Strong-field-approximation theory of high-order harmonic generation by polyatomic molecules

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A theory of high-order harmonic generation by arbitrary polyatomic molecules is introduced. A polyatomic molecule is modeled by an ($N + 1$)-particle system, which consists of N heavy atomic (ionic) centers and an electron. After the separation of the center-of-mass coordinate, the dynamics of this system is reduced to the relative electronic and nuclear coordinates. Various versions (with or without the dressing of the initial and/or final molecular state) of the molecular strong-field approximation are introduced. For neutral polyatomic molecules the derived expression for the T-matrix element takes a simple form. The interference minima in the harmonic spectrum are explained as a multiple-slit type of interference. This is illustrated by numerical examples for the ozone (O_3) and carbon dioxide (CO_2) molecules.

I. INTRODUCTION

High-order harmonic generation (HHG) is a unique highly nonlinear process which has attracted the attention of experimental and theoretical physicists over the past three decades. In this process a strong laser field removes an electron from the parent atom or molecule to the continuum where it gains energy from the laser field and subsequently recombines with the parent ion, emitting a high-energy photon of energy which is an integer multiple of the fundamental field photon energy. As coherent extreme ultraviolet and soft x-ray radiation, high harmonics have important applications in time-resolved spectroscopy and attoscience [1–10].

Molecules have more complex structures than atoms so molecular HHG can lead to new physical phenomena. In particular, for diatomic molecules a double-slit-type interference effect in HHG spectra was discovered. HHG can serve to reveal nuclear, electronic, vibrational, and rotational dynamics of molecules, structural information such as internuclear distance, symmetry of the highest occupied molecular orbitals (HOMOs), etc. (see, for example, the review articles [11–13] and references therein).

Because of the molecular orientation dependence, HHG in molecules can provide a unique time-resolved probe of the electronic orbital structure. Mostly these studies have been confined to simple diatomic and triatomic linear molecules. Experiments with polyatomic molecules were performed in Refs. [14–19]. In Ref. [14], using the SF_6 molecule as an example, it was shown that HHG is a very sensitive probe of vibrational dynamics, while in Ref. [15] the dependence of the harmonic yield on the angle between the molecular axis and the polarization of the driving laser field is seen to contain the fingerprint of the HOMOs in acetylene and allene. Using the N_2O_4 molecule as an example, in Ref. [16] it was shown that HHG can reveal coupled electronic and nuclear dynamics in polyatomic molecules. The theoretical approach based on quantitative rescattering theory for calculation of HHG from polyatomic molecules in ultrashort linearly polarized intense laser pulses, using the example of the CCl_4 molecule, is considered in Ref. [20]. Very recently, in Ref. [21], using SF_6 as an example, a method for extending high-harmonic

spectroscopy to polyatomic molecules has been demonstrated. In Ref. [22], using high-harmonic spectroscopy as a tool and spatially oriented CH_3F and CH_3Br as generic examples of polar polyatomic molecules, researchers performed accurate measurement of the intensity ratios of even and odd harmonics and of the emission from aligned and unaligned molecules, and showed that a substantial modification of the molecular electronic structure by the external laser field can be revealed.

Whereas direct numerical solution of the time-dependent Schrödinger equation can be used for atomic and simple linear molecular targets within the single-active-electron approximation, such an approach is not practical for polyatomic molecules [23,24]. Since *ab initio* HHG calculations for polyatomic molecules thus far have not been possible in any detail, it is clear that sophisticated models and theories have to be developed. The most popular such theories are based on the strong-field approximation (SFA), according to which the electron, between the ionization and recombination, is described by the Volkov states so that its interaction with the laser field is treated exactly, while the influence of the atomic or molecular binding potential is neglected [25]. Generalization of the SFA from atoms to molecules is not so straightforward as one might expect. Our SFA approach to HHG for arbitrary diatomic molecules is explained in Refs. [26,27].

The ozone molecule plays an important role in the terrestrial atmosphere. In particular, the discovery of the Antarctic ozone hole has stimulated the research of processes in which the O_3 molecule takes place (see, for example, [28] and references therein). As a triatomic molecule, the ozone is very suitable for testing three-point interference. We have investigated above-threshold ionization spectra of O_3 in our previous publications [29]. In the present paper we will consider HHG by the O_3 and CO_2 molecules using the length gauge version of the SFA with the dressed initial and the undressed final bound state, which is in accordance with our previous results given in Refs. [26,27]. We use the fixed-nuclei approximation and neglect the vibrational degree of freedom. Our aim is to explore the influence of the interference of the recombining electron wave packets at different molecular centers. It has recently been shown that for a broad range of molecules in

strong ultrashort laser pulses, vibrational dynamics does not play an important role in the ionization process [30].

In Sec. II we present our polyatomic molecular SFA theory of HHG, while in Sec. III we apply this theory to neutral polyatomic molecules. We show how a factor with the recombination matrix element can be separated and used to identify interference structures in the HHG spectra. Section IV contains our numerical results and discussions and, finally, our conclusions are given in Sec. V.

II. THEORY OF MOLECULAR HHG

We will formulate an SFA-based theory of HHG by polyatomic molecules exposed to a laser field described by the electric field vector $\mathbf{E}(t)$. Our approach is based on the S-matrix theory from Ref. [31] which was applied to HHG by diatomic molecules in Ref. [26] and to above-threshold ionization of diatomic [32,33] and polyatomic molecules [29].

The S-matrix element for emission of a harmonic photon having the frequency $\omega_{\mathbf{K}}$, wave vector $\mathbf{K}$, and the polarization $\hat{\mathbf{e}}_{\mathbf{K}}$, is [31,34]

$$S_{\text{fi}} \propto \int dt \, e^{i\omega_{\mathbf{K}}t} \, \mathbf{d}_{\text{fi}}(t) \cdot \hat{\mathbf{e}}_{\mathbf{K}}^*, \quad (1)$$

where $\mathbf{d}_{\text{fi}}(t)$ is the time-dependent dipole matrix element between the initial and final molecular states in the laser field. We should determine $\mathbf{d}_{\text{fi}}(t)$ in the case of polyatomic molecules.

A polyatomic molecule was considered in Refs. [29] as a system of N atomic (ionic) centers and an active electron. After the separation of the center-of-mass coordinate, the Hamiltonian H which describes this molecule in the laser field is expressed using a set of $(N-1)$ relative (Jacobi) coordinates of atomic (ionic) centers $\{\mathbf{R}\} \equiv (\mathbf{R}_1, \ldots, \mathbf{R}_{N-1})$ and the vector $\mathbf{R}_N$, which describes the relative motion of the electron with respect to the center of mass of all these centers. We denote the momenta, coordinates, masses, and charges of N centers and electron by $\mathbf{p}_k$, $\mathbf{r}_k$, m_k, and e_k, $k = 1, \ldots, N$, and $\mathbf{p}_e$, $\mathbf{r}_e$, m_e, and e, respectively. We also introduce the relative momenta $\mathbf{P}_k$, the reduced masses $\mu_j = m_{j+1}\lambda_j$ (with $\lambda_j = M_j/M_{j+1}$ and $M_j = \sum_{k=1}^{j} m_k$), and the relative charges $\tilde{e}_j = \lambda_j e_{j+1} - \kappa_{j+1} \sum_{k=1}^{j} e_k$ (with $\kappa_j = m_j/M_j$). The laser-free interaction is written as the sum of all electron kth molecular center potentials $V_k(\mathbf{r}_e - \mathbf{r}_k)$ and the potential energy of these centers $V_{\text{C}}(\{\mathbf{R}\})$. In the length gauge and dipole approximation the interaction with the laser field is given by

$$V_{\text{F}}(\mathbf{R}_N, \{\mathbf{R}\}, t) = -\sum_{k=1}^{N} \tilde{e}_k \mathbf{R}_k \cdot \mathbf{E}(t). \quad (2)$$

With this notation the Hamiltonian of our problem is

$$H = \sum_{k=1}^{N} \left[\frac{\mathbf{P}_k^2}{2\mu_k} + V_k(\mathbf{r}_e - \mathbf{r}_k) \right] + V_{\text{C}}(\{\mathbf{R}\}) + V_{\text{F}}. \quad (3)$$

In the SFA the interaction of the electron with the atomic (ionic) centers is neglected in intermediate states and the Hamiltonian H is approximated by H_{F}, where

$$H_{\text{F}} = h_{\text{e}}^{\text{F}} + H_{\text{C}} - \mathbf{E}(t) \cdot \left(\sum_{k=1}^{N-1} \tilde{e}_k \mathbf{R}_k \right),$$

$$h_{\text{e}}^{\text{F}} = \frac{\mathbf{P}_N^2}{2\mu_N} - \tilde{e}_N \mathbf{E}(t) \cdot \mathbf{R}_N, \quad H_{\text{C}} = \sum_{k=1}^{N-1} \frac{\mathbf{P}_k^2}{2\mu_k} + V_{\text{C}}. \quad (4)$$

For calculation of the time-dependent dipole we need the molecular Volkov Green's operator

$$G_{\text{F}}^{(+)}(t,t') = -i\theta(t-t') \sum_{\nu} \int d^3\mathbf{k} |\Phi_{\mathbf{k}\nu}^{\text{F}}(t)\rangle\langle\Phi_{\mathbf{k}\nu}^{\text{F}}(t')|, \quad (5)$$

where the summation is over the vibrational degree of freedom ν, the integration is over the electron momenta $\mathbf{k} \equiv \mathbf{k}_N$, and $\Phi_{\mathbf{k}\nu}^{\text{F}}(t)$ are the solutions of the time-dependent Schrödinger equation (TDSE) with the Hamiltonian H_{F} which can be approximated by

$$\Phi_{\mathbf{k}\nu}^{\text{F}}(\mathbf{R}_N, \{\mathbf{R}\}, t) \approx \phi_{\text{e}\mathbf{k}}(\mathbf{R}_N, t)\varphi_{\text{C}\nu}(\{\mathbf{R}\})e^{-iE_{\text{C}\nu}t},$$

$$\phi_{\text{e}\mathbf{k}}(\mathbf{R}_N, t) = (2\pi)^{-3/2} e^{i[\mathbf{k} - \tilde{e}_N \mathbf{A}(t)]\cdot\mathbf{R}_N - iS_{\mathbf{k}}(t)}, \quad (6)$$

where $\phi_{\text{e}\mathbf{k}}$ is the electronic Volkov state with $S_{\mathbf{k}}(t) = \int_{-\infty}^{t} dt'[\mathbf{k} - \tilde{e}_N \mathbf{A}(t')]^2/2$, $\mathbf{A}(t) = -\int_{-\infty}^{t} \mathbf{E}(t')dt'$, and $\varphi_{\text{C}\nu}$ and $E_{\text{C}\nu}$ are the eigenstates and eigenenergies of the Hamiltonian H_{C}. We will also need the initial and final bound states Φ_j, $j =$ i,f, which also can be written as the product of the N-center wave function $\varphi_{\text{C}\nu_j}(\{\mathbf{R}\}) \exp(-iE_{\text{C}\nu_j}t)$ and the bound electronic wave function $\phi_{\text{e}j}^q = \varphi_{\text{e}j}^q(\mathbf{R}_N; \{\mathbf{R}\}) \exp[-iE_{\text{e}j}(\{\mathbf{R}\})t]$ with $E_{\text{e}j}$ the bound-state electron energy and the state $\varphi_{\text{e}j}^q$ written as a linear combination of atomic orbitals ψ_a. We will use two forms of the functions $\varphi_{\text{e}j}^q$, the undressed ($q = $ u) and dressed ($q = $ d), which are defined by the relations $\varphi_{\text{e}j}^q = \sum_{l=1}^{N} g_q(\boldsymbol{\rho}_l, t) f_l(\mathbf{r}_e - \mathbf{r}_l)$, $g_{\text{u}}(\boldsymbol{\rho}_k, t) = 1$, and $g_{\text{d}}(\boldsymbol{\rho}_k, t) = \exp[-i\tilde{e}_N \boldsymbol{\rho}_k \cdot \mathbf{A}(t)]$, where $\boldsymbol{\rho}_k(\{\mathbf{R}\}) = \lambda_{k-1}\mathbf{R}_{k-1} - \sum_{j=k}^{N-1} \kappa_{j+1}\mathbf{R}_j$, $f_l(\mathbf{r}) = \sum_a c_{la}\psi_a(\mathbf{r})$, and $\mathbf{r}_e - \mathbf{r}_l = \mathbf{R}_N - \boldsymbol{\rho}_l(\{\mathbf{R}\})$.

With the above definitions, the dominant part of the time-dependent dipole is

$$\mathbf{d}_{\text{fi}}(t) \approx \prod_{j=1}^{N} \left[\int d^3\mathbf{R}_j \right] \Phi_{\text{f}}^*(\mathbf{R}_N, \{\mathbf{R}\}, t)$$

$$\times \left(-\sum_{k=1}^{N} \tilde{e}_k \mathbf{R}_k \right) \int dt' \prod_{j'=1}^{N} \left[\int d^3\mathbf{R}'_{j'} \right]$$

$$\times \langle \mathbf{R}_N, \{\mathbf{R}\}| G_{\text{F}}^{(+)}(t,t') |\mathbf{R}'_N, \{\mathbf{R}'\}\rangle$$

$$\times V_{\text{F}}(\mathbf{R}'_N, \{\mathbf{R}'\}, t') \, \Phi_{\text{i}}(\mathbf{R}'_N, \{\mathbf{R}'\}, t'). \quad (7)$$

Separating the Franck-Condon factor $S_{\nu_{\text{f}}\nu_{\text{i}}} = \prod_{j=1}^{N-1} [\int d^3\mathbf{R}_j]\varphi_{\text{C}\nu_{\text{f}}}^*(\{\mathbf{R}\})\varphi_{\text{C}\nu_{\text{i}}}(\{\mathbf{R}\})$ and denoting all possible choices of the dressing of initial or final states by the upper index qq', in the fixed-nuclei approximation $\{\mathbf{R}\} = \{\mathbf{R}_0\}$, we

obtain

$$\mathbf{d}_{\mathrm{fi}}^{qq'}(t) = -i \sum_{\nu} S_{\nu_{\mathrm{f}}\nu} S_{\nu\nu_{\mathrm{i}}} e^{i(E_{\mathrm{C}\nu_{\mathrm{f}}} - E_{\mathrm{C}\nu})t} \int_{-\infty}^{t} dt' e^{i(E_{\mathrm{C}\nu} - E_{\mathrm{C}\nu_{\mathrm{i}}})t'}$$

$$\times \int d^3\mathbf{k} \langle \phi_{\mathrm{ef}}^q(t) | \left(-\sum_{k=1}^{N} \tilde{e}_k \mathbf{R}_k \right) | \phi_{\mathrm{e}\mathbf{k}}(t) \rangle$$

$$\times \langle \phi_{\mathrm{e}\mathbf{k}}(t') | V_{\mathrm{F}}(t') | \phi_{\mathrm{ei}}^{q'}(t') \rangle. \tag{8}$$

Solving the integral over $\mathbf{k}$ using the saddle-point method, with the notation $\tau = t - t'$ and $\mathbf{k}_{\mathrm{st}} = \tilde{e}_N \int_{t-\tau}^{t} \mathbf{A}(t'') dt'' / \tau$, and supposing that $\nu_{\mathrm{f}} = \nu_{\mathrm{i}} = \nu$, we finally obtain

$$\mathbf{d}_{\mathrm{fi}}^{qq'}(t) = -i \left(\frac{2\pi}{i} \right)^{3/2} \int_0^{\infty} \frac{d\tau}{\tau^{3/2}} e^{i[S_{\mathbf{k}_{\mathrm{st}}}(t') - S_{\mathbf{k}_{\mathrm{st}}}(t) + E_{\mathrm{ef}}t]}$$

$$\times e^{-iE_{\mathrm{ei}}t'} \mathbf{m}_{\mathrm{f}\mathbf{k}_{\mathrm{st}}}^q(t) \mathbf{E}(t') \cdot \mathbf{m}_{\mathrm{i}\mathbf{k}_{\mathrm{st}}}^{q'*}(t'), \tag{9}$$

$$\mathbf{m}_{j\mathbf{k}}^q(t) = \langle \phi_{\mathrm{e}j}^q | \left(-\sum_{k=1}^{N} \tilde{e}_k \mathbf{R}_k \right) | \mathbf{k} - \tilde{e}_N \mathbf{A}(t) \rangle. \tag{10}$$

For a laser field having period $T = 2\pi/\omega$ the rate of emission of a harmonic photon with the frequency $\omega_{\mathbf{K}} = n\omega + E_{\mathrm{ei}} - E_{\mathrm{ef}}$, wave vector $\mathbf{K}$, and the unit complex polarization vector $\hat{\mathbf{e}}_{\mathbf{K}}$, into a solid angle $d\Omega_{\hat{\mathbf{K}}}$ is ([31,34]; in atomic units)

$$w_n^{qq'} = \frac{1}{2\pi} \left(\frac{\omega_{\mathbf{K}}}{c} \right)^3 \left| T_n^{qq'} \right|^2, \tag{11}$$

with

$$\mathbf{T}_n^{qq'} = \int_0^T \frac{dt}{T} e^{in\omega t} \mathbf{d}_{\mathrm{fi}}^{qq'}(t) = T_n^{qq'} \hat{\mathbf{e}}_{\mathbf{K}} = \sum_{\xi=x,y,z} T_{n\xi}^{qq'} \hat{\mathbf{e}}_{\xi}, \tag{12}$$

and

$$\mathbf{d}_{\mathrm{fi}}^{qq'}(t) = -i \left(\frac{2\pi}{i} \right)^{3/2} \int_0^{\infty} \frac{d\tau}{\tau^{3/2}} e^{i[S_{\mathbf{k}_{\mathrm{st}}}(t') - S_{\mathbf{k}_{\mathrm{st}}}(t) + E_{\mathrm{ei}}\tau]}$$

$$\times \sum_{l=1}^{N} \sum_a c_{la} \eta_q(\boldsymbol{\rho}_l, t) \langle \psi_a | \tilde{e}_N \mathbf{r} + \boldsymbol{\rho}_{\mathrm{C}_l} | \mathbf{k}_{\mathrm{st}} - \tilde{e}_N \mathbf{A}(t) \rangle$$

$$\times \sum_{j=1}^{N} \sum_{a'} c_{ja'} \eta_{q'}^*(\boldsymbol{\rho}_j, t')$$

$$\times \langle \mathbf{k}_{\mathrm{st}} - \tilde{e}_N \mathbf{A}(t') | (\tilde{e}_N \mathbf{r} + \boldsymbol{\rho}_{\mathrm{C}_j}) \cdot \mathbf{E}(t') | \psi_{a'} \rangle, \tag{13}$$

where the substitution $\mathbf{r} = \mathbf{R}_N - \boldsymbol{\rho}_l$ is used, $\boldsymbol{\rho}_{\mathrm{C}_l} = \tilde{e}_N \boldsymbol{\rho}_l + \sum_{j=1}^{N-1} \tilde{e}_{j_l} \mathbf{R}_j$, $\eta_{\mathrm{d}}(\boldsymbol{\rho}_j, t) = \exp\{i\mathbf{k}_{\mathrm{st}} \cdot \boldsymbol{\rho}_j\}$, and $\eta_{\mathrm{u}}(\boldsymbol{\rho}_j, t) = \exp\{i[\mathbf{k}_{\mathrm{st}} - \tilde{e}_N \mathbf{A}(t)] \cdot \boldsymbol{\rho}_j\}$. The index l on $\tilde{e}_j$ means that the charge distribution is such that the electron is ionized from (recombined with) the center l.

III. HHG BY NEUTRAL POLYATOMIC MOLECULES AND THE INTERFERENCE CONDITION FOR ARBITRARILY ORIENTED LINEARLY POLARIZED LASER FIELD

In this section we consider HHG by neutral polyatomic molecules and present a condition for appearance of the interference minima in the HHG spectrum. For neutral polyatomic molecules we have $\tilde{e}_N = -1$ and $\boldsymbol{\rho}_{\mathrm{C}l} = \mathbf{0}$, $l = 1, \ldots, N$,

so that the expression for the time-dependent dipole (13) simplifies.

Let us first check that our new result reduces to our earlier results for atoms and diatomic molecules. For $N = 1$ we have $\boldsymbol{\rho}_j = \mathbf{0}$ and $\eta_q = 1$ so that our result reduces to the standard length-gauge atomic SFA. For $N = 2$ we have $\boldsymbol{\rho}_1 = -\kappa_2 \mathbf{R}_1$ and $\boldsymbol{\rho}_2 = \lambda_1 \mathbf{R}_1$. Introducing the mass asymmetry parameter $\lambda = (m_1 - m_2)/(m_1 + m_2)$, we obtain $\boldsymbol{\rho}_l = -(s - \lambda)\mathbf{R}_1/2$, where $s = +1$ for $l = 1$ and $s = -1$ for $l = 2$, so that in Eq. (13) we can replace the sums over l and j by the sum over $s = \pm 1$ and $s' = \pm 1$, respectively. For $\lambda = 0$ this result reduces to the modified molecular SFA in length gauge for homonuclear diatomic molecules from Refs. [26,27], while for $\lambda \neq 0$ this result reduces to an analogous result for heteronuclear diatomic molecules from Ref. [35].

In the case of diatomic molecules we observed and explained the interference minima in the HHG spectra in Refs. [26,35]. In order to examine the possibility of appearance of similar interference minima in the HHG spectra of polyatomic molecules, we apply the saddle-point method and solve the integrals over the times t and τ in Eqs. (12) and (13). This means that the partial derivatives over τ and t of the action $S_{\mathbf{k}_{\mathrm{st}}}(t') - S_{\mathbf{k}_{\mathrm{st}}}(t) + E_{\mathrm{ei}}\tau + n\omega t$ are equal to zero, which gives the following system of equations for the variables $t' = t - \tau$ and t:

$$[\mathbf{k}_{\mathrm{st}} + \mathbf{A}(t')]^2 = 2E_{\mathrm{ei}}, \tag{14}$$

$$[\mathbf{k}_{\mathrm{st}} + \mathbf{A}(t)]^2 = 2(n\omega + E_{\mathrm{ei}}), \tag{15}$$

which express the energy-conserving conditions at the ionization time t' and the recombination time t. In this way the double integral over the times t and τ is replaced by a sum over all saddle-point solutions which we denote by the index s [36].

For a linearly polarized laser field the vector potential $\mathbf{A}(t)$ and the intermediate electron momentum $\mathbf{k}_{\mathrm{st}}$ are parallel to the laser electric field unit vector $\hat{\mathbf{e}}_{\mathrm{L}}$, so that, for $n\omega > -E_{\mathrm{ei}} = I_{\mathrm{p}}$, we can write Eq. (15) in the following form

$$p = -[k_{\mathrm{st}} + A(t_s)] = \sqrt{2(n\omega - I_{\mathrm{p}})}. \tag{16}$$

We have neglected the small imaginary part of the recombination time t_s and have chosen $t \in [0,T]$, so that the saddle-point solutions are such that $p > 0$ [36]. In the Cartesian
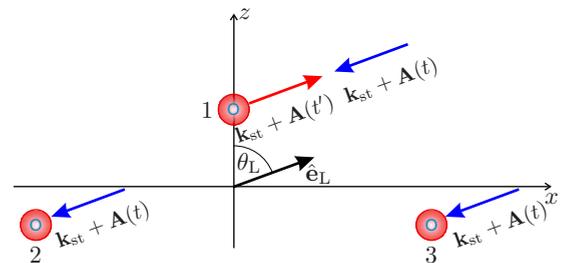
FIG. 1. Schematic presentation of the HHG process initiated by ionization from the center 1 with possible recombination to the same center as well as to the other two centers. The orientation of the laser electric field unit vector $\hat{\mathbf{e}}_{\mathrm{L}}$ relative to the z axis is defined by the angle θ_{L}.
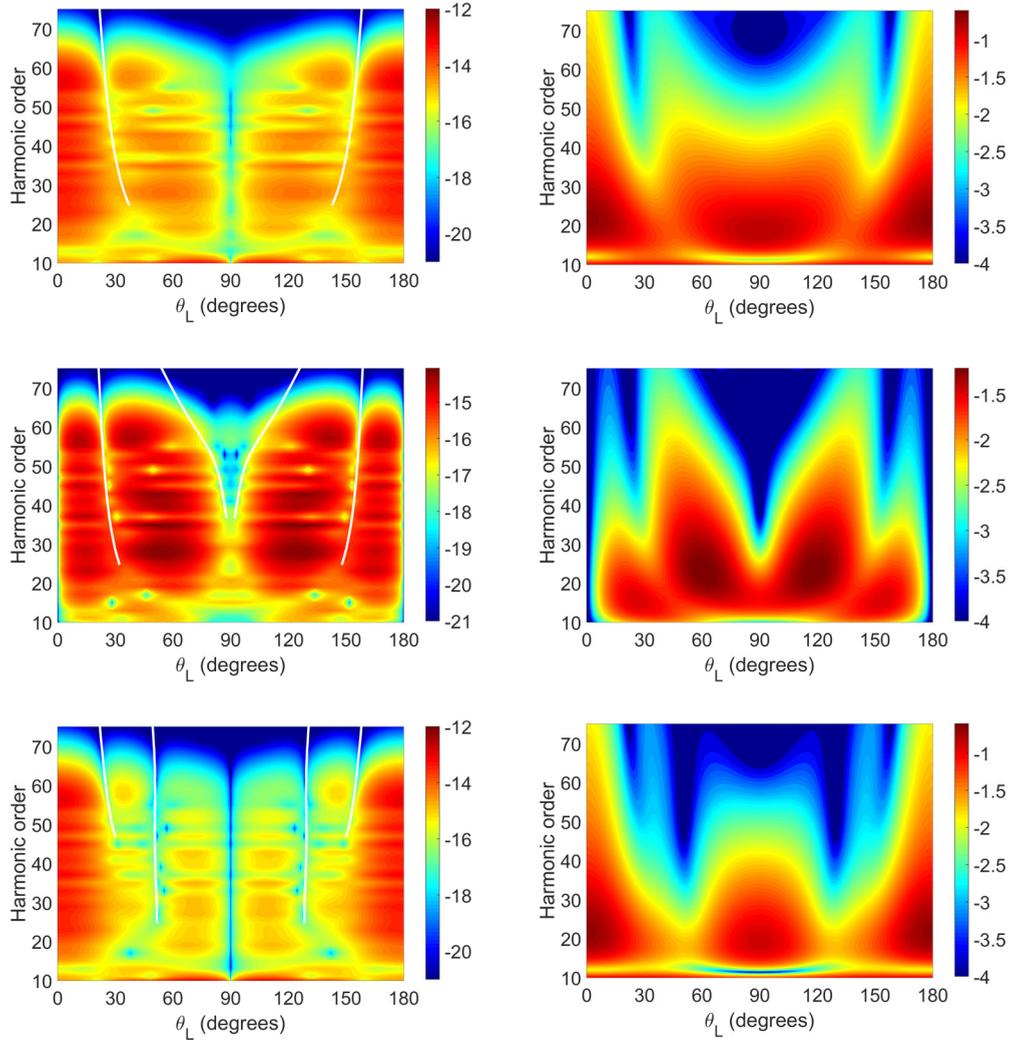
FIG. 2. HHG spectra of the O_3 molecule (left panels) and logarithm of the absolute square of the interference factors (right panels). The angle θ_L is plotted along the horizontal axis, while the harmonic order n is along the vertical axis. Laser field is linearly polarized having the intensity 4×10^{14} W/cm^2 and the wavelength 800 nm. The initial state is dressed ($q' = $ d), while the final state is undressed ($q = $ u). The results for the logarithm of the HHG rates shown in false colors in the left panels are obtained using both (top panel), only the x (middle panel), and only the z (bottom panel) components of the T-matrix element. In the right panels we show in false colors the logarithm of $|I_x|^2 + |I_z|^2$ (top panel), $|I_x|^2$ (middle panel), and $|I_z|^2$ (bottom panel). The white lines in the left panels follow the interference minima which are obtained using the results of the right panels.

coordinates xyz, which are defined by the molecular system, we have $\hat{\mathbf{e}}_L = \sin\theta_L \cos\varphi_L \hat{\mathbf{e}}_x + \sin\theta_L \sin\varphi_L \hat{\mathbf{e}}_y + \cos\theta_L \hat{\mathbf{e}}_z$, where θ_L and φ_L are the polar and azimuthal angles, respectively. In this case the recombination matrix element $\mathbf{m}_a(\mathbf{k}_{st}, t_s) = \langle \psi_a | (-\mathbf{r}) | \mathbf{k}_{st} + \mathbf{A}(t_s) \rangle = -i\hat{\mathbf{e}}_L \partial \psi_a^* / \partial p$ does not depend on the times t_s and τ_s. In addition to this, for the undressed final state we have $\eta_u = \exp(-ip\hat{\mathbf{e}}_L \cdot \boldsymbol{\rho}_l)$ which also does not depend on the times t_s and τ_s. Therefore, the recombination factor from Eqs. (12) and (13),

$$I_\xi(n, \theta_L, \varphi_L) = \hat{\mathbf{e}}_L \cdot \hat{\mathbf{e}}_\xi \sum_{l=1}^{N} e^{-ip\hat{\mathbf{e}}_L \cdot \boldsymbol{\rho}_l} \sum_a c_{la} \frac{\partial \psi_a^*}{\partial p}, \quad (17)$$

can be withdrawn in front of the sum over s so that the $\xi = x, y, z$ component of the T-matrix element for emission of the

nth harmonic is proportional to

$$T_{n\xi}^{qq'} \propto I_\xi \sum_s \left\{ \tau_s^{-3/2} e^{i[n\omega t_s + S_{\mathbf{k}_{st}}(t_s') - S_{\mathbf{k}_{st}}(t_s) - I_p \tau_s]} \right.$$
$$\left. \times \sum_{j=1}^{N} \sum_{a'} c_{ja'} \eta_{q'}^*(\boldsymbol{\rho}_j, t_s') \mathbf{m}_{a'}^*(\mathbf{k}_{st}, t_s') \cdot \mathbf{E}(t_s') \right\}. \quad (18)$$

The interference factor I_ξ, Eq. (17), is a sum of N plane waves with different weights and for some specific values of n, θ_L, and φ_L interference structures can be expected. In the next section we will explain three-center interference using the ozone and carbon dioxide molecules as examples.

IV. NUMERICAL RESULTS

A. O_3 molecule

Similar to that in Refs. [29], we will illustrate our theory of HHG by polyatomic molecules using the ozone molecule as an example. The O_3 molecule is a planar molecule which consists of three oxygen atoms placed in the xz plane (see Fig. 1). We calculate the HOMO of O_3 using the cc-pVTZ basis set from the GAMESS quantum chemistry package [37]. We will use the ionization potential $I_p = -E_{ei} = 12.73$ eV as in our previous papers [29]. The time-dependent dipole in the case of O_3 is given by Eq. (13) with $N = 3$, $\tilde{e}_N = -1$, $\boldsymbol{\rho}_{Cj} = \mathbf{0}$, $\boldsymbol{\rho}_j \approx \mathbf{r}_j$, and $j = 1,2,3$.

We suppose that the laser field is linearly polarized with the electric field vector $\mathbf{E}(t) = E_0 \sin(\omega t)\hat{\mathbf{e}}_L$. For analysis of the three-center interference in HHG, we fix the laser field in the xz plane ($\varphi_L = 0$) and change the polar angle $\theta_L \in [0°, 180°]$. From Fig. 1 we see that the electron, emitted in the process of ionization from the center 1 with the initial velocity $\mathbf{k}_{st} + \mathbf{A}(t')$, moves away from this center in the direction determined by the angle θ_L and returns along the same direction to one of the three centers denoted by 1, 2, and 3, having the velocity $\mathbf{k}_{st} + \mathbf{A}(t)$ at the recombination time. It is obvious that three recombination amplitudes contribute to the HHG process. This leads to the three-center interference structures.

In the upper left panel of Fig. 2 in false colors we show the logarithm of the harmonic emission rate, Eq. (11), as a function of the angle θ_L and the harmonic order n. In the remaining left panels we show the rates obtained using only the x (middle panel) and only the z (bottom panel) component of the T-matrix element, Eq. (12). One can see that the contribution of the z component is dominant. However, the contribution of the x component is important in the regions of the (θ_L, n) plane where the x component exhibits the interference minima (denoted by white lines), as well as along the nodal plane $\theta_L = 90°$ [for the z component from Eq. (17) it follows that the interference factor $I_z \propto \hat{\mathbf{e}}_L \cdot \hat{\mathbf{e}}_z = \cos\theta_L = 0$ for $\theta_L = 90°$, and analogously $I_x \propto \hat{\mathbf{e}}_L \cdot \hat{\mathbf{e}}_x = \sin\theta_L = 0$ for $\theta_L = 0°$ and $180°$]. Additional interference minima can be read from the right panels of Fig. 2 where we presented the logarithm of the absolute square of the corresponding interference factors. It is evident that these minima fit well the false color minima which appear in the numerical results.

B. CO_2 molecule

As the next example we present the HHG spectra for the CO_2 molecule. The CO_2 molecule is a linear molecule with a C-O distance of 1.162 Å and a vertical ionization energy of 13.78 eV. The HOMO of the CO_2 molecule is calculated using the same method as for the O_3 molecule. We present our results for the parameters of Ref. [38]. In this paper a long-wavelength laser was used and it was found that multielectron effects are negligible.

Our results presented in Fig. 3 agree well with the result presented in the left panel of Fig. 2 from Ref. [38]. Similar to the O_3 case, the spectra exhibit pronounced interference minima for a wide range of angles. We added to our false-color figure two curves obtained using our interference formula (17). The white curve is obtained taking into account all three centers of the CO_2 molecule, while the lower red
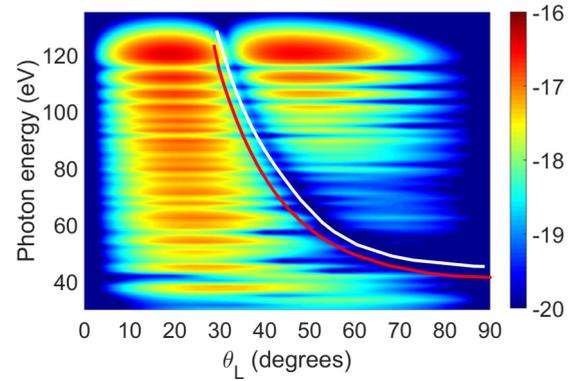
FIG. 3. Logarithm of the HHG rates for CO_2 molecule shown in false colors. The angle θ_L is plotted along the horizontal axis, while the harmonic photon energy (in eV) is along the vertical axis. Laser field is linearly polarized having the intensity $I = 1.7 \times 10^{14}$ W/cm^2 and the wavelength of 1450 nm. The white line follows the interference minima which are obtained taking into account contributions of all three atomic centers, while the red line is obtained taking into account only the contributions from the two O atomic centers.

curve is obtained taking into account only two O centers. It is obvious that the white curve fits numerical results much better than the red one. This confirms that the formalism introduced in our paper works well.

V. CONCLUSIONS

We have presented an SFA-based theory of high-order harmonic generation by polyatomic molecules. In our model, a polyatomic molecule is considered as a system of $N + 1$ particles: N atomic (ionic) centers and one valence electron, emitted by strong-field ionization. In the Born-Oppenheimer and the fixed-nuclei approximation we derived an expression for the harmonic emission T-matrix element. Our theory is formulated in such a way that the strong-field approximation with the laser-field dressed or undressed initial and final states can be treated on the same footing. Based on our previous work given in Ref. [26] we have chosen the version of the molecular SFA where in the initial (ionization) and the final (recombination) step the molecular states are treated as dressed and undressed, respectively. For neutral polyatomic molecules the T-matrix element is simplified and we were able to extract its recombination part as a factor. This factor is responsible for a multicenter interference of the recombining electronic wave packets.

We have applied our theory to high-order harmonic generation by O_3 and CO_2 molecules. The logarithm of the harmonic emission rate is presented as a function of the harmonic order and the angle between the molecular z axis and the laser polarization direction. We confirmed that the minima in the harmonic spectra are caused by the interference of the three wave packets in the moment of recombination for different oxygen atoms (for O_3) or two oxygen atoms and one carbon atom (for CO_2), i.e., they originate from the multicenter interference.

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