Center of Mass and Relative Motion in Time Dependent Density Functional Theory

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It is shown that the theorem asserting separability of the center of mass motion for a system of interacting particles in a harmonic external potential is satisfied in the time dependent density functional theory, provided that the exchange-correlation potential satisfies a simple symmetry under transformation to an accelerated frame of reference. Examples of approximations for the exchange-correlation potential which satisfy or violate this symmetry are given.

Time dependent density functional theory (TDFT) [1–3] is a very useful tool for the study of the dynamic behavior of correlated electronic systems under the influence of external probes. This formalism maps the time dependent many-body problem onto a set of one-electron, self-consistent Hartree-like equations, which include, in addition to the Hartree potential, a local time dependent exchange-correlation potential. The range of problems to which TDFT is successfully applied is expanding [3,4]: it includes the calculation of atomic photoabsorption cross sections [5], the dynamics of electrons in quantum wells under very strong electromagnetic fields [6], and the calculation of excitation energies in atoms, molecules, and solids [7]. Crucial to the success of the theory is the availability of simple approximations for the exchange-correlation potential $V_{xc}[n; \vec{r}, t]$, which is an ordinary function of $\vec{r}$ and t, but a complicated, nonlocal functional of the density distribution $n(\vec{r}', t')$ for times t' earlier than t. Examples of approximations for V_{xc} are the adiabatic time dependent local density approximation (TDLDA) of Zangwill and Soven [5], and the local linear response approximation, with a frequency-dependent exchange-correlation kernel, of Gross and Kohn [2]. In constructing such approximations, it is desirable to satisfy as many of the known exact properties of the functional as possible. One example of rigorous constraints on approximate functionals is provided by the scaling relations for the static density functional theory [8]. Another type of constraint, which is peculiar to the time dependent theory, has been recently pointed out by Dobson [9]. In a system of interacting electrons confined by an external harmonic potential $V_h(\vec{r}) = (\frac{1}{2})\vec{r} \cdot \mathbf{K} \cdot \vec{r}$ the dynamics of the center of mass is completely decoupled from that of the internal degrees of freedom [10,11]. When a uniform time dependent electric field $\vec{E}(t)$ is applied to such a system, the density distribution is rigidly transported, according to the equation

$$n(\vec{r}, t) = n_0(\vec{r} - \vec{R}_{CM}(t)), \qquad (1)$$

where $n_0(\vec{r})$ is the static electronic density in the absence of the field, and $\vec{R}_{CM}(t)$ is the solution of the classical equation of motion

$$m \frac{d^2 \vec{R}_{CM}(t)}{dt^2} = - e\vec{E}(t) - \mathbf{K} \cdot \vec{R}_{CM}(t)$$
$$- \frac{e}{c} \frac{d\vec{R}_{CM}(t)}{dt} \times \vec{B}. \qquad (2)$$

This property of the exact density will be referred to as the "harmonic potential theorem" (HPT) [9]. Dobson's discovery [9] is that the HPT is not automatically satisfied in approximate versions of TDFT. For example, the Zangwill-Soven [5] adiabatic TDLDA does satisfy the HPT, but he Gross-Kohn [2] linearized response theory, which includes a frequency dependence in the exchange-correlation kernel, does not.

In this Letter, we demonstrate that the validity of the HPT in TDFT is guaranteed if the exchange-correlation potential satisfies a simple symmetry which is required in the *exact* theory. The approximations that Dobson finds to satisfy HPT are the ones that satisfy this symmetry, and those that violate the HPT are the ones that violate this symmetry. Furthermore, we present a general procedure whereby the correct symmetry of the exchange-correlation potential as a functional of density can be built into an approximation.

We begin by stating a few exact properties of the time dependent Schrödinger equation

$$\left(i \frac{\partial}{\partial t} - \hat{H} - \hat{V}(t) \right) |\psi(t)\rangle = 0, \qquad (3)$$

where

$$\hat{H} = \sum_{i=1}^{N} \frac{1}{2m} \left(\vec{p}_i + \frac{e}{c} \vec{A}(\vec{r}_i) \right)^2 + \frac{e^2}{2} \sum_{i,j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \qquad (4)$$

is the familiar Hamiltonian for N interacting electrons in the presence of a uniform magnetic field $\vec{B}$ described by the vector potential $\vec{A}(\vec{r}) = \vec{B} \times \vec{r}/2$, and $\hat{V}(t) = \sum_{i=1}^{N} V(\vec{r}_i, t)$ is the time dependent potential. The time dependent density $n(\vec{r}, t)$ is defined as the expectation value $\langle \psi(t)|\hat{n}(\vec{r})|\psi(t)\rangle$ of the density operator $\hat{n}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$.

Let us look at the system from the point of view of an accelerated observer whose position, relative to the

original reference frame, is given by the vector $\vec{x}(t)$. It is assumed that the accelerated observer uses Cartesian axes that remain parallel to the axes of the original reference frame and that $\vec{x}(t_0) = d\vec{x}(t)/dt(t = t_0) = 0$, so that both the density and the wave function seen by the accelerated observer coincide with those seen by the inertial observer at an "initial" time t_0. The accelerated observer describes the time evolution of the wave function in terms of the Schrödinger equation (3), in which the time dependent potential $V(\vec{r}, t)$ is replaced by

$$V'(\vec{r}, t) = V(\vec{r} + \vec{x}(t), t) + m\vec{a}(t)$$

$$\cdot \sum_{i=1}^{N} \vec{r}_i + (e/c)[\vec{v}(t) \times \vec{B}] \cdot \sum_{i=1}^{N} \vec{r}_i + f(t), \quad (5)$$

where $\vec{a}(t)$ and $\vec{v}(t)$ are the second and first derivatives of $\vec{x}(t)$ with respect to time, and $f(t) = N(-mv^2(t)/2 + (e/2c)[\vec{B} \times \vec{x}(t)] \cdot \vec{v}(t))$. The wave function ψ' in the accelerated reference frame is related to the wave function ψ in the original frame by the transformation

$$|\psi'(t)\rangle = \hat{U}(t)|\psi(t)\rangle, \quad (6)$$

where the unitary operator $\hat{U}(t) = \prod_{i=1}^{N} \hat{U}_i(t)$ is defined by

$$\hat{U}_i(t) = \exp\left[-i\vec{r}_i \cdot \left(m\vec{v}(t) - \frac{e}{2c}\vec{B} \times \vec{x}(t) \right) \right]$$

$$\times \exp[i\vec{p}_i \cdot \vec{x}(t)]. \quad (7)$$

The mathematical proof of the key equations (5) and (6) follows from the application of $\hat{U}(t)$ to the time dependent Schrödinger equation. However, the correctness of these equations is physically evident. Equation (5) says that the potential seen by the accelerated observer is the original potential expressed in terms of the new coordinate, plus a uniform inertial force $-m\vec{a}(t)$, and a uniform electric field $\vec{v} \times \vec{B}/c$ that arises from the transformation of the magnetic field. Equation (7) says that the new wave function is obtained from the former by translating the coordinate of each electron by $\vec{x}(t)$ and the momentum of each electron by $m\vec{v}(t)$. When the magnetic field is present an additional translation of the momentum by $-e\vec{B} \times \vec{x}(t)/2c$ is required. Notice that, for a system in a static harmonic potential, an applied uniform time dependent electric field can be eliminated by transforming to an accelerated reference frame moving according to Eq. (2). This observation proves the HPT.

Let us now turn our attention to time dependent density functional theory. The basic theorem here is the Runge-Gross theorem, according to which, for any time dependent density $n(\vec{r}, t)$ defined within an appropriate class of functions in the interval $t_0 < t < t_1$, and evolving from a *fixed* initial state $\psi(t_0)$, there exists an essentially unique time dependent potential $V(\vec{r}, t)$, such that the solution of the time dependent Schrödinger equation (3) yields $n(\vec{r}, t)$ as the expectation value of the density

operator. The expression "essentially unique" refers to the possibility of adding to $V(\vec{r}, t)$ an arbitrary function $c(t)$ of time, which causes the wave function to be multiplied by a phase factor $\exp[i \int c(t) dt]$ without affecting the density. The "appropriate class" of densities includes all the densities for which the potential $V(\vec{r}, t)$ exists, and is Taylor expandable, with finite convergence radius, in a neighborhood of t_0. Under the assumption that at time t_0 the system is in the ground state—an assumption that we make in the rest of this paper—the Runge-Gross theorem establishes the existence of an essentially unique mapping from time dependent densities to time dependent potentials and wave functions.

The exchange-correlation potential is constructed as follows. First, one defines the action functional [1]

$$\tilde{A}[n] = \int_{t_0}^{t_1} \langle \psi(t)|i \frac{\partial}{\partial t} - \hat{H}|\psi(t)\rangle dt, \quad (8)$$

where $|\psi(t)\rangle$ is the wave function that corresponds to $n(\vec{r}, t)$ according to the Runge-Gross theorem. The *noninteracting* action functional is similarly constructed

$$\tilde{A}_s[n] = \int_{t_0}^{t_1} \langle \psi_s(t)|i \frac{\partial}{\partial t} - \hat{T}|\psi_s(t)\rangle dt, \quad (9)$$

where ψ_s is the wave function corresponding to the density $n(\vec{r}, t)$ in a *noninteracting* system, and $\hat{T}$ is the kinetic energy operator. Then, following Runge and Gross, one defines the exchange-correlation part of the action functional via the equation

$$\tilde{A}[n] \equiv \tilde{A}_s[n] + A_H[n] + A_{xc}[n], \quad (10)$$

where the Hartree part of the functional is

$$A_H[n] = -\frac{e^2}{2} \int_{t_0}^{t_1} dt \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}, t)n(\vec{r}', t)}{|\vec{r} - \vec{r}'|}. \quad (11)$$

Finally, the exchange-correlation potential $V_{xc}[n; \vec{r}, t]$ is defined as the first functional derivative of the action $V_{xc}[n; \vec{r}, t] \equiv \delta A_{xc}[n]/\delta n(\vec{r}, t)$.

Let us now consider the action functional in the accelerated reference frame. The density seen by the accelerated observer is $n'(\vec{r}, t) = n(\vec{r} + \vec{x}(t), t)$. Using Eqs. (5) and (6), it is easy to see that the transformed action is

$$\tilde{A}[n'] = \tilde{A}[n] + N \int_{t_0}^{t_1} \left[m\vec{a}(t) \cdot \vec{R}_{CM}(t) + \frac{e}{c}[\vec{v}(t) \times \vec{B}] \right.$$

$$\cdot \vec{R}_{CM}(t) + \frac{mv^2(t)}{2}$$

$$\left. - \frac{e}{2c}[\vec{B} \times \vec{x}(t)] \cdot \vec{v}(t) \right] dt, \quad (12)$$

where

$$\vec{R}_{CM}(t) = \frac{1}{N} \int \vec{r} n(\vec{r}, t) d\vec{r} \quad (13)$$

is the coordinate of the center of mass of the density distribution. *Exactly the same transformation applies to*

the noninteracting action functional $\tilde{A}_s[n]$. Since the Hartree term in the action is manifestly invariant under the transformation $n \rightarrow n'$, we conclude, comparing the transformation equations for $\tilde{A}$ and $\tilde{A}_s$, that A_{xc} is invariant under this transformation:

$$A_{xc}[n'] = A_{xc}[n]. \tag{14}$$

This is the most important result in this paper. The transformation law for the exchange correlation potential is derived in the following way. We consider the difference between the xc action calculated for two neighboring densities n and $n + \delta n$:

$$A_{xc}[n + \delta n] - A_{xc}[n] = \int_{t_0}^{t_1} dt' \int d\vec{r} \, V_{xc}[n; \vec{r}', t'] \\ \times \delta n(\vec{r}', t'), \tag{15}$$

which follows from the definition of V_{xc} as a first functional derivative of A_{xc} with respect to the density. We can write the same relation for the transformed densities n' and $n' + \delta n'$, and, using Eq. (14), we easily establish the transformation

$$V_{xc}[n'; \vec{r}, t] = V_{xc}[n; \vec{r} + \vec{x}(t), t]. \tag{16}$$

Another interesting property of V_{xc} that follows directly from Eq. (14) is

$$\int \vec{\nabla} V_{xc}[n; \vec{r}, t] n(\vec{r}, t) \, d\vec{r} = 0, \tag{17}$$

for any density. This is nothing but the statement that the exact exchange-correlation potential (as well as the Hartree potential) does not exert a *net* force on the system, in compliance with the requirement of Newton's third law of motion.

We now show that an exchange-correlation potential that correctly transforms according to Eq. (16) automati-

cally satisfies the harmonic potential theorem. We suppose that for $t \leq t_0$ the density of the N interacting electron system is described by the static Kohn-Sham equation with a *time independent* external *harmonic* potential $V_h(\vec{r})$, and a static Hartree potential $V_H(n_0; \vec{r})$ and exchange-correlation potential $V_{xc}[n_0; \vec{r}]$. $n_0(\vec{r})$ is the static ground-state density, given by the sum of the square amplitudes of N single particle orbitals $\phi_i(\vec{r}, t) = \phi_i(\vec{r}) \exp[-i\epsilon_i t]$, with ϵ_i's the N lowest eigenvalues of the static Kohn-Sham equation. These orbitals satisfy the equation

$$\left[i \frac{\partial}{\partial t} - \hat{T} - V_h(\vec{r}) - V_H[n_0; \vec{r}] - V_{xc}[n_0; \vec{r}] \right] \\ \times \phi_i(\vec{r}, t) = 0. \tag{18}$$

The system is now perturbed by a uniform time dependent electric field $\vec{E}(t)$. Our task is to show that $n(\vec{r}, t) = n_0(\vec{r} - \vec{R}_{CM}(t))$, where $\vec{R}_{CM}(t)$ is the solution of the equation of motion (2), is a self-consistent solution of the time dependent Kohn-sham equation *in the presence of the driving electric field:*

$$\left[i \frac{\partial}{\partial t} - \hat{T} - V_h(\vec{r}) - V_H[n; \vec{r}, t] - V_{xc}[n; \vec{r}, t] \\ - e\vec{E}(t) \cdot \vec{r} \right] \phi_i^E(\vec{r}, t) = 0. \tag{19}$$

To prove this fact, we observe that Eq. (19) can be generated starting from Eq. (18), simply by applying to the latter a transformation to an accelerated frame of reference with $\vec{x}(t) = -\vec{R}_{CM}(t)$. Starting from Eq. (6), it is easy to prove that the transformed wave functions $\phi_i'(\vec{r}, t) = \hat{U}\phi_i(\vec{r}, t)$ satisfy the equation

$$\left[i \frac{\partial}{\partial t} - \hat{T} - V_0(\vec{r} - \vec{R}_{CM}(t)) - V_H[n_0; \vec{r} - \vec{R}_{CM}(t)] - V_{xc}[n_0; \vec{r} - \vec{R}_{CM}(t)] + m\vec{a}_{CM}(t) \cdot \vec{r} + \frac{e}{c} [\vec{v}_{CM}(t) \times \vec{B}] \cdot \vec{r} \right.$$

$$\left. + \frac{mv_{CM}^2(t)}{2} - \frac{e}{2c} [\vec{B} \times \vec{R}_{CM}(t)] \cdot \vec{v}_{CM}(t) \right] \phi_i'(\vec{r}, t) = 0. \tag{20}$$

Now, we substitute the harmonic potential form for

$$V_h(\vec{r} - \vec{R}_{CM}) = V_h(\vec{r}) - \vec{R}_{CM} \cdot \mathbf{K} \cdot \vec{r} \\ + \frac{1}{2} \vec{R}_{CM} \cdot \mathbf{K} \cdot \vec{R}_{CM}, \tag{21}$$

and we make use of the symmetry of the Hartree and exchange-correlation potentials $V_{xc}[n_0; \vec{r} - \vec{R}_{CM}(t)] = V_{xc}[n; \vec{r}]$. Using the equation of motion (2) to eliminate terms that depend on $\vec{R}_{CM}(t)$ we see that Eq. (20) is essentially equivalent to the Kohn-Sham equation (19) in the presence of the driving field. The only difference is a time dependent additive term in the potential which can be eliminated by further multiplying each wave function by the phase factor $\exp[iS(t)]$, where $S(t)$ is the classical action for the motion of the center of mass.

Since the orbitals $\phi_i^E = \phi_i' \exp[iS(t)]$ yield the density $n = n_0(\vec{r} - \vec{R}_{CM}(t))$ and satisfy the time dependent Kohn-Sham equation, in the presence of the driving field, with Hartree and exchange-correlation potentials evaluated at that same density n, we conclude that they *are* the self-consistent solution of the driven Kohn-Sham equation. Any approximation for V_{xc} that satisfies Eq. (16) will automatically satisfy the HPT.

Consider the adiabatic TDLDA [5]. The action functional in this approximation has the form

$$A_{xc}[n(\vec{r}, t)] = - \int_{t_0}^{t_1} dt \int d\vec{r} \, \epsilon_{xc}(n(\vec{r}, t)), \tag{22}$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy *density* of the uniform electron gas of density n. This expression is manifestly invariant under the transformation $n \to n'$ since the latter amounts to a simple change of variable in the space part of the integral. Therefore, the HPT is satisfied.

On the other hand, consider the linear response theory of Gross and Kohn [2] for V_{xc}. It has the form

$$V_{xc}[n; \vec{r}, t] = \mu_{xc}(n_0(\vec{r}))$$
$$+ \int_{t_0}^{t} f_{xc}[n_0(\vec{r}), t - t']\delta n(\vec{r}, t') \, dt', \quad (23)$$

where it is assumed that the density $n(\vec{r}, t) = n_0(\vec{r}) + \delta n(\vec{r}, t)$ deviates only slightly from the static equilibrium density. $\mu_{xc}(n_0(\vec{r}))$ is the exchange-correlation part of the chemical potential of the uniform electron gas of density n_0. The kernel $f_{xc}(n_0(\vec{r}), t - t')$ [2] is a function of a time difference, but only one position. In the case of harmonically confined electrons we know from Eq. (1) that $\delta n(\vec{r}, t) \sim -\vec{R}_{CM}(t) \cdot \vec{\nabla} n_0(\vec{r})$ if $\vec{R}_{CM}(t)$ is small. From Eq. (16), we also know that $V_{xc}[n; \vec{r}, t] = V_{xc}[n_0, \vec{r} - \vec{R}_{CM}(t)] \sim V_{xc}[n_0, \vec{r}] - \vec{R}_{CM}(t) \cdot \vec{\nabla}V_{xc}[n_0; \vec{r}]$, and $V_{xc}[n_0; \vec{r}] = \mu_{xc}(n_0(\vec{r}))$. Substituting this into Eq. (23) we see that the integral on the right-hand side must equal $\vec{\nabla}V_{xc}[n_0, \vec{r}] \cdot \vec{R}_{CM}(t)$. Because this must be true for an arbitrary (small) driven motion of $\vec{R}_{CM}(t)$, we see that the only admissible time dependence of $f_{xc}(n_0(\vec{r}), t - t')$ is proportional to a δ function of $t - t'$, i.e., the only admissible approximation in this class must be local in time as well as in space. Since the Gross-Kohn potential is nonlocal in time, it violates Eq. (16) and therefore also the harmonic potential theorem.

How can one make sure that approximate forms of the exchange-correlation potential satisfy Eq. (16)? A general way is to start from an action that depends only on the "relative density" defined as

$$n_{rel}(\vec{r}, t) \equiv n(\vec{r} + \vec{R}_{CM}(t), t), \quad (24)$$

where $\vec{R}_{CM}(t)$ is constructed from Eq. (13). By construction, n_{rel} is invariant with respect to transformation to an arbitrary accelerated frame of reference. Therefore, if the action functional is written as a functional of the relative density $A_{xc}[n(\vec{r}, t)] = \bar{A}_{xc}[n_{rel}(\vec{r}, t)]$, it will automatically satisfy the symmetry of Eq. (14). The exchange-correlation potential will then be given by

$$V_{xc}[n; \vec{r}, t] = \bar{V}_{xc}[n_{rel}; \vec{r} - \vec{R}_{CM}(t), t], \quad (25)$$

where $\bar{V}_{xc}[n_{rel}, \vec{r}, t] \equiv \delta \bar{A}_{xc}[n_{rel}]/\delta n_{rel}(\vec{r}, t)$. As a first application of this method we construct an approximate exchange-correlation functional for small displacements from equilibrium, which is frequency dependent in the spirit of the Gross-Kohn treatment, but sat-

isfies the HPT. We write the relative density as $n_{rel}(\vec{r}, t) = n_0(\vec{r}) + \delta n_{rel}(\vec{r}, t)$, where $n_0(\vec{r})$ coincides with the absolute initial density, because the center of mass is initially at the origin of the coordinates. The correction δn_{rel} vanishes in the case of uniformly driven harmonically confined system, but it need not vanish in more general cases. The exchange-correlation potential is approximated as

$$\bar{V}_{xc}[n_{rel}; \vec{r}, t] = \mu_{xc}(n_0(\vec{r}))$$
$$+ \int_{t_0}^{t} dt' f_{xc}[n_0(\vec{r}); t - t']\delta n_{rel}(\vec{r}, t'), \quad (26)$$

where $f_{xc}[n_0, t - t']$ is the Gross-Kohn exchange-correlation kernel. $\vec{R}_{CM}(t)$ itself must be determined self-consistently from the knowledge of the full density, according to Eq. (13).

We note, in closing, that all our results could be easily generalized to the case of a uniform time dependent magnetic field. The HPT generalizes to this case. The only difference is the appearance of the additional electric field $(e/2c)d\vec{B}(t)/dt \times \vec{x}(t)$ in Eq. (5).

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