

Memory in Time-Dependent Density Functional Theory

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Exact time-dependent density functionals remember both the entire history of the density and the initial wave function. We show that the two effects are intimately related, and all history dependence can be written as initial-state dependence, including that of the exchange-correlation kernel. For states that can be evolved from a ground state, all initial-state dependence is a dependence on a pseudo-prehistory, providing a route to excited-state densities from time-dependent density functional theory.

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Ground-state density functional theory (DFT) is a promising alternative to wave function calculations for electronic structure and properties. Modern DFT is in principle exact, built on the Hohenberg-Kohn theorem [1]: The ground-state density of an interacting N -electron system in a static external potential completely determines all of its properties (e.g., energy, bond lengths, even excited states). The practical power of DFT lies in mapping the system to a fictitious noninteracting system of the same ground-state density, the Kohn-Sham (KS) system [2], with a one-body potential. Solution of these self-consistent orbital equations is far faster than solution of the Schrödinger equation, allowing calculations on large systems of interest in materials science and chemistry, and employing increasingly accurate approximations to the exchange-correlation (XC) energy [3].

There has been a recent explosion of interest in time-dependent DFT (TDDFT) which treats interacting electrons in time-dependent (TD) external potentials, and leads to TD KS equations for fictitious noninteracting electrons. For example, atoms and molecules in intense laser fields can be treated. Furthermore, the response to weak external fields is now calculated in many quantum chemistry codes, giving accurate predictions of electronic transition frequencies, oscillator strengths, polarizabilities, etc. The first TDDFT calculations of the optical response of solids have begun to appear [4,5].

Most of these calculations use a simple approximation for the XC contribution to the TD KS potential $v_S(\mathbf{r}t)$. In the ubiquitous adiabatic local density approximation (ALDA), $v_{XC}^{ALDA}(\mathbf{r}t) = v_{XC}^{unif}[n(\mathbf{r}t)]$, where $v_{XC}^{unif}[n]$ is the XC potential of a uniform electron gas of density n . While modern generalized gradient approximations and hybrids with exact exchange cure some of the drawbacks of the spatially local approximation, it is well understood that the exact KS potential depends in general on the entire history of the density, not just on its value at the given instant in time [6]. The XC kernel, $f_{XC}[n](\mathbf{r}t, \mathbf{r}'t') = \delta v_{XC}[n](\mathbf{r}t) / \delta n(\mathbf{r}'t')$, is not simply proportional to $\delta(t - t')$, as it is in any adiabatic approximation. There have been several

attempts to model these history effects [7–11]. The history effect in fully TD calculations has been explored in recent work [12] where we studied Hooke's atom with a TD force constant, beginning in the ground state. The correlation potential is a highly non-local-in-time functional of the density, and the correlation energy can become positive. This is impossible for ground states, and would be missed by any adiabatic density functional.

A much less-studied difference from the ground-state theory is that in TDDFT the mapping between densities and potentials is unique only for a specified initial state [13], e.g., $v_S[n, \Phi(0)](\mathbf{r}t)$, where $\Phi(0)$ is the initial KS wave function. This initial-state dependence is usually avoided by starting the system in its ground state which, if nondegenerate, is then a functional of the initial density [1]. Attempts to approximate history dependence have all begun from the ground state.

Recently, it has been shown [14] how to construct the potential for a given TD density and suitable initial wave function, and two of us have performed this construction for two noninteracting electrons, finding that different TD KS wave functions can produce the same evolving density, by starting from different initial KS wave functions [15]. The KS potentials of the two systems are quite different, as in the one-dimensional example of Fig. 1. If we imagine these systems to be the KS systems of an interacting problem, then the difference in the KS potentials is the difference in the XC potentials. Any approximate TD XC potential lacking initial-state dependence predicts the same potential for each case. We return to this figure shortly.

Here we demonstrate an intimate relation between the two memory effects: initial-state dependence and history. One can express history effects as initial-state effects and vice versa. Often initial-state dependence can be completely expressed as a history dependence. Functional differentiation of this result expresses the XC kernel in terms of initial-state dependence. The logical consequences of these results are profound, especially in application of TDDFT to non-ground-state situations. We discuss a conundrum arising for certain excited states.

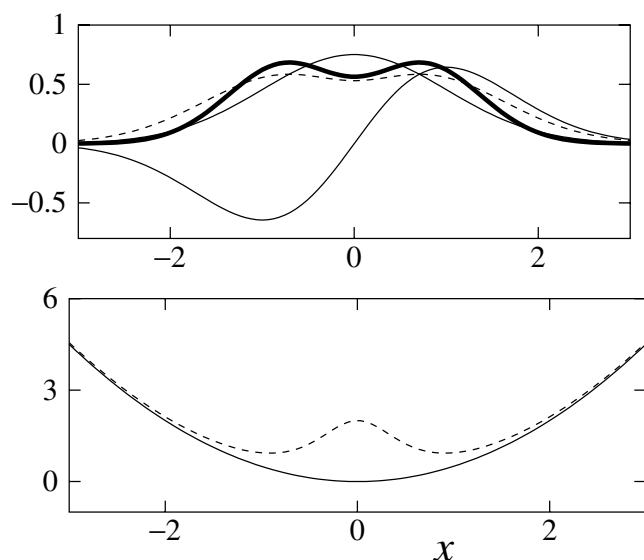


FIG. 1. In the top panel is the density (thick solid line) of a two electron singlet excited state; the KS orbitals are the solid lines, and v_S is the harmonic oscillator (solid line in bottom panel). The dashed line is the doubly occupied orbital resulting from evolving, with TD KS equations, a singlet ground state to a state of the same density as the excited state. The KS potential in which this is an eigenstate (the ground state) is the dashed line in the lower panel.

A system begins with wave function $\Psi(0)$ at time $t = 0$, and evolves according to

$$\hat{H}(t)\Psi(t) = i\partial\Psi(t)/\partial t, \quad (1)$$

where $\hat{H}(t)$ consists of a kinetic-energy operator, an inter-particle interaction, and a TD one-body external potential, $v_{\text{ext}}(\mathbf{r}t)$. The single-particle density is then determined by

$$n_0(\mathbf{r}t) = N \sum_{\sigma} \int dx_2 \cdots dx_N |\Psi(x, x_2, \dots, x_N, t)|^2, \quad (2)$$

where we have added the subscript to indicate the start time of this density (see below). The variables $x_i = (\mathbf{r}_i, \sigma_i)$ represent the spatial and spin coordinates. The Runge-Gross (RG) theorem states that, for a given particle interaction and statistics, $v_{\text{ext}}(\mathbf{r}t)$ is uniquely determined by $n_0(\mathbf{r}t_1)$ for all $0 < t_1 < t$ and $\Psi(0)$.

However, we could equally well consider some intermediate time t' , $0 < t' < t$, as the *initial* time. For this initial time, the initial wave function is $\Psi(t') = U(t')\Psi(0)$, where $U(t)$ is the unitary evolution operator, and the subsequent wave function, density, and external potential are those of the original case; i.e.,

$$v_{\text{ext}}[n_{t'}, \Psi(t')](\mathbf{r}t) = v_{\text{ext}}[n_0, \Psi(0)](\mathbf{r}t) \quad \text{for } t \geq t', \quad (3)$$

where

$$n_{t'}(\mathbf{r}t) = n(\mathbf{r}t) \quad \text{for } t \geq t', \quad (4)$$

and $n_{t'}(\mathbf{r}t)$ is undefined for $t < t'$. To see why this trivial statement in quantum mechanics has profound implications for TDDFT, apply it also to the fictitious noninter-

acting KS system with the same time-evolving density:

$$v_S[n_{t'}, \Phi(t')](\mathbf{r}t) = v_S[n_0, \Phi(0)](\mathbf{r}t) \quad \text{for } t \geq t', \quad (5)$$

where $\Phi(0)$ is an allowed KS initial state at time 0 (which means both its density and the divergence of its current match those of $\Psi(0)$ [13,14]), and $\Phi(t') = U_S(t')\Phi(0)$, where $U_S(t')$ is the KS time-evolution operator. Since $v_{\text{XC}} = v_S - v_{\text{ext}} - v_H$, where v_H is the instantaneous Hartree potential which depends only on the density at that instant in time (i.e., has no memory), then

$$v_{\text{XC}}[n_{t'}, \Psi(t'), \Phi(t')](\mathbf{r}t) = v_{\text{XC}}[n_0, \Psi(0), \Phi(0)](\mathbf{r}t), \quad (6)$$

for $t \geq t'$. This is the central result of this paper. Any dependence of the XC potential on the density at prior times may be transformed into an initial-state dependence and vice versa.

As in other exact conditions [8,16], Eq. (6) may be used as a test of approximate functionals. By ignoring both history dependence *and* initial-state dependence, ALDA trivially satisfies this relation. But any of the recent attempts to include history dependence, while ignoring initial-state dependence, must fail, since the histories on either side of Eq. (6) differ. If we restrict their application only to systems beginning in the ground state (discussed in more detail below), then Eq. (6) may be treated as the *definition* of an implied initial-state dependence. Still Eq. (6) produces a strict test of such functionals. Imagine an exact TD calculation beginning in the ground state of some system, as in Ref. [12], at $t = 0$. Later, when $\Psi(t')$ is no longer a ground state, we evolve *backwards* in time in an alternative external potential, and find a pseudo-prehistory beginning from a different ground state at a different initial time. Then, according to Eq. (6), the XC potential for all times greater than t' should be the same for both the original evolution and the evolution along the alternative path. The extent to which these two differ is a measure of the error in a given history-dependent approximation, even applied only to initial ground states. (Note that any adiabatic approximation ignoring initial-state dependence produces no difference.)

Although RG was proven only for analytic potentials (i.e., those that equal their Taylor series expansions at t in a neighborhood of t in $[0, \infty)$ for all $t \geq 0$) [13], it holds also for piecewise analytic potentials, i.e., potentials that are analytic in each of a finite number of intervals. The potential $v(t)$ need not have the same Taylor expansion in one interval as it does in another, so the points where they join may be points of nonanalyticity [17]. Consider evolving the same initial state in two piecewise analytic potentials $v_{\text{ext}}(t)$ and $v'_{\text{ext}}(t)$ which differ by more than a purely TD function. We break up time into a finite number of intervals $[t_n, t_{n+1}]$ so that $v_{\text{ext}}(t)$ and $v'_{\text{ext}}(t)$ are both analytic on each interval. If the two Taylor series at $t = 0$, in the first time interval, differ at some order by more than a purely TD function, then the proof of the RG paper applies directly. If they coincide (up to a purely TD function),

one then considers the next time interval. Let us say they coincide, for example, up to the n th segment and differ in the $(n + 1)$ st. Since the potential is uniquely determined on the interval $[0, t_n]$ (up to a purely TD function) and the wave function $\Psi(0)$ is specified (up to an irrelevant purely TD phase), then $\Psi(t_n)$ is determined uniquely. This is the initial wave function for the segment starting at t_n , in which the Taylor series at $t = t_n$ to the right for the two potentials differ, and, hence, the RG proof follows directly once more. This extension of RG is used in many present-day applications of TDDFT [18], e.g., an atom in a laser field that is turned off after a finite time.

This means that different allowed pseudo-prehistories can connect to the same wave function at some later time.

$$\sum_{\alpha} \int d^3 r_1 \frac{\delta v_S[n_{t'}, \Phi(t')](\mathbf{r}t)}{\delta \phi_{t', \alpha}(\mathbf{r}_1)} \phi_{t', \alpha}^{(1)}(\mathbf{r}_1) - \int dx_1 \cdots dx_N \frac{\delta v_{\text{ext}}[n_{t'}, \Psi(t')](\mathbf{r}t)}{\delta \Psi_{t'}(x_1 \cdots x_N)} \Psi_{t'}^{(1)}(x_1 \cdots x_N) + \text{c.c.} = \int d^3 r_1 \int_0^{t'} dt_1 f_{\text{XC}}[\bar{n}](\mathbf{r}\mathbf{r}_1, t - t_1) n^{(1)}(\mathbf{r}_1, t_1), \quad (7)$$

where the derivatives in the first two terms are the functional derivatives of the KS potential with respect to the “initial” KS state $[\bar{\phi}_{t', \alpha}(r_1) = e^{-i\bar{\epsilon}_{\alpha} t'} \bar{\phi}_{\alpha}(r_1, 0)]$, and of the external potential with respect to the initial interacting state $[\bar{\Psi}_{t'}(x_1 \cdots x_N) = e^{-i\bar{E}_o t'} \bar{\Psi}(x_1 \cdots x_N, 0)]$ at time t' , respectively. The XC kernel of linear response theory $f_{\text{XC}}[\bar{n}](\mathbf{r}\mathbf{r}', t - t') = \delta v_{\text{XC}}[\bar{n}](\mathbf{r}t) / \delta n(\mathbf{r}'t')$ can thus be written entirely in terms of initial-state dependence.

Returning to the general case, in the usual formulation of TDDFT, one may choose any initial KS state which reproduces the density and divergence of the current of the interacting initial state [14]. Here, this choice is translated into the choice of which ground state the interacting wave function $\Psi(0)$ evolves back to, together with the pseudo-prehistory of the density thus generated. For a given wave function $\Psi(0)$, there may be many paths which evolve back to some ground state, each path generating a different pseudo-prehistory. Only for those which result in the same KS wave function $\Phi(0)$ [and of course interacting wave function $\Psi(0)$] will the XC potentials be identical after time 0.

For a given interaction, when is an arbitrary wave function Ψ evolvable from a ground state? This is a quantum control question [20,21], but of a different nature to those usually addressed. All ground states can be reached arbitrarily closely from a specific one by adiabatically changing v_{ext} . Then we ask, is the orbit of that ground state, i.e., the space of all states generated by all possible one-body potentials $v_{\text{ext}}(\mathbf{r}t)$, equal to the entire space of N -electron wave functions? The answer is no, because of the limitations on the allowed TD potentials: The space of all N -electron states is much larger than those reachable by all multiplicative *one-body* operators. Arguments using the Baker-Hausdorff-Campbell formula, or using standard results from quantum control theory [21], imply that

This raises the possibility of eliminating initial-state dependence altogether: If we can evolve the initial interacting wave function backwards in time to a nondegenerate ground state, then the initial-state dependence may be completely absorbed into a history dependence along this pseudo-prehistory.

Next, consider a system in its ground state, perturbed by a weak external field, i.e., $v_{\text{ext}}(\mathbf{r}t) = \bar{v}_{\text{ext}}(\mathbf{r}) + \epsilon v_{\text{ext}}^{(1)}(\mathbf{r}t)$, where $v_{\text{ext}}^{(1)}(\mathbf{r}t) = 0$ at $t = 0$. Then, to first order in the perturbation, the KS wave function at time t is $e^{-i\bar{E}_o t} \bar{\Phi}_0 + \epsilon \Phi^{(1)}(t)$, and the density evolves as $\bar{n} + \epsilon n^{(1)}(t)$, where $n^{(1)}(\mathbf{r}t) = 2 \sum_{\alpha} \Re \bar{\phi}_{\alpha}^*(\mathbf{r}) \phi_{\alpha}^{(1)}(\mathbf{r}t)$, where α is the index for the spin orbital. Taking the corresponding small variations in Eq. (6) then yields [19]

the unitary evolution operator has the form $\exp[i(\hat{T} + \hat{V}_{\text{ee}})t] \exp[i\hat{H}_1(t)]$, where \hat{H}_1 is a one-body operator. The first factor, having only one parameter t , can add only one dimension to the space of states generated by \hat{H}_1 . In general, it can be shown that the space of states (even arbitrarily close to those) reachable by such operators from the given initial state is much smaller than the N -electron Hilbert space. In most cases, not all wave functions are ground-state evolvable.

Next, what are the densities of bound excited states predicted by TDDFT and what is the nature of the corresponding Kohn-Sham state? Suppose one begins an experiment in an excited state Ψ^* . Assuming Ψ^* is interacting ground-state evolvable and we know the appropriate pseudo-prehistory, we would begin our KS calculation in the KS ground-state corresponding to that (earlier) ground-state density. The resulting KS state at the true initial time is not necessarily an excited state. For a general pseudo-prehistory, one could imagine the density and external potential (and interacting wave function, up to a purely TD phase) becoming static forever onwards, but with the XC potential (and Kohn-Sham wave function) continuing to evolve in time. The exact XC functional would be ultra-non-local in time [22].

In practice, we work with an approximate XC functional, and those so far suggested are not ultra-non-local in time. We now argue that then we do not need to find such a pseudo-prehistory. In the simplest case, consider an adiabatic XC approximation, such as ALDA. Again, imagine a pseudo-prehistory between the ground and target excited states. When the system is in an interacting eigenstate of the external potential, the density becomes static when the external potential does. But in this case, it will also be in a KS eigenstate, because the KS potential in the adiabatic

approximation will be static. In general, this KS state will *not* be an eigenstate of the ground-state KS potential corresponding to $v_{\text{ext}}(\mathbf{r})$, but rather an eigenstate of the potential $v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n^*](\mathbf{r}) + v_{\text{XC}}[n^*](\mathbf{r})$, where n^* is the excited-state density, rather than the ground-state density. These states are precisely those found by TDDFT response theory [23,24], which yields the transition frequency to the excited state from the ground state, if we require the initial KS state to be the ground KS state. We have here provided a route to the corresponding density, which is just the density of a type of Δ SCF calculation [25]. The same reasoning applies for *any* XC functional that is not ultra-non-local in time. Any history dependence that has a vanishing effect after sufficiently long time, such as the semi-instantaneous approximation of Vignale and Kohn [9], will produce the same excited states as ALDA, since it reduces to ALDA for *static* densities.

However, this leads to an unfortunate difficulty for excited states in TDDFT when the approximate functionals are not ultra-non-local in time. Imagine the density in Fig. 1 as the endpoint of evolving a singlet interacting two-electron system into an excited state. If we make the natural choice of allowing two different orbitals to produce this density, the KS potential is a harmonic well. But, for any calculation with a functional without explicit initial-state dependence, we must regard this state as having evolved from a singlet state with one doubly occupied ground-state orbital. During the pseudoevolution, this orbital remains doubly occupied, and will arrive at the required density with a KS potential given by the dashed line in the lower panel. These considerations apply equally to finding the $1s2p$ excited state of He. Any single Slater determinant, as in the KS He ground state, evolving under the one-body evolution operator (even spin dependent) of the KS system, will remain a single Slater determinant. This is a case of severe static correlation, such as in stretched H_2 , where a single Slater determinant is an unnatural description of such an excitation. For example, the orbital will have no well-defined angular momentum, being proportional to $\sqrt{n^*}(\mathbf{r})$. To understand this state, assume that the exact KS potential eventually becomes static. Then the final orbital would be a pure eigenstate of this potential [26]; since it has no nodes, it must be the ground state and the potential must be highly nonspherical. Alternatively, the exact XC and KS potentials change forever, despite the static density. ALDA is unlikely to provide a good approximation in either case.

We end by noting that the difficulties with excited-state densities are caused by driving the system entirely into a single excited state, and occur even in an orbital-dependent theory [27]. This is irrelevant to the success of TDDFT for extracting transition frequencies and oscillator strengths in the linear response regime, in which there are only infinitesimal perturbations around the ground state.

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