a weak shift of the poles but also to connections between those functions $\tilde{\Theta}$ which have identical poles.

If we are interested only in the pole part of the function $\widetilde{\Theta}$, then after changing over to the Fourier transforms Eq. (42) breaks up into a series of independent systems of equations, each of which corresponds to a definite pole of the function $\widetilde{\Theta}_0$.

Thus, the pole lying in the vicinity of zero corresponds to the system

$$\widetilde{\Theta}(\sigma_1, \sigma_3|\omega) = \widetilde{\Theta}_0(\sigma_1, \sigma_3|\omega) + (2\pi)^2 \sum_{\sigma_5\sigma_7} \widetilde{\Theta}(\sigma_1, \sigma_5|\omega) A(\sigma_5, \sigma_5; \sigma_7, \sigma_7|\omega) \widetilde{\Theta}(\sigma_7, \sigma_3|\omega), \quad (43)$$

where

$$\widetilde{\Theta}(\sigma_1, \sigma_3|\omega) \equiv \widetilde{\Theta}(\sigma_1, \sigma_1; \sigma_3, \sigma_3|\omega),$$

$$\widetilde{\Theta}_0(\sigma_1, \sigma_3|\omega) = \frac{i}{2\pi} \frac{\delta_{\sigma_1\sigma_3}}{\omega + 2i\gamma(\sigma_1)}.$$

The function Re $\widetilde{A}(\sigma_5, \sigma_5; \sigma_7, \sigma_7|\omega)$ is even, and accordingly the imaginary part is odd. Therefore

$$\sum_{\sigma_2} \{(\omega + 2i\gamma(\sigma_1))\delta_{\sigma_1\sigma_2} - 2\pi i J(\sigma_2, \sigma_1; \sigma_1, \sigma_2|\omega(\sigma_2) - \omega(\sigma_1))\} \cdot \widetilde{\Theta}(\sigma_2, \sigma_3|\omega) = \frac{i}{2\pi} \delta_{\sigma_1\sigma_3}. \quad (44)$$

Summing both parts of (44) with respect to σ_1, we obtain

$$\sum_{\sigma_1} \widetilde{\Theta}(\sigma_1, \sigma_3|\omega) = \frac{i}{2\pi} \frac{1}{\omega + i\varepsilon}.$$

Thus, as expected, among the poles of the function $\widetilde{\Theta}$ there is a pole lying at the point $\omega = 0$.

Equation (44) can be transformed into an equation for the populations. Taking the inverse Fourier transform of (44) multiplied by $\langle \psi^+(\sigma_3, t^*)\psi(\sigma_3, t^*)\rangle$, we obtain for $t > t^*$ the equation

$$\frac{dp(\sigma_1)}{dt} = -\sum_{\sigma_2} w(\sigma_2, \sigma_1) p(\sigma_1) + \sum_{\sigma_2} w(\sigma_1, \sigma_2) p(\sigma_2), \quad (45)$$

where

$$w(\sigma_1, \sigma_2) = 2\pi J(\sigma_2, \sigma_1; \sigma_1, \sigma_2|\omega(\sigma_2) - \omega(\sigma_1))$$

and

$$p(\sigma) = \langle \psi_r^+(\sigma, t)\psi_r(\sigma, t)\rangle.$$

We have thus obtained the ordinary kinetic equation. We note that

$$w(\sigma_1, \sigma_2) = e^{\beta\hbar(\omega(\sigma_2) - \omega(\sigma_1))} w(\sigma_2, \sigma_1),$$

by virtue of which Eq. (45) has a stationary solution

$$p(\sigma) = \frac{e^{-\beta\hbar\omega(\sigma)}}{\sum_{\sigma'} e^{-\beta\hbar\omega(\sigma')}}. \quad (46)$$

5. DISCUSSION OF RESULTS

The problem of the interaction of an N-level system with a thermostat was considered in detail by Wangsness and Bloch[5]. The technique proposed by them in connection with this problem was further developed by Bloch[6], Hubbard[7], and Faĭn[8]. The authors of these papers tend, first of all, to reduce the initial Neumann equation to a simpler form, and go over to observables only in the last stage. The method of solving the problem is such that it leads by virtue of its very idea to equations describing a Markov process. This, naturally, forces the authors to impose a number of serious limitations both on the character of the interaction and on the initial conditions.

On the other hand, the method proposed in[1] and developed in the present paper leads to equations describing processes with memory, i.e., non-Markov processes, and only in some particular cases can they be approximately represented as Markov processes. Argyres and Kelley[9] likewise arrive at equations describing non-Markov processes. Unlike the cited papers, the initial equations are transformed into equations for observables already in the first stage. We regard such an approach as more natural. Indeed, it is well known that although the density matrix does carry a tremendous amount of information on the behavior of the systems, it nevertheless does not make it possible to calculate many-time correlation functions. It is known from experience that only a small number of observables satisfy only simple phenomenological equations. One can therefore hope (or even be convinced) that these equations can be derived from the dynamic ones. In addition, it is known that the phenomenological equations contain precisely many-time correlation functions. The "simplicity" requirement imposed on the density matrix is too strong and unnecessary. For the same reasons, knowledge of the density matrix will hardly yield an equation for observables of a wide class of processes. On the other hand, the proposed method makes it possible to calculate the mean values of different operators and many-time correlation functions in accordance with a single scheme. Finally, within the framework of this method there are no fundamental difficulties for changing over to higher approximations.

We call attention to one more important circumstance in connection with the Bloch equations (29) and (30). They contain five parameters, four of which can be expressed in terms of the fifth one $1/T_1$, specified as a function of the constant external field. This possibility permits, first, at least in principle, to verify experimentally the validity of the made statements; second, it determines the maximum information that can be obtained within the framework of a given experimental method. Thus, in the given particular case it is clear that the entire information is contained in $1/T_1$, and measurement of the remaining parameters will not yield anything new.

The author is grateful to B. Ya. Zel'dovich and L. V. Keldysh for a discussion of the results.

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Translated by J. G. Adashko
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