Adiabatic Approximation in Nonperturbative Time-Dependent Density-Functional Theory

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We construct the exact exchange-correlation potential of time-dependent density-functional theory and the approximation to it that is adiabatic but exact otherwise. For the strong-field double ionization of the Helium atom these two potentials are virtually identical. Thus, memory effects play a negligible role in this paradigm process of nonlinear, nonperturbative electron dynamics. We identify the regime of high-frequency excitations where the adiabatic approximation breaks down and explicitly calculate the nondiabatic contribution to the exchange-correlation potential.

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Progress in laser technology has provided the experimental tools to study and manipulate electron dynamics on atomic scales [1]. On the theoretical side, this strong-field regime can in principle be accessed by solving the many-electron time-dependent Schrödinger equation (TDSE). In practice, however, a first-principles approach in this vein is ruled out by the tremendous computational cost of solving the TDSE for more than two electrons in three dimensions. Time-dependent density-functional theory (TDDFT) [2] offers a computationally attractive approach to strong-field electron dynamics [3,4] which is in principle exact, but in practice requires approximations for the time-dependent exchange-correlation (xc) potential v_{xc}(r,t).

Up to now applications of TDDFT almost exclusively rely on “adiabatic approximations” [e.g., the adiabatic local density approximation (ALDA)], which are obtained by plugging the time-dependent density into one of the existing ground-state density functionals for v_{xc}. Approaches of this type have also been used to calculate the double ionization (DI) of the helium atom, one of the most prominent effects in the regime of strong-field electron dynamics. Its importance as a benchmark for theoretical tools to study and manipulate electron dynamics on the intensities and frequencies that are usually considered in the context of strong-field electron dynamics, and specifically for the helium DI, the adiabatic approximation works extremely well. Thus, an accurate description requires nonlocality in space more than nonlocality in time.

For the definition of the “adiabatically exact approximation” one should recall that, for the initial state being the ground state, the exact xc potential shows “memory” as at any given time it is a nonlocal functional of the exact time-dependent density n at all previous times, i.e., v_{xc}^{ex}(r,t) = v_{xc}^{ex}[n(r',t')]\langle r, t \rangle where t' ≤ t. By definition it is related to the exact Kohn-Sham (KS) potential v_{xc}^{ks}[n(r',t')]\langle r, t \rangle by

\[ v_{xc}^{ex}(r,t) = v_{xc}^{ks}(r,t) - \nu_h(r,t) - \nu_{ext}(r,t), \]  

where \nu_{ext} is the external potential and \nu_h is the Hartree potential, which is a functional of the density only at t' = t. By virtue of the Runge-Gross theorem, the potential v_{xc}^{ex} corresponding to the exact time-dependent density is unique, and it can be shown to exist [29].

The adiabatic approximation is defined by treating the time-dependent density at a fixed time t = t_0 as a ground-state density, i.e., n_0(r) = n(r, t_0). Consequently, the adiabatically exact KS potential v_{ks,ex}^{adi}(r) is the local potential which yields n_0(r) as the solution of the noninteracting,
single-particle Schrödinger equation. The correspondence between \( n_0 \) and \( v_{\text{xc}}^{\text{adia,ex}} \) is unique according to Hohenberg and Kohn [30]. Following standard ground-state DFT, the xc contribution to \( v_{\text{adia,ex}}^{\text{xc}}(r) \) is given by

\[
v_{\text{xc}}^{\text{adia,ex}}(r) = v_{\text{s}}^{\text{adia,ex}}(r) - v_h(r, t_0) - v_{\text{ext},0}(r), \tag{2}
\]
i.e., this defines the adiabatically exact xc potential at \( t = t_0 \). Here, \( v_h \) is again the Hartree potential corresponding to the given density \( n_0 \) and \( v_{\text{ext},0}(r) \) is the local external potential which yields \( n_0 \) as the solution of the interacting many-particle Schrödinger equation. Also the mapping between \( n_0 \) and \( v_{\text{ext},0}(r) \) is unique according to Hohenberg and Kohn. Therefore, \( v_{\text{adia,ex}}^{\text{xc}}(r) \) is uniquely defined by Eq. (2) and is a numerical representation of the unknown exact ground-state xc potential functional. The existence of the ground-state potentials is also guaranteed [31]. Comparing \( v_{\text{xc}}^{\text{adia}} \) and \( v_{\text{adia,ex}}^{\text{xc}} \) will directly reveal the nonadiabatic effects.

Using these definitions in practice requires the exact time-dependent density as an input. For the helium atom the latter can be calculated at bearable computational cost from the solution of the TDSE by using a one-dimensional model which reproduces the essential features of the DI process [10,11,16,17,32]. In this model, the helium atom in a time-dependent external potential \( v_{\text{ext}}(z, t) \) is described by the Hamiltonian

\[
H = \sum_{j=1,2} \left( \frac{p_j^2}{2m} + v_{\text{ext}}(z_j, t) \right) + W(z_1 - z_2) \tag{3}
\]
with electron coordinates \( z_1, z_2 \), momenta \( p_1, p_2 \), electron mass \( m \) and the soft-core interaction \( W(z) = e^2/\sqrt{z^2 + 1} \). The external potential \( v_{\text{ext}}(z, t) = -2W(z) - ezE(t) \) contains the electron-nucleus interaction and the potential of the time-dependent electrical field \( E(t) \). Taking the spatial wave function to be symmetric under exchange of electrons, the time-dependent Schrödinger equation \( i\hbar \partial_t \psi = H\psi \) is solved numerically. The two-electron wave function obtained in this way allows to calculate the exact time-dependent density \( n(z, t) = 2 \int |\psi(z', t)|^2 dz' \) and, via the inversion of the time-dependent KS equation (TDKS) [20,33], the exact time-dependent KS potential \( v_{\delta}(z) \). From the latter, the exact correlation potential \( v_{\text{c}}^{\text{adia}} = v_{\text{c}}^{\text{adia}} - v_{\text{s}} \) follows by Eq. (1), as for a two-electron singlet system \( v_{\text{dia}} := v_h + v_s = 1/2 v_h \) with \( v_h(z, t) = \int n(z', t)W(z - z')dz' \).

Thus, \( v_{\text{dia,ex}}^{\text{adia}} \) can readily be calculated. However, obtaining \( v_{\text{adia,ex}}^{\text{adia}} \) is a formidable task even in the one-dimensional model. Calculating the adiabatically exact total KS potential is still easy: Making the above described identification \( n_{0}(z) = n(z, t_0) \), the adiabatically exact total KS potential follows from the inversion of the static KS equation,

\[
v_{\text{s}}^{\text{adia,ex}}(z) = \frac{\hbar^2}{m} \frac{1}{2\varphi(z)} \frac{d^2\varphi(z)}{dz^2} + \text{const.} \tag{4}
\]
where \( \varphi(z) = \sqrt{n_0(z)/2} \). The challenge is posed by the exact xc part according to Eq. (2): finding \( v_{\text{ext},0}(r) \) requires the inversion of the interacting static Schrödinger equation \( H_0\psi_0 = E_0\psi_0 \) (SE) for the ground state \( \psi_0 \) which satisfies the constraint \( n_0(z) = 2 \int |\psi_0(z', z)|^2 dz' \). Here,

\[
H_0 = \sum_{j=1,2} \left( \frac{p_j^2}{2m} + v_{\text{ext},0}(z_j) \right) + W(z_1 - z_2). \tag{5}
\]
To find \( v_{\text{ext},0} \) for a given \( n_0 \) we implemented a generalization of an iterative scheme [34]. Starting with an initial guess \( v_{\text{ext},0}^{(1)} \) for \( v_{\text{ext},0} \) we calculate [33] the corresponding ground-state wave function, which in turn yields the density \( n_0^{(1)} \) corresponding to \( v_{\text{ext},0}^{(1)} \). Then a new potential is constructed according to the rule

\[
v_{\text{ext},0}^{(i+1)}(z) = v_{\text{ext},0}^{(i)}(z) + w(z)(n_0^{(i-1)}(z) - n_0(z)), \tag{6}
\]
where \( i = 2 \) for the first step. \( w(z) = \alpha |z|^{\beta} \) (with parameters \( \alpha, \beta > 0 \)) is a weight function allowing to increase the contribution of the density-fall-off region. The thus obtained \( v_{\text{ext},0}^{(2)} \) in turn leads to a \( n_0^{(2)} \) via solution of the SE. These steps are iterated until the density \( n_0^{(i)} \) has converged to \( n_0 \) according to the criterion

\[
\int |n_0(z) - n_0(z)|dz \leq \Delta, \tag{7}
\]
where \( \Delta \) is a measure for the desired accuracy. Once we have obtained \( v_{\text{ext},0}(z) \), the adiabatically exact correlation potential \( v_{\text{c}}^{\text{adia,ex}}(z) \) follows from Eq. (2) with \( v_{\text{hx}} \) being identical for the time-dependent and static case.

In order to assess the validity of the adiabatic approximation, we solve the two-electron TDSE for given potentials \( v_{\text{ext}}(z, t) \) representing paradigm cases of strong-field electron dynamics (discussed in detail below). At every time step \( t \) we then construct \( v_{\text{c}}^{\text{adia}} \) and \( v_{\text{c}}^{\text{adia,ex}} \) according to the procedure described above.

In our first study we take \( E(t) \) to be a dc electric field that is ramped up during 27 a.u. (0.65 fs) to a maximum value \( E_0 = 0.141 \) a.u. and held constant afterwards. Starting from the two-electron ground state this leads to field-induced ionization of the system with the electrons escaping to \( z \to \infty \). To avoid numerical problems caused by strongly accelerated electrons, the interaction with the field is truncated at a distance of 35 a.u. from the nucleus [20]. The resulting time-evolution of the density and the potentials is shown in Fig. 1. \( v_{\text{a}}^{\text{adia}} \) and \( v_{\text{c}}^{\text{adia,ex}} \) are defined only up to an additive time-dependent constant, which has been adjusted so that the boundary condition \( v_{\text{a}}^{\text{adia}}(z, t) \to 0 \) for \( z \to \infty \) is fulfilled. The free additive constant in \( v_{\text{s}}^{\text{adia,ex}} \) and \( v_{\text{ext},0} \) cannot be fixed, thus all adiabatically exact potentials are shifted to match the exact ones at \( z = 0 \). As with other known density-inversion schemes, our procedures work accurately only in regions of space where a sufficient amount of density is located. As a rule of thumb, regions where \( n(z) > 10^{-2} \) a.u. can safely be considered.
Restricting the analysis to regions of space where the density obtained with the iterative scheme also reproduces the one from the TDSE with high accuracy acts as a further safeguard against numerical artefacts.

Figure 1 shows that the exact and adiabatically exact versions of the total KS potential $v_\text{t}$ differ substantially and qualitatively. This reflects the fact that the former corresponds to an excited density in the presence of the linear laser potential, and the latter to a bound ground state in a global potential minimum. However, the surprising result is that the lowest line of panels in Fig. 1 undoubtedly reveals that the correlation contributions to the potentials, i.e., $v_{c}\text{ex}(z)$ and $v_{c,\text{adia,ex}}(z)$, agree extremely well at all times (also for times much longer than what is shown in Fig. 1). This indicates that memory effects in the correlation potential are practically negligible for this process. Also the buildup of a steplike structure in $v_c$ at later times as identified in [20] is well reproduced by the adiabatically exact approximation.

To probe the regime where nonadiabatic effects manifest themselves in the correlation potential, we consider as our second study an external potential in which the density is deformed more rapidly than during the ramping process. Instead of adding an external laser field to the electron-nucleus interaction, we directly perturb the soft-core potential according to

$$v_{\text{ex}}(z, t) = -\frac{2e^2}{\sqrt{(z - 0.5 \text{ a.u.})^2 + 1}}. \quad (8)$$

This forcing mimics an oscillatory motion of the nucleus. It has the benefit of keeping the density relatively well localized, thus allowing for stable solutions in the TDKS-inversion-scheme. The chosen frequency $\omega = 0.9$ a.u. is close to the frequency range investigated in earlier work on two-electron systems in the nonadiabatic regime [25,26]. Figure 2 shows that for the external potential (8) the density gets rapidly and strongly deformed and does not return to its initial shape after a full cycle of the forcing. To contain such a density as a ground state, the adiabatically exact KS potential produces additional minima which are not present in its exact, nonadiabatic counterpart. The resulting $v_{c,\text{adia,ex}}$ displayed in the lowest line of Fig. 2 differs markedly from $v_{c}\text{ex}$, showing that nonadiabatic effects become important.

Finally, in our third study we turn our attention to the practically most relevant case of strong, time-dependent external fields due to powerful laser pulses of the 780 nm wavelength that is typically used in strong-field experiments. The oscillation here is of moderate frequency but the density is strongly displaced from its initial position. This is a setup for which ALDA is known to fail badly [18].

The results shown below are obtained during a 4-cycle pulse with linear turn-on and -off for two cycles each. Our comparison now is done in the way that is most useful to assess the accuracy of the adiabatically exact approximation in practice: We propagate [33] the KS orbital while using at every time step the adiabatically exact approximation of $v_c$ that is obtained self-consistently from the KS density [35].

The TDSE is solved as the exact reference and now is used only for that purpose. To compare the results of the adiabatically exact TDKS calculation to those of the TDSE, we focus on the number of bound electrons,

$$N_b(t) = \int_{-a}^{a} n(z, t) dz,$$

with $|z| \leq a = 5 \text{ a.u.}$ This is a decisive quantity for the
Figure 3 shows the time evolution of the total ionization, the density without making additional approximations. This is crucial for the description of phenomena like, e.g., double excitations, our results show that they are negligible for typical strong-field excitations, and, in particular, for the paradigm process of the helium DI. Here, the adiabatically exact TDDFT approach yields excellent results.

In summary, we calculated the adiabatic xc potential by inverting the interacting SE. Thus, we were able to visualize the nonadiabatic effects in \( v_{xc}(r, t) \) exactly, providing a procedure to directly track down this fundamental but elusive feature of TDDFT. As a test of immediate practical relevance we have performed a nonlinearized, nonperturbative Kohn-Sham calculation of strong-field ionization which consistently used the adiabatically exact approximation for \( v_{xc} \). While memory effects in \( v_{xc} \) are known to be crucial for the description of phenomena like, e.g., double excitations, our results show that they are negligible for typical strong-field excitations, and, in particular, for the paradigm process of the helium DI. Here, the adiabatically exact TDDFT approach yields excellent results.

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**Reference Notes**

35. A similar procedure has been used in H. O. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. 100, 056404 (2008).