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Variational Principle for Derivation of Macroscopic Equations

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It is pointed out that the Schwinger variational principle of scattering theory applies to the case of linear and nonlinear relaxation problems in quantum statistics. By means of this principle it is possible to derive closed sets of equations for expectation values. To illustrate this variational method and to clarify the connection to other standard approaches some simple examples are treated for which the equations of motion are already known.

KEY WORDS: Variational principle; von Neumann equation; equations for macroscopic observables; relaxation.

1. INTRODUCTION

For classical dynamic correlation functions of linear response a Schwinger-type variational principle has been formulated.[1] Later the same idea of such a variational principle has independently been introduced for quantum systems.[2] It is the purpose of this paper to point out that this variational principle, formally taken from scattering theory, can be extended to the case of general dynamics of macroscopic observables. In this general form the variational principle can be used to derive closed systems of equations for macroscopic variables from the microscopic von Neumann equation. In this paper we will give no new equations of motion. We wish only to establish the variational principle and to demonstrate how it works. To this end we treat simple physical examples and show how standard equations of statistical mechanics emerge from this variational approach. The examples considered can be a guide to find a suitable variational ansatz in complicated cases.

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2. STATIONARY VARIATIONAL PRINCIPLE

Consider a system with time-independent Hamiltonian $\mathcal{H}$ described by a statistical operator ρ. Then the time evolution of any observable A_v can be expressed as follows:

$$\langle A_v\rangle(t) = \mathrm{Tr}\, \rho e^{iLt} A_v \tag{1}$$

where the Liouvillian L is defined by

$$LA = (1/\hbar)[\mathcal{H}, A] \tag{2}$$

Now from (1) it is evident that the Laplace transform of $\langle A_v\rangle(t)$ can be written as a resolvent

$$\langle A_v\rangle(z) = -i\int_0^\infty dt\, e^{izt}\langle A_v\rangle(t) = \mathrm{Tr}\, \rho(z+L)^{-1}A_v \tag{3}$$

The calculation of a resolvent is a basic mathematical problem in scattering theory.[3] Hence we can transfer the methods used there to quantum statistics and write down a Schwinger-type functional

$$F[\phi', \phi_v] = \mathrm{Tr}\, \phi' A_v + \mathrm{Tr}\, \rho\phi_v - \mathrm{Tr}\, \phi'(z+L)\phi_v \tag{4}$$

which has to be varied with respect to ϕ' and ϕ_v. It is a simple matter to show that F is stationary for

$$\phi_{v\,\mathrm{st}} = (z+L)^{-1}A_v = A_v(z) \tag{5a}$$

$$\phi'_{\mathrm{st}} = (z-L)^{-1}\rho = \rho(z) \tag{5b}$$

and the stationary value of F is given by

$$F[\phi'_{\mathrm{st}}, \phi_{v\,\mathrm{st}}] = \mathrm{Tr}\, \rho(z+L)^{-1}A_v = \langle A_v\rangle(z) \tag{6}$$

Starting from the functional (4) and a suitable ansatz for ϕ' and ϕ_v one can find approximations for $\langle A_v\rangle(z)$. This is in practice possible if one has some idea in which part of the Liouville space the stationary values (5) of ϕ' and ϕ_v will be. Then this subset can be parametrized, and the parameters can be determined from $\delta F = 0$.

In the next section we shall use linear parametrizations of the chosen subsets, in section 4 we will introduce nonlinear parametrizations as well. Common to all variational principles, the accuracy of the results will crucially depend on the chosen subsets. The variational method will be demonstrated in each section by well-known physical examples.

3. LINEAR VARIATIONAL ANSATZ

Let φ_v and φ'_v be two sets of vectors such that linear combinations of φ_v and of φ'_v lead to approximate expressions for $A_v(z)$ and $\rho(z)$, respectively. The question how to find these sets will be discussed later (see Section 3.2).

Now, according to the desired expression (5) for ϕ_v and ϕ' it is reasonable to take the following ansatz:

$$\phi_v = \sum_{\mu} c_{v\mu} \varphi_{\mu} \tag{7a}$$

$$\phi' = \sum_{\mu} c'_{\mu} \varphi'_{\mu} \tag{7b}$$

Inserting the ansatz (7) into (4) we find for F

$$F[c', c] = \sum_{\mu} c'_{\mu} \operatorname{Tr} \varphi'_{\mu} A_v + \sum_{\mu} c_{v\mu} \operatorname{Tr} \rho \varphi_{\mu} - \sum_{\mu,\lambda} c'_{\mu} c_{v\lambda} \operatorname{Tr} \varphi'_{\mu}(z + L)\varphi_{\lambda} \tag{8}$$

The stationary conditions of F read

$$\sum_{\lambda} c_{v\lambda} \operatorname{Tr} \varphi'_{\mu}(z + L)\varphi_{\lambda} - \operatorname{Tr} \varphi'_{\mu} A_v = 0 \tag{9a}$$

$$\sum_{\lambda} c'_{\lambda} \operatorname{Tr} \varphi'_{\lambda}(z + L)\varphi_{\mu} - \operatorname{Tr} \rho \varphi_{\mu} = 0 \tag{9b}$$

Equations (9) determine the stationary values

$$\begin{aligned} (c_{v\mu})_{st} &= c_{v\mu}(z) \\ (c'_{\mu})_{st} &= c'_{\mu}(z) \end{aligned} \tag{10}$$

which depend on the frequency z. Using the equations (9), we find for the stationary value of F

$$F_{st}(z) = F[\phi'_{st}, \phi_{v\,st}] = \operatorname{Tr} \rho \phi_{v\,st}(z) = \operatorname{Tr} \phi'_{st}(z) A_v \tag{11}$$

where

$$\begin{aligned} \phi_{v\,st}(z) &= \sum_{\mu} (c_{v\mu})_{st} \varphi_{\mu} \\ \phi'_{st}(z) &= \sum_{\mu} (c'_{\mu})_{st} \varphi'_{\mu} \end{aligned} \tag{12}$$

approximate $A_v(z)$ and $\rho(z)$, respectively. It suffices, however, to solve one of the decoupled systems of equations (9a) or (9b).

3.1. A Linear System of Differential Equations for Expectation Values

Transforming the equations (9a) or (9b) into the time region, and taking appropriate linear combinations, we find the following system of linear equations for $F_{st}(t) = \langle A_v \rangle(t)$:

$$\langle \dot{A}_v \rangle - i \sum_{\lambda} \langle A_{\lambda} \rangle \Lambda_{\lambda v} = 0 \tag{13a}$$

where the kinetic matrix Λ is defined by

$$\begin{aligned} \Lambda &= \alpha^{-1} L \beta^{-1} \alpha \\ \alpha_{v\mu} &= \operatorname{Tr} \varphi_v' A_\mu \\ \beta_{v\mu} &= \operatorname{Tr} \varphi_v' \varphi_\mu \\ L_{v\mu} &= \operatorname{Tr} \varphi_v' L \varphi_\mu \end{aligned} \tag{13b}$$

According to (9) the initial conditions are

$$\langle A_v \rangle (t=0) = \sum_\mu \operatorname{Tr} \rho \varphi_\mu (\beta^{-1}\alpha)_{\mu v} \tag{14}$$

In (13) we have derived a system of equations for expectation values $\langle A_v \rangle$. Because of

$$\phi_{\rm st}'(t) = \sum_\mu (c_\mu')_{\rm st}(t) \varphi_\mu' \tag{15}$$

we alternatively can use equations (9b) to derive a master equation for the relevant statistical operator $\rho_{\rm rel}(t) = \phi_{\rm st}'(t)$. We will discuss this aspect later by means of a special example (see Section 3.6).

3.2. Conditions on φ_v and φ_v'

In equations (13) the kinetic matrix Λ remains still undetermined as long as the vectors φ_v and φ_v' are not specified. For a given set of observables $\{A_v\}$ and a given set of initial statistical operators $\{\rho\}$ we now discuss an appropriate choice of the subspaces $\{\varphi_v\}$ and $\{\varphi_v'\}$.

It is physically reasonable to demand that the solution of (13) with initial conditions (14) would become exact for $t = 0$. This implies

$$\langle A_v \rangle (t=0) = \operatorname{Tr} \rho A_v \tag{16}$$

From (14) one sees that condition (16) is fulfilled if either

$$\rho = \sum_\mu r_\mu \varphi_\mu' \tag{17}$$

holds for all statistical operators ρ to be considered or

$$A_v = \sum_\mu a_{v\mu} \varphi_\mu \tag{18}$$

where r_μ and $a_{v\mu}$ are c numbers.

3.3. Simplest Choice of φ_v and φ_v'

The simplest ansatz, which fulfills the physically reasonable condition (16), is given by

$$\begin{aligned} \varphi_v &= A_v \\ \varphi_v' &= R_v \end{aligned} \tag{19}$$

Here we have introduced a basis $\{R_v\}$ of the space spanned by the statistical operators ρ which are to be considered:

$$\rho = \sum_v r_v R_v \tag{20}$$

The ansatz (19) obviously fulfills (17) and (18) and, therefore, equation (16). This means: The solution (11) is exact for $z \to \infty$

$$F_{\text{st}}(z \to \infty) = \langle A_v \rangle_{\text{exact}}(z \to \infty) \tag{21}$$

Because of $\beta = \alpha$ we find for the matrix Λ

$$\begin{aligned} \Lambda &= \alpha^{-1} L \equiv \Omega \\ \alpha_{v\mu} &= \operatorname{Tr} R_v A \mu \\ L_{v\mu} &= \operatorname{Tr} R_v L A_\mu \end{aligned} \tag{22}$$

Inspection of the equation of motion (13a) shows that the result (22) for the matrix Λ implies the correct values for the derivatives $\langle \dot{A}_v \rangle$ at $t = 0$. The solution of (13a), therefore, represents an extrapolation of the short-time behavior of $\langle A_v \rangle(t)$. Normally, this procedure does not lead to a description of damping phenomena. To describe such effects it is necessary to find a solution of $\langle A_v \rangle(t)$ which is meaningful for long times, too. We will treat this problem in the next section.

3.4. Choice of φ_v and φ_v' for "Slow Variables"

Now let us seek a more useful ansatz, which would give the exact result for two different values of z, say $z \to \infty$ and $z = z_0$. We already know that the ansatz $\varphi_v' = R_v$ gives the exact result for $\langle A_v \rangle(z)$ at $z \to \infty$, $F_{\text{st}}(z \to \infty) = \langle A_v \rangle_{\text{exact}}(z \to \infty)$, whatever the ansatz for φ_v may be. Vice versa, the ansatz $\varphi_v = A_v(z_v)$ yields the exact result for $\langle A_v \rangle(z)$ at $z = z_v$, $F_{\text{st}}(z_v) = \langle A_v \rangle_{\text{exact}}(z_v)$, whatever we may have used for φ_v'. This follows from (9b) and (11). We therefore expect that the ansatz

$$\begin{aligned} \varphi_v' &= R_v \\ \varphi_v &= A_v(z_v) \end{aligned} \tag{23}$$

would give an appropriate interpolation for $\langle A_v \rangle(z)$ between the exact values $\langle A_v \rangle(z_v)$ and $\langle A_v \rangle(z \to \infty)$.

In order for this interpolation between the two frequencies $z = \infty$ and $z = z_v$ to represent a useful approximation of the exact result, we have to postulate some properties of the observables A_v: Let us assume that $e^{-i\omega_v t} A_v(t)$ is a "slowly varying quantity," which means that its Fourier transform is peaked at $\omega = 0$, or the Fourier transform of $A_v(t)$ is peaked at $\omega = -\omega_v$, respectively. If $e^{-i\omega_v t} A_v(t)$ were constant in time, we would have

$$A_v(z) = c_v(z) A_v(z_v) \tag{24}$$

so that the ansatz

$$\varphi_v = A_v(z_v) \tag{25}$$

would lead to the exact result for $\langle A_v \rangle(z)$. Hence we expect for "slowly varying" $e^{-i\omega_v t}A_v(t)$ the variational ansatz $\varphi_v = A_v(z_v)$ to be adequate.

To find the frequency ω_v in the Fourier spectrum of $A_v(t)$ we use perturbation theory and demand that there exists a main part L_0 of the Liouvillian $L = L_0 + gL_1$ with

$$L_0 A_v = \omega_v A_v \tag{26}$$

In this case we choose $z_v = -\omega_v + i\eta$. Then equation (26) leads to

$$A_v(z_v) = -i\int_0^\infty d\tau\, e^{iz_v\tau}e^{iL\tau}A_v = -i\int_0^\infty d\tau\, e^{-\eta\tau}e^{iL\tau}e^{-iL_0\tau}A_v \tag{27}$$

Since we will use the linear ansatz

$$\phi_v = \sum_\mu c_{v\mu}\varphi_\mu = \sum_\mu c_{v\mu}A_\mu(z_\mu) \tag{28}$$

we can take linear combinations of A_v in (27) as well. From this we conclude the following:

Given a set $\{A_v\}$ invariant under L_0

$$L_0 A_v = \sum_\mu L^0_{v\mu}A_\mu \tag{29}$$

then a suitable ansatz for φ'_v and φ_v is

$$\begin{aligned} \varphi'_v &= R_v \\ \varphi_v &= -i\int_0^\infty d\tau\, e^{-\eta\tau}e^{iL\tau}e^{-iL_0\tau}A_v \end{aligned} \tag{30}$$

Now ansatz (30) leads to the following result for the matrix Λ defined in (13b):

$$\Lambda = \Omega + i\Gamma \tag{31}$$

where the expression for the matrix Ω reads

$$\begin{aligned} (\alpha\Omega)_{v\mu} &= \operatorname{Tr} R_v L A_\mu \\ \alpha_{v\mu} &= \operatorname{Tr} R_v A_\mu \end{aligned} \tag{32}$$

This term has already been found by means of the simple ansatz (19) [compare Eq. (22)], where it was the only contribution to Λ. The matrix Γ is expressed as

$$(\alpha\Gamma)_{v\mu} = g^2\int_0^\infty d\tau\, e^{-\eta\tau}\operatorname{Tr} R_v L'_1 e^{iL_0\tau}L_1 e^{-iL_0\tau}A_\mu + O(g^3) \tag{33}$$

where α is given by (32) and L'_1 is defined by

$$L'_1 X = L_1 X - \sum_{\mu,v} L_1 A_\mu (\alpha^{-1})_{\mu v}\operatorname{Tr} R_v X \tag{34}$$

To arrive at formula (33) we have used the result of first-order perturbation theory for the time-evolution operator e^{iLt}.[2]

The basic results of our linear variational method are presented in equations (9) and (11). These equations can be rewritten as a linear system of differential equations (13) for the expectation values of observables A_v. The kinetic matrices involved may be specialized to yield the expressions (22) or (31), (32) and (33) respectively. These variational results comprise various projection-operator approaches. This fact will be discussed in the Appendix. Here we only want to illustrate this connection by simple examples.

3.5. Example: Linear Relaxation of Parallel Magnetization

First let us discuss the relaxation of a magnetization M_z parallel to a static magnetic field H if the field is changed by a small amount ΔH. The purpose of this example is to illustrate the connection to a Markovian approximation of Mori's theory[4] of linear Langevin equations. Consider a system described by the Hamiltonian

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + g\mathcal{H}_1 \\ \mathcal{H}_0 &= -HM_z + \mathcal{H}_0(H=0), \qquad \left[M_z, \mathcal{H}_0(0)\right] = 0 \end{aligned} \tag{35}$$

and the statistical operator at $t = 0$

$$\begin{aligned} \rho = R(\Delta H) &= \left[Z(\Delta H)\right]^{-1} e^{-\beta(\mathcal{H} - \Delta H M_z)}, \qquad \beta = (kT)^{-1} \\ &= R(0) + \Delta H \left.\frac{\partial R}{\partial \Delta H}\right|_{\Delta H = 0} \end{aligned} \tag{36}$$

for small ΔH. Thus the space of considered statistical operators $\{\rho\}$ is spanned by $R_1 = R(0)$ and $R_2 = (\partial R / \partial \Delta H)|_{\Delta H = 0}$. We therefore choose

$$\begin{aligned} &A_1 = 1, \qquad A_2 = M_z - \langle M_z \rangle_\infty, \qquad \langle M_z \rangle_\infty = \mathrm{Tr}\, R(0) M_z \\ &R_1 = R(0), \qquad R_2 = \left.\frac{\partial R}{\partial \Delta H}\right|_{\Delta H = 0} \end{aligned} \tag{37}$$

Since equation (29) is fulfilled, we can consider A_1 and A_2 to be "slow variables." Applying ansatz (30) we immediately find from (32), (33), and (13a): $\Omega = 0$, $\alpha_{11} = 1$, $\alpha_{22} = \chi$, and

$$\begin{aligned} \langle \dot{M}_z \rangle &= -\Gamma(\langle M_z \rangle - \langle M_z \rangle_\infty) \\ \langle M_z \rangle(0) &= \langle M_z \rangle_\infty + \Delta H \chi \end{aligned} \tag{38}$$

[2] In the case where $L_1' = L_1$ and equation (26) holds, we directly find expression (33) for Γ by the ansatz

$$\varphi_v = \left\{(z_v + L_0)^{-1} - (z_v + L_0)^{-1} L_1 (z_v + L_0)^{-1}\right\} A_v$$

where the damping constant Γ is given by

$$\Gamma = \chi^{-1}\left(\frac{g}{\hbar}\right)^2 \int_0^\infty d\tau\, e^{-\eta\tau}\, \mathrm{Tr}\, \frac{\partial R}{\partial \Delta H}\bigg|_{\Delta H=0} \left[\mathcal{H}_1, \left[\mathcal{H}_1(\tau), M_z\right]\right] \qquad (39)$$
$$\mathcal{H}_1(\tau) = e^{(i/\hbar)\mathcal{H}_0\tau}\mathcal{H}_1 e^{-(i/\hbar)\mathcal{H}_0\tau}$$

For convenience we have introduced the isothermal magnetic susceptibility $\chi = (\partial M_z/\partial H)_T$. Equations (38) and (39) are usually derived by Mori's theory[4] and are a standard result in linear magnetic relaxation theory.

3.6. Example: Master Equation for the Statistical Operator R_s of a Subsystem

In our second example we consider a system $\mathcal{H}_s$ in contact with a heat reservoir $\mathcal{H}_B$. Let the Hamiltonian be

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_B + g\mathcal{H}_1 \qquad (40)$$

The equilibrium statistical operator of the heat reservoir is denoted by

$$R_B = Z_B^{-1} e^{-\beta\mathcal{H}_B} \qquad (41)$$

We now use ansatz (30) and equation (9b) to derive the standard master equation for the relevant statistical operator R_s of the subsystem $\mathcal{H}_s$. Let

$$A_v = A_v^{(s)}$$
$$R_v = R_B \cdot R_v^{(s)} \qquad (42)$$

where both sets $\{A_v^{(s)}\}$ and $\{R_v^{(s)}\}$ span a complete basis of the Liouville space of the subsystem. Then condition (29) is fulfilled and ansatz (30) immediately yields the following differential equation for R_s[3]:

$$R_s(t) = \mathrm{Tr}_B\, \phi'(t) = \sum_v c_v'(t) R_v^{(s)}$$
$$\dot{R}_s = -iL_s R_s - \left(\frac{g}{\hbar}\right)^2 \int_0^\infty d\tau\, e^{-\eta\tau}\, \mathrm{Tr}_B\left[\mathcal{H}_1, \left[\mathcal{H}_1(-\tau), R_B R_s\right]\right] \qquad (43)$$

which is the standard result for the time evolution of the reduced density operator.[5]

4. NONLINEAR VARIATIONAL ANSATZ

In Section 3 we have considered linear parametrizations of the various sets $\{\phi'\}$ and $\{\phi_v\}$. They lead to linear systems of equations for expectation values of macroscopic observables A_v, or to linear master equations for relevant statistical operators R_s, respectively. In this section we want to

[3]We have taken $\langle\mathcal{H}_1\rangle_B = \mathrm{Tr}_B\, R_B \mathcal{H}_1 = 0$.

discuss a nonlinear parametrization of the set $\{\phi'\}$. We, therefore, drop the condition that ϕ' be only linearly dependent on the variational parameters $\{c'_v\}$ and write

$$\phi'(z) = -i\int_0^\infty dt\, e^{izt}\phi'(c'_v(t))$$
$$\phi_v = \sum_\mu c_{v\mu}\varphi_\mu \tag{44}$$

The nonlinear function $\phi'(c'_v)$ will be defined later. Inserting the ansatz (44) into (4) we find for our functional

$$F[c',c] = \operatorname{Tr}\phi'(z)A_v + \sum_\mu c_{v\mu}\operatorname{Tr}\rho\varphi_\mu - \sum_\mu c_{v\mu}\operatorname{Tr}\phi'(z)(z+L)\varphi_\mu \tag{45}$$

Variation with respect to the parameters $c_{v\mu}$ gives

$$\operatorname{Tr}\phi'(z)(z+L)\varphi_\mu - \operatorname{Tr}\rho\varphi_\mu = 0 \tag{46}$$

These equations determine the stationary values of c'_v, which will be denoted by $\lambda_v(t)$

$$(c'_v(t))_{\text{st}} = \lambda_v(t) \tag{47}$$

Using relation (46) and the definition

$$R(z) = (\phi'(z))_{\text{st}} \tag{48}$$

we can write for the stationary value of F

$$F_{\text{st}} = \operatorname{Tr}R(z)A_v \tag{49}$$

Transforming equations (46) into the time region, we find for $R(t) = \phi'(\lambda_v(t))$ the following differential equations:

$$\operatorname{Tr}\varphi_\mu(\dot{R} + iLR) = 0 \tag{50}$$

which have to be solved with the initial conditions

$$\operatorname{Tr}\varphi_\mu R(t=0) = \operatorname{Tr}\varphi_\mu\rho \tag{51}$$

Equations (50) and (51) are equivalent to (46).

We now want to choose an explicit form of the function $\phi'(c'_v)$. For a given set of macroscopic observables A_v we will consider the following set of initial statistical operators:

$$\rho(\lambda_v^0) = \exp\left(-\sum_v \lambda_v^0 A_v\right) \tag{52}$$

where the parameters λ_v^0 are considered to be given by the expectation values of A_v at $t = 0$.

In the following we will suppose that the unity operator is a linear combination of A_v:

$$1 = \sum_v a_v A_v \tag{53}$$

From the form (52) we are led to take the following function $\phi'(c'_v)$ as an ansatz in (44):

$$\phi'(c'_v) = \exp\Big(-\sum_v c'_v A_v\Big) \tag{54}$$

The "relevant statistical operator" (49) then reads

$$R(t) = \exp\Big[-\sum_v \lambda_v(t) A_v\Big] \tag{55}$$

The parameters $\lambda_v(t)$ are the stationary values of $c'_v(t)$, and are to be calculated from equations (50) together with the initial condition (51): $\lambda_v(0) = \lambda_v^0$.

Let us summarize: Our nonlinear variational ansatz (44) and (54) has led to the system of equations (50) for $R(t)$, the form of which is given by (55). Choosing the same set φ_v as in Section 3, we now can derive a closed system of nonlinear equations for the expectation values $\langle A_v\rangle(t)$. This procedure will be outlined in the following section.

4.1. A Nonlinear System of Differential Equations for Expectation Values

Equation (49) defines $\langle A_v\rangle(t)$ as a function of $\lambda_v(t)$:

$$\langle A_v\rangle(t) = \langle A_v\rangle(\lambda_\mu(t)) \tag{56}$$

Conversely, the stationary functions $\lambda_v(t)$ and the statistical operator $R(t)$ (55) depend on the time t by the functions $\langle A_v\rangle(t)$: $R(t) = R(\langle A_v\rangle(t))$. Now because of relation (53) $R(t)$ may be expressed as[6]

$$R = \sum_\lambda \langle A_\lambda\rangle \frac{\partial R}{\partial\langle A_\lambda\rangle} \tag{57}$$

By means of the identity (57) we can transform equations (50) into the following nonlinear differential equations:

$$\begin{aligned} \langle\dot{A}_v\rangle - i\sum_\lambda \langle A_\lambda\rangle \Lambda_{\lambda v}(\langle A_\kappa\rangle) &= 0^4 \\ \Lambda &= L\beta^{-1} \\ L_{v\mu} &= \mathrm{Tr}\frac{\partial R}{\partial\langle A_v\rangle} L\varphi_\mu \\ \beta_{v\mu} &= \mathrm{Tr}\frac{\partial R}{\partial\langle A_v\rangle}\varphi_\mu \end{aligned} \tag{58}$$

[4] An equivalent form to the equation of motion (58) reads

$$\langle\dot{A}_v\rangle - i\sum_\lambda \mathrm{Tr}\, RL\varphi_\lambda(\beta^{-1})_{\lambda v} = 0$$

The system (58) is the analog to the system (13). Contrary to equations (13), however, (58) generally constitutes a system of *nonlinear* differential equations, because the kinetic matrix Λ depends on $\langle A_v \rangle$.

It holds that $R(t=0) = \rho$, hence it follows from the relation $F_{\text{st}} = \operatorname{Tr} R(t) A_v$, that $F_{\text{st}}(t)$ becomes the exact value of $\langle A_v \rangle(t) = 0$, whatever the special choice for φ_v may be.

In section 3, possible choices of φ_v were discussed. Let us use here the same two sets

$$\varphi_v = A_v \tag{59a}$$

and

$$\varphi_v = -i \int_0^\infty d\tau \, e^{-\eta\tau} e^{iL\tau} e^{-iL_0\tau} A_v \tag{59b}$$

If it holds that $L_0 A_v = \omega_v A_v$, then the φ_v of (59b) again lead to the exact values of $\langle A_v \rangle(z)$ at $z = z_v = -\omega_v + i\eta$. This fact follows from (46), (48), and (49):

$$\operatorname{Tr} \rho A_v(z_v) = \operatorname{Tr} R(z_v) A_v = F_{\text{st}}(z_v) \tag{60}$$

Applying the φ_v of (59) we can rewrite the kinetic matrix (58). In case (59a) we find

$$\begin{aligned} \beta &= 1 \\ \Lambda &= \Omega \\ \Omega_{v\mu} &= \operatorname{Tr} \frac{\partial R}{\partial \langle A_v \rangle} L A_\mu \end{aligned} \tag{61}$$

In case (59b) we have

$$\Lambda = \Omega + i\Gamma \tag{62}$$

where Ω has already been defined by (61) and Γ is given by

$$\begin{aligned} \Gamma_{v\mu} &= g^2 \int_0^\infty d\tau \, e^{-\eta\tau} \operatorname{Tr} \frac{\partial R}{\partial \langle A_v \rangle} L_1'(t) e^{iL_0\tau} L_1 e^{-iL_0\tau} A_\mu + 0(g^3) \\ L_1'(t) X &= L_1 X - \sum_\mu L_1 A_\mu \operatorname{Tr} \frac{\partial R}{\partial \langle A_\mu \rangle} X \end{aligned} \tag{63}$$

To illustrate the nonlinear formalism outlined above, we will apply it to some simple examples in the next sections.

4.2. Example: Time-Dependent Hartree–Fock Equation

As a first example for the nonlinear system (58) let us apply ansatz (59a). Consider a quantum gas of bosons or fermions with two-particle interactions:

$$\mathcal{H}_0 = \sum_1 \epsilon_1 a_1^+ a_1$$
$$\mathcal{H}_1 = \frac{1}{2N} \sum_{11'22'} V_{121'2'} a_1^+ a_2^+ a_{2'} a_{1'} \tag{64}$$

We choose

$$A_0 = 1$$
$$A_v = a_1^+ a_2 \tag{65}$$
$$\phi'(c_0', c_{12}') = \exp\Big(-\sum_{12} c_{12}' a_1^+ a_2 - c_0'\Big)$$

The kinetic matrix (61) can be evaluated explicitly. From (58) we arrive at the following nonlinear system of equations for the one-particle density matrix $\langle a_1^+ a_2\rangle(t) = \langle 2|\rho^{(1)}(t)|1\rangle$

$$\begin{aligned}\frac{\partial}{\partial t}\langle 2|\rho^{(1)}(t)|1\rangle = {} & -(i/\hbar)(\epsilon_2 - \epsilon_1)\langle 2|\rho^{(1)}(t)|1\rangle \\ & + (i/\hbar)\frac{1}{2N}\sum_{344'}\{(V_{424'3} \pm V_{244'3})\langle 4'|\rho^{(1)}(t)|4\rangle\langle 3|\rho^{(1)}(t)|1\rangle \\ & - (V_{434'1} \pm V_{344'1})\langle 4'|\rho^{(1)}(t)|4\rangle \\ & \times \langle 2|\rho^{(1)}(t)|3\rangle\}\end{aligned} \tag{66}$$

They are the well-known Hartree–Fock equations.[7]

4.3. Example: Nonlinear Heat Conduction

To discuss ansatz (59b) let us consider the heat conduction between two reservoirs $\mathcal{H}_1$ and $\mathcal{H}_2$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + g\mathcal{H}_{12}, \qquad [\mathcal{H}_1, \mathcal{H}_2] = 0 \tag{67}$$

We take

$$A_0 = 1$$
$$A_v = \mathcal{H}_v, \qquad v = 1,2 \tag{68}$$
$$\phi'(c_v') = \exp\Big(-\sum_v c_v' \mathcal{H}_v - c_0'\Big)$$

From (50) and (59b) we directly find the equation for heat conduction

$$\langle\dot{\mathcal{H}}_1\rangle = -\Gamma(\beta_v)(\beta_2 - \beta_1) = -\langle\dot{\mathcal{H}}_2\rangle \tag{69}$$

where the thermal conductivity $\Gamma(\beta_v)$ is given by

$$\begin{aligned}
\Gamma(\beta_v) &= \int_0^{\infty} d\tau\, e^{-\eta\tau} \int_0^1 d\lambda\, \mathrm{Tr}\, R^{1-\lambda}\dot{\mathcal{H}}_1(\tau) R^{\lambda} \dot{\mathcal{H}}_1 + O(g^3) \\
R(\beta_v) &= \left[Z(\beta_v(t))\right]^{-1} \exp\Big(-\sum_v \beta_v(t)\mathcal{H}_v\Big) \\
\dot{\mathcal{H}}_1 &= (i/\hbar) g[\mathcal{H}_{12}, \mathcal{H}_1] \\
\dot{\mathcal{H}}(\tau) &= e^{(i/\hbar)(\mathcal{H}_1+\mathcal{H}_2)\tau}\dot{\mathcal{H}}_1 e^{(-i/\hbar)(\mathcal{H}_1+\mathcal{H}_2)\tau}
\end{aligned} \tag{70}$$

The thermal conductivity Γ itself depends on $\beta_v(t)$; thus (69) represents a nonlinear system of heat conduction equations.[8]

4.4. Example: Nonlinear Dynamics of a Spin System

In Sections 4.2 and 4.3 we have regarded examples where the kinetic matrices Λ were given by $\Lambda = \Omega$ or by $\Lambda = i\Gamma$, respectively. We now want to treat a simple example where both terms Ω and Γ contribute to Λ.

Consider the physical system of Section 3.6, where we now specialize the subsystem S to be constituted of N spins $s = 1/2$ in an external magnetic field H. Thus we write

$$\begin{aligned}
\mathcal{H}_s &= -\gamma H \sum_i S_i^z \\
g\mathcal{H}_1 &= g\sum_i (B_i^+ S_i^- + B_i^- S_i^+) \\
\langle B_i^{\pm}\rangle &= \mathrm{Tr}_B\, R_B B_i^{\pm} = 0, \qquad R_B = Z_B^{-1} e^{-\beta\mathcal{H}_B}
\end{aligned} \tag{71}$$

Now let us take

$$\begin{aligned}
A_0 &= 1 \\
A_v &= \sum_i S_i^v, \qquad v = +, -, z \\
\phi'(c_0', c_v') &= R_B \cdot \exp\Big(-\sum_v c_v' \sum_i S_i^v - c_0'\Big)
\end{aligned} \tag{72}$$

and use ansatz (59b). Then a straightforward calculation of (58) yields the following nonlinear equation for $\mathbf{M} = \gamma\sum_i\langle \mathbf{S}_i\rangle$:

$$\dot{\mathbf{M}} = -\gamma(\mathbf{M}\times\mathbf{H}) - D\cdot(\mathbf{M}-\mathbf{M}_\infty) - \gamma'\mathbf{M}\times M_z\mathbf{e}_z + \gamma''(\mathbf{M}\times(\mathbf{M}\times\mathbf{H})) \tag{73}$$

where

$$\mathbf{H} = \begin{bmatrix} 0 \\ 0 \\ H \end{bmatrix} \mathbf{M}_\infty = \begin{bmatrix} 0 \\ 0 \\ M_\infty \end{bmatrix}, \qquad M_\infty = \frac{N\gamma\hbar}{2} \tanh \frac{\gamma\hbar H}{2kT}$$

$$D = \begin{bmatrix} 1/\tau & & 0 \\ & 1/\tau & \\ 0 & & 2/\tau \end{bmatrix} \tag{73a}$$

$$\gamma\gamma' = -2g^2 \mathrm{Re}\left(\frac{1}{N^2} \sum_{i \neq j} \chi_{ij}(\gamma H) \right)$$

$$\gamma H \gamma'' = -2g^2 \mathrm{Im}\left(\frac{1}{N^2} \sum_{i \neq j} \chi_{ij}(\gamma H) \right)$$

$$\gamma\tau^{-1} = -(g^2/2) M_\infty^{-1} \mathrm{Im}\left(\sum_i \chi_{ii}(\gamma H) \right) \tag{73b}$$

$$\chi_{ij}(\omega) = \frac{1}{\hbar} \int_0^\infty dt\, e^{i\omega t} \langle [B_i^+(t), B_j^-] \rangle$$

The first term on the right of equation (73) constitutes the linear reversible motion, the second term is the Bloch damping, the third renormalizes the reversible motion by a molecular field:

$$(\dot{\mathbf{M}})_{\mathrm{rev}} = -\gamma(\mathbf{M} \times \mathbf{H}_{\mathrm{eff}})$$

$$\mathbf{H}_{\mathrm{eff}} = \left(H + \frac{\gamma'}{\gamma} M_z \right) \mathbf{e}_z \tag{74}$$

and the last term is the Landau–Lifschitz damping[9].

5. CONCLUSIONS

It has been shown that the Schwinger variational principle of scattering theory is suited for quantum statistics, where it allows a derivation of macroscopic equations of motion.

The variational method might be useful to improve known results by optimizing parameters, or will make it possible to attack complicated problems if the dynamics for different limiting cases is known and one wants to treat an intermediate situation.

APPENDIX

To point out the connection of our result of linear relaxation problems to standard "projection-operator" approaches, let us define the following idempotent operator P:

$$PX = \sum_{v,\mu} A_v (\alpha^{-1})_{v\mu} \operatorname{Tr} R_\mu X \tag{A.1}$$

where α is given by (22). Then by means of (A.1), relation (11) can be cast into the following form:

(a) In case of ansatz (19) one obtains

$$F_{\mathrm{st}}(z) = \operatorname{Tr} \rho (z + PLP)^{-1} A_v \tag{A.2}$$

(b) In case of ansatz (30) and $L_0 A_v = 0$ for all v one arrives at

$$F_{\mathrm{st}}(z) = \operatorname{Tr} \rho \left[z + PLP - M(i\eta) \right]^{-1} A_v \tag{A.3}$$

where

$$M(z) = PLQ(z + QLQ)^{-1} QLP, \qquad Q = 1 - P \tag{A.4}$$

Inspection of the results (A.2) and (A.3), (A.4) and the exact expression for $\langle A_v \rangle (z)$

$$\langle A_v \rangle (z) = \operatorname{Tr} \rho (z + PLP - M(z))^{-1} A_v \tag{A.5}$$

shows that the ansatz (19) in the variational method neglects memory effects, but gives an exact description of the systematic part of dynamics, whereas ansatz (30) corresponds to a Markovian approximation in the memory kernels.

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