Strong-field ionization of Li and Be: a time-dependent density functional theory with self-interaction correction

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ABSTRACT

In the framework of the time-dependent density functional theory, we have performed 3D calculations of multiphoton ionization of Li and Be atoms by strong near-infrared laser fields. The results for the intensity-dependent probabilities of single and double ionization are presented. We make use of the time-dependent Krieger-Li-Iafrate exchange-correlation potential with self-interaction correction (TD-KLI-SIC). Such a potential possesses an integer discontinuity which improves description of the ionization process. However, we have found that the discontinuity of the TD-KLI-SIC potential is not sufficient to reproduce characteristic feature of double ionization.

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1. Introduction

The first experiments on double multiphoton ionization of He atoms by strong near-infrared laser fields [1,2] revealed a non-sequential nature of this process, with the exception of very high intensities ($>3 \times 10^{15}$ W/cm^2) where the sequential ionization takes place. Different theoretical models have been suggested for description of the non-sequential double ionization (NSDI) (see, for example, review [3]). However, further experimental investigations [4–6] unambiguously pointed out that the dominant contribution to NSDI in the tunneling ionization regime can be explained by the recollision mechanism [7]. According to the classical rescattering model [7], an electron removed from the atom by the external field can return to the parent ion after some period of time. When it returns, its kinetic energy can be as large as $3.17U_p$ due to acceleration by the external field (U_p is ponderomotive potential; for linearly polarized laser fields, $U_p = F^2/(2\omega)^2$ where F is the peak electric field strength and ω is the laser frequency). The returning electron can undergo elastic or inelastic scattering or it can recombine with the core. The latter possibility leads to emission of a photon (high-order harmonic generation, HHG), and elastic scattering contributes to above-threshold ionization (ATI). Inelastic scattering results in excitation of the core or ejection of another electron through $(e, 2e)$ process; removal of multiple electrons is also possible. Of course, these inelastic processes can take place only if they obey the energy conservation.

Experimentally confirmed $(e, 2e)$ mechanism of NSDI in the tunneling regime implies that proper account of the electron–electron interaction is crucial for correct description of this process. It is not surprising that single active electron (SAE) theoretical models are unable to reproduce NSDI characteristics even qualitatively since such models do not include multielectron dynamics. On the contrary, the time-dependent density functional theory (TDDFT), in principle, contains all multielectron effects through the exchange-correlation functional. However, early attempts to apply TDDFT with various known exchange-correlation functionals for calculations of NSDI [8,9] were unsuccessful. The calculations failed to describe the experimental results on double ionization of He atoms even qualitatively: the famous "knee" structure in the intensity dependence of the double ionization probability [1,2] couldn't be reproduced. Nowadays it is understood that the problem is not in TDDFT itself but in quality of the exchange-correlation functionals. Most of approximate exchange-correlation functionals lack the important property of the exact functional, the discontinuity of its derivative with respect to the number of particles N, when N passes through integer values [10]. It was shown [11] that the derivative discontinuity is crucial for correct description of double ionization: a simple model correlation potential with the discontinuity, being used in the time-dependent Kohn–Sham equations, produced the intensity dependence of the double ionization probability with the "knee" structure, in qualitative agreement with the experiment. In the ground-state density functional theory, the exchange-correlation potentials with the discontinuity can be constructed with the help of the optimized effective

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potential (OEP) method and its simplified version, the Krieger-Li-lafrate (KLI) approximation [12]. Both OEP and KLI methods can be extended to the TDDFT domain [13], and the constructed time-dependent exchange-correlation potential retains the discontinuity property. Moreover, it was demonstrated [14] that the discontinuity of the exchange-correlation potential is explicitly built up during the time propagation of the time-dependent Kohn–Sham orbitals.

2. Method

In this paper, we use TDDFT to study multiphoton ionization of Li and Be atoms by strong near-infrared laser fields. The single-particle potential with the discontinuity is constructed by means of the time-dependent KLI (TDKLI) procedure with self-interaction correction (SIC) [15]. For the TD-KLI-SIC procedure [15] adopted here, we extend Perdew and Zunger's SIC form [16] to the time domain. It has been shown [15] that the TDKLI procedure [13] can be simplified considerably without the need of using the nonlocal Hartree–Fock energy functional, in the construction of the time-dependent OEP. Thus the TD-KLI-SIC procedure [15] is computationally more efficient and yet maintains high accuracy in the calculation of the ground state energies, ionization potentials, excited autoionizing resonances [17], as well as multiphoton ionization dynamics [15,18]. Within the adiabatic approximation, well justified in the case of low-frequency laser fields [19], the TD-KLI-SIC single-particle potential can be expressed as follows:

$$V_\sigma^s(\boldsymbol{r},t) = \sum_{n=1}^{N_\sigma} \frac{\rho_{n\sigma}(\boldsymbol{r},t)}{\rho_\sigma(\boldsymbol{r},t)}\left[v_{n\sigma}(\boldsymbol{r},t) + \overline{V}_{\sigma n}^s - \bar{v}_{n\sigma}\right]. \tag{1}$$

Here indices n and σ enumerate spin-orbitals (σ corresponds to the spin projection, N_σ is the total number of electrons with the spin σ); $\rho_{n\sigma}$ and ρ_σ are the spin-orbital density and the total spin-density, respectively:

$$\rho_{n\sigma}(\boldsymbol{r},t) = |\psi_{n\sigma}(\boldsymbol{r},t)|^2,$$
$$\rho_\sigma(\boldsymbol{r},t) = \sum_{n=1}^{N_\sigma} \rho_{n\sigma}(\boldsymbol{r},t) \tag{2}$$

($\psi_{n\sigma}(\boldsymbol{r},t)$ is the Kohn–Sham spin-orbital). The orbital-dependent potential $v_{n\sigma}(\boldsymbol{r},t)$ includes the Hartree and exchange-correlation parts as well as self-interaction corrections. The mean values $\overline{V}_{\sigma n}^s$, $\bar{v}_{n\sigma}$ are calculated with the spin-densities $\rho_{n\sigma}(\boldsymbol{r},t)$:

$$\overline{V}_{\sigma n}^s = \int d^3 r \rho_{n\sigma}(\boldsymbol{r},t) V_\sigma^s(\boldsymbol{r},t),$$
$$\bar{v}_{n\sigma} = \int d^3 r \rho_{n\sigma}(\boldsymbol{r},t) v_{n\sigma}(\boldsymbol{r},t). \tag{3}$$

Eq. (1) defines the potential $V_\sigma^s(\boldsymbol{r},t)$ up to an arbitrary constant. However, since the exchange-correlation potential vanishes at infinity in the space domain, its expectation value with the highest-occupied spin-orbital $\psi_{m\sigma}(\boldsymbol{r},t)$ must be equal to that of the orbital-dependent potential $v_{m\sigma}(\boldsymbol{r},t)$ [12]:

$$\overline{V}_{\sigma m}^s = \bar{v}_{m\sigma}. \tag{4}$$

The constraint (4) makes the potential (1) unique, and all unknown constants $\overline{V}_{\sigma n}^s$ ($n < m$) can be obtained solving a set of linear equations [12]. It is the constant $\overline{V}_{\sigma n}^s - \bar{v}_{n\sigma}$ in Eq. (1) that ensures discontinuous behavior of the TD-KLI-SIC potential with respect to the particle number N_σ [12,14].

For Li and Be atoms, the procedure is particularly straightforward since N_σ does not exceed 2. For the open-shell Li atom (the electronic structure ($1s^2 2s$)), the TD-KLI-SIC potential is spin-dependent and can be explicitly written as follows, for the spin up (↑) and spin down (↓), respectively:

$$V_\uparrow^s(\boldsymbol{r},t) = \frac{\rho_{1\uparrow}(\boldsymbol{r},t)}{\rho_\uparrow(\boldsymbol{r},t)}\left\{v_{1\uparrow}(\boldsymbol{r},t) + \left[\int d^3 r \frac{\rho_{2\uparrow}(\boldsymbol{r},t)\rho_{1\uparrow}(\boldsymbol{r},t)}{\rho_\uparrow(\boldsymbol{r},t)}\right]^{-1}\right.$$
$$\times \int d^3 r \frac{\rho_{2\uparrow}(\boldsymbol{r},t)\rho_{1\uparrow}(\boldsymbol{r},t)}{\rho_\uparrow(\boldsymbol{r},t))}\left[v_{2\uparrow}(\boldsymbol{r},t) - v_{1\uparrow}(\boldsymbol{r},t)\right]\Bigg\}$$
$$+ \frac{\rho_{2\uparrow}(\boldsymbol{r},t)}{\rho_\uparrow(\boldsymbol{r},t)}v_{2\uparrow}(\boldsymbol{r},t), \tag{5}$$

$$V_\downarrow^s(\boldsymbol{r},t) = v_{1\downarrow}(\boldsymbol{r},t). \tag{6}$$

For the closed-shell Be atoms ($1s^2 2s^2$), the TD-KLI-SIC potential is spin-independent and takes the form (5) for both spin projections. For the orbital-dependent potentials $v_{n\sigma}(\boldsymbol{r},t)$, we use the exchange-only approximation in the local spin-density (LSD) form, and include Perdew-Zunger [16] self-interaction corrections:

$$v_{n\sigma}(\boldsymbol{r},t) = v_H[\rho_\uparrow + \rho_\downarrow](\boldsymbol{r},t) + v_x^{LSD}[\rho_\sigma](\boldsymbol{r},t) - v_H[\rho_{n\sigma}](\boldsymbol{r},t)$$
$$- v_x^{LSD}[\rho_{n\sigma}](\boldsymbol{r},t), \tag{7}$$

where $v_H[\rho](\boldsymbol{r},t)$ and $v_x^{LSD}[\rho](\boldsymbol{r},t)$ are the Hartree and LSD exchange potentials, respectively:

$$v_H[\rho](\boldsymbol{r},t) = \int d^3 r' \frac{\rho(\boldsymbol{r}',t)}{|\boldsymbol{r} - \boldsymbol{r}'|},$$
$$v_x^{LSD}[\rho](\boldsymbol{r},t) = -\left[\frac{6}{\pi}\rho(\boldsymbol{r},t)\right]^{1/3}. \tag{8}$$

The spin-orbital energies computed by the time-independent DFT using these potentials are listed in Table 1. They are in very good agreement with the results of Ref. [12] where the exact exchange potential was used.

To obtain the time-dependent electron densities and calculate the ionization probabilities, one has to solve a set of the time-dependent Kohn–Sham equations for the spin-orbitals $\psi_{n\sigma}(\boldsymbol{r},t)$:

$$i\frac{\partial}{\partial t}\psi_{n\sigma}(\boldsymbol{r},t) = \left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + V_\sigma^s(\boldsymbol{r},t) + v_{ext}(\boldsymbol{r},t)\right]\psi_{n\sigma}(\boldsymbol{r},t),$$
$$n = 1, \ldots, N_\sigma. \tag{9}$$

Besides the discussed single-particle potential V_σ^s, the right-hand side of Eq. (9) contains the Coulomb interaction with the nucleus (Z is the nucleus charge) and interaction with the external laser field $v_{ext}(\boldsymbol{r},t)$. In our calculations we use a linearly polarized laser pulse; the wavelength of the carrier is 800 nm, and the envelope has a sine-squared shape and contains 8 optical cycles:

$$v_{ext}(\boldsymbol{r},t) = (\boldsymbol{F}(t) \cdot \boldsymbol{r}), \tag{10}$$

$$\boldsymbol{F}(t) = \boldsymbol{F}_0 \sin^2 \frac{\pi t}{T} \sin \omega_0 t, \quad T = \frac{16\pi}{\omega_0}. \tag{11}$$

To solve the set (9), we apply the time-dependent generalized pseudospectral (TDGPS) method which proved accurate and efficient in our previous TDDFT calculations (see, e.g., Refs. [21,20]). For the TDGPS discretization in the present calculations, we use 80 radial and 32 angular grid points, and the time step 0.027 a.u. The Eq. (9) are solved in space within a sphere with the radius

Table 1
Absolute values of spin-orbital energies of Li and Be atoms. (A) Present calculations (a.u.). (B) Ref. [12] (a.u.).

Atom	Spin-orbital	A	B
Li	1s↑	1.993	
	1s↓	2.476	
	2s↑	0.196	0.196
Be	1s	4.039	
	2s	0.308	0.309