Several Theorems in Time-Dependent Density Functional Theory

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The time dependence of the exchange-correlation energy in density functional theory is given in terms of the exchange-correlation potential. The virial theorem for the exchange-correlation potential is shown to hold for *time-dependent* electronic systems and is illustrated by an exactly solved model: Hooke's atom with a time-dependent force constant. A relation between the coupling constant and functionals evaluated on scaled densities is derived. [S0031-9007(98)08169-1]

Ground-state electronic density functional theory (DFT) has long been used to perform electronic structure calculations of solids and has recently become popular in quantum chemistry [1]. Many useful properties can be derived from calculations of ground-state electronic energies, such as geometric and vibrational structure and static response functions.

An important part of making DFT results useful to the broad community of users has been in improving the accuracy of approximations to the exchange-correlation energy functional, $E_{XC}[n]$, the only part of the energy which must be approximated in a Kohn-Sham calculation [2]. A vital part of this approach, in turn, has been the study of exact conditions satisfied by density functionals, especially the exchange and correlation energies. A simple example is that the correlation energy is never positive, and always finite [3]. Satisfaction of energetically relevant conditions is often used to guide construction of approximations, such as the Perdew-Burke-Ernzerhof generalized gradient approximation [4]. This functional is now commonly used in electronic structure calculations.

In the past several years, interest has grown in *time-dependent* density functional theory (TDDFT), which is now a very active research area [5]. There is a wealth of applications for an accurate theory, such as atoms, molecules, and solids in intense laser fields [6], dynamic response properties [7], and electronic spectroscopy [8]. A fully developed TDDFT would allow, e.g., study of optical limiting materials [9] or electron dynamics on a femtosecond time scale [10].

While formal TDDFT was put on solid ground with the Runge-Gross theorem [11] (the analog of the Hohenberg-Kohn theorem), exploration of the exact properties of time-dependent functionals is still in its infancy. Several exact conditions have been found, including Newton's third law [12], which implies that the net exchange-correlation force must vanish, and translational invariance, which states that the time-dependent exchange-correlation potential $v_{XC}(\mathbf{r}t)$ for a boosted static density will be that of the unboosted density, evaluated at the boosted point. The latter theorem, applied to a harmonic potential, showed that the Gross-Kohn

approximation [13] for frequency-dependent response properties violates the Kohn theorem [14]. This led to several new approximations [15], which overcome this difficulty, but remain largely untested.

In this work, we take a different approach from previous workers, in that we consider the energy components of the system, even though the total energy is not conserved. We find several simple relations satisfied by these energy components, which are then restrictions which approximate functionals should satisfy. We also derive the relation between coordinate scaling and the adiabatic coupling constant.

We begin our proofs with the Heisenberg equation of motion for any operator $\hat{A}$ on a quantum-mechanical system:

$$\dot{A} = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle, \tag{1}$$

where $A = \langle \hat{A} \rangle$, and the dot denotes a time derivative. We apply this to a system of N identical particles, with $\hat{H} = \hat{T} + \hat{V}$, where $\hat{T}$ is the kinetic energy operator, and $\hat{V}$ is the potential energy operator. For interacting electronic systems, the potential consists of a time-dependent one-body contribution, $V_{ext}(t)$, and a two-body contribution, V_{ee}, the Coulomb interaction between the electrons. Applying Eq. (1) to $\hat{A} = \hat{H}$ itself, we find

$$\dot{T} + \dot{V}_{ee} + \dot{V}_{ext} = \left\langle \frac{\partial V_{ext}}{\partial t} \right\rangle. \tag{2}$$

Since $V_{ext} = \int d^3r \, n(\mathbf{r}t) v_{ext}(\mathbf{r}t)$,

$$\dot{T} + \dot{V}_{ee} = -\int d^3r \, \dot{n}(\mathbf{r}t) v_{ext}(\mathbf{r}t). \tag{3}$$

So far, we have simply derived a general result for time-dependent quantum mechanics. But we now apply this to the Kohn-Sham system, i.e., that fictitious system of noninteracting particles which has the same time-dependent density $n(\mathbf{r}t)$. Thus

$$\dot{T}_S = -\int d^3r \, \dot{n}(\mathbf{r}t) v_s(\mathbf{r}t), \tag{4}$$

where T_S is the noninteracting kinetic energy and $v_S(\mathbf{r}t)$ is the Kohn-Sham potential. Analogous to the ground

state [2], we write $T_C = T - T_S$ and $E_{XC} = V_{ee} - U + T_c$, where U is the Hartree energy, while $v_S = v_{ext} + v_H + v_{XC}$, where v_H is the Hartree potential. These are all time-dependent quantities here, and energy is not conserved. Since $\dot{U} = \int d^3r\, \dot{n}(\mathbf{r}t)v_H(\mathbf{r}t)$, we find, subtracting Eq. (4) from (3),

$$\frac{dE_{XC}}{dt} = \int d^3r\, \dot{n}(\mathbf{r}t)v_{XC}(\mathbf{r}t). \qquad (5)$$

The time dependence of the exchange-correlation energy is solely determined by the exchange-correlation potential.

Another simple result is the virial theorem. We write $\hat{A} = \sum a(\mathbf{r}_i, \mathbf{p}_i)$, where $\mathbf{r}_i$ is the position of the ith particle and $\mathbf{p}_i$ is its momentum, and choose $a = (\mathbf{r} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{r})/2$:

$$\frac{1}{2}\frac{d}{dt}\langle(\mathbf{r} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{r})\rangle = 2T - \left\langle \sum_i \mathbf{r}_i \cdot \nabla_i V \right\rangle. \qquad (6)$$

For a stationary state, the left-hand side vanishes, yielding the customary virial theorem [16]. Since V_{ee} is homogeneous of degree -1 in the coordinates, its virial is equal to minus itself, yielding

$$\frac{1}{2}\frac{d}{dt}\langle(\mathbf{r} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{r})\rangle = 2T + V_{ee} - \langle\mathbf{r} \cdot \nabla v_{ext}\rangle. \qquad (7)$$

To further simplify the left-hand side above, we consider Eq. (1) for $a = r^2$, finding $md\langle r^2\rangle/dt = \langle\mathbf{r} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{r}\rangle$. Insertion into Eq. (7) yields

$$\frac{m}{2}\frac{d^2}{dt^2}\langle r^2\rangle = 2T + V_{ee} - \langle\mathbf{r} \cdot \nabla v_{ext}\rangle. \qquad (8)$$

In the Kohn-Sham system, this becomes

$$\frac{m}{2}\frac{d^2}{dt^2}\langle r^2\rangle = 2T_s - \langle\mathbf{r} \cdot \nabla v_s\rangle. \qquad (9)$$

Since the left side of Eq. (8) depends only on the density, it is the same in both the physical and the Kohn-Sham systems. Since the Hartree energy is also homogeneous of degree -1, we find

$$E_{XC}[n](t) + T_C[n](t)$$
$$= -\int d^3r\, n(\mathbf{r}t)\mathbf{r} \cdot \nabla v_{XC}[n](\mathbf{r}t). \quad (10)$$

In deriving Eq. (10), we never require v_{XC} to be a functional derivative, thereby avoiding the need to define an action [5]. Equation (7) also implies an exact condition on the Kohn-Sham density matrix:

$$\int d^3r\, \mathbf{r} \cdot \nabla\gamma(\mathbf{r}\mathbf{r}'t)|_{\mathbf{r}'=\mathbf{r}} = \int d^3r\, \mathbf{r} \cdot \nabla\gamma_S(\mathbf{r}\mathbf{r}'t)|_{\mathbf{r}'=\mathbf{r}}. \qquad (11)$$

A last theorem relates coordinate scaling to the coupling constant for the electron-electron repulsion [17]. The Schrödinger equation for N electrons is

$$\left\{\hat{T} + \hat{V}_{ee} - i\frac{\partial}{\partial t}\right\}\Psi(\mathbf{r}_1\ldots\mathbf{r}_Nt) = -\hat{V}_{ext}\Psi(\mathbf{r}_1\ldots\mathbf{r}_Nt). \qquad (12)$$

[Note that we could have derived Eq. (7) by replacing $\mathbf{r}_i$ by $\mathbf{r}'_i/\gamma$ everywhere and taking $d/d\gamma|_{\gamma=1}$ of both sides.]

Consider $\Psi^\lambda[n]$ to be the solution of Eq. (12), but with electron-electron repulsion $\lambda\hat{V}_{ee}$, and $v_{ext}^\lambda(\mathbf{r}, t)$ chosen to keep the density fixed (at its $\lambda = 1$ value). Then let $\mathbf{r}_i \to \gamma\mathbf{r}'_i$ and $t \to \beta t'$ and multiply through by γ^2. If we define

$$\Psi_{\gamma\beta}(\mathbf{r}_1\ldots\mathbf{r}_Nt) = \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1\cdots\gamma\mathbf{r}_N\beta t), \qquad (13)$$

we find Eq. (12) becomes

$$\left\{\hat{T} + \lambda\gamma\hat{V}_{ee} - i\frac{\gamma^2}{\beta}\frac{\partial}{\partial t}\right\}\Psi_{\gamma\beta}^\lambda[n] = -\gamma^2\hat{V}_{ext}^\lambda\Psi_{\gamma\beta}^\lambda[n]. \qquad (14)$$

By choosing $\beta = \gamma^2$ and $\gamma = 1/\lambda$, we find $\Psi_{1/\lambda,1/\lambda^2}^\lambda[n]$ satisfies Eq. (12), i.e., is equal to $\Psi[n]$. (By the Runge-Gross theorem, the potentials must be identical if the densities are the same for both wave functions.)   Thus

$$\Psi^\lambda[n] = \Psi_{\lambda\lambda^2}[n_{1/\lambda,1/\lambda^2}] \qquad (15)$$

and, by subtracting out Hartree and Kohn-Sham contributions,

$$v_{XC}^\lambda[n](\mathbf{r}t) = \lambda^2 v_{XC}[n_{1/\lambda,1/\lambda^2}](\lambda\mathbf{r}, \lambda^2 t). \qquad (16)$$

Thus any functional of the density, evaluated at coupling constant λ, can be written in terms of the physical functional, evaluated on a scaled density at the scaled coordinates. For example, following arguments first applied to the ground state [16],

$$E_X[n_{\gamma\gamma^2}](t) = \gamma E_X[n](\gamma^2 t). \qquad (17)$$

Highly accurate calculations on time-dependent systems are usually extremely demanding [5], making tests of exact theorems and approximations very difficult in TDDFT. We performed exact numerical calculations on Hooke's atom, two interacting electrons in parabolic potential, with a time-dependent force constant, $k(t) = m\omega^2(t)$. This model is solvable because

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Phi(\mathbf{R}, t)\phi(\mathbf{u}, t), \qquad (18)$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$. Each wave function satisfies a single-particle time-dependent Schrödinger equation, e.g.,

$$\left(-\frac{1}{2\mu}\nabla^2 + \frac{\mu\omega^2(t)}{2}u^2 + \frac{1}{u}\right)\phi = i\dot{\phi}, \qquad (19)$$

where $\mu = m/2$ is the reduced mass. Then ϕ is expanded in the adiabatic basis of instantaneous eigenstates of its Hamiltonian:

$$\phi(u, t) = \sum_j b_j(t)\chi_j[\omega(t); u]e^{-i\epsilon_j[\omega(t)]t}, \qquad (20)$$

where

$$\left(-\frac{1}{2\mu}\nabla^2 + \frac{\mu\omega^2}{2}u^2 + \frac{1}{u}\right)\chi_j(\omega; u) = \epsilon_j(\omega)\chi_j(\omega; u). \qquad (21)$$

These eigenstates in turn are solved by expanding the wave function in a power series in u times a Gaussian [18]. The coefficients b_k satisfy

$$\dot{b}_k = i\dot{\epsilon}_k b_k t - \sum_{j \neq k} b_j \langle j|\dot{V}(t)|k\rangle e^{-i(\epsilon_j - \epsilon_k)t}/(\epsilon_j - \epsilon_k),$$
(22)

where $\dot{V} = \mu\omega\dot{\omega}u^2$, and are solved numerically.

We start our system in the ground state at $t = 0$ with $\omega = \omega_0$ and then let $\omega(t) = \omega_0 + (\omega_1 - \omega_0)\{\sin[\pi(t/t_1 - \frac{1}{2})] + 1\}/2$, as shown in Fig. 1. We show results for the time evolution with $\omega_0 = 0.5$, $\omega_1 = 1$, and $t_1 = 1$ in atomic units ($e^2 = m = \hbar = 1$). The first three occupation numbers (in u) and the time-dependent frequency are shown in Fig. 1. By $t = 1.6$, the system is about 30% excited. After $t = 1.6$, the number of u levels in our calculation (12) were no longer sufficient to guarantee the accuracy needed for the calculations shown below.

In Fig. 2, we plot T, V_{ext}, and V_{ee} as a function of time, as well as $\frac{1}{2}md^2\langle r^2\rangle/dt^2$. Here $\langle \mathbf{r} \cdot \nabla v_{\text{ext}}\rangle = 2V_{\text{ext}}$. We find the virial theorem of Eq. (8) to be satisfied to within 0.1 millihartree. If we contrast our results with an adiabatic situation (in which the system remains in the instantaneous ground state for all times), we see that T remains remarkably low, as the wave function takes time to respond to the stimulus. V_{ext} grows, but then drops after $t = 0.9$, while ω is still increasing. The Coulomb repulsion barely changes during the entire run. Finally, the large value of $2(T - V_{\text{ext}}) + V_{\text{ee}}$ contrasts with its vanishing in any single eigenstate.

Next, we calculate the exact Kohn-Sham potential for this two-electron system. We have a single orbital, doubly occupied, but the calculation is more involved than for a ground state, as the phase of the wave function becomes important. We write $\phi(\mathbf{r}t) = e^{i\alpha}\sqrt{n/2}$ and insert this form into the time-dependent Kohn-Sham equation. Requiring that the imaginary part of $v_s(\mathbf{r}t)$ be

zero yields

$$\alpha' = -\frac{1}{n(r,t)r^2}\int_0^r \dot{n}(r',t)r'^2 dr',$$
(23)

where the prime indicates d/dr, and

$$v_S = \frac{1}{2r}\left(\frac{n'}{n}\right) + \frac{n''}{4n} - \frac{1}{8}\left(\frac{n'}{n}\right)^2 - \frac{1}{2}\alpha'^2 - \dot{\alpha}.$$
(24)

The last two terms arise purely from the time dependence of the density. Even for a noninteracting system, they are nonzero. The exchange-correlation contribution is then found by subtracting the external and Hartree potentials.

In Fig. 3, we plot $v_c(\mathbf{r}t)$ at several times during the excitation. We do not plot $v_X(\mathbf{r}t)$, as this is just $-v_H(\mathbf{r}t)/2$ for two electrons. These curves are qualitatively similar to those in the adiabatic ground states. The strange behavior beyond $r = 3$ for $t = 1.5$ is due to numerical inaccuracy. We tested Eq. (5) on these potentials, finding it satisfied within the accuracy of the calculations.

Next, we plot the quantities appearing in Eq. (10) in Fig. 4. We subtract out the exchange contribution, which trivially satisfies the virial theorem in this case ($E_X = -U/2$). The line denoted virial is just the virial of the correlation potential and is indistinguishable from $E_C + T_C$ until about $t = 1.4$, where numerical inaccuracies arise. As noted above, V_{ee} is very unresponsive to the external potential, and this is reflected in E_C. The kinetic correlation energy follows T and starts to grow at about $t = 0.8$. What is remarkable is that this means that the sum $E_C + T_C$, which has never been found to be positive in any ground state, becomes *positive* around 1.2. This shows that time-dependent energy components can behave very differently from their ground-state analogs.

To illustrate our scaling theorem, Eq. (15), consider the plasmon frequency of a uniform gas, ω_p where $\omega_p^2 = 4\pi e^2 n/m$. Under scaling, $n \to \gamma^3 n$ and $\omega \to \omega/\gamma^2$, so
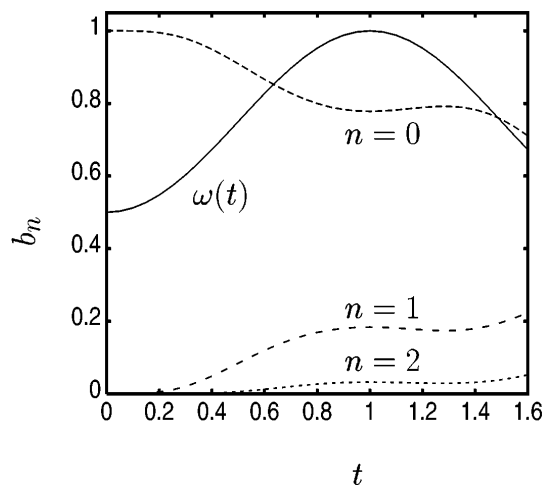

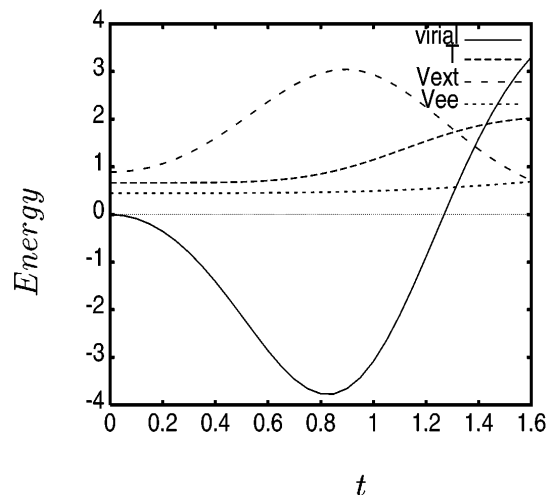FIG. 1. Occupation numbers for the u wave function and $\omega(t)$ (atomic units).

FIG. 2. Energy components for the time-dependent Hooke's atom (hartrees); virial $= 2(T - V_{\text{ext}}) + V_{\text{ee}}$.
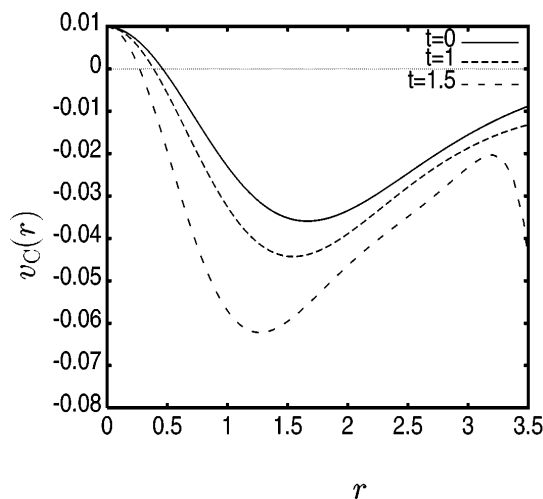
FIG. 3.   Time-dependent correlation potentials (atomic units).

that, according to Eq. (15), $(\omega_p^\lambda)^2 = 4\pi e^2 \gamma^3 n/(m\gamma^4) = \lambda\omega_p^2$, correctly. The importance of Eq. (16) is that it applies to all inhomogeneous systems also.

Last, we discuss the implications of Eqs. (5) and (10) for the construction of approximate time-dependent functionals. These are usually written as approximations to the exchange-correlation potential. If an approximation implies an assumption about energy components, then Eqs. (5) and (10) should be checked. If not, then Eqs. (5) and (10) can be used to construct energy components. An adiabatic approximation employs only the instantaneous density to approximate the potential at any given time. Such an approximation satisfies Eqs. (5) and (10) if it satisfies them in the ground state. If it is an accurate approximation for the energy components, it will then be accurate for the virial of the potential, providing a constraint on the approximate potential. This may explain the "surprising" accuracy of approximate potentials in Ref. [19]. The oldest and most commonly used [20] is adiabatic local-density approximation (ALDA),
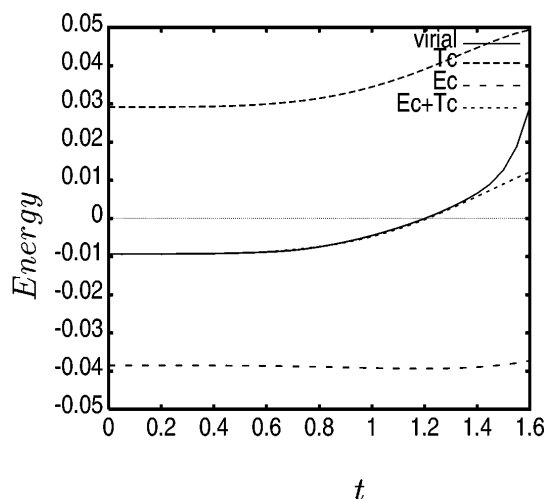
which simply constructs properties, such as the time-dependent exchange-correlation potential, using ground-state uniform gas functions, at the given instant in time. On the other hand, in regions where the time-dependent energy components differ qualitatively from their ground-state counterparts, such approximations will fail badly. For example, $E_C^{\text{ALDA}} + T_C^{\text{ALDA}} < 0$ always.

FIG. 4.   Time-dependent energy components (hartrees).

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Erratum: Several Theorems in Time-Dependent Density Functional Theory
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The dependence on the initial wave function, $\Psi(0) = \Psi(\mathbf{r}_1 \cdots \mathbf{r}_N, t = 0)$, was missing from the relations between the scaling and coupling constant. By considering $\Psi^\lambda[n; \Psi(0)]$, the wave function with electron-electron repulsion $\lambda \hat{V}_{ee}$ generating n from an initial wave function $\Psi(0)$, one finds

$$\Psi^\lambda[n; \Psi(0)] = \Psi_{\lambda\lambda^2}[n_{1/\lambda, 1/\lambda^2}; \Psi_{1/\lambda}(0)], \tag{15}$$

where $\Psi_\gamma(0) = \gamma^{3N/2}\Psi(\gamma\mathbf{r}_1 \cdots \gamma\mathbf{r}_N, t = 0)$. Thus Eq. (16) becomes

$$v_{\mathrm{xc}}^\lambda[n; \Psi(0), \Phi(0)](\mathbf{r}t) = \lambda^2 v_{\mathrm{xc}}[n_{1/\lambda, 1/\lambda^2}; \Psi_{1/\lambda}(0), \Phi_{1/\lambda}(0)](\lambda\mathbf{r}, \lambda^2 t), \tag{16}$$

where $\Phi(0)$ is the initial state in the Kohn-Sham system, while Eq. (17) becomes

$$E_{\mathrm{x}}[n_{\gamma\gamma^2}; \Phi_\gamma(0)](t) = \gamma E_{\mathrm{x}}[n; \Phi(0)](\gamma^2 t). \tag{17}$$

[We also note that, in Eq. (14), the coordinates in the external potential should have been scaled.]

We thank Robert van Leeuwen for bringing this oversight to our attention.