Adiabatic Approximation of the Correlation Function in the Density-Functional Treatment of Ionization Processes

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The ionization of a one-dimensional model helium atom in short laser pulses using time-dependent density-functional theory is investigated. We calculate ionization probabilities as a function of laser intensity by approximating the correlation function of the system adiabatically with an explicit dependence on the fractional number of bound electrons. For the correlation potential we take the derivative discontinuity at integer numbers of bound electrons explicitly into account. This approach reproduces ionization probabilities from the solution of the time-dependent Schrödinger equation, in particular, the so-called knee due to nonsequential ionization.

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Experimental double ionization yields for helium atoms in laser fields of $\lambda = 614$ nm [1] and $\lambda = 780$ nm [2] show a knee structure as a function of intensity, i.e., double ionization is enhanced over the expected yields for sequential ionization by several orders of magnitude and was therefore named nonsequential double ionization (NSDI).

Theoretically, the problem was addressed successfully using the strong-field approximation (see, e.g., [3] and references therein) and classical methods [4]. The widely accepted mechanism behind NSDI relies on the rescattering of the first electron with its parent ion, collisionally ionizing (or exciting) the second electron.

However, investigations using time-dependent density-functional theory (TDDFT) [5] failed to reproduce the characteristic knee of the double ionization probability [6–8]. This failure is especially important given the fact that TDDFT offers the possibility to treat the strong-field dynamics of atomic and molecular systems from first principles in a numerically tractable way, whereas the solution of the Schrödinger equation in full dimensionality [9] is limited to two active electrons. Other methods used to tackle the NSDI problem from first principles are R-Matrix Floquet theory [10] or multiconfigurational time-dependent Hartree-Fock [11,12], which, however, have not yet reproduced NSDI knees either.

Two reasons for the failure of TDDFT in the context of NSDI were identified [13]: the approximation of the exchange-correlation functional v_{xc} and the approximation of the functionals for the calculation of the ionization probabilities. Initial attempts to overcome these problems were not successful [13]. Recent progress in approximating v_{xc} has been made by including the derivative discontinuity at integer numbers of bound electrons [14–16]. In this work we therefore focus our attention on the open problem of constructing functionals for the calculation of the ionization probabilities. We show that by using a rather simple adiabatic approximation of the correlation function, the ionization yields for a model He atom in few-cycle laser pulses (for which we have the exact time-dependent Schrödinger solutions at hand) are remarkably well reproduced.

We investigate helium in linearly polarized $N = 3$-cycle laser pulses of duration $T = N2\pi/\omega$ with a $\sin^2$-pulse envelope in dipole approximation, i.e., the vector potential is of the form $A(t) = \hat{A}\sin^2(\frac{\omega}{2N}t)\sin(\omega t)$ for $0 \le t \le T$. Two different pulses with frequencies used in experimental work [1,2] are chosen: $\omega = 0.058$ and $\omega = 0.074$ (atomic units are used throughout this work unless otherwise indicated). The linear polarization of the laser pulses allows to model helium by a one-dimensional atom with soft-core potentials for the Coulomb interactions. It is known that the essential features of the nonsequential double ionization process are described well by this model [6,7,11,14,16,17]. For different effective peak intensities $I = I(\hat{A})$ of the laser pulses we solve the time-dependent Schrödinger equation (TDSE) $i\partial_t\psi = \hat{H}\psi$ with the Hamilton operator

$$\hat{H} = \sum_{k=1,2}\left[-\frac{1}{2}\partial_{x_k}^2 + V(x_k, t)\right] + W(x_1 - x_2), \quad (1)$$

where $\hat{H} = \hat{H}(x_1, x_2, t)$, the external potential $V(x, t) = -iA(t)\partial_x - 2/\sqrt{x^2 + \epsilon_{\mathrm{ce}}}$ (the A^2 term has been transformed away), and the electron-electron interaction potential $W(x) = 1/\sqrt{x^2 + \epsilon_{\mathrm{ee}}}$. The solution is the two-electron wave function $\psi(x_1, x_2, t)$ in a spin singlet state. Therefore, we have just one Kohn-Sham orbital fulfilling $i\partial_t\phi = \hat{H}_{\mathrm{KS}}\phi$ with $\phi = \phi(x, t)$ and $\hat{H}_{\mathrm{KS}}(x, t) = -(1/2)\partial_x^2 + V(x, t) + v_{\mathrm{hxc}}(x, t)$. The Hartree-exchange part $v_{\mathrm{hx}} = v_{\mathrm{h}} + v_{\mathrm{x}}$ of the potential $v_{\mathrm{hxc}} = v_{\mathrm{h}} + v_{\mathrm{x}} + v_{\mathrm{c}}$ is known exactly for the helium atom, $v_{\mathrm{h}}(x, t) = \int dx' 2|\phi(x', t)|^2 W(x - x')$ and $v_{\mathrm{x}}(x, t) = -\frac{1}{2}v_{\mathrm{h}}(x, t)$. A simple model for the correlation potential which takes into account the derivative discontinuity at integer numbers of bound electrons is that recently proposed by Lein and Kümmel [14]

$$v_{\mathrm{hxc}}^{\mathrm{LK}}(x,t) = \frac{N_0/N(t)}{1+\exp[C(N_0/N(t)-2)]} v_{\mathrm{hx}}(x,t), \qquad (2)$$

where $N(t) = \int_{-a}^{+a} dx 2|\phi(x,t)|^2$ is the number of bound electrons and $N_0 = N(t=0)$. C is a positive, sufficiently large number, e.g., $C = 50$. We choose $\epsilon_{\mathrm{ce}} = 0.5$ which yields the correct $I_p^{(2)} = 2.0$. In order to reproduce $I_p^{(1)} = 0.904$ in the Schrödinger equation $\epsilon_{\mathrm{ee}} = 0.329$ and in the TDDFT calculation $\epsilon_{\mathrm{ee}} = 0.343$ are used (results do not change qualitatively for a different choice of ϵ_{ce} and ϵ_{ee}). To encompass the bound states, the parameter a is set to $a = 6$ throughout this work. The Schrödinger and Kohn-Sham equations are solved numerically by a split-operator time propagator on a numerical grid (see, e.g., [18] and references therein).

For our model atom, the diagonal of the two-electron density matrix is the pair density $\rho(x_1, x_2, t) = 2|\psi(x_1, x_2, t)|^2$. The exact density of the system

$$n(x,t) = \int dx' \rho(x, x', t) \qquad (3)$$

can, in principle, be calculated from the Kohn-Sham orbital of a TDDFT calculation with the correct exchange-correlation potential v_{xc} as $n(x,t) = 2|\phi(x,t)|^2$. Using v_{xc} in the LK approximation yields approximate densities n_{LK}. The time-dependent correlation function of the model atom is $g_{\mathrm{xc}}[n](x_1, x_2, t) = \rho(x_1, x_2, t)/n(x_1, t)n(x_2, t)$. The conditional probability to find at time t an electron at x_2 in dx_2 *if* there is an electron at x_1 is given by $n(x_2, t)g_{\mathrm{xc}}(x_1, x_2, t)dx_2$. Since the probability is an observable, the Runge-Gross theorem [5] assures that g_{xc} can in principle be expressed exactly as a functional of the density [13].

For a system with a two-electron wave function that can be expressed as a product of single-electron orbitals, g_{xc} simplifies to $g_{\mathrm{xc}} = g_{\mathrm{x}} = \frac{1}{2}$. The correlation contribution to the correlation function is thus defined as

$$g_{\mathrm{c}}[n](x_1, x_2, t) = \frac{\rho(x_1, x_2, t)}{n(x_1, t)n(x_2, t)} - \frac{1}{2}. \qquad (4)$$

Because of Eq. (3), g_{c} fulfills the integration constraints $\int dx_i n(x_i, t) g_{\mathrm{c}}[n](x_i, x_{j\neq i}, t) = 0$ with $i, j \in \{1, 2\}$.

A quantity of central importance to our work is the number of electrons bound to the helium core at time t,

$$N(t) = \int_{-a}^{+a} dx n(x,t), \qquad (5)$$

which also plays a central role in the exchange-correlation potential v_{xc} in ionization processes, as in Eq. (2).

In the two-electron space of the model atom we attribute areas to single ionization P^+ (either $|x_1| > a$ and $|x_2| \leq a$ or $|x_1| \leq a$ and $|x_2| > a$) and double ionization P^{2+} ($|x_1| > a$ and $|x_2| > a$). Integration of $|\psi(x_1, x_2, T)|^2$ over these areas yields the ionization probabilities. This procedure to calculate ionization probabilities is well established [6,7,11] and leads to ionization probabilities depicted in Fig. 1. Substituting the density and the correlation function for the pair density in the integrals and using $P^0 + P^+ + P^{2+} = 1$ (P^0 being the probability for the atom to remain neutral) yields the exact ionization probabilities [13]

$$P^+(t) = 2p(t)[1 - p(t)] - I_{\mathrm{c}}(t), \qquad (6)$$

$$P^{2+}(t) = [1 - p(t)]^2 + \tfrac{1}{2} I_{\mathrm{c}}(t), \qquad (7)$$

where $p(t) = \frac{1}{2}\int_{-a}^{+a} dx n(x,t)$ and the correlation integral is given by

$$I_{\mathrm{c}}(t) = \int_{-a}^{+a} dx_1 \int_{-a}^{+a} dx_2 n(x_1) n(x_2) g_{\mathrm{c}}(x_1, x_2), \qquad (8)$$

with the density and the correlation function depending on time t and $g_{\mathrm{c}} = g_{\mathrm{c}}[n]$.

It is important to note that Eqs. (6)–(8) assure that only the exact density in the range $-a \leq x \leq +a$ and the exact correlation function for $-a \leq x_1, x_2 \leq +a$ are required to calculate the exact ionization probabilities.

The functional dependence of g_{c} on n is not known and the calculation of the pair density ρ at time $t = T$ is computationally demanding even for the one-dimensional helium model atom. Therefore, it is necessary to find a suitable approximation for $g_{\mathrm{c}}[n](x_1, x_2, T)$ to calculate I_{c}. Setting $I_{\mathrm{c}}(t) = 0$ corresponds to assuming the two-electron wave function to be a product of identical single-electron orbitals. This interpretation of the Kohn-Sham orbitals as electron orbitals has been widely used [6,7,13,14]. However, this approach leads to ionization probabilities which differ significantly from the exact probabilities even when the exact density (3) is used [7], as shown in Fig. 1. The LK approximation for v_{xc} leads to probabilities which closely resemble the probabilities calculated from the exact densities.

The TDSE solution yields the exact pair density. This allows us to calculate the exact g_{c} and I_{c} as a reference for approximations of g_{c}. Figure 2 reveals a structure of the integrand of $I_{\mathrm{c}}(T)$ which is remarkably simple. This is

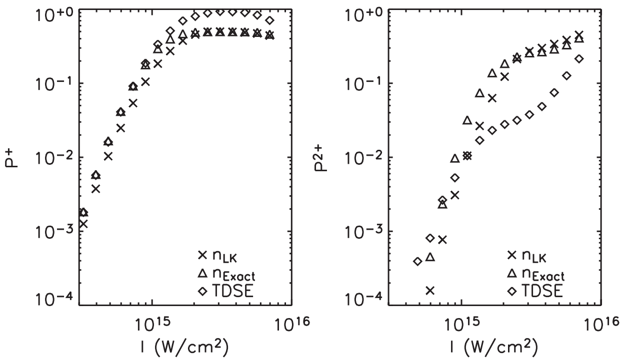

FIG. 1. Single and double ionization probabilities for exact and LK densities using $I_{\mathrm{c}} = 0$ compared to the TDSE solution for a $\lambda = 780$ nm laser pulse.

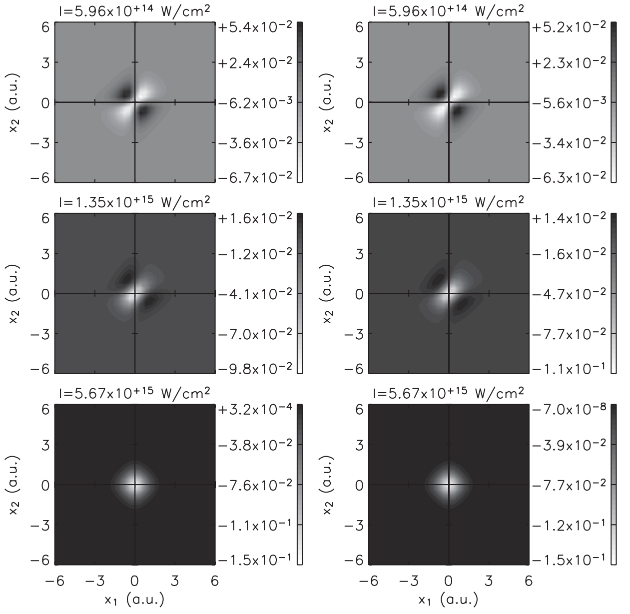

FIG. 2. Comparison of the integrand of the exact $I_c(T)$ (left) and the adiabatic approximation $I_c^A(T)$ (right) for different effective peak intensities of a $\lambda = 780$ nm laser pulse.

caused by the multiplication of g_c by the density at x_1 and at x_2, which exhibits a maximum at the origin. For the other laser pulse the integrand of I_c reveals a qualitatively similar structure.

The values of $I_c(T)$ for the two laser pulses are depicted in the left panel of Fig. 3 as a function of the number of bound electrons $N(T)$. I_c shows a quantitatively similar behavior for both laser pulses: a minimum value for I_c is reached when the number of electrons is equal to one. This result points to the importance of the quantity $N(T)$ for the value of $I_c(T)$.

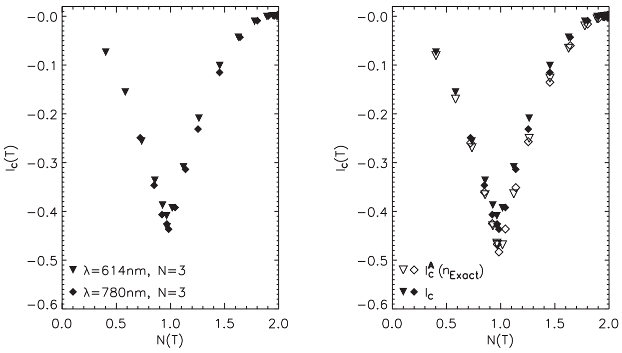

FIG. 3. Value of the exact $I_c(T)$ as a function of the number of bound electrons (left). Value of $I_c^A(T)$ using exact densities compared to the exact $I_c(T)$ (right). Results for both laser pulses are shown together with differently shaped symbols.

We shall now introduce our adiabatic approximation for g_c. The starting point is our assumption that the system in the vicinity of the helium core after the laser pulse closely resembles a ground state system with a fractional number of electrons given by the number of bound electrons $N(T)$. We approximate numerator and denominator of the correlation function separately as linear combinations of the ground state densities n_i and ground state pair densities ρ_i of i-electron systems. The density of the model helium atom is expressed as [14]

$$n^A = \begin{cases} (1-N)n_0 + Nn_1 & 0 \leq N \leq 1 \\ (2-N)n_1 + (N-1)n_2 & 1 \leq N \leq 2 \end{cases}, \tag{9}$$

where $n^A = n^A(x,t)$, $n_i = n_i(x)$, and $N = N(t)$ is given by (5). Using $n^A(t)$ in the ground state Kohn-Sham equation to calculate $v_c(t)$ and consequently employing $v_c(t)$ in the time propagation has been shown to improve ionization probabilities compared to $v_c = 0$ [16]. Since $n(x)dx$ is the probability to find an electron at x in dx, the density of the zero-electron system vanishes: $n_0 = 0$. Assuming the same adiabatic dependence of $\rho^A(t)$ on $N(t)$ the pair density is approximated as

$$\rho^A = \begin{cases} (1-N)\rho_0 + N\rho_1 & 0 \leq N \leq 1 \\ (2-N)\rho_1 + (N-1)\rho_2 & 1 \leq N \leq 2 \end{cases}, \tag{10}$$

where $\rho^A = \rho^A(x_1, x_2, t)$, $\rho_i = \rho_i(x_1, x_2)$ and $N = N(t)$. The pair density $\rho(x_1, x_2)$ gives the joint probability to find an electron at x_1 in dx_1 and an electron at x_2 in dx_2. Corresponding to our consideration for the density, the pair densities of the zero- and one-electron systems are zero: $\rho_0 = 0$, $\rho_1 = 0$. For our model atom, $n_1(x)$ is the ground state density of He$^+$. It is calculated from the solution of the respective one-dimensional stationary Schrödinger equation with $\epsilon_{ce} = 0.5$. Consistently we use $n_2(x) = n(x, t = 0)$ where n denotes the density utilized to calculate $N(t)$ in (5). Our adiabatic approximation of g_c thus is

$$g_c^A = \begin{cases} -\dfrac{1}{2} & 0 \leq N \leq 1 \\ \frac{\rho^A(x_1,x_2,t)}{n^A(x_1,t)n^A(x_2,t)} - \dfrac{1}{2} & 1 \leq N \leq 2 \end{cases}, \tag{11}$$

with $g_c^A = g_c^A(x_1, x_2, t)$. Although for $N(T) = 1$ one has $g_c^A = 1/2$ which yields the unphysical value $P^{2+}(T) = 0$, good results are already acquired for $N(T)$ only slightly smaller or larger than 1, as is shown below.

In this form the approximation recovers the exact correlation function for the ground state. This approximation can only be valid in the immediate vicinity of the helium core. However, as pointed out above, this is sufficient to calculate the correlation integral $I_c^A(T)$. The integration constraints $\int dx_i n(x_i, t) g_c[n](x_i, x_{j\neq i}, t) = 0$ with $i, j \in \{1, 2\}$ are not fulfilled since for $|x_i| > a$ we have $n \neq 0$ and $g_c \neq 0$ but set $g_c^A = 0$. The same densities as in Eq. (5) are used in the integrand of I_c^A.

The ground state inputs needed to calculate g_c^A are accessible numerically also for more complex systems than helium. Moreover, in the three-dimensional case the ground state pair density can be calculated approximately via one of the well-known approximations for the ground state correlation function [19,20].

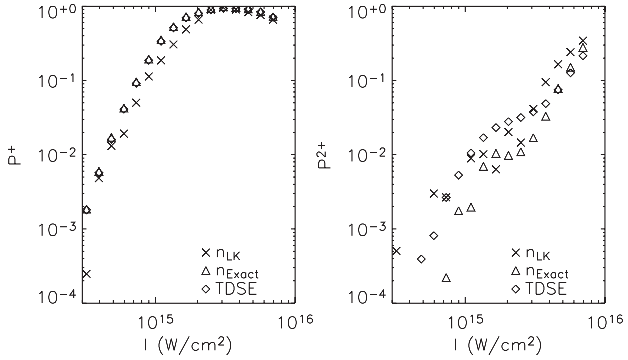

FIG. 4. Single and double ionization probabilities for exact and LK densities using the adiabatic approximation of the correlation integral I_c^A compared to the TDSE solution for a $\lambda = 780$ nm laser pulse.

The right-hand side of Fig. 2 shows the integrand of $I_c^A(T)$ using the exact densities. The qualitative agreement with the exact integrand of $I_c(T)$ is good. Furthermore, the maximum and minimum values of the integrand are close to the exact values. This is a strong indication that the adiabatic approximation of g_c captures the essential features which contribute to I_c. In the right plot of Fig. 3 the adiabatic approximation I_c^A is compared to the exact values I_c for both laser pulses as a function of $N(T)$. The adiabatic approximation exhibits a very similar dependence on N as the exact values. However, for $N(T) \approx 1.0$ the values differ from the exact results. In our adiabatic approximation for $N(t) \leq 1$ all correlation effects vanish, as can be seen from (11). This might indicate the necessity to include memory effects in a refined approximation of ρ.

Figure 4 shows the ionization probabilities calculated from the exact and the LK densities using the approximated $I_c^A(T)$ for the $\lambda = 780$ nm laser pulse. Single ionization probabilities agree very well with the exact probabilities from the TDSE for both exact and LK densities. The systematically too low values for $I_c = 0$ are corrected. Double ionization probabilities show a good agreement for high intensities. For low intensities the double ionization probabilities (and I_c^A) are so small that already small deviations of I_c^A from the exact I_c lead to relatively large deviations in the logarithmic plot of the ionization probabilities and to minima and maxima in the double ionization probability. Since $g_c^A = 1/2$ at $N(T) = 1$, the adiabatically corrected probabilities for the two laser pulses examined show a minimum at intensities when the second derivative of the exact probabilities changes its sign at the onset of the knee structure [where $N(T) \simeq 1$]. Comparison with the values for $I_c = 0$ (Fig. 1) evidences a significant improvement of the TDDFT ionization probabilities using our approximation of the correlation function (11).

In summary, to acquire the exact, multiple ionization probabilities of atoms in strong laser fields from time-dependent density-functional calculations, knowledge of the correlation integral $I_c(T)$ is vital. For a one-dimensional helium model atom, an adiabatic approximation of the correlation function g_c close to the helium core yields an approximation of I_c which agrees qualitatively and quantitatively well with the exact I_c. The exact single ionization probabilities and the knee structure in the double ionization probability are reproduced. The (pair) density of helium after the laser pulse can be approximated by a linear combination of atomic and ionic ground state (pair) densities using the fractional number of bound electrons. This method opens the possibility to apply the adiabatic approximation in three dimensions and to the ionization of more complex atoms.

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