Dynamical core polarization of two-active-electron systems in strong laser fields

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The ionization of two-active-electron systems by intense laser fields is investigated theoretically. In comparison with time-dependent Hartree-Fock and exact two-electron simulation, we show that the ionization rate is overestimated in single-active-electron approximation. A modified single-active-electron model is formulated by taking into account the dynamical core polarization. Applying our approach to Ca atoms, it is found that the polarization of the core can be considered instantaneous and the large polarizability of the cation suppresses the ionization by 50% while the photoelectron cutoff energy increases slightly. The existing tunneling ionization formulation can be corrected analytically by considering core polarization.

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Various nonperturbative phenomena occurring during atom-laser interactions are started with single ionization, e.g., above threshold ionization (ATI) and high harmonic generation (HHG). Although they have been successfully interpreted by the rescattering model based on single-active-electron (SAE) approximation (see reviews, e.g., [1,2]), detailed examination showed that multielectron effects are embedded in the photon and electron spectra [3–9]. It is found that HHG from molecules records interference of different channels, suggesting that more than one molecular orbitals are involved [3] and electron rearrangement is occurring [4], which is certainly beyond the scope of the SAE theory. On the other hand, two-electron events such as nonsequential double ionization cannot be explained, either, without considering the electron-electron interaction [10]. It is thus desirable to examine in detail the multielectron effects occurring in the ionization of atomic systems beyond SAE.

The single ionization of atoms in strong laser fields can be pictured as the tunneling of one electron through the barrier formed by the atomic potential and the laser-atom dipole interaction. The Keldysh parameter measures the ratio of tunneling time to the optical period, $\gamma = \sqrt{I_p/2U_p}$, where $I_p = \kappa^2/2$ is the ionization potential and $U_p = E^2/4\omega^2$ is the ponderomotive energy of a free electron in a laser field of strength E and frequency ω. When $\gamma < 1$, tunnel ionization occurs so rapidly that the electric field can be considered as a static field at each instant. The so-called adiabatic approximation is the root of Ammosov-Delone-Krainov (ADK) and similar theories [11] for obtaining ionization rates. Based on this picture, the rate is mainly determined by the unitless quantity κ^3/E, with κ^3 representing the atomic field strength at the classical radius of the electron motion.

It is obvious that the adiabatic approximation will break down if the atomic potential acting on the tunneling electron is varying sooner than the tunneling time. For more than one electron systems, the core can be polarized by the laser fields, and hence the atomic potential is time varying. In the case of absence of resonant excitation, the polarization is instantaneously following the laser field. One therefore expects that ionization rates from single-active-electron theory need to be corrected by taking the dynamical core polarization (DCP) into account [12]. Recently we have incorporated the DCP into simulations [13], successfully interpreting the experimentally measured alignment-dependent ionization rate of CO molecules [14]. In this work, we further investigate the effects of DCP on the photoelectron spectra of alkaline-earth-metal atoms that have two strongly correlated valence electrons. In particular, we benchmark the various related theories by comparison with exact solution of the time-dependent Schrödinger equation (TDSE) for a model hydrogen molecule with both electrons moving in one dimension.

We start with the SAE approximation and then take into account the multielectron symmetry [15–18] and the core polarization induced by laser fields. For a N-e^- system interacting with laser fields, the valence electrons will be strongly perturbed compared to the inner electrons. After the liberation of one electron, the ion becomes more tightly bounded, giving rise to higher secondary ionization potential. Therefore the SAE approximation is usually adopted assuming the ionic core is frozen. The effective TDSE for the active electron in a laser field takes the form of

$$i\frac{\partial}{\partial t}\psi = \left[-\frac{\nabla^2}{2} + V_n + V_L\right]\psi, \tag{1}$$

where $V_L = \vec{r}\cdot\vec{E}$ is the interaction of the active electron with the external laser field $\vec{E}$ and V_n is the effective potential from the *frozen* core (atomic units are used throughout unless indicated otherwise). One of the approaches to obtain the effective potential is approximating the Hartree-Fock potential in the local-density approximation, which gives the correct asymptotic behavior of $V_n \to -\frac{1}{r}$ as the active electron is detached from the atomic system. The initial wave function can be taken as the the Hartree-Fock orbital of the valence electron. We will refer to this treatment as the SAE theory.

The SAE theory assumes the electrons can be distinguished as the active electron and the core electrons. Although the static (both Coulombic and exchange) potentials from the core electrons are taken into account, the antisymmetrization of the total wave function due to the Pauli exclusion principle is disregarded in the dynamics driven by external fields. It can be partly remedied by requiring the wave function $\psi(\vec{r},t)$ to be orthogonal to the occupied orbitals during the time

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propagation, and therefore, for many-electron systems, the orbitals occupied by the core electrons limit the configuration space that the active electron can occupy. We refer this treatment as SAE + O theory.

Another shortcoming of SAE theory is that it fails when the dynamic response of the core electrons comes into play, such as for systems that have more than one weakly bounded electron. The interplay between electrons would lead to complex multielectron effects, including multiorbital (multichannel) and multipole effects [19]. Here we focus on the effect of the adiabatic evolution or polarization of the ionic core induced by the external laser field. Within the adiabatic approximation, it is possible to derive an effective Hamiltonian of the active electron which takes into account the laser-induced core polarization [20–22]. We give a brief description in the following.

Denoting the polarizability tensor of the atomic core as $\hat{\beta}^+$, the induced dipole moment is given by $\vec{d} = \hat{\beta}^+ \vec{E}$, where $\vec{E}$ is the external laser field. For the symmetric atomic core, the polarizability is uniform in all directions, the induced dipole moment is parallel to the external field, and the potential due to laser-induced core polarization is given by [20,22]

$$V_{\rm cp} = -\frac{\beta^+ \vec{E}\cdot\vec{r}}{r^3}. \tag{2}$$

When the active electron is close to the atomic core, the form of polarization potential is not valid because of the electron screening. Therefore the polarization potential is cut to zero below r_0, which is estimated from the atomic polarizability ($\approx r_0^3$) [13,20]. It can be seen that the magnitude of the potential from the polarized core is proportional to the strength of the external electric field. In the strong-field regime, it is comparable to or larger than the interaction of the active electron with the permanent dipole moment of the atomic core if which exists.

The effective TDSE for the active electron turns into

$$i\frac{\partial}{\partial t}\psi = \left[-\frac{\nabla^2}{2} + V_n + V_{\rm cp} + V_L\right]\psi. \tag{3}$$

The method of directly propagating Eq. (3) will be named as SAE + CP. Similar to the SAE theory discussed previously, the initial wave function is taken as the Hartree-Fock orbital of the valence electron. Note that, in this theory, we neglect the polarization of the core induced by the Coulombic field of the outer electron as well as the permanent dipole moment.

Different from the theories presented above, the time-dependent Hartree-Fock theory in principle takes all electrons into account based on the mean-field approximation. We limit ourselves to the case of two valence electrons that form a singlet state and keep the other N-2 electrons frozen. Restricting the two electrons occupying the same orbital, and using the effective potential from the other N-2 electrons which forms the closed-shell core, we have the following nonlinear equation:

$$i\frac{\partial}{\partial t}\psi = \left[-\frac{\nabla^2}{2} + V_{N-2} + \langle\psi|\frac{1}{r_{12}}|\psi\rangle + V_L\right]\psi, \tag{4}$$

where $V_{N\text{-}2}$ is the effective potential from the core constituted by the other N-2 electrons, which has asymptotic behavior as $-\frac{2}{r}$. This method will be referred as the time-dependent restricted Hartree (TDRH) method. The repulsive Coulomb potential from the other valence electron is evaluated at each time as

$$\langle\psi|\frac{1}{r_{12}}|\psi\rangle = \int d\vec{r}_2 |\Psi(\vec{r}_2,t)|^2 \frac{1}{|\vec{r}-\vec{r}_2|}, \tag{5}$$

which includes the induced polarization from the interaction of the laser field with the other valence electron. Here we have made a crude assumption that the two valence electrons have the same time-dependent orbital. Note that if the potential in Eq. (5) is evaluated with the initial field-free Hartree-Fock valence orbital we again obtain the TDSE given in Eq. (1).

Now we apply those theories to the ionization of an alkaline-earth-metal atom Ca by a laser field at a wavelength of 1600 nm and intensity of 1×10^{13} W/cm^2. The laser pulse has a duration of 15 fs; $E(t) = f(t)\sin\omega t$, with a Gaussian envelope $f(t)$. The Ca atom has a configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ with two valence electrons outside a closed shell. The Hartree-Fock calculation gives an ionization potential of 0.1955 a.u. The polarizability of Ca is found to be 154 a.u. After obtaining the effective potential from HF calculation using the local-density approximation, we perform the SAE calculation and obtain a similar ionization energy at 0.1947 a.u. The ponderomotive energy U_p is about 3.08 times that of the photon energy, and the Keldysh parameter is close to 1; therefore tunneling ionization dominates.

The equations of motion, Eqs. (1), (3), and (4), are solved, respectively, in a spherical box of 1600 a.u. with 20 partial waves using the pseudospectral grid and split-operator propagation method [23,24]. The photoelectron spectra are obtained by projecting the final wave function to the continuum states:

$$P_E = \sum_{l=1}^{20} |\langle\phi_{El}|\psi(T_f)\rangle|^2, \tag{6}$$

where ϕ_{El} is the energy normalized continuum state of given energy E and angular momentum l. In the SAE calculation, the ionization probability is directly given by $p_i = \int P_E dE$, while in TDRH the ionization probability of the system is given by $P_I = 1-(1-p_i)^2$, where independent particle approximation is applied.

In Fig. 1, we present the photoelectron energy spectra for Ca calculated with the various theories. All calculations capture the main feature of above threshold ionization, that there exist two main peaks located at $2U_p$ and $10U_p$. The $2U_p$ peak corresponds to those electrons that directly escape from the atom after tunneling through the barrier formed by the atomic potential and the dipole interaction with the laser field. The $10U_p$ is the maximum energy that the tunneling electron can gain after being rescattered backward by the atomic core [25]. In the SAE + O calculation, we keep the outer electron wave function orthogonal to the other occupied orbitals, which implies that the core cannot be penetrated. However, the spectra intensity shows only a little increase compared to the SAE calculation. Note that the carrier-envelope phase has profound effects on the ATI spectra for few-cycle laser pulses,

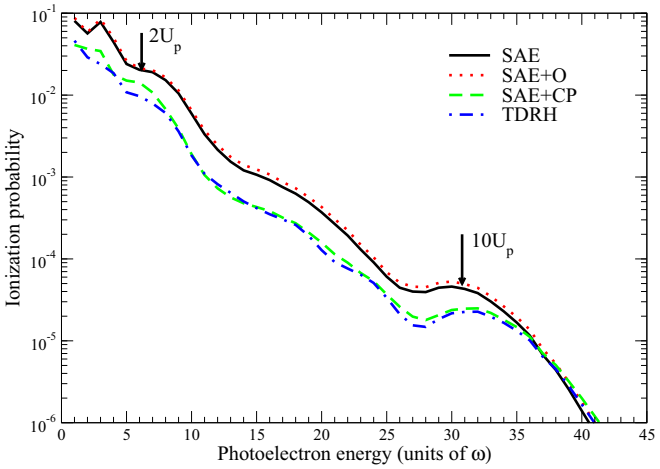

FIG. 1. (Color online) Photoelectron spectra of the Ca atom calculated in various approximations. The arrows indicate the maximum energy of the directly escaped and rescattered electron, with U_p as the ponderomotive energy.

as shown in [26,27]. In order to have a full rescattering, we chose the laser field as given previously.

When the core is polarized by the laser fields, it takes more energy for the electron to move from inside the core to the outer region. However, once it tunnels outside the barrier, the polarization potential repels the electron away, resulting in a slight increase of the cutoff energy, as demonstrated by the comparison of SAE results with the SAE + CP results multiplied by 2 shown in Fig. 1. We see that the core polarization causes the suppression of ionization rates and marginally increases the maximum energy that electrons can gain. The ionization suppression has also been found from time-dependent density-functional theory [28]. The reason for the marginal increase of the cutoff energy lies in the rescattering electron dynamics [25,29]. Based on the classical trajectory analysis, the laser field is close to zero when the electron collides with the atomic core with maximum kinetic energy. The corresponding instantaneous polarization of the atomic core is small, and thus it makes little impact on the cutoff energy of the photoelectron. However, changing the carrier-envelope phase could lead to the enhancement of the polarization effects, since the laser field is not necessary small. Different from ATI, it can be expected that the harmonic spectra can be modified by the core polarization due to different recombination instants and the resulting polarization even for a long pulse, as shown in [12].

Note that we use the available polarizability of the neutral atom found in the database. The polarizability of the Ca^+ is about 20% smaller, which makes a small change to the ionization rate. We also perform a different check by calculating the time-dependent induced dipole moment from propagating the Ca^+ in the same laser field, and then we use it in the simulation of the outer electron dynamics. The results show almost no difference, suggesting the polarization is indeed instantaneous, and therefore the phase lag due to a different time response of the outer electron and the atomic core to the laser field has no effect in the present study. However, this might not be true when resonant excitation is present, which is beyond the scope of the present study. To further justify the consideration of the core polarization, TDRH calculation is performed as well. The resulting spectrum, shown in Fig. 1, is very close to that computed from SAE + CP calculation, indicating that the core polarization cannot be neglected for the laser intensity we considered.

The suppression of the ionization rate due to the core polarization can be understood within the tunneling picture. The potential barrier along the laser polarization direction is given by

$$V(z) = V_n(z) - Ez + V_{\rm cp}, \tag{7}$$

where $V_{\rm cp} = \beta^+ E/z^2$. In the standard theory of tunnel ionization, the core polarization is not taken into account, and the potential barrier takes the form of $V_0(z) = V_n(z) - Ez$. According to the ADK model [11], the tunnel ionization rate when disregarding the core polarization can be estimated by

$$w_0 \approx \exp\left[-2\int_{z0}^{z_1}\sqrt{\kappa^2 + 2V_0(z)}dz\right], \tag{8}$$

where κ is related to the ionization potential I_p by $I_p = \kappa^/2$ and z_0 and z_1 are the inner and outer turning points, respectively. When the core polarization is taken into account, the correction of the ionization rate can be approximated by [21,30–32]

$$R_c = w/w_0 \approx \exp\left[-2\int_{z0}^{z_1}\frac{V_{\rm cp}}{\kappa}dz\right]. \tag{9}$$

The potential barrier of the Ca atom in the laser field is plotted in Fig. 2. The polarization potential is cut to zero below $r_0 = 5$ a.u., which is estimated from the atomic polarizability ($\approx r_0^3$) and is consistent with the size of the Ca atom. Taking $z_0 = r_0$ as the inner turning point. The outer turning point is determined by I_p/E. At the laser intensity of 10^{13} W/cm^2, the outer turning point is 12 a.u. from the nucleus. According to Eq. (9), we found the correction factor is 0.386, while the numerical simulation shows that total photoelectron spectra intensity in SAE + CP calculation is about 52% of that

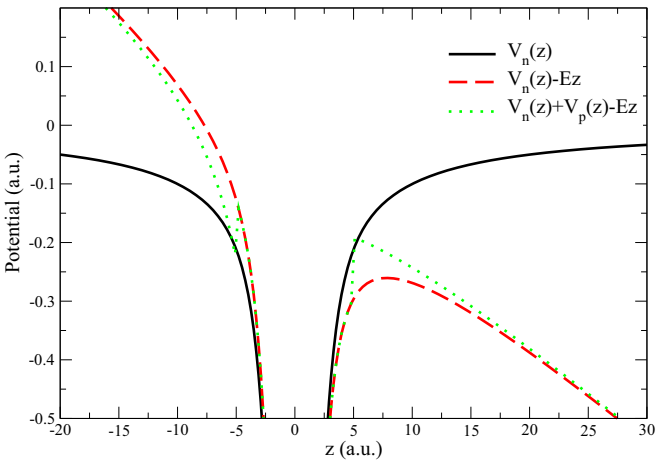

FIG. 2. (Color online) Illustration of the effective potentials for the laser-free (solid line), laser field included (dashed lines), and core-polarization considered (dotted lines) cases.

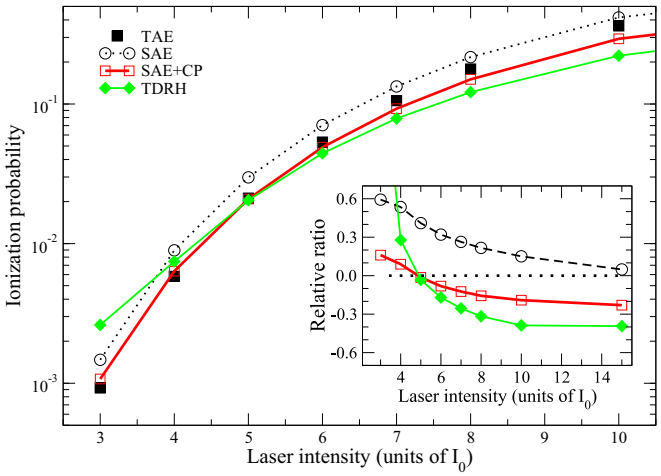

FIG. 3. (Color online) Ionization probability of a model hydrogen molecule calculated from exact two-electron calculation (TAE, filled squares), one-electron TDSE using the effective potential (SAE, dotted lines with open circles), modified SAE calculation by considering the core polarization (SAE + CP, solid line with open squares), and TDRH (solid line with diamonds). Inset: Relative ratios comparing to the TAE calculation from the other three theories.

obtained from SAE calculation, in good agreement with the analytical correction.

In order to further check the validity of our theory, we perform exact two-active-electron (TAE) calculation for a model hydrogen molecule with both electrons moving in one dimension. The soft-core Coulomb potential has the form of $|V(x)| = \frac{1}{\sqrt{\epsilon+x^2}}$ with $\epsilon_N = 0.7$ and $\epsilon_e = 1.2375$ for the electron-nucleus and electron-electron interaction [33]. The energies of the neutral and the cation are found to be -2.2085 and -1.4103 a.u., respectively. The laser pulse has the same shape as previously but with a duration of two cycles with a wavelength of 1200 nm. Varying the carrier-envelope phase (not shown) does not change the analysis below.

The calculated ionization probability from the theories above is shown in Fig. 3. For laser intensities less than $5I_0$ ($I_0 = 10^{14}$ W/cm^2), the ionization probability obtained from TDRH calculation is higher than that from the exact TAE calculation. The failure of TDRH at low laser intensity might be caused by two facts. First, the HF ground-state energy differs from the exact two-electron energy by the correlation energy (0.025 a.u.). When the ionization rate is less than the correlation energy, it has been shown that the correlation of the two electrons has profound effects [34]. The threshold laser intensity at which the correlation cannot be neglected might be estimated from that of the dipole interaction energy at the classical radius, which is on the order of the correlation energy. In the presently studied system, the averaged distance is $\langle r \rangle \approx 1.2$ a.u., such that the threshold laser intensity is roughly $0.2I_0$. For laser intensities much higher, the difference of the ionization energy and the initial wave function in the restricted Hartree-Fock theory from the exact calculation can be neglected due to the strong interaction with the laser field. Second, however, the two electrons are treated as equivalent and independent particles in TDRH, which is not appropriate during ionization, when the two electrons in fact can be distinguished as the inner and the outer electron. After the removal of the first electron, it will be very difficult to further ionize the ionic core. Therefore the total ionization probability defined by $P_I = 1 - (1 - p_i)^2$ is not proper anymore and needs to be replaced by p_i, neglecting the ionization of the second electron.

For higher laser intensity, the correlation plays less role in the ionization process. When the ionization rate is much larger than the correlation energy, the difference of the inner and outer electron orbital is not the main cause any more. At the laser intensity of $5I_0$, the TDRH gives the same ionization probability to the TAE calculation. However, as laser intensity keeps increasing, the rates from TDRH become smaller than the TAE results. The reason lies in the assumption that the two electrons are equivalent and are occupying the same time-dependent orbital. When the ionization probability is large, less norm from the orbital is bounded. The nuclear charge is less shielded and the potentials on the electrons become unphysical due to this self-interaction in the TDRH theory, such that further ionizing is incorrectly suppressed. Therefore TDRH theory fails in both low and high laser intensities.

As shown in Fig. 3, the rates from the SAE calculation are larger than the TAE results for the laser intensity considered. When introducing the core-polarization potential, we see that the deviation is reduced to less than 20% for laser intensity $<8I_0$. Noted for a laser intensity above $8I_0$, the ionization mechanism switches from tunnel ionization to over the barrier ionization (OTB). In the OTB regime, the removal of one electron is so rapid, there is no time for the two electrons exchanging energy, such that SAE theory works better, as shown in the inset of Fig. 3.

In conclusion, we have shown that it is necessary to consider core polarization in strong-field ionization of multielectron atoms. By incorporating the polarization potential into theory the tunneling ionization theory can be improved within the framework of SAE. Comparing with exact two-electron model calculations and time-dependent restricted Hartree-Fock calculation, we show that single-active-electron approximation overestimates the ionization rate due to the additional barrier from the dipole potential. The maximum photoelectron energy is found to be increased slightly by the core polarization.

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[1] M. Protopapas, C. H. Keitel, and P. L. Knight, Rep. Prog. Phys. **60**, 389 (1997).

[2] T. Brabec and F. Krausz, Rev. Mod. Phys. **72**, 545 (2000).

[3] O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villenenve, P. Corkum, and Y. Ivanov, Nature (London) **460**, 972 (2009).

[4] Y. Mairesse *et al.*, Phys. Rev. Lett. **104**, 213601 (2010).

[5] M. Spanner, J. Mikosch, A. Gijsbertsen, A. E. Boguslavskiy, and A. Stolow, New J. Phys. **13**, 093010 (2011).
[6] A. D. Shiner *et al*., Nat. Phys. **7**, 464 (2011).
[7] A. E. Boguslavskiy *et al*., Science **335**, 1336 (2012).
[8] B. Bergues *et al*., Nat. Comm. **3**, 813 (2012).
[9] S. Pabst and R. Santra, Phys. Rev. Lett. **111**, 233005 (2013).
[10] D. N. Fittinghoff, P. R. Bolton, B. Chang, and K. C. Kulander, Phys. Rev. Lett. **69**, 2642 (1992).
[11] M. V. Ammosov, N. B. Delone, and V. P. Krainov, Zh. Eksp. Teor. Fiz. **91**, 2008 (1986) [Sov. Phys. JETP **64**, 1191 (1986)].
[12] G. Jordan and A. Scrinzi, New J. Phys. **10**, 025035 (2008).
[13] B. Zhang, J. Yuan, and Z. Zhao, Phys. Rev. Lett. **111**, 163001 (2013).
[14] J. Wu, L. P. H. Schmidt, M. Kunitski, M. Meckel, S. Voss, H. Sann, H. Kim, T. Jahnke, A. Czasch, and R. Dörner, Phys. Rev. Lett. **108**, 183001 (2012).
[15] S. Patchkovskii, Z. Zhao, T. Brabec, and D. M. Villeneuve, Phys. Rev. Lett. **97**, 123003 (2006).
[16] R. Santra and A. Gordon, Phys. Rev. Lett. **96**, 073906 (2006).
[17] Z. Zhao, J. Yuan, and T. Brabec, Phys. Rev. A **76**, 031404 (2007).
[18] Z. Zhao, J. Wu, and J. Yuan, J. Phys. B **41**, 155601 (2008).
[19] S. Pabst, L. Greenman, D. A. Mazziotti, and R. Santra, Phys. Rev. A **85**, 023411 (2012).
[20] I. B. Bersuker, Opt. Spectrosc. **9**, 363 (1960).
[21] T. Brabec, M. Côté, P. Boulanger, and L. Ramunno, Phys. Rev. Lett. **95**, 073001 (2005).
[22] V. L. Sukhorukov, I. D. Petrov, M. Schäfer, F. Merkt, M.-W. Ruf, and H. Hotop, J. Phys. B **45**, 092001 (2012).
[23] X. M. Tong and S. I. Chu, Chem. Phys. **217**, 119 (1997).
[24] X. Chu and S.-I. Chu, Phys. Rev. A **63**, 013414 (2000).
[25] G. G. Paulus, W. Becker, W. Nicklich, and H. Walther, J. Phys. B **27**, L703 (1994).
[26] F. Lindner, G. G. Paulus, H. Walther, A. Baltuška, E. Goulielmakis, M. Lezius, and F. Krausz, Phys. Rev. Lett. **92**, 113001 (2004).
[27] C. Altucci, V. Tosa, R. Velotta, and C. H. Nam, Phys. Rev. A **70**, 065402 (2004).
[28] X. Chu, Phys. Rev. A **82**, 023407 (2010).
[29] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[30] Z. X. Zhao and T. Brabec, J. Phys. B **39**, L345 (2006).
[31] Z. Zhao and T. Brabec, J. Modern. Optics **54**, 981 (2007).
[32] B. Zhang and Z. Zhao, Phys. Rev. A **82**, 035401 (2010).
[33] J. Zhao and Z.-X. Zhao, Chin. Phys. Lett. **27**, 063301 (2010).
[34] A. J. Tolley, J. Phys. B **32**, 3449 (1999).