Time-dependent effective potential for the ultrafast correlated electron dynamics of molecules in intense laser fields: Application to anisotropic ionization of CO

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Abstract. By using the multiconfiguration time-dependent (TD) Hartree-Fock (MCTDHF) method, we simulated the multielectron dynamics of a CO molecule irradiated by near-IR two-cycle pulses with different carrier envelope phases. The ionization rate calculated is higher when the laser electric field $\mathbf{\epsilon}(t)$ points from the nucleus C to O than the opposite case, in agreement with the results of two-color ionization experiments. The mechanism of anisotropic tunnel ionization in CO was examined by converting the obtained multielectron dynamics to the representation in terms of TD natural orbitals $\{\phi_j(t)\}$. Within the framework of MCTDHF, we derived the unitary equations of motion for $\{\phi_j(t)\}$. From the derived equations, we defined the TD effective potentials $v_{\text{eff}}^j(t)$ that govern the dynamics of $\{\phi_j(t)\}$. In $v_{\text{eff}}^5(t)$ for the $5\sigma$ HOMO, a narrow hump that originates from two-body electron-electron repulsion is formed on the top of the field-induced distorted barrier near the nucleus C when $\mathbf{\epsilon}(t)$ points from C to O, which is responsible for the directional anisotropy of tunnel ionization. For $4\sigma$ HOMO-2, a high barrier to suppress ionization is formed in $v_{\text{eff}}^4(t)$ when $\mathbf{\epsilon}(t)$ points from C to O, in correlation with the electron-electron interaction with a $5\sigma$ electron on route to ionization. For the opposite phase, $v_{\text{eff}}^4(t)$ becomes barrierless, which enhances high-harmonic generation through $\phi_{4\sigma}(t)$.

1. Introduction

Electronic motion induced by external fields is one of the fundamental processes that trigger various physical or chemical phenomena in a wide range of timescale. Intense, ultrashort laser pulses are utilized to induce/manipulate large amplitude electronic motions such as tunnel ionization and subsequent high-order harmonic generation (HHG). Ti:Sapphire near-infrared (IR) laser systems can now provide ultrafast few cycle pulses of focused intensity greater than $10^{14}$ W cm$^{-2}$. A number of experimental and theoretical researches have been devoted to profoundly understanding the intense-field induced electron dynamics in atoms [1], molecules [2], solids [3], and biological systems [4]. The electronic response of
an atom or a molecule can be categorized into adiabatic and nonadiabatic regimes with respect to
temporal change in the applied laser electric field [5]. Accordingly, ionization induced by intense fields
is usually characterized by the Keldysh parameter $\gamma = \left( \omega / f_{\text{max}} \right)^{1/2}$ [6] (in atomic units), where $\omega$
is the angular frequency of the applied laser field, $f_{\text{max}}$ is the maximum of the electric field envelope,
and $I_p$ is the ionization potential. The ionization mechanism is classified as adiabatic “quasistatic”
tunnel ionization or multiphoton ionization according as $\gamma < 1$ or $\gamma > 1$.

Diverse theoretical approaches have been developed to investigate the field-induced ionization of
atoms and molecules and to quantify the ionization rate or probability. When the light intensity of the
laser is beyond a certain limit, conventional perturbation theory is insufficient for the description of
ionization. Epoch-making in the development of nonperturbative approaches is the one proposed by
Keldysh [6], in which intense-field ionization is formulated as an electronic transition from the ground
state of an atom to Volkov states (quantum states of an electron freed in an oscillating laser electric
field). In this approach, the ground state is not perturbed by the applied field and the detailed atomic
energy structure is not taken into account in determining the ionization probability. Another defect in
Keldysh’s approach was its neglect of the Coulomb interaction of the electron released in the laser field
with the parent ion. To remedy the defect, Perelomov et al. developed a method, called the Perelomov-
Popov-Terent’ev (PPT) approach [7], where the long-range Coulomb interaction is included as the first-
order correction in the quasi-classical action of the electron. These types of approaches have been
generalized by $S$-matrix theory for obtaining the transition probability of a quantum process. An element
of the $S$-matrix is in general equivalent to the transition amplitude obtained by the standard prescription
of projection of the total wave function of the system onto the final state. Since the early days of
nonperturbative ionization of atoms or molecules in intense laser fields, several versions of the $S$-matrix
approach have been introduced which are together known as the Keldysh-Faisal-Reiss (KFR) theory or
Strong Field Approximation (SFA) [8].

As the field intensity becomes higher and its optical period $2\pi/\omega$ becomes longer (i.e. $\gamma \to 0$), an
electron penetrates (or goes beyond) the distorted “quasistatic” barrier for ionization before the sign of
the laser electric field changes. In this case, quasiadibatic tunneling theory, namely the Ammosov–Delone–
Krainov (ADK) model [9], is most commonly used. The ADK model is the quasistatic limit ($\gamma \to 0$) of
the PPT approach. Tong et al. extended the tunnelling ionization ADK model to molecules by
considering the symmetry property and the asymptotic behaviour of the molecular electronic wave
function (named MO-ADK theory) [10]. Adiabatic theory of intense field ionization for finite-range
potentials has now been completed by Tolstikhin and Morishita [11].

The above approaches are developed within the framework of the single active electron (SAE)
approximation where only the atomic or molecular orbital under consideration is allowed to interact
with the applied field and the other orbitals are kept fixed at the shapes obtained for the ground-state
calculation. There are ways of including the effects of field-induced dynamic polarization on other
orbitals. It is possible to estimate dynamic polarization effects by constructing an “effective potential”
semiempirically [12] or by systematically expanding the $S$-matrix of a multielectron system to different
ionization processes. In fact, only the leading term associated with an ionization process is evaluated in
a systematic series expansion of the $S$-matrix [13].

Time-dependent processes can be explicitly described beyond the SAE approximation by numerically
solving the time-dependent (TD) Schrödinger equation of a multielectron system. Among such methods
are the time-dependent Hartree-Fock (TDHF) method and the multiconfiguration time-dependent
Hartree-Fock (MCTDHF) method [14-16]. In the TDHF, the multielectron wave function, as a function
of time $t$, is approximated by a single Slater determinant and the time evolution of orbitals is formulated
under the mean field approximation. This basic approach takes into account the electron-electron
interaction but not correlated electron motion. On the other hand, the total wave function $\Phi(t)$ in the
MCTDHF method is expanded in terms of many Slater determinants corresponding to various electron
configurations, by which the correlated electron motion can be described beyond the mean field
approximation. In this method, both the orbitals and the coefficients of Slater determinants are optimized
in compliance with the Dirac-Frenkel variational principle. For the simulation of the electron dynamics
of large systems, real-time real-space time-dependent density functional theory (TDDFT) is utilized [17, 18], where the quantification of electron correlation depends on the specific property of the exchange-correlation functional employed. The variations of the electron density and correlation energy in time could be analyzed, but the description of correlated electron motion by TDDFT is incomplete because only the total electron density is determined.

More reliable and detailed information can be obtained as the level of the theory employed is higher. Accordingly, the results obtained becomes complicated to analyze. For example, the TD orbitals in the MCTDHF method reflect the effects of electron-electron (two-body) interaction or electron correlation, but it is not straightforward to extract those effects from the time evolution of orbitals. The temporal change in orbitals cannot be linearly decomposed into those due to the one-body interaction (interaction of an electron with nuclei and external fields) and due to the two-body interaction. In previous papers, we have proposed a way of converting the multielectron wave function $\Phi(t)$ obtained by MCTDHF to a single orbital picture [19, 20]. For this purpose, using the TD natural spin-orbitals $\{V_i(t)\}$ [21], which diagonalize the first-order reduced density matrix of electrons constructed from $\Phi(t)$, we derived the corresponding effective potentials $v_i^{\text{eff}}(r,t)$ for $V_i(t)$ as a function of the spatial coordinates of an electron, $r$ [21]. The TD effective potential $v_i^{\text{eff}}(t)$ for $V_i(t)$ can be decomposed into $v_i^{\text{eff}}(t) = v_i(t) + v_{ij}(t)$, where $v_i(t)$ is the one-body interaction and $v_{ij}(t)$ arises from the two-body interaction. Modern laser technology enables us to tailor the form and phase of a laser field for manipulation of the dynamics of molecules on a femtosecond or even attosecond time scale. The two-color field can also be used to answer the fundamental question, i.e., to investigate the anisotropy in electron dynamics, for example, unidirectional ionization of heteronuclear diatomics such as CO. The emission direction of C$^+$ or O$^+$ from CO molecules in two-color ionization experiments indicates that ionization is enhanced when the electric field points from the nucleus C to the nucleus O [22]. This type of experiment can now be combined with the field-free molecular orientation technique applied to CO [23]. By using MCTDHF, we calculated the effective potentials of natural orbitals for CO in an intense near-IR field to investigate the mechanism of anisotropic ionization of CO [20]. The results indicated that when the laser electric field points from C to O, tunnel ionization from the C atom side is enhanced and that a hump structure originating from two-body electron-electron repulsion is then formed near the C nucleus on the top of the field-induced distorted barrier of the effective potential for the 5$\sigma$ highest occupied molecular orbital (HOMO). We attributed this hump formation to the directional anisotropy of tunnel ionization.

Effective potential is a versatile tool to analyze intrinsic multielectron nature in electronic dynamics. Correlation in dynamics between natural orbitals can be revealed by examining the temporal change in the corresponding effective potential, though the effective potential is a one-body quantity. In the present paper, we show that the dynamics of the HHG of the 4$\sigma$ (HOMO-2) orbital in CO is correlated with the 5$\sigma$ ionization dynamics: When the laser electric field points from O to C, HHG from 4$\sigma$ is enhanced while the ionization from 5$\sigma$ is reduced. In the following, we present a brief summary of the effective potential approach and the numerical results for the effective potentials of the 4$\sigma$ and 5$\sigma$ orbitals.

2. Effective potential for natural orbitals in the MCTDHF framework
The equation we solve is the TD Schrödinger equation for an $N$-electron system in intense laser fields

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = \hat{H}(t)\Phi(t),$$

(1)

where $\Phi(t)$ is the TD wave function and $\hat{H}(t)$ is the electronic Hamiltonian including the interaction with the applied field $\mathcal{E}(t)$. We solve (1) by using the MCTDHF method where $\Phi(t)$ is expanded in terms of electron configurations $\{\Phi_i(t)\}$ (Slater determinants or configuration state functions) [15,16]:

$$\Phi(t) = \sum_{i=1}^{M} C_i(t)\Phi_i(t),$$

(2)

where $M$ is the number of $\Phi_i(t)$ and $C_i(t)$ are the configuration interaction (CI) coefficients for $\Phi_i(t)$. Each electron configuration is constructed of $N$ spin orbitals (SOs) $\{\psi_k(t)\}$. A SO $\psi_k(t)$ is the product of a one-electron spatial orbital and a one-electron spin function; $\psi_k(t) = \langle x | \hat{k}(t) \rangle$, where $x = (r, \mu)$ denotes the spatial coordinates $r$ and the spin coordinate $\mu$ of an electron. The number of SOs used, $N_0$, is...
is larger than \( N \) (\( N_o = N \) in TDHF). The working equations of motion (EOMs) of \( \{ \psi_j(t) \} \) and \( \{ C_i(t) \} \) have been derived by applying the Dirac-Frenkel TD variational principle to possible variations of \( \Phi(t) \).

The resulting EOMs for \( \psi_k(t) \), from which the effective potentials \( v_j(r,t) \) are derived, are expressed as

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} |\psi_k(t)\rangle = \hat{h}(t)|\psi_k(t)\rangle + \sum_{j} A^{\ast}_j(t)_{kj} |\hat{V}_j(t) - A_j(t)\rangle |\psi_l(t)\rangle , \tag{3}
\]

where \( \hat{h}(t) \) is the one-body Hamiltonian including the electric dipole interaction \( r \cdot \xi(t) \) with laser electric fields \( \xi(t) \), \( \hat{V}_j(t) \) is the orbital coupling between \( i \) and \( j \) mediated by other orbitals (depending on \( \{ C_i(t) \} \) ), \( A_{\ast} \) is the \((k,m)\) matrix element of the 1st order reduced density matrix (1RDM), where \( \hat{a}_\ast \) and \( \hat{a}_\dagger \) denote, respectively, the annihilation and creation operators for an electron in \( \psi_j(t) \). \( A_j(t) \) is the following Lagrange multiplier

\[
A_j(t) = \sum_{m} \langle \psi_j(t) \rangle \left[ \hat{V}_m(t) + A_m(t) \hat{g}(t) \right] |\psi_k(t)\rangle , \tag{4}
\]

where \( \hat{g}(t) \) is to be determined so that the orthonormalization condition \( \langle \psi_j(t) \rangle |\psi_k(t)\rangle = \delta_{jk} \) is maintained.

Equation (3) can be rewritten as

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} |\psi_k(t)\rangle = \left[ \hat{h}(t) - \hat{g}(t) \right] |\psi_k(t)\rangle + \hat{Q}(t) \left[ \hat{g}(t) |\psi_k(t)\rangle + \sum_{j} A^{\ast}_j(t)_{kj} \hat{V}_j(t) |\psi_k(t)\rangle \right] , \tag{5}
\]

where \( \hat{Q}(t) = 1 - \sum_{m} |s(t)\rangle \langle s(t)| \) is the projector to the complement to the current orbital space. Since the time propagation is unitary if \( \hat{g}(t) \) is a Hermitian operator like \( \hat{g}(t) = \sum_{m} |s(t)\rangle \langle s(t)| \), to ensure the numerical stability in solving the EOMs for \( \{ \psi_j(t) \} \) and \( \{ C_i(t) \} \), we choose \( \hat{g}(t) = \hat{h}(t) \); then, \( \langle \psi_j(t) \rangle \hat{c}_\ast \psi_j(t) \langle \hat{g}(t) |\psi_j(t)\rangle = 0 \) for \( i = j \) and \( i \neq j \), i.e., the orthonormalization condition holds in the time-propagation of \( |\psi_j(t)\rangle \). Equation (5) are coupled with the EOMs for \( \{ C_i(t) \} \).

The 1RDM at \( t \) is calculated from \( \{ \psi_j(t) \} \) and \( \{ C_i(t) \} \), which is given by

\[
\rho(x,x',t) = \sum_{k} |A_{\ast} \rangle_{ij} \langle \phi_i(x,t) \psi_j(x',t) \rangle . \tag{7}
\]

For \( \hat{g}(t) = \hat{h}(t) \), \( A_j(t) \neq 0 \). The rhs in (7) can be diagonalized by a unitary transformation from \( \{ \psi_j(t) \} \) to \( \{ \phi_j(t) \} \)

\[
\rho(x,x',t) = \sum_{\phi} \sum_{k} |A_{\ast} \rangle_{ij} \langle \phi_i(x,t) \phi_j(x',t) \rangle . \tag{8}
\]

In this case, \( A_j(t) = 0 \) for \( i \neq j \) and the orbitals that satisfy (8) are called natural orbitals [21]. The diagonal elements for natural orbitals, \( n_j(t) = A_j(t) \), is the occupation number of \( \phi_j(t) \). The expectation value \( \langle d(t) \rangle \) of any one-particle operator \( d \), such as the field-induced dipole moment, is expressed as \( \langle d(t) \rangle = \sum_{j} n_j(t) \langle d(t) \rangle \phi_j(t) \phi_j(t) \rangle \). We shown for LiH that the dynamics of \( \phi_j(t) \) is correlated with the “time-dependent chemical potential” of \( \phi_j(t) \) [19]. The natural orbital representation provides a bridge connecting the multielectron dynamics to a single electron picture.

The matrix elements of the 1RDM obey in general the following equation [20]:

\[
d A_{mn}(t)/dt = -i[\hat{W}_{mn}(t) - W_{mn}(t) + g_{mn}(t)(n_m(t) - n_n(t))] . \tag{9}
\]

Here, \( W_{mn}(t) \) is defined as \( W_{mn}(t) = \left[ W_{mn}(t) \right]_{ij} = \frac{dx \psi_i(x) \psi_j(x)}{[\phi_i(x), \phi_j(x)]} [n_j(t) - n_i(t)] \psi_i(x) \psi_j(x) \). Suppose that \( \psi_j(t_0) = \phi_j(t_0) \) at \( t = t_0 \). To satisfy \( A_j(t) = 0 \) for \( i \neq j \), we set \( g_{mn}(t) \) in (9) as

\[
g_{mn}(t) = \left[ W_{mn}(t) - W_{nm}(t) \right] / [n_n(t) - n_i(t)] . \tag{11}
\]

Substitution of (11) into (5) yields the EOMs for the natural orbitals

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} |\phi_j(t)\rangle = \left[ \hat{T} + v_j(r,t) \right] |\phi_j(t)\rangle + \sum_j |U_j(t)| \langle \phi_j(t) \rangle , \tag{12}
\]
\[ \hat{T} \] is the kinetic energy operator of an electron, the one body interaction term \( V_1(r,t) \) consists of the electric dipole interaction \( r \cdot \mathbf{g}(t) \) and the Coulomb attractive interaction between an electron and the nuclei, and the coupling between \( \phi_k(t) \) and \( \tilde{U}_k(t) \), is given by
\[
\tilde{U}_k(t) = (1 - \delta_{ij}) \frac{W_{ij}(t) - W'_{ij}(t)}{n_i(t) - n_j(t)} + Q(t) \frac{\tilde{V}_{ij}(t)}{n_i(t)}.
\] (13)

In the present treatment, the spatial part of the natural SO is independent of its spin state. Equation (12) can then be formally rewritten as
\[
i\hbar \frac{\partial \phi_k(r,t)}{\partial t} = \left[ \hat{T} + v^\text{eff}_k(r,t) \right] \phi_k(r,t),
\] (14)
where the one-body quantity \( v^\text{eff}_k(r,t) \) is considered the effective potential that determines the dynamics of \( \phi_k(t) \) under multielectron interaction
\[
v^\text{eff}_k(r,t) = v_i(r,t) + \sum_{j} \langle r | \tilde{U}_k(t) | \phi_j(t) \rangle \langle \phi_j(t) | \phi_k(r,t) \rangle = v_i(r,t) + v_{ij}(r,t).
\] (15)

Multielectron dynamics can be analyzed by examining separately the temporal change in the one-body term \( v_i(r,t) \) and that in the two-body term \( v_{ij}(r,t) \). We designate the expectation value of \( \hat{T} + v^\text{eff}_k(r,t) \) over \( \phi_k(t) \) as the real-valued effective energy \( \mathcal{E}_k(t) \). In practice, we obtain the “instantaneous” natural orbitals \( \{ \phi_j(t) \} \) at time \( t \) from \( \Phi(t) \) that are the numerical solutions of (5) for \( \hat{g}(t) = \hbar(t) \). \( v^\text{eff}_k(r,t) \) can be plotted as function of \( r \) by inserting \( \{ \phi_j(t) \} \) and the corresponding \( \{ C_{ji} \} \) (different from those for \( \hat{g}(t) = \hbar(t) \)) into (15).

3. Results and discussion

We briefly introduce the results [20] related to the ionization and HHG dynamics of a CO molecule interacting with an intense near-IR two-cycle pulse and present the TD effective potentials for the 4\( \sigma \) and 5\( \sigma \) natural orbitals in the dynamics. In the numerical simulation, we considered 10 spatial orbitals constructed mainly from 1s, 2s, 2p orbitals of C and O atoms, that is, 1\( \sigma \), 2\( \sigma \), 3\( \sigma \), 4\( \sigma \), 2\( \times \)1\( \pi \), 5\( \sigma \), 2\( \times \)2\( \pi \) (LUMO) and 6\( \sigma \). We chose the high lying six orbitals of 2\( \times \)1\( \pi \), 5\( \sigma \), 2\( \times \)2\( \pi \) and 6\( \sigma \) as the active orbitals that construct the complete configuration space to accommodate 14–8=6 electrons. The lower lying SOs are treated to be occupied by one electron but the shapes of orbitals vary according to the EOMs for the SOs. This calculation scheme is referred to as the time-dependent complete active space self-consistent field (TD-CASSCF) method, developed in [16]. The cylindrical coordinates \( z \) and \( \rho \) are used for numerical grid point representation of the spatial orbitals; \( z \) is chosen parallel to the molecular axis. The nuclei C and O are placed on the \( z \) axis (\( \rho = 0 \)): \( z = -1.066 \, a_0 \) for C and \( z = 1.066 \, a_0 \) for O, where \( a_0 \) is the Bohr radius (the difference is equal to the equilibrium internuclear distance \( R_e = 2.132 \, a_0 \)).

The polarization direction of the applied electric field \( \mathbf{g}(t) \) was assumed to be parallel to the C-O axis. The frequency of \( \mathcal{E}(t) \) is \( \hbar \omega = 0.06 \, E_{\text{th}} = 1.64 \, \text{eV} \) (wavelength \( \lambda = 760 \, \text{nm} \), optical period \( T_o = 2\pi / \omega = 2.53 \, \text{fs} \)), where \( E_{\text{th}} \) is the Hartree. The electric field \( \mathcal{E}(t) \) is assumed to have a form
\[
\mathcal{E}(t) = f(t) \cos(\alpha t - \varphi),
\] (16)
where \( \varphi \) is the carrier-envelope phase (CEP) and the envelope function \( f(t) \) takes the form of \( f(t) = f_{\text{max}} \sin^2(\pi t / 2T) \) so that \( f(t) \) attains its maximum value of \( f_{\text{max}} = 0.06 \, E_{\text{th}} / (e a_0) = 3.1 \times 10^{10} \, \text{V/m} \) (the corresponding light intensity \( I_{\text{max}} = 1.3 \times 10^{14} \, \text{W/cm}^2 \)) at \( t = T_c \) and then returns to zero at \( t = 2T_c \) (two-cycle pulse). The electric field \( \mathcal{E}(t) \) for \( \varphi = 0 \) is shown in figure 1. The sign of the field is reversed when \( \varphi = 0.5 \pi \). The conditions of the numerical simulation such as grid intervals to describe MOs are given in [20].

3.1. Ionization of CO

The Keldysh parameter \( \gamma \) is \( \sim 1.0 \) in the present condition of the applied pulse. The simulated ionization processes are thus categorized as tunnel ionization. According to the results of the TD-CASSCF numerical simulation [20], ionization exclusively occurs from the 5\( \sigma \) HOMO natural orbital when \( \mathcal{E}(t) > 0 \), i.e., the laser electric field points from the nucleus C to O (for instance, around \( t = t_1 \) in figure 1). The electric field exerts a force on electrons toward the side of \( z < 0 \) (from O to C) when \( \mathcal{E}(t) > 0 \). We have also confirmed that ionization from 5\( \sigma \) is significantly reduced when \( \mathcal{E}(t) < 0 \). In the present
condition, the calculated ionization probability around the second peak of \( \mathcal{E}(t) \) (at \( t = t_1 \)) is five times smaller for \( \varphi = 0.5\pi \) than for \( \varphi = -0.5\pi \). The ionization components from \( 4\sigma \) and \( 1\pi \) are orders of magnitude less than that of \( 5\sigma \). This is in accord with previous experimental and theoretical works, where the ionization rate takes the maximum when \( \mathcal{E}(t) > 0 \) and takes the minimum when \( \mathcal{E}(t) < 0 \). This is attributed to the fact that the \( 5\sigma \) orbital has a large lobe protruding from the C atom. The total ionization probabilities for the two-cycle pulses of \( \varphi = \pm 0.5\pi \) obtained by the TDHF method are about 20 times smaller than those obtained by the TD-CASSCF.

![Figure 1. Electric field profile \( \mathcal{E}(t) \) of the two-cycle pulse of (16) for CEP \( \varphi = -0.5\pi \) and the corresponding induced dipole moment \( d_{\sigma\sigma}(t) \) of the \( 5\sigma \) natural orbital: \( \omega = 0.06 \frac{E_{\text{in}}}{h} (\lambda = 760 \text{ nm}) \), maximum field strength \( \mathcal{E}_{\text{max}} = 0.052 \frac{E_{\text{in}}}{(e\omega_0)} = 2.7 \times 10^{10} \text{ V/m at } t \approx t_1 \).](image1.png)

![Figure 2. High-harmonic spectra \( S(\omega_{hh}) \) of the \( 4\sigma \) (broken lines) and \( 5\sigma \) (solid lines) paths of CO for the two-cycle pulses of (a) \( \varphi = -0.5\pi \) and (b) \( \varphi = 0.5\pi \). The polarization direction is parallel to the C-O axis. * denotes the highest peak in each path.](image2.png)

### 3.2. HHG

HHG spectra \( S(\omega_{hh}) \) are also affected by anisotropic ionization, where \( \omega_{hh} \) is the frequency of HHG. The HHG spectrum of a single molecule can be calculated from the Fourier transform of the dipole acceleration \( \mathbf{d}(t) \) (See \( d_{\sigma\sigma}(t) \) in figure 1). \( S(\omega_{hh}) \) of CO for two-cycle pulses of (16) are shown in figure 2. We decompose the HHG spectrum into different paths associated with respective natural orbital (i.e., \( \mathbf{d}(t) \approx \sum_{n=1}^{\infty} n_i(t) \mathbf{d}_i(t) \)). As shown in figure 2(a) for \( \varphi = -0.5\pi \), the HHG generated by \( \phi_{\sigma\sigma}(t) \), denoted as the \( 5\sigma \) path, is much larger than those of the other paths, especially in the range of \( \omega_{hh}/\omega \leq 9 \) (The HHG cutoff energy for \( 5\sigma \) is \( \approx 18h\omega \)). This is due to the recombination of the ionization component from \( 5\sigma \) born at \( t = t_1 \approx 2 \text{ fs} \) (around the second peak of \( \mathcal{E}(t) \)), which demonstrates that ionization leading to HHG mainly proceeds from \( 5\sigma \) when \( \mathcal{E}(t) > 0 \). The ionization component from \( 5\sigma \) born at the third peak of \( \mathcal{E}(t) \) \(( < 0 \text{ at } t = t_2 \approx 3 \text{ fs}) \) is relatively small and the fourth peak is much weaker (confirmed by wavelet analysis). Only the ionization component born at \( t \approx t_1 \) contributes to the HHG.

The results for \( \varphi = 0.5\pi \) are shown in figure 2(b). The HHG of the \( 5\sigma \) path for \( \varphi = 0.5\pi \), which originates from the electron freed at \( \mathcal{E}(t_2) > 0 \), is weaker than for \( \varphi = -0.5\pi \). This is because the fourth peak of \( \mathcal{E}(t) \) is weaker than the third peak at \( t \approx t_2 \) (for \( \varphi = -0.5\pi \), \( \mathcal{E}(t_1) \approx \mathcal{E}(t_2) \)). The HHG of the \( 5\sigma \) path is generated in either case by a \( 5\sigma \) electron freed when \( \mathcal{E}(t) > 0 \). The opposite trend is observed for the \( 4\sigma \) path in figure 2. For the \( 4\sigma \) path, the 5th order peak for \( \varphi = -0.5\pi \) originates from ionization at \( t \approx t_2 \) and the 8th order peak for \( \varphi = 0.5\pi \) originates from ionization at \( t \approx t_1 \). Both are due to the ionization component of \( 4\sigma \) generated when \( \mathcal{E}(t) < 0 \). For \( \varphi = 0.5\pi \), the 8th order peak of the \( 4\sigma \) path is a prominent peak, which is much higher than the 8th order peak of the \( 5\sigma \) path.

### 3.3. Effective potential

We here investigate the mechanism of anisotropic near-IR induced ionization of CO by analysing multielectron (correlated) dynamics in terms of the TD effective potentials of natural orbitals defined by (15). The intrinsic multielectron nature in ionization of each natural orbital can be revealed by examining the temporal change in the corresponding effective potential, i.e., by resorting to the language of a single electron picture. Plotted in figure 3 are effective potentials \( \phi_{5\sigma}(t) = \mathbf{v}_1(t) + \mathbf{v}_{2,5\sigma}(t) \) of the
5σ at t₁=2 fs, where ρ is fixed at 0.755 a₀. The potentials in figure 3(a) and 3(b) are obtained by TDHF and TD-CASSCF, respectively. At t=t₁, ε(t) points from C to O. The change in v₁(t) is governed by the dipole interaction, i.e., v₁(t) ≈ v₁(0) + zε(t); thus, v₁(t) + v₂,5σ(0) linearly slants. The change in v₂,5σ(t) differs between the two cases. In the z-range shown in figure 3, while v₂,5σ(t) − v₂,5σ(0) > 0 for TDHF, v₂,5σ(t) − v₂,5σ(0) for TD-CASSCF has a hump structure formed on the top of the field-induced distorted barrier v₁(t) + v₂,5σ(0). As a result, the total one of veff,5σ(t) = v₁(t) + v₂,5σ(t) has a hump thin barrier for tunnelling, formed at z ≈ −3 a₀ near the C nucleus. This is favourable for ionization toward negative z. When the phase of ε(t) is reversed at t ≈ t₂, the tunnel barrier formed is far away from the nuclei (z≈15 a₀), which is responsible for suppressed tunnel ionization when ε(t) < 0. These features of veff,5σ(t) are consistent with the directional anisotropy of tunnel ionization of CO. As shown in figure 3(a), hump formation cannot be described by TDHF. The formation of the hump is hence attributed to correlated electron motion. As expected from the comparison between figure 3(a) and (b), the ionization probability for TDHF is less than 1/20 of the TD-CASSCF value [20].

Figure 3. Effective potentials veff,5σ(t) = v₁(t) + v₂,5σ(t) of the 5σ at t=t₁=2 fs of the two-cycle pulse (16): (a) TDHF and (b) TD-CASSCF (M=400). v₁(t) is the one-body part in veff,5σ(t) and v₂,5σ(t) is the two-body part. The horizontal dotted line denotes the effective energy Εeff,5σ.

Figure 4. 2D plots of TD-CASSCF effective potentials at t = t₁=2 fs of the two-cycle pulse (16) of φ = −0.5π : (a) veff,5σ(t) and (b) veff,4σ(t). The heights of contour lines are given in units of E₀.

The TD-CASSCF effective potentials of veff,5σ(t) and veff,4σ(t) are depicted in figure 4 as functions of z and ρ. Figure 4(a) shows that the barrier around z=−3 a₀ of veff,5σ(t) lowers as ρ increases, which reflects the fact that the electron mostly moves along the C-O axis in the case where the polarization direction is parallel to the C-O axis. At t ≈ t₁, the electron density is peaked near the position of z=−3 a₀ and ρ = 0, which we call an exit zone of ionization. veff,5σ(t) has thus a hump in the same exit zone of ionization, which results from interactions between orbitals through electron-electron repulsion. As shown in figure 4(b), veff,4σ(t) has a high barrier originating from v₂,4σ(t), in correlation with the electron-electron interaction with a 5σ electron on route to ionization. The high barrier formed at a radius of ~7 a₀ from the nuclei suppresses the birth of a 4σ electron that contributes to HHG (See figure 2(a)). On the other
hand, for $\varphi = 0.5\pi$, $v_{\text{eff}}^\varphi(t)$ at $t \approx t_1$ ($\varphi(t_1) < 0$) is nearly barrierless [20]. The electron released then has more space for rescattering, which enhances the HHG of the 4$\sigma$ path as shown in figure 4(b).

4. Concluding remarks

We proposed an effective potential approach to analyze the multielectron dynamics of molecules in external fields. Within the framework of MCTDHF, we defined the TD effective potentials $\{v_{\text{eff}}^\varphi(t)\}$ that govern the dynamics of natural orbitals $\{\phi_j(t)\}$: $v_{\text{eff}}^\varphi(t) = v_{1j}(t) + v_{2j}(t)$, where $v_{1j}(t)$ is the one-body interaction including the interaction with the applied laser field $\varphi(t)$ and $v_{2j}(t)$ is due to the two-body electron-electron repulsion. The mechanism of intense near-IR field ionization in CO was investigated by examining the temporal change in $v_{\text{eff}}^\varphi(t)$ for the 5$\sigma$ HOMO. We found that for CO, the hump formed near the C atom (an exit zone of ionization), which is due to the change in electron-electron interaction (or electron correlation), is responsible for the anisotropic ionization observed. Two-body interaction can significantly modify the shape of the tunnel barrier in the effective potential. We also found that the suppression of 5$\sigma$ ionization is correlated with the enhancement of 4$\sigma$ HHG, which can be experimentally confirmed by combining two-cycle near-IR pulses of different carrier envelope phases with orientation experiments of CO [23].

Another approach in line with the concept of effective potential is developed by Kato and Yamanouchi [24], where an effective potential itself, from which SOs are obtained, is formulated as an optimization target in the framework of multiconfiguration expansion. Further development of effective potential theory is inevitable to grasp the core of multielectron correlation dynamics.

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