Quantum dynamics of molecular motions based on a functional method

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A time-dependent functional formalism of molecular positions is developed in order to study nonequilibrium problems. It is based on the Liouvillean quantum field dynamics and is different from the density-functional framework. It provides a direct self-consistent approach to molecular dynamics of a system which is initially in thermodynamic equilibrium and is subjected to time-dependent external force.

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A wide variety of problems concerning the equilibrium states of matter is successfully treated by the density-functional theory of systems of atoms or molecules treated as point particles [1] which we generically call molecules in this paper. This formalism (be it classical or quantum) is based on the principle of minimum free energy of the system as a functional of molecular density. The purpose of this work is to formulate a time-dependent functional theory of self-consistent dynamical motions of the molecules which may also find use (e.g., dynamical structure factor) in dealing with a large body of dynamical questions, the resolution of which is outside the scope of near-equilibrium approaches. Instead of an extension of the density-functional theory to include the time-dependent density functional, we employ the molecular positions themselves as the dynamical variables. The use of molecular positions themselves as the dynamical variables was successfully employed in a many-body theoretical framework for studying many physical phenomena, a review of which may be found in Ref. [1]. The spirit of this work is the same as our recent work [2–4] on the time-dependent functional theory which generalized the density-functional theory for time-dependent electronic systems [5,6] to include ionic and electromagnetic fields. This theory would provide a formal framework for investigations of self-consistent molecular dynamics simulations of nonequilibrium states of matter under a large class of situations, which may be either classical or quantal.

A description of essentially nonequilibrium quantum systems, e.g., a system of electrons in a strong electric field as in a resonant tunneling device (RTD) subjected to a time-dependent external bias, and nonequilibrium superconductivity, are usually studied by means of the time-ordered path and similar methods [7,8] in Hilbert space (H space). The drawback of this nonequilbirium H-space scheme is that a functional theory of the many-body effects cannot be readily formulated. Recently a convenient and powerful reformulation of the quantum statistical mechanics, called the nonequilibrium thermofield dynamics, has been introduced; it possesses several advantages over the time-path method [9–11] in H space, even though it is equivalent to it. This theory employs superoperators acting on the Liouville space (L space) with a doubled number of degrees of freedom and is sometimes called the twin formulation of quantum statistical mechanics such that any physical property of the system under consideration can be expressed in terms of the twins. In this sequel we will call this Liouvillean quantum field dynamics (LQFD). In LQFD, the conventional equation for the density matrix is replaced by a Schrödinger-like equation in the L space and the known "zero-temperature" diagrammatic techniques are then easily transcribed in this framework. The drawback of the conventional H-space scheme, namely incorporating the initial condition of the system which is in thermodynamic equilibrium, has been surmounted in this alternative formalism, because a stationary action principle for determining the time-dependent density matrix is readily obtained for setting up the nonequilibrium time-dependent functional theory.

The purpose of the present work is to employ the new stationary action principle in this L space given in Ref. [4]. This has enabled us to develop a time-dependent functional theory, which in the conventional pure state H-space framework has proven to be successful in its numerical implementation and hence its usefulness [5,6].

We begin with a brief description of this twin formulation as given by Schmutz [11] for the sake of completeness. We consider a system of interacting molecules in the sense described above expressed in the usual H space.

The Hamiltonian operator in the H space is

$$\check{H}=\check{T}_N+\check{U}_N \ . \tag{1}$$

$\check{T}_N$ is the kinetic energy of molecules of type κ with mass M_κ in the lth unit cell,

$$\check{T}_N=\sum_{l\kappa}\frac{\check{\mathbf{P}}^2(l\kappa)}{2M_\kappa} \tag{2a}$$

(we consider $\kappa=1,\ldots,s$, so that there are s molecules in the unit cell of the crystal), and mutual molecular interaction energy is, for example, a two-body interaction,

$$\check{U}_N=\sum_{l\kappa,l'\kappa'}\check{W}(\check{\mathbf{R}}(l\kappa),\check{\mathbf{R}}(l'\kappa')) \ . \tag{2b}$$

We may note that the formalism to be developed is applicable equally when the molecules are not located on lattice sites, as in a liquid, for example, and when the mutual interactions involve multiparticle forces.

A c-number time-dependent local force $\mathbf{F}(l\kappa t)$ acting on the molecule at position $\check{R}(l\kappa)$ is represented by the appropriate Hamiltonian operator

$$\check{V}(t)=\sum_{l\kappa}\mathbf{F}(l\kappa t)\cdot\check{\mathbf{R}}(l\kappa) \ . \tag{3}$$

This is added to $\check{H}$ in setting up the time-dependent (TD) functional theory where the TD Hamiltonian is defined by

$$\check{H}_t=\check{H}+\check{V}(t) \ . \tag{4}$$

The Cartesian components of molecular position and momentum operators $\check{R}(l\kappa)$, $\check{P}(l\kappa)$, respectively, obey the standard commutation rules in H space,

$$\begin{aligned}&[\check{R}(l\kappa\alpha),\check{R}(l'\kappa'\alpha')]_-=0=[\check{P}(l\kappa\alpha),\check{P}(l'\kappa'\alpha')]_- \ , \\ &[\check{R}(l\kappa\alpha),\check{P}(l'\kappa'\alpha')]_-=i\hbar\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\alpha'} \ .\end{aligned} \tag{5}$$

This is to be contrasted with the conventional procedure [1] where Eq. (3) is replaced by terms involving the density of molecules coupled to a TD potential, and thus leading to a density-functional theory. Equation (3) thus allows us to formulate a molecular-position-functional theory suitable for discussing the detailed TD dynamics of molecular motions of the system.

If $\check{\rho}(t)$ is the density matrix of the system obeying the usual von Neumann equation, given that at the initial time the system is in the thermal equilibrium described by the density matrix $\check{\rho}_{\rm eq}$,

$$\begin{aligned}&i\hbar\frac{\partial\check{\rho}(t)}{\partial t}=[\check{H}_t,\check{\rho}(t)]_- \ , \\ &\check{\rho}(t_0)\equiv\check{\rho}_{\rm eq}=\exp[-\beta(\check{H}_{t_0}-\mu\check{N})]/Z(\beta) \ , \\ &Z(\beta)=\mathrm{Tr}\exp[-\beta(\check{H}_{t_0}-\mu\check{N})] \\ &\qquad\qquad\text{with } \mathrm{Tr}\check{\rho}(t)=1 \ \text{ for all } t \ ,\end{aligned} \tag{6}$$

where β is the usual inverse temperature, $(k_BT)^{-1}$, and μ is the chemical potential corresponding to the fixed number of molecules in the system, $\check{N}$ being the total number operator. It may be recalled that $\check{\rho}_{\rm eq}$ is determined from a free energy minimum principle. The well-known formal solution of Eq. (6) is

$$\begin{aligned}&\check{\rho}(t)=\check{U}(tt_0)\check{\rho}(t_0)\check{U}(t_0t), \\ &\qquad\text{where } i\hbar\frac{\partial}{\partial t}\check{U}(tt_0)=\check{H}_t\check{U}(tt_0) \ , \\ &\qquad\text{with } \check{U}(t_0t_0)=1 \ .\end{aligned} \tag{6'}$$

We will now reformulate the above in terms of the L space which meets all our needs in the construction of a time-dependent functional approach to the problem in parallel to the pure state formalism of Gross and Kohn [6] in ordinary H space provided we make the necessary translation of the H-space theory to the L-space formalism. We give here a brief account of this explicitly for the system described above.

A general operator $\check{A}$ in the H space is represented by the superoperator twin set $(\hat{A},\tilde{A})$ and the algebra of the superoperators $\hat{A}$ ($\tilde{A}$) is a linear (antilinear) representation of the algebra of the operators $\check{A}$. Operators such as the Hamiltonian, position, and momentum in the H space become, respectively, twin pairs of superoperators in the L space:

$$\begin{aligned}&\check{H}_t\rightarrow(\hat{H}_t,\tilde{H}_t), \quad \mathbf{R}(l\kappa)\rightarrow(\hat{\mathbf{R}}(l\kappa),\tilde{\mathbf{R}}(l\kappa)), \\ &\check{\mathbf{P}}(l\kappa)\rightarrow(\hat{\mathbf{P}}(l\kappa),\tilde{\mathbf{P}}(l\kappa)) \ .\end{aligned} \tag{7}$$

Defining the unit superket

$$|1\rangle\rangle=\sum_\alpha|\alpha,\alpha\rangle\rangle$$

$$\text{such that } \hat{H}_t|1\rangle\rangle=\tilde{H}_t|1\rangle\rangle=\langle\langle 1|\hat{H}_t=\langle\langle 1|\tilde{H}_t \ , \tag{8}$$

where $|\alpha,\alpha\rangle\rangle=||\alpha\rangle\langle\alpha|\rangle\rangle$ with $\{|\alpha\rangle\}$ any complete set of kets in the ordinary H space, then an operator $\check{A}$ in the H space becomes a superket in the L space defined by

$$|A\rangle\rangle=\hat{A}|1\rangle\rangle=\tilde{A}^\dagger|1\rangle\rangle \ . \tag{9a}$$

More generally, a product of any two operators $\check{A}$ and $\check{B}$ in the H space becomes a superoperator acting on a superket in the following manner:

$$|AB\rangle\rangle=\hat{A}|B\rangle\rangle, \quad |BA\rangle\rangle=\tilde{A}^\dagger|B\rangle\rangle \ . \tag{9b}$$

(For fermions, A has to be a number conserving operator for this equation to hold.) The superket in this space, $|\rho(t)\rangle\rangle$, is here a vector corresponding to the density matrix in the usual H space, and obeys the "supervector" equation corresponding to Eq. (6) which in the L space assumes the form

$$\begin{aligned}\left|i\hbar\frac{\partial\rho(t)}{\partial t}\right\rangle\!\!\right\rangle&\equiv i\hbar D_t|\rho(t)\rangle\rangle \\ &=|[\check{H}_t,\check{\rho}(t)]_-\rangle\!\rangle\equiv\overline{H}_t|\rho(t)\rangle\rangle \ ,\end{aligned} \tag{10}$$

where $\overline{H}_t=\hat{H}_t-\tilde{H}_t$ and

$$i\hbar D_t=\left[\widehat{i\hbar\frac{\partial}{\partial t}}\right]-\left[\widetilde{i\hbar\frac{\partial}{\partial t}}\right]$$

in the same sense as Schmutz [11], with the condition that the state is initially in thermal equilibrium as described above, namely, $|\rho(t_0)\rangle\rangle=|\rho_{\rm eq}\rangle\rangle$. As stated earlier, this initial state is itself determined from a free energy minimum principle which will be incorporated in this sequel. This procedure is important in maintaining self-consistency of the formalism at all levels and on equal footing. The time derivative operator in the H space is a superoperator, D_t, in view of Eq. (9b), defined in the sense shown in the left hand side of Eq. (10). We may then state the usual normalization condition on the density matrix in the form of a matrix element [11] in the superspace:

$$\mathrm{Tr}\check{\rho}(t)=\langle\langle 1|\rho(t)\rangle\rangle=1 \ . \tag{11}$$

Also the expectation value of any operator $\check{A}(\mathbf{r}t)$ in the ordinary H space is just a matrix element of either of its twin operators $\hat{A}(\mathbf{r}t)$ or $\tilde{A}(\mathbf{r}t)$ in the L space [11]:

$$\langle \breve{A}(\mathbf{r}t)\rangle = \mathrm{Tr}[\breve{\rho}(t)\breve{A}(\mathbf{r}t)] = \mathrm{Tr}[\breve{\rho}(t_0)\breve{A}(\mathbf{r}t,t_0)] ,$$
$$\text{where } \breve{A}(\mathbf{r}t,t_0) = \breve{U}(t_0 t)\breve{A}(\mathbf{r}t)\breve{U}(tt_0) . \quad (12)$$

This is also expressed as

$$\langle\langle 1|\hat{A}(\mathbf{r}t)|\rho(t)\rangle\rangle = \langle\langle 1|\tilde{A}^{\dagger}(\mathbf{r}t)|\rho(t)\rangle\rangle . \quad (12')$$

The second line in Eq. (12) expresses the Heisenberg representation of the operator $\breve{A}(\mathbf{r}t)$.

We can now restate Eq. (10) as a stationary action principle in this superspace:

$$A(t_0,t_1) = \tfrac{1}{2}\int_{t_0}^{t_1} dt\,\langle\langle \Phi(t)|(i\hbar D_t - \overline{H}_t)|\rho(t)\rangle\rangle \quad (13)$$

subject to the initial condition, given in Eq. (10), by varying the left supervector and setting the result equal to zero. Also, by varying the right supervector, we obtain the corresponding equation for the superbra. The factor $\frac{1}{2}$ in Eq. (13) is chosen, to account for the presence of the twins in Eq. (13), so that this expression reduces to the correct action in the special case when the density matrix represents a pure state and the left superbra is the unit vector introduced above. Furthermore, the physical action functional is obtained when we choose the left superbra to be the unit supervector and the right supervector to be that associated with the density matrix, in view of Eq. (11). We will now prepare the initial density matrix superket to be the equilibrium state or equivalently the equilibrium density matrix, by a minimum free energy principle, with the free energy given by

$$\Omega = \mathrm{Tr}\breve{\rho}_{\mathrm{eq}}(\theta)[\breve{H}_{t_0} + \beta^{-1}\ln\breve{\rho}_{\mathrm{eq}}(\theta)]$$
$$\equiv \langle\langle 1|(\hat{H}_{t_0} - T\hat{S})|\rho_{\mathrm{eq}}(\theta)\rangle\rangle , \quad (14)$$

where $|\rho_{\mathrm{eq}}(\theta)\rangle\rangle$ is the variational thermal state. The corresponding entropy superoperator in the L space is

$$\hat{S} = -k_B(\widehat{\ln\rho}) . \quad (15)$$

In Eq. (14) the first form is the well-known free energy expression in the usual H space. The variation of Ω with respect to $\breve{\rho}_{\mathrm{eq}}(\theta)$ yields the equilibrium state and the value of Ω at the minimum is the free energy of the system given initially. In the complex time domain, this leads to the well-known periodicity, to be discussed subsequently [discussion following Eq. (40)]. A functional theory holds for this equilibrium state also and thus the two principles together lead to a new procedure which maintains self-consistency at all levels and treats in tandem the stationary action principle and its initial state specification on equal footing. The notations used here are slightly modified from those in Ref. [11]. With this at hand, it is now straightforward to formulate the generalization for the pure state time-dependent functional theory of Gross and co-workers (Ref. [6] contains a good review of the work in this subject) to include the initial thermal equilibrium condition. We enunciate here the essential theorems of this formalism along with their proofs and point out the advantages of this method outlined here. We choose to work in this asymmetric formulation of the L-space quantum dynamics since it has the distinct advantage that the Green functions of the many-particle systems defined in this space go over to the real time matrix Green functions, as was shown by Schmutz [11]. It thus makes it possible to derive the matrix Green function equations in the functional formalism which in turn is amenable to numerical implementation.

Quite generally, the time evolution of the expectation value of any operator $\breve{A}(\mathbf{r}t)$, defined as above, is given by

$$i\hbar\frac{d}{dt}\langle\langle 1|\hat{A}(\mathbf{r}t)|\rho(t)\rangle\rangle$$
$$= \langle\langle 1|\left[\widehat{i\hbar\frac{\partial\breve{A}(\mathbf{r}t)}{\partial t}}\right] + [\widehat{\breve{A}(\mathbf{r}t),\breve{H}_t}]_-|\rho(t)\rangle\rangle , \quad (16)$$

where the time derivative on the left hand side is the ordinary time derivative of a c-number function. This equation is best understood if we recall the corresponding H-space version of it and then transform it to the L-space by the procedures outlined above. Using this equation, we follow the steps given in Ref. [6] to deduce the important theorems of the nonequilibrium time-dependent functional formalism in LQFD.

The molecular position and momentum operators have the expectation values

$$\mathbf{R}(l\kappa t) = \mathrm{Tr}\breve{\rho}(t)\breve{R}(l\kappa) \equiv \langle\langle 1|\hat{\mathbf{R}}(l\kappa)|\rho(t)\rangle\rangle$$
$$= \langle\langle 1|\hat{\mathbf{R}}(l\kappa tt_0)|\rho(t_0)\rangle\rangle , \quad (17)$$

$$\mathbf{P}(l\kappa t) = \mathrm{Tr}\breve{\rho}(t)\breve{P}(l\kappa) \equiv \langle\langle 1|\hat{\mathbf{P}}(l\kappa)|\rho(t)\rangle\rangle$$
$$= \langle\langle 1|\hat{\mathbf{P}}(l\kappa tt_0)|\rho(t_0)\rangle\rangle . \quad (18)$$

The last terms in the above serve to define the corresponding Heisenberg representation in LQFD. We will now state and prove the mapping theorem.

Theorem 1. For every force $\mathbf{F}(l\kappa t)$ on the molecules which can be expanded into respective Taylor series in the time coordinate around $t = t_0$, a map

$$\mathbf{F}(l\kappa t) \rightarrow \mathbf{R}(l\kappa t)$$

is defined by solving the time-dependent Liouville equation with a fixed initial state and calculating the corresponding coordinate and momentum at later times. This map is invertible.

Proof. It is important to note that the minimum free energy principle assures us of the above mapping at the initial time. This follows by a *reductio ad absurdum* argument similar to the one given for equilibrium situations in Ref. [12]. The Taylor expansion then provides the mapping for succeeding times after t_0 as in Ref. [2]. We supply the details below.

The first step follows from the minimal property of the free energy associated with the initial density matrix,

$$\breve{\rho}(t_0) = \breve{\rho}_{\mathrm{eq}}(\theta) ,$$
$$\Omega_{\mathbf{F}}[\breve{\rho}'] = \langle\langle 1|(\hat{H}_{t_0} - T\hat{S})|\rho\rangle\rangle > \Omega_{\mathbf{F}}[\breve{\rho}] \quad \text{for } \breve{\rho}' \neq \breve{\rho} . \quad (19)$$

We examine the map $\mathbf{F}(l\kappa t_0) \rightarrow \mathbf{R}(l\kappa t_0)$ by considering the Hamiltonian $\breve{H}'_{t_0} = \breve{H}_{t_0} + \breve{V}'(t_0) - \breve{V}(t_0)$, with its density matrix $\breve{\rho}'(t_0)$, the average ion positions $\mathbf{R}'(l\kappa t_0)$, and

the associated free energy $\Omega_{\mathbf{F}'}[\check{\rho}']$ which is manipulated to the form

$$\begin{aligned}\Omega_{\mathbf{F}'}[\check{\rho}'] &= \langle\langle 1|(\hat{H}'_{t_0} - T\hat{S}')|\rho'\rangle\rangle \\ &= \Omega_{\mathbf{F}}[\check{\rho}'] + \sum_{l\kappa}[\mathbf{F}'(l\kappa t_0) - \mathbf{F}(l\kappa t_0)]\cdot\mathbf{R}'(l\kappa t_0) \\ &> \Omega_{\mathbf{F}}[\check{\rho}] + \sum_{l\kappa}[\mathbf{F}'(l\kappa t_0) - \mathbf{F}(l\kappa t_0)]\cdot\mathbf{R}'(l\kappa t_0) \ .\end{aligned} \tag{20}$$

The last line follows upon using the minimal property of Ω. In the same fashion reversing the primed and unprimed quantities above we obtain

$$\Omega_{\mathbf{F}}[\check{\rho}] > \Omega_{\mathbf{F}'}[\check{\rho}'] + \sum_{l\kappa}[\mathbf{F}(l\kappa t_0) - \mathbf{F}'(l\kappa t_0)]\cdot\mathbf{R}(l\kappa t_0) \ . \tag{21}$$

We see at once that the assumption $\mathbf{R}(l\kappa t_0) = \mathbf{R}'(l\kappa t_0)$ leads to contradiction. Thus different forces $\mathbf{F}(l\kappa t_0)$ and $\mathbf{F}'(l\kappa t_0)$ always lead to different equilibrium positions. In other words, the initial positions determine the initial forces and the density matrix can thus be considered as a function of the initial positions of the ions.

The second step is to demonstrate that the ion positions and momenta evolving from a common initial density matrix of the system in thermodynamic equilibrium under the influence of two different TD forces $\mathbf{F}(l\kappa t)$ and $\mathbf{F}'(l\kappa t)$ which are identical at the initial time are always different provided the forces obey some conditions to be specified presently. We assume that these forces can be expanded in respective Taylor series around t_0. Then there must exist a non-negative integer k' such that

$$\left[\frac{\partial}{\partial t}\right]^{k'} [\mathbf{F}(l\kappa t) - \mathbf{F}'(l\kappa t)] \neq 0 \ . \tag{22}$$

We will now prove that $\mathbf{R}(l\kappa t)$ and $\mathbf{R}'(l\kappa t)$ are different if Eq. (22) holds for $k' \neq 0$. First we show that the momenta $\mathbf{P}(l\kappa t)$ and $\mathbf{P}'(l\kappa t)$ are different. Remembering that we consider only those density matrices that evolve from the given initial equilibrium density matrix, upon using Eq. (16), we have

$$\begin{aligned} i\hbar\frac{d}{dt}[\mathbf{P}(l\kappa t) - \mathbf{P}'(l\kappa t)]_{t=t_0} &= \langle\langle 1|[\hat{\mathbf{P}}(l\kappa), \hat{H}_{t_0} - \hat{H}'_{t_0}]_-|\rho(t_0)\rangle\rangle \\ &= i\hbar[\mathbf{F}(l\kappa t_0) - \mathbf{F}'(l\kappa t_0)] \ . \end{aligned} \tag{23}$$

If $\mathbf{F}(l\kappa t)$ and $\mathbf{F}'(l\kappa t)$ are not equal at $t = t_0$, i.e., Eq. (22) holds for $k' = 0$, then the right hand side of Eq. (23) will be nonzero and so $\mathbf{P}(l\kappa t)$ and $\mathbf{P}'(l\kappa t)$ will not be equal for t infinitesimally later than t_0. If the minimum integer k' for which Eq. (22) holds is greater than zero, then Eq. (16) has to be applied k' times, so that we have

$$\left[i\hbar\frac{d}{dt}\right]^{k'+1} [\mathbf{P}(l\kappa t) - \mathbf{P}'(l\kappa t)]_{t=t_0} = i\hbar\left\{\left[i\hbar\frac{d}{dt}\right]^{k'} [\mathbf{F}(l\kappa t) - \mathbf{F}'(l\kappa t)]\right\}_{t=t_0} \ . \tag{24}$$

This implies that $\mathbf{P}(l\kappa t)$ and $\mathbf{P}'(l\kappa t)$ are different at infinitesimally later times than t_0. We now make use of the relation

$$\frac{d}{dt}[\mathbf{R}(l\kappa t) - \mathbf{R}'(l\kappa t)] = \frac{1}{M_\kappa}[\mathbf{P}(l\kappa t) - \mathbf{P}'(l\kappa t)], \tag{25}$$

which follows from Eq. (16), and is the well-known relationship between average position and the average of its conjugate momentum of a particle (Ehrenfest). Taking the $(k'+1)$ the derivative of this equation and using Eq. (24) we obtain

$$\left[\frac{d}{dt}\right]^{k'+2} [\mathbf{R}(l\kappa t) - \mathbf{R}'(l\kappa t)]_{t=t_0} = \frac{1}{M_\kappa}\left\{\left[\frac{d}{dt}\right]^{k'} [\mathbf{F}(l\kappa t) - \mathbf{F}'(l\kappa t)]\right\}_{t=t_0} \ . \tag{26}$$

Following the same arguments as in Refs. [5,6] if Eq. (22) holds, the right hand side of Eq. (26) cannot vanish. Thus the ion positions become different infinitesimally later than t_0.

Since we consider, by construction, only density matrices $\check{\rho}(t)$ and $\check{\rho}'(t)$ that evolve from the same initial state $\check{\rho}(t_0)$, the positions as well as the momenta of the ions are identical at the initial time and evolve subsequently to be different as demonstrated above. Thus, we have established the 1 to 1 correspondence between the time-dependent positions of the ions and the external forces; the external forces, on the other hand, uniquely determine the time-dependent density matrix, which can therefore be considered as a functional of the time-dependent positions:

$$\check{\rho}(t) = \check{\rho}[\mathbf{R}](t) \ . \tag{27}$$

As a consequence, the average value of any quantum mechanical operator is a unique functional of the ionic positions:

$$A(\mathbf{r}t) = \mathrm{Tr}\check{\rho}(t)\check{A}(\mathbf{r}t) \equiv A[\mathbf{R}](\mathbf{r}t) \ . \tag{28}$$

These arguments, it may be noted, run parallel to those used in the pure state theory in Refs. [5,6]. The consequences of this theorem will now be explored in the same spirit as in these references.

Theorem 2. There exists a functional $\mathbf{D}[\mathbf{R}(l\kappa t)]$ such that

$$\frac{\partial}{\partial t}\mathbf{R}(l\kappa t) = M_\kappa^{-1}\mathbf{P}(l\kappa t) \ , \tag{29}$$

and

$$\frac{\partial}{\partial t}\mathbf{P}(l\kappa t)=\mathbf{D}[\mathbf{R}(l\kappa t)]\ , \tag{30}$$

with the given initial conditions

$$\mathbf{R}(l\kappa t_0)\ \text{ and }\ \mathbf{P}(l\kappa t_0)\ .$$

Proof. The proofs of these statements follow from Eq. (16) and the definitions, Eqs. (17) and (18). Equation (29) is easily derived whereas Eq. (30) needs a little manipulation. We obtain

$$i\hbar\frac{\partial}{\partial t}\mathbf{P}(l\kappa t)=\langle\langle 1|[\hat{\mathbf{P}}(l\kappa),\hat{H}_t]_-|\rho(t)\rangle\rangle$$
$$=\langle\langle 1|\{-i\hbar\mathbf{F}(l\kappa t)+[\hat{\mathbf{P}}(l\kappa),\hat{H}]_-\}|\rho(t)\rangle\rangle$$

and hence

$$\mathbf{D}[\mathbf{R}(l\kappa t)]=-\mathbf{F}(l\kappa t)-\langle\langle 1\left|\frac{\partial\hat{U}_N}{\partial\hat{\mathbf{R}}(l\kappa)}\right|\rho(t)\rangle\rangle \tag{31}$$

after working out the commutators and using the general result, Eq. (28). A more practical result is obtained by using the stationary action principle, which we shall now discuss.

Theorem 3. The physical action

$$A[\mathbf{R}(l\kappa t)]=\tfrac{1}{2}\int_{t_0}^{t_1}dt\,\langle\langle 1|(i\hbar D_t-\bar{H}_t)|\rho(t)\rangle\rangle \tag{32}$$

may now be represented as a functional of the molecular positions. It can be rewritten as

$$A[\mathbf{R}]=B[\mathbf{R}]-\int_{t_0}^{t_1}dt\sum_{l\kappa}\mathbf{F}(l\kappa t)\cdot\mathbf{R}(l\kappa t)\ , \tag{33}$$

where $B[\mathbf{R}]$ is a *universal* functional of molecular position, which holds for any external force, $\mathbf{F}(l\kappa t)$. The action, Eq. (32), is stationary at the exact molecular positions of the system, which can be computed from the stationarity condition

$$\frac{\delta A[\mathbf{R}]}{\delta\mathbf{R}(l\kappa t)}=0\ \text{ with given }\mathbf{R}(l\kappa t_0),\ \ \mathbf{P}(l\kappa t_0)\ . \tag{34}$$

The given initial conditions are themselves determined from the equilibrium free energy functional Ω given by Eq. (14):

$$\frac{\delta\Omega}{\delta\mathbf{R}(l\kappa t_0)}=0\ \text{ and }\ \mathbf{P}(l\kappa t_0)=M_\kappa\dot{\mathbf{R}}(l\kappa t_0)\ . \tag{35}$$

Proof. The proof follows in two steps as in the proof of Theorem 1. We first observe that the initial density matrix is a functional of $\mathbf{R}(l\kappa t_0)$. Then, following arguments similar to the one in proving Theorem 1, we show that the subsequent density matrix is a functional of $\mathbf{R}(l\kappa t)$, as in Eq. (28). These arguments then directly establish explicitly that $B[\mathbf{R}]$ is a functional $\mathbf{R}(l\kappa t)$ and is given by

$$B[\mathbf{R}]=\tfrac{1}{2}\int_{t_0}^{t_1}dt\,\langle\langle 1|(i\hbar D_t-\bar{H})|\rho(t)\rangle\rangle\ . \tag{36}$$

Since the action is stationary for the exact solution of the density matrix equation the corresponding functional given above must also be stationary for the exact time-dependent molecular positions of the system. A more familiar version of the equations of motion is obtained by introducing the corresponding noninteracting density matrix $|\rho_s(t)\rangle\rangle$ and action $B_s[\mathbf{R}]$ for the molecules, given by $B^s[\mathbf{R}]=\frac{1}{2}\int_{t_0}^{t_1}dt\,\langle\langle 1|(i\hbar D_t-\bar{T}_N)|\rho_s(t)\rangle\rangle$ so that we obtain the equation

$$M_\kappa\ddot{\mathbf{R}}(l\kappa t)=-\mathbf{F}_{\text{eff}}(l\kappa t)\ , \tag{37}$$

$$\mathbf{F}_{\text{eff}}(l\kappa t)=\mathbf{F}(l\kappa t)-\frac{\delta B_1}{\delta\mathbf{R}(l\kappa t)}\ , \tag{38}$$

where $B_1[\mathbf{R}]=B^s[\mathbf{R}]-B[\mathbf{R}]$, with the given initial conditions. It is useful to express these equations in terms of the Green functions defined by [13]

$$D_{\alpha\beta}(l\kappa t;l'\kappa' t')=\frac{\delta R_\alpha(l\kappa t)}{\delta F_\beta(l'\kappa' t')} \tag{39}$$

so that we now have the equation for it in the form for real times,

$$M_\kappa\frac{\partial^2}{\partial t^2}D_{\alpha\beta}(l\kappa t;l'\kappa' t')=-\delta_{\alpha\beta}\delta_{ll'}\delta_{\kappa\kappa'}\delta(t-t')-\sum_{l_1\kappa_1\gamma_1}\int dt_1\frac{\delta^2B_1[\mathbf{R}]}{\delta R_\alpha(l\kappa t)\delta R_{\gamma_1}(l_1\kappa_1 t_1)}D_{\gamma_1\beta}(l_1\kappa_1 t_1;l'\kappa' t')\ . \tag{40}$$

In equilibrium, Eq. (40) is replaced by a similar equation with the Green function D replaced by its equilibrium counterpart, which possesses periodicity in the imaginary time domain, and the functional B_1 replaced by its corresponding free energy functional, Ω_1, given by $\Omega^s-\Omega$, with Ω given by Eq. (14) and Ω^s defined as the free energy of the noninteracting molecular system as above. Moreover, the time t_1 integration is replaced by $\int_{t_0}^{t_0-i\beta}dt_1$.

It may be worthwhile to point out the relationship of the equilibrium part of the above theory with the self-consistent phonon theory [14] whose basis is the free energy, Eq. (14) and approximations thereof. This theory therefore provides us with Ω_1 mentioned above and hence also the equivalent dynamical force constants which are just the second derivatives of Ω_1 with respect to positions.

In summary, we have here developed a time-dependent functional theory of molecular motions which addresses a different class of self-consistent molecular dynamics problems than the molecular-density-functional theory. This theory is applicable to nonequilibrium situations as well.

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