

Universal Dynamical Steps in the Exact Time-Dependent Exchange-Correlation Potential

P. Elliott,^{1,*} J. I. Fuks,² A. Rubio,^{2,3} and N. T. Maitra¹

¹*Department of Physics and Astronomy, Hunter College and the Graduate Center of the City University of New York, 695 Park Avenue, New York, New York 10065, USA*

²*Nano-Bio Spectroscopy Group and ETSF, Departamento de Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Avenida Tolosa 72, E-20018 San Sebastián, Spain*

³*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

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We show that the exact exchange-correlation potential of time-dependent density-functional theory displays dynamical step structures that have a spatially nonlocal and time nonlocal dependence on the density. Using one-dimensional two-electron model systems, we illustrate these steps for a range of nonequilibrium dynamical situations relevant for modeling of photochemical or physical processes: field-free evolution of a nonstationary state, resonant local excitation, resonant complete charge transfer, and evolution under an arbitrary field. A lack of these steps in the usual approximations yields inaccurate dynamics, for example, predicting faster dynamics and incomplete charge transfer.

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The vast majority of applications of time-dependent density-functional theory (TDDFT) today deal with calculating the linear electronic spectra and response of molecules and solids and provide an unprecedented balance between accuracy and efficiency [1,2]. TDDFT also applies to any real-time electron dynamics, not necessarily starting in a ground state and possibly subject to strong or weak time-dependent fields. Time-resolved dynamics are particularly important and topical for TDDFT for two reasons. First, there is really no alternative practical method for accurately describing correlated electron dynamics, and second, many fascinating new phenomena and technological applications lie in this realm. These include attosecond control of electron dynamics [3], photoinduced coupled electron-ion dynamics (for example, in describing light-harvesting and artificial photosyntheses), and photochemical or physical processes [4,5] generally. TDDFT in theory yields all observables exactly, solely in terms of the time-dependent density; however, in practice, approximations must be made both for the observable as a functional of the density and for the exchange-correlation (xc) functional. Thus, the question arises as to whether the approximate functionals that have been successful for excitations predict well the dynamics in the more general time-dependent context. In particular, the exact xc contribution to the Kohn-Sham (KS) potential at time t functionally depends on the history of the density $n(\mathbf{r}, t' < t)$, the initial interacting many-body state Ψ_0 , and the choice of the initial KS state Φ_0 : $v_{XC}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$. However, almost all calculations today use an *adiabatic* approximation, $v_{XC}^A = v_{XC}^{g.s.}[n(t)]$ that inputs the instantaneous density into a ground-state xc functional [6,7], completely neglecting both the history and initial-state dependence. Functionals that have explicit dependence on the KS orbitals do contain some memory dependence [8]. Further, the ground-state

functional $v_{XC}^{g.s.}$ must be approximated; hybrid functionals are most popular for molecular spectra, while the spatially local density approximation and semilocal generalized gradient approximations are most popular for solids (see Ref. [2] and references therein).

Although understanding when such approximations are expected to work well or fail has advanced significantly in the linear response regime [2], considerably less is known about the performance of approximate TDDFT for general nonlinear dynamics [9–11]. Part of the reason for this is due to the lack of exact, or highly accurate, results with which to compare. Moreover, even in the case where an accurate calculation is available, it is very complicated to extract the exact xc potential (see Refs. [12,13] for significant progress). It is critical for the reliability of TDDFT for describing fundamental dynamical processes in the applications mentioned earlier to first test available xc approximations on systems for which the exact xc potential can be extracted. One such case is that of two electrons in a spin singlet, chosen to start in a KS single-Slater determinant. We show that, in this case, the usual adiabatic and semilocal approximations *typically* fail to capture a critical and fundamental structure in the exact correlation potential: a time-dependent step that has a spatially ultranlocal and nonadiabatic dependence on the density. This feature is missing in all available TDDFT approximations today. Even the exact adiabatic functional misses it. This leads to erroneous dynamics; e.g., faster time scales are observed in the adiabatic approximations for examples where the step opposes the density evolution.

For two electrons in a spin singlet, we choose, as is usually done, the initial KS state as a doubly occupied spatial orbital, $\phi(\mathbf{r}, t)$. Then, the exact KS potential for a given density evolution can be found easily [14]. In one dimension (1D), we have

$$v_S(x, t) = -\frac{[\partial_x n(x, t)]^2}{8n^2(x, t)} + \frac{\partial_x^2 n(x, t)}{4n(x, t)} - \frac{u^2(x, t)}{2} - \int^x \frac{\partial u(x', t)}{\partial t} dx', \quad (1)$$

where $u(x, t) = j(x, t)/n(x, t)$ is the local “velocity,” $n(x, t)$ is the one-body density, and $j(x, t)$ is the current density. We numerically solve the exact time-dependent Schrödinger equation for the two-electron interacting wave function, obtain $n(x, t)$ and $j(x, t)$, and insert them into Eq. (1). The exchange potential in this case is simply $v_X(x, t) = -v_H(x, t)/2$, with $v_H(x, t) = \int w(x', x)n(x', t)dx'$, in terms of the two-particle interaction $w(x', x)$. Therefore, we can directly extract the correlation potential using

$$v_C(x, t) = v_S(x, t) - v_{\text{ext}}(x, t) - v_H(x, t)/2, \quad (2)$$

where $v_{\text{ext}}(x, t)$ is the external potential applied to the system. The two electrons in all our examples interact via the soft-Coulomb interaction [15], $w(x', x) = 1/\sqrt{(x' - x)^2 + 1}$. We use atomic units throughout.

We start the analysis with some purely (or largely) two-state systems, in which the exact interacting wave function, $|\Psi(t)\rangle$, can be expanded in a basis consisting of the ground state, $|\Psi_g(t)\rangle$, and the first excited singlet state, $|\Psi_e(t)\rangle$:

$$|\Psi(t)\rangle = a_g(t)|\Psi_g\rangle + a_e(t)|\Psi_e\rangle, \quad (3)$$

where $a_g(t)$ and $a_e(t)$ are coefficients given by

$$i\partial_t \begin{pmatrix} a_g(t) \\ a_e(t) \end{pmatrix} = \begin{pmatrix} E_g - d_{gg}\mathcal{E}(t) & -d_{eg}\mathcal{E}(t) \\ -d_{eg}\mathcal{E}(t) & E_e - d_{ee}\mathcal{E}(t) \end{pmatrix} \begin{pmatrix} a_g(t) \\ a_e(t) \end{pmatrix}, \quad (4)$$

where E_g and E_e are the energy eigenvalues of the two states, $d_{ab} = \int \Psi_a^*(x_1, x_2)(x_1 + x_2)\Psi_b(x_1, x_2)dx_1dx_2$ is the transition dipole moment, and $\mathcal{E}(t) = A \cos(\omega t)$ is an applied electric field of strength A and frequency ω . In the weak amplitude limit, with $\omega \gg |d_{eg}A|$ and ω close to the resonant frequency, this reduces to the textbook Rabi problem. By solving Eq. (4), we can easily construct the current and density at any time, their time derivatives, and hence all pieces entering Eq. (1).

In our first example, we consider a “1D He atom,” where $v_{\text{ext}} = -2/\sqrt{x^2 + 1}$, subject to a weak electric field of strength $A = 0.00667$ au and frequency $\omega = 0.533$ au, resonant with the first singlet excitation [16,17]. The system oscillates from one state to the other over a Rabi cycle of period $T_R = 2\pi/(|d_{eg}A|)$. Figure 1 shows snapshots of $v_C(x, t)$ over one Rabi cycle, while Fig. 2 shows snapshots over one optical period centered around $T_R/4$. (Note that the system is not exactly periodic over T_R , as the optical frequency and the Rabi frequency are not commensurate).

The most salient feature of the correlation potential is the presence of time-dependent steps that oscillate on the time scale of the optical field. These steps arise from the

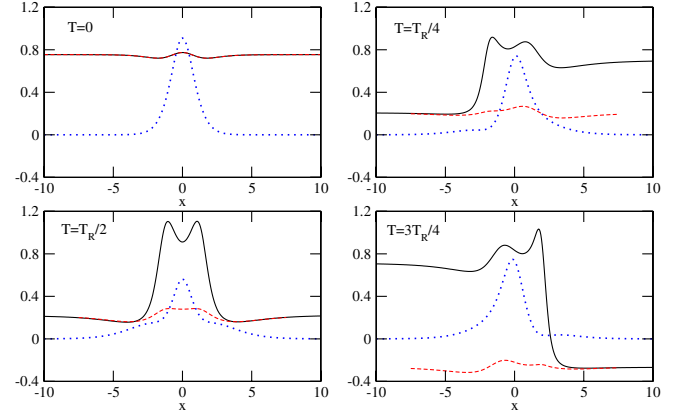


FIG. 1 (color online). Snapshots of the exact correlation potential (solid black line), density (dotted blue line), and exact adiabatic (dashed red line) over one Rabi cycle for the 1D He atom. At $T_R/2$, the density of the first excited state is essentially exactly reached. In all graphs, the correlation potentials are plotted up to an irrelevant time-dependent constant.

fourth term of Eq. (1): Whenever there is a net “acceleration,” $\partial_t u(x, t)$, through the system, the spatial integral is finite, resulting in a potential rising from one end of the system to the other. The correlation potential thus has a spatially ultranlocal dependence on the density, as it changes far from the system.

Further, the time dependence of the steps is nonadiabatic, meaning that the instantaneous density is not enough to determine the correlation potential functional. One is tempted to point to the time derivatives in the fourth term in Eq. (1) as evidence for the nonadiabatic dependence; however, caution would be needed for such an argument, as time nonlocality in v_S is not the same as time nonlocality in v_C [2]. The fourth term may be written as v_{ext} plus other terms, and, although v_{ext} typically has strongly nonadiabatic dependence, this is irrelevant because it is never approximated as a functional in practice [2,18]; rather, it is taken from the problem at hand. Only the xc potential must be approximated, and its functional dependence cannot be deduced directly from Eq. (1). Instead, to unambiguously show the nonadiabatic dependence of the step, we plot the “adiabatically exact” correlation potential in Fig. 1. This is defined by the exact correlation potential

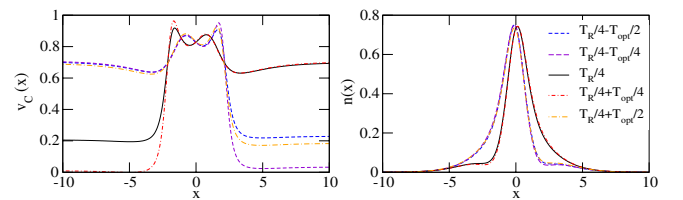


FIG. 2 (color online). Snapshots of the correlation potential (left) and corresponding density (right) for the 1D He atom at times indicated on the right.

for which both the interacting and KS wave functions are ground-state wave functions with density equal to the instantaneous one, i.e., $v_C^{\text{adia-ex}}[n] = v_S^{\text{adia}}[n] - v_{\text{ext}}^{\text{adia}}[n] - v_H[n] - v_X[n]$ [19], where $v_{\text{ext}}^{\text{adia}}[n]$ is the external potential for two interacting electrons whose ground state has density n and $v_S^{\text{adia}}[n]$ is the exact ground-state KS potential for this density [given by the first two terms in Eq. (1)]. We find $v_{\text{ext}}^{\text{adia}}[n]$ using similar techniques to Ref. [19] (see also Ref. [20]). Figure 1 shows that $v_C^{\text{adia-ex}}[n]$ does not capture the dynamical step structure.

Before turning to our next example, we verify that the two-state approximation is accurate enough for our purposes. One aspect of the potentials we find is actually an artifact of the two-state approximation: The correlation potential asymptotically has a slope that exactly cancels the externally applied electric field. This is because the two-state approximation cannot correctly describe polarization arising from occupying many excited states in time. The KS potential obtained from the two-state approximation is flat asymptotically, as it cannot describe states that are polarized asymptotically. The field is so weak that this effect is hardly noticeable in Figs. 1 and 2, but, to check that our conclusions regarding the dynamics step structure are unaffected by the two-level approximation, we computed the KS potential using the density, current, and their time derivatives from the numerically exact wave function, found using OCTOPUS [21–23]. Apart from some extra structure in the tail region (small peaks and steps as we move away from the atom) and the small linear field-counteracting term, the correlation potential agrees with that from the two-state model.

Dynamical step features have arisen in TDDFT in earlier studies; Refs. [19,24] showed they appear in ionization processes and linked them to a time-dependent derivative discontinuity, related to fractional charges. In time-resolved transport, step structures have been shown to be essential for describing Coulomb-blockade phenomena [25], again related to the discontinuity. In the response regime, field-counteracting steps develop across long-range molecules [26]. In open-systems TDDFT, Ref. [27] shows that steps arise when using a closed KS system to model an open interacting one. The linear response xc kernel for charge-transfer excitations displays frequency-dependent steps [28]. Here, we argue that the dynamical step structures we find are generic: They *typically* arise in dynamics and, moreover, unlike most of the above cases [19,24–26], cannot be captured by an adiabatic approximation. They appear with no need for ionization or subsystems of fractional charge or any applied field (see the next example), unlike in Refs. [19,24–26]. In this sense, our results are more akin to Ref. [12], which studies the physically very different situation when an electron freely propagates through a wire. The large range of the examples we present suggests that such nonadiabatic and nonlocal steps *generically* arise in electron dynamics.

Our second example accentuates the fact that dynamical step structures need neither ionization nor an external field to appear. We begin in an equal linear superposition of the ground and first-excited states of the 1D He and let it evolve freely, so that

$$|\Psi(t)\rangle = (e^{-iE_g t}|\Psi_g\rangle + e^{-iE_e t}|\Psi_e\rangle)/\sqrt{2}. \quad (5)$$

It oscillates back and forth between the two states with frequency $\omega_0 = E_e - E_g$. The two-state approximation is exact at all times. Again, we see large steps in the correlation potential, as shown in Fig. 3. To support the discussion and provide a microscopic insight behind this phenomenon, we also plot in Fig. 3 the acceleration, $a(x, t) = \partial_t u(x, t)$, and its spatial integral with the external potential subtracted out. The position and magnitude of the step at each time are heavily dependent on this term. Peaks in the acceleration, when integrated, become local steps in the potential, and the asymptotic value of the step in $v_C(x, t)$ is given by the total step in the spatial integral of $a(x, t)$. Although local steplike features may be canceled out by the other terms in Eq. (1), the net magnitude of the step is determined from the asymptotic values of this integral.

Note that we have the freedom to choose the initial state of the KS system as long as it has the same density and first derivative in time of the exact density [29], and the shape of the exact correlation potential depends on this choice [20]. We used a doubly occupied orbital in the previous example. A different choice, with a configuration more similar to that of the interacting initial state, could well yield a more gentle correlation potential [20], with less dramatic step structure.

The generality of the dynamical step feature is further supported by considering different resonant excitations. Consider a double well as a model of a molecule:

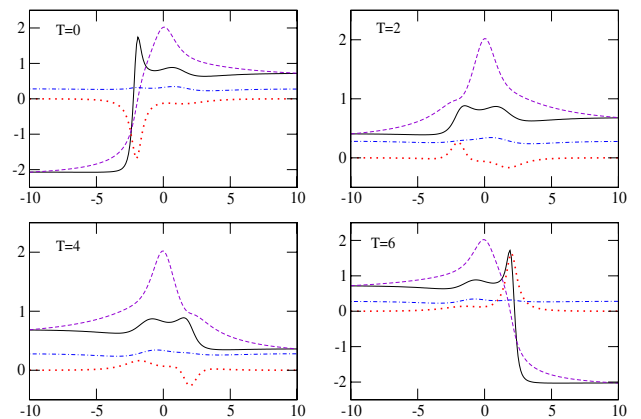


FIG. 3 (color online). The exact correlation potential (solid black line) at times indicated for the two-state example [Eq. (5)]. Also shown are the local acceleration (dotted red line), $-\int^x \partial_t u(x', t) dx' - v_{\text{ext}}$ (dashed purple line), and the adiabatically exact correlation potential (dash-dotted blue line).

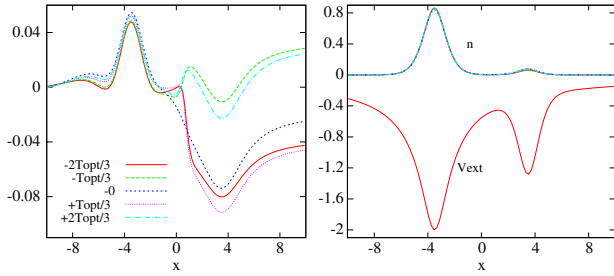


FIG. 4 (color online). The correlation potential (left) and density and external potential (right) shown at snapshots of time $T_R/8 \pm$ fractions of the optical period, $T_{\text{opt}} = 2\pi/0.112$ au for the two-well potential model Eq. (6) under resonant charge-transfer excitation conditions.

$$v_{\text{ext}}(x, t) = -\frac{2}{\sqrt{(x+3.5)^2 + 1.0}} - \frac{1}{\cosh^2(x-3.5)} - \mathcal{E}(t)x, \quad (6)$$

with $\mathcal{E}(t) = 0.006 \cos(0.112t)$. Here, the ground state has two electrons in the left well and Ψ_e is a charge-transfer excited state, with one electron in each well, at a frequency of 0.112 au. Using the ground state and Ψ_e in Eq. (3), we solve for the occupations using Eq. (4); we again checked the two-state result against the exact numerical solution using OCTOPUS. The system behaves as the Rabi problem with a nonzero ground-state dipole moment [30,31]. Figure 4 shows the correlation potential for several times within an optical cycle around $T_R/8$. Again, dynamical steps oscillating on the optical frequency time scale emerge. The situation is more complicated as a step related to the delocalization of the density during the charge-transfer process slowly develops (on the time scale of $T_R/2$) [32]. The dynamical step can then increase, decrease, or even reverse this charge-transfer step. Approximations unable to develop steps lead to incomplete charge transfer. This, along with other details of time-resolved charge transfer, is investigated in more detail in Ref. [32]. For the present purposes, it is sufficient to note that dynamical steps are again present to capture the exact dynamics.

Finally, we explicitly demonstrate that the nonlocal non-adiabatic step feature is a generic aspect of the correlation potential in the following way. We subject the 1D He atom to a field that is chosen somewhat arbitrarily: It is relatively strong and linearly switched on over two optical cycles, with an off-resonant frequency. In Fig. 5, we show the exact correlation potential at four times. The time-dependent step in the exact v_c is once again evident, and again the adiabatically exact approximation fails to capture it.

In summary, dynamical steps in the correlation potential are a generic feature of electron dynamics. The step features arise from part of the fourth term of Eq. (1), which suggests that, any time there is a net acceleration across the system, there is a step that has a very nonlocal spatial dependence on the density and is nonadiabatic.

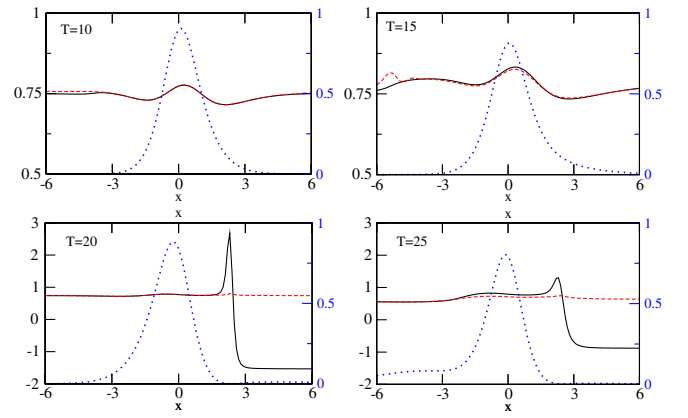


FIG. 5 (color online). The exact correlation potentials (solid black line) during propagation under strong nonresonant field ($A = \frac{1}{2\sqrt{2}} \frac{0.3}{4\pi}$, $\omega = 0.3$). This field induces the population of many empty states (over fifty); therefore, we are well beyond the two-level Rabi physics. Also shown are the adiabatically exact correlation potentials (dashed red line) and the density (dotted blue line, scale on the right).

This represents a type of time-dependent screening, where the electron-electron interaction hinders electron movement to certain regions. Although two-electron systems were studied here, we expect that, except for special cases (such as field driven harmonic potential motion), steps are a more general feature of electron dynamics, as supported by the recent Ref. [12], and are a topic for future investigation.

The lack of the step in approximations leads to incorrect dynamics. Faster time scales in adiabatic approximations were found for the field-free dynamics of a linear superposition state, where the direction of the step tended to oppose the density's motion. The exact dipole and adiabatic exact-exchange (AEXX) dipole for this case are shown in Fig. 6. We computed the dynamics of the local excitation of Figs. 1 and 2 using AEXX, adiabatic local density approximation, and adiabatic self-interaction-corrected local density approximation. The dipole oscillation time scale in all cases was faster than in the true case. These approximations yet provide good linear response spectra [17]. The steps are likely a feature of non-linear dynamics, intimately connected with having an

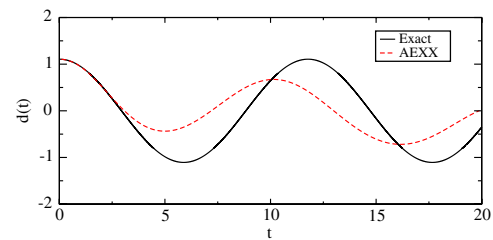


FIG. 6 (color online). Dipole moments in field-free propagation of the state Eq. (5), where the time-dependent KS calculation starts in the exact singlet doubly occupied orbital.

appreciable population in excited states; this will be investigated closely in the future.

Note that the xc electric field, defined as the gradient of the xc potential, has a more local character than the potential. This suggests that considering functional approximations to this field (including hydrodynamical ones [33]) or, more generally, to an xc vector potential [12,34] may point to an easier path to develop approximations containing step features. Including explicit orbital dependence suggests another fruitful avenue to explore, as orbitals themselves have nonlocal and nonadiabatic dependence on the density [8,35].

As applications of TDDFT continue to expand, it is crucial to further study the impact of the missing steps in the approximations on their predictions. When starting in the ground state, the exact adiabatic potential may follow well the exact dynamics at short times, but, as soon as there is an appreciable change in the occupation of an excited state, the exact solution develops the dynamical step, entirely missing in the adiabatic one. This result is general and applies to all available functionals. It raises an important issue when applying TDDFT to fundamental photoinduced processes (e.g., photovoltaics, artificial photosynthesis, photoactivated chemistry, photophysics, etc.): All these involve a significant change of state population. Clearly, the population of many-body states due to the external field is not a linear process and requires functionals able to cope with the generic features of the dynamical step that we have unveiled in the present Letter.

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*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle (Saale), Germany.

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