Exact Time-Dependent Exchange-Correlation Potentials for Strong-Field Electron Dynamics

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(Received 25 October 2004; published 14 April 2005)

By solving the time-dependent Schrödinger equation and inverting the time-dependent Kohn-Sham scheme we obtain the *exact* time-dependent exchange-correlation potential of density-functional theory for the strong-field dynamics of a correlated system. We demonstrate that essential features of the exact exchange-correlation potential can be related to derivative discontinuities in stationary density-functional theory. Incorporating the discontinuity in a time-dependent density-functional calculation greatly improves the description of the ionization process.

DOI: 10.1103/PhysRevLett.94.143003 PACS numbers: 31.15.Ew, 32.80.Rm, 34.80.Kw

Time-dependent density-functional theory (TDDFT) [1,2] is a well established approach to the calculation of excitations in many-electron systems. One of its very attractive features is that not only the linear but also the nonlinear and the nonperturbative response [3–6] can be calculated efficiently. TDDFT thus allows one to access on a first-principles basis the regime of strong-field dynamics that is becoming ever more important due to the rapid progress in laser technology. The need for a computationally tractable yet accurate theory is also particularly urgent here because the computational cost of *ab initio* wave-function methods, which are already expensive for ground-state calculations, simply becomes overwhelming in the nonperturbative, time-dependent case.

In analogy to ground-state DFT, TDDFT is in principle exact, but in practice one needs approximations for the time-dependent exchange-correlation (xc) potential $v_{\mathrm{xc}}(\mathbf{r}, t)$. It incorporates the many-body effects into the theory and is thus the central quantity in TDDFT. So far, applications of TDDFT rely almost exclusively on the "adiabatic approximation"; i.e., one feeds the time-dependent density into a known ground-state functional and hopes that this gives a reasonable description of the dynamics. Using continuum functionals, this approach has met impressive successes as well as dramatic failures. In this Letter we investigate the strong-field double ionization of the helium atom as one of the most prominent examples of complete failure [7–9], and also a particularly severe one since, as stated above, it is the strong-field dynamics where TDDFT in principle has huge advantages and is most urgently needed.

It is well established by experiment [10,11] and theory [7,8,12–14] that in laser-induced ionization of noble-gas atoms, electron correlations lead to a substantial enhancement of the double-ionization yield in the region of low laser intensities ("nonsequential ionization"). Consequently, the transition from nonsequential to sequential ionization appears as a famous "knee structure" [10,11] in the intensity dependence of the double-ionization probability. Serious efforts were made to investigate this effect using TDDFT [7–9,15]. But no matter which of the known functionals was employed, all calculations failed to reproduce the knee even qualitatively. From the two TDDFT problems—having to approximate v_{xc} and the functional for the ionization probability—we focus on the former, since a mean-field way of calculating the ionization yields leads to a knee structure if the exact density is used [8,9]. Double ionization has thus become a paradigm example for the failure of v_{xc} approximations.

The aim of this Letter is to analyze this failure by constructing the *exact* time-dependent $v_{\mathrm{xc}}(\mathbf{r}, t)$. As demonstrated below, our analysis reveals that there is a connection between the time-dependent xc potential of the two-electron system and the ground-state xc potential of a system with noninteger particle number between 2 and zero. Thus, the qualitative failure of previous TDDFT calculations for the He double ionization can be understood in terms of the integer derivative discontinuity of ground-state DFT [16] which is missing in the continuum approximations that were employed so far. We will see that incorporating the discontinuity greatly improves the description of the ionization process.

Two hurdles must be taken for generating an exact xc potential: A quasiexact density must be calculated and an algorithm is needed that allows one to construct the Kohn-Sham (KS) potential (the effective single-particle potential) corresponding to a given density. Along these lines the exact static KS potential of ground-state DFT has been calculated [17–19]. For the time-dependent case, however, apart from pioneering works [20,21] little has been achieved so far since both of the above-mentioned steps are significantly more complicated. Even for a simple system like the He atom, solving the two-body three-dimensional time-dependent Schrödinger equation is a computational task that stretches the capacities of modern computers to their limits, and, in particular, this is the case for the long-ranged dynamics that is associated with the strong low-frequency fields generated by the lasers typically used in experiments. Also the inversion that leads from the density to the potential is more difficult in the time-dependent case since one has to work with complex-valued KS orbitals.

In order to circumvent the problems with the full-dimensional two-electron Schrödinger equation, we work instead with a reduced-dimensional model which is motivated by the nearly one-dimensional nature of the strong-field dynamics. The He model atom in an electric field $E(t)$ is described by the Hamiltonian

$$H = \sum_{j=1,2}\left(\frac{p_j^2}{2m} + v_0(z_j, t)\right) + W(z_1 - z_2) \tag{1}$$

with electron coordinates z_1, z_2, momenta p_1, p_2, and the soft-core interaction $W(z) = e^2/\sqrt{z^2+1}$. The external potential is $v_0(z,t) = -2W(z) + ezE(t)$. This model has been demonstrated to capture the essential physics of the He double-ionization process [7,8,13,22,23].

The spin degrees of freedom are omitted and the spatial wave function is taken to be symmetric under exchange of electrons; i.e., a singlet configuration is chosen. The time-dependent Schrödinger equation $i\hbar\partial\Psi/\partial t = H\Psi$ is solved numerically by means of the split-operator method [24] on a grid that is chosen large enough to contain the entire wave function. From the two-electron wave function, we calculate the density and current

$$n(z,t) = 2\int |\Psi(z,z',t)|^2 dz', \tag{2}$$

$$j(z,t) = \frac{2\hbar}{m}\,\mathrm{Re}\int \Psi^*(z,z',t)\frac{\partial}{i\partial z}\Psi(z,z',t)dz'. \tag{3}$$

TDDFT replaces the system of interacting particles by a system without electron-electron interaction that is required to have the same density as the interacting system. This KS system evolves under the influence of an effective single-particle potential

$$v_s(z,t) = v_0(z,t) + v_h(z,t) + v_{xc}(z,t), \tag{4}$$

where $v_h(z,t) = \int n(z',t)W(z-z')dz'$ is the Hartree potential. The xc potential $v_{xc}(z,t)$ is defined by Eq. (4) and can be split into its exchange (v_x) and correlation (v_c) parts.

According to the Runge-Gross theorem [1], the KS potential is determined up to a purely time-dependent constant by the initial state and the time-dependent density. The initial KS state Ψ_{s0} must be chosen such that it reproduces the initial density and time derivative of the initial density of the interacting system [20]. In our case, we describe each of the two electrons by the same initial orbital $\varphi_0(z)$, i.e., $\Psi_{s0}(z_1,z_2) = \varphi_0(z_1)\varphi_0(z_2)$, and with this choice, both electrons are described by the same KS orbital $\varphi(z,t)$ for all times. We then have $v_x(z,t) = -v_h(z,t)/2$, and the orbital can be written as

$$\varphi(z,t) = \sqrt{n(z,t)/2}\,e^{i\alpha(z,t)}. \tag{5}$$

The phase α can be calculated up to a time-dependent constant from the relation $j = j_{KS}$, i.e.,

$$\partial\alpha(z,t)/\partial z = (m/\hbar)j(z,t)/n(z,t), \tag{6}$$

where the current and density are taken from the exact solution. After the construction of the KS orbital, the KS potential is obtained by inversion of the split-operator time propagator:

$$v_s(z,t) = -\frac{\hbar}{2\delta t}\arcsin\mathrm{Im}\frac{e^{+iT\delta t/\hbar}\varphi(z,t+\delta t)}{e^{-iT\delta t/\hbar}\varphi(z,t-\delta t)} + \mathrm{const}, \tag{7}$$

where T is the single-particle kinetic-energy operator. The operators $e^{\pm iT\delta t/\hbar}$ are applied by multiplication in momentum space. An appropriate time-dependent constant is added to the resulting potential to enforce the boundary condition $v_s(z,t) \to 0$ for $z \to \infty$. Once we have obtained v_s, we easily calculate the Hartree-exchange-correlation potential $v_{hxc} = v_s - v_0$, which contains all effects due to the electron-electron interaction, and the correlation potential $v_c = v_{hxc} - v_h - v_x$.

We consider the ionization of the correlated two-electron atom by an external dc electric field, starting from the two-electron ground state. Field-induced ionization is the first stage of the recollision mechanism [25] which appears to be responsible for nonsequential double ionization [26,27]: after single-electron ionization, the outgoing electron is driven back by the laser field and knocks out or excites the second electron. In our model calculation, the direction of the field is chosen such that the electrons can escape towards $z \to \infty$. To avoid numerical problems with strongly accelerated electrons, the interaction with the field is truncated at a distance of $z_t =$ 35 a.u. from the nucleus; i.e., $v_0(z,t) = -2W(z) + ez_tE(t)$ for $z > z_t$. The field is ramped up over a time interval of 27 a.u. (0.65 fs) to a maximum value $E_0 = 0.141$ (corresponding to the peak amplitude of a laser pulse with 7×10^{14} W/cm^2 peak intensity) and is held constant afterwards.

The left-hand side of Fig. 1 shows on a logarithmic scale the calculated electron density at equally spaced instants in time. Initially, the system is in the ground state. At later times, the field drives part of the density towards $z \to \infty$. It is apparent from the plot that the decay is exponential. On the right-hand side of the figure, we plot the corresponding potentials v_{hxc} and v_c. At $t = 0$, the correlation part is small, indicating that an exchange-only treatment could be reasonable. In the course of time, however, we observe a dramatic increase in the correlation potential and, finally, v_{hxc} develops a pronounced plateau in the region around the nucleus followed by a steplike structure.

To understand this time evolution we estimate the number of bound electrons by integrating the density over the interval $|z| < a = 5$ a.u. For the four instants shown in Fig. 1, $N_b(t) = \int_{-a}^{a} n(z,t)dz = 2.000$, 1.228, 1.032, and 1.004. This indicates that the probability for removal of the second (more tightly bound) electron is negligible and that the plateau and step appear when the removal of the first electron is nearly completed.

We argue that the step is essentially the same as the discontinuity [16] Δ_{xc} that in ground-state DFT is known to

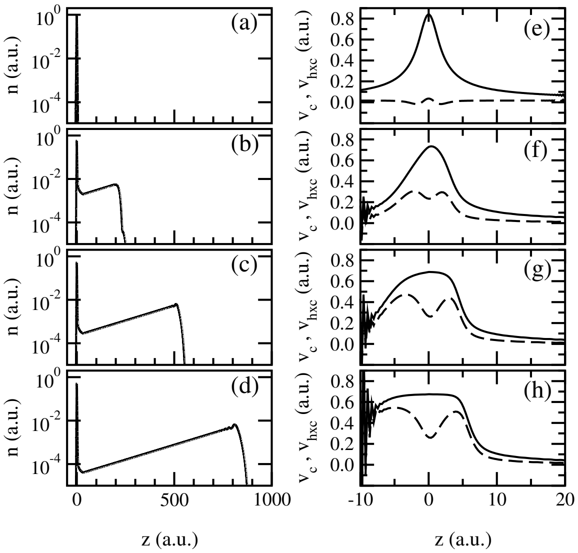

FIG. 1. Density $n(z, t)$ and potentials $v_{\mathrm{hxc}}(z, t)$ (solid curves), $v_{\mathrm{c}}(z, t)$ (dashed curves) at various times during the interaction of the two-electron atom with a static field. (a),(e) $t = 0$; (b),(f) $t = 108$ a.u.; (c),(g) $t = 215$ a.u.; (d),(h) $t = 323$ a.u. [The oscillations around $z = -10$ a.u. are artifacts due to the vanishing density which leads to very small numbers in the denominators of Eqs. (6) and (7) and thus makes reliable reconstruction of the potential impossible.]

appear in the xc potential when the electron number passes through an integer N:

$$\Delta_{\mathrm{xc}} = \lim_{\epsilon\to 0}\{v_{\mathrm{xc}}(\mathbf{r})|_{N+\epsilon} - v_{\mathrm{xc}}(\mathbf{r})|_{N-\epsilon}\}. \tag{8}$$

To corroborate this idea, we calculate the exact static potentials for noninteger electron numbers $1 + \epsilon$ in our model atom. Here, the exact density $n_{1+\epsilon}(z)$ is obtained from the one- and two-electron ground-state densities $n_1(z)$ and $n_2(z)$ as

$$n_{1+\epsilon}(z) = (1 - \epsilon)n_1(z) + \epsilon n_2(z), \tag{9}$$

and inserting the KS orbital $\varphi(z) = \sqrt{n_{1+\epsilon}(z)/(1 + \epsilon)}$ into the stationary single-particle Schrödinger equation yields the KS potential

$$v_{\mathrm{s}}(z) = \frac{\hbar^2}{m}\frac{1}{2\varphi(z)}\frac{d^2\varphi(z)}{dz^2} + \mathrm{const}. \tag{10}$$

The result is shown in Fig. 2 for three different occupation numbers. With decreasing ϵ, we observe a behavior that resembles closely the time-evolution in field-induced ionization: when one of the two electrons is almost removed, a plateau in v_{hxc} is formed and a "softened" step appears. As the electron number approaches unity from above, the step becomes sharper, moves farther out, and for distances far from the center, the plateau is built exclusively from v_{c}. Numerically we cannot follow this process arbitrarily close to $\epsilon = 0$, but it is clear that the step will reach infinity as $\epsilon = 0$ is reached. Requiring that the potential should tend to zero at infinity then enforces a downward shift of the potential by an amount corresponding to the height of the step; i.e., the potential jumps discontinuously by a constant. The same behavior has been observed for the exact KS exchange potential [28,29]. The difference is that here, the step is in the correlation potential since our electrons are of opposite spin and thus not coupled by exchange.

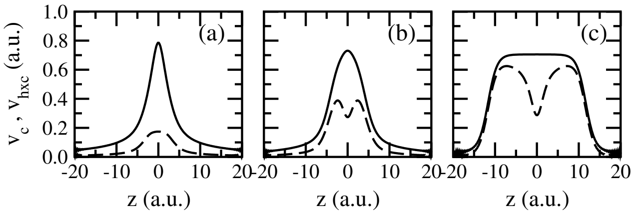

FIG. 2. Static potentials $v_{\mathrm{hxc}}(z)$ (solid curves) and $v_{\mathrm{c}}(z)$ (dashed curves) for ground states with noninteger electron number $1 + \epsilon$. (a) $\epsilon = 0.5$; (b) $\epsilon = 0.1$; (c) $\epsilon = 0.0001$.

In view of the physics of the ionization process it is clear that the derivative discontinuity must play a prominent role. As one electron leaves the system, the remaining electron is bound much more strongly. But since both electrons occupy identical KS orbitals, the difference in the ionization potentials can come only through the derivative discontinuity. This reasoning is supported by the fact that in our calculations, the height of the plateau is found to be in good agreement with the difference Δ between the ionization potentials $I_+ = 1.48$ a.u., $I_0 = 0.75$ a.u. of the one- and two-electron systems. Δ is known as the derivative discontinuity of the total energy in ground-state DFT and obeys the relation $\Delta = \Delta_{\mathrm{KS}} + \Delta_{\mathrm{xc}}$ [30], where Δ_{KS} is the energy difference between the lowest unoccupied and the highest occupied KS orbital of the N-electron system. In our case ($N = 1$), $\Delta_{\mathrm{KS}} = 0$ leads to $\Delta = \Delta_{\mathrm{xc}}$ in agreement with our numerical results.

In the following, we show that a double-ionization knee is reproduced in a TDDFT calculation where we introduce a quasidiscontinuous behavior "by hand." A simple approximation for the correlation potential that captures the relevant physics is

$$v_{\mathrm{c}}(z, t) = [c(N_{\mathrm{b}}(0)/N_{\mathrm{b}}(t)) - 1][v_{\mathrm{h}}(z, t) + v_{\mathrm{x}}(z, t)], \tag{11}$$

where $c(x) = x/(1 + e^{50(x-2)})$ and $N_{\mathrm{b}}(t)$ again estimates the number of bound electrons. The purpose of Eq. (11) is to initially compensate for the loss of bound electrons: in the regime $1 < N_{\mathrm{b}}(t) \leq 2$, we have $c \approx 2/N_{\mathrm{b}}(t)$. Around $N_{\mathrm{b}}(t) = 1$, the function $c(x)$ goes quickly to zero, causing a sudden change in the ionization potential and thus mimicking the derivative discontinuity. The parameter 50 was chosen just to provide a fast change; any other similarly large number will lead to practically the same results. Using the functional Eq. (11), we perform TDDFT calculations for our model atom subject to trapezoidally shaped 8-cycle 780 nm laser pulses with two-cycle turn-on and turn-off times. The single- and double-ionization probabilities P_1 and P_2 at the end of the propagation are obtained via the single-particle approximation [8,9] $P_1 = N_{\mathrm{b}}(1 - N_{\mathrm{b}}/2)$, $P_2 = (1 - N_{\mathrm{b}}/2)^2$. Within our TDDFT approach,

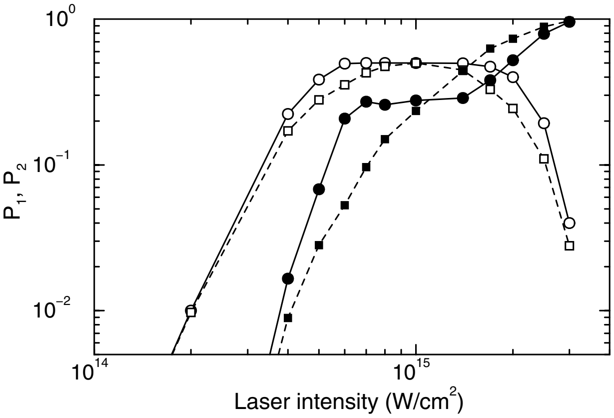

FIG. 3. Probabilities for laser-induced single- ionization (open symbols) and double ionization (filled symbols) from TDDFT (circles) and TDHF (squares) calculations.

the time-dependent Hartree-Fock (TDHF) method is recovered by setting $v_c = 0$.

In Fig. 3 we compare the intensity dependence of the single- and double-ionization yields obtained with Eq. (11) to TDHF results. While the single-ionization result is quite similar to TDHF, the double-ionization signal exhibits a clear knee structure which is absent in the TDHF curve. Thus, we see that a TDDFT calculation can produce a double-ionization knee similar to exact two-electron calculations [8,31].

In summary, we have calculated the exact time-dependent KS potential for the strong-field ionization of a two-electron system. Our calculations show that the derivative discontinuity plays an important role for the correct description of the ionization process. The correlation potential takes care of the fact that the singly charged ion is much harder to ionize than the neutral atom, and that the chemical potential changes discontinuously when the electron number passes through an integer. Conventional approximations for the xc potential such as the local-density approximation do not incorporate the derivative discontinuity but replace it by a smooth interpolation between the two ionization potentials. This "averaging out" of the discontinuity is at the heart of why conventional approximations do not produce a knee in the double-ionization probability. Including the derivative discontinuity, even in a rather simple-minded way, corrects this failure of TDDFT. This shows that TDDFT can describe situations which so far have been regarded as beyond its capabilities, and it stresses the importance of the further development of functionals that include the discontinuity. The time-dependent optimized effective potential [32] appears as a promising concept that may allow one to take the time-dependent discontinuity into account in a natural way.

S. K. acknowledges financial support under a DFG Emmy-Noether grant.

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