Three-Step Model for High-Harmonic Generation in Many-Electron Systems

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The three-step model (TSM) of high-harmonic generation (HHG) is generalized to atomic and molecular many-electron systems. Using many-body perturbation theory, corrections to the standard TSM due to exchange and electron-electron correlations are derived. It is shown that canonical Hartree-Fock orbitals represent the most appropriate set of one-electron states for calculating the HHG spectrum. To zeroth order in many-body perturbation theory, a HHG experiment allows direct access, in general, to a combination of occupied Hartree-Fock orbitals rather than to the highest occupied molecular orbital by itself.

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High-harmonic generation (HHG) is well understood within the framework of the three-step model [1,2] (TSM) when the Keldysh parameter [2] is small. (See also Ref. [3].) An electron in the atom or molecule is ionized, is accelerated in the laser field, and recombines with the ion core emitting a HHG photon. The probability amplitude for emitting a HHG photon is given by the product of the three probability amplitudes assigned to each step [4].

The shape of the HHG spectrum is predominantly determined by the recombination amplitude. If the effect of the binding potential on the electron continuum states is neglected, the latter can be replaced by plane waves, which results in the well-known expression for the recombination amplitude a^{rec} obtained by Lewenstein *et al.* [2]:

$$a^{\mathrm{rec}}_{\mathrm{Lew}}(\boldsymbol{k}) = \langle 0|d|\boldsymbol{k}\rangle. \tag{1}$$

Here, d is the dipole operator, $|\boldsymbol{k}\rangle$ is a momentum eigenstate (a plane wave), and $|0\rangle$ is the ground state.

When propagation effects play a negligible role, a^{rec} can in principle be extracted from experimental HHG spectra. Therefore, according to Eq. (1), HHG can be used to measure the ground-state *wave function* (not merely the probability density). This idea was exploited in a recent groundbreaking work [5].

Equation (1) strictly applies only to a single-electron system. At the heart of this Letter lies the derivation of an expression that generalizes Eq. (1) to many-electron systems. This expression leads to three results. First, to the extent that the HHG process can be assigned to one-particle wave functions, it is the Hartree-Fock orbitals that are imprinted in the HHG spectrum. Electron-correlation effects appear in lower order in many-body perturbation theory than corrections due to the difference between, say, Dyson orbital and Hartree-Fock orbital. Second, we show that the HHG recombination amplitude in many-electron systems is sensitive to all occupied orbitals rather than to the highest occupied orbital alone. Third, we find the leading correction to the single-particle picture due to many-body effects. Computational treatments of HHG in many-electron systems may be found, e.g., in Refs. [6,7].

The vast majority of stable molecules exhibit a closed-shell electronic structure (total spin $S = 0$). This is the case we will focus on in this Letter. Of the three TSM amplitudes [4], this study is concerned with the recombination amplitude alone because it is considered [2,4,5] the most influential factor on the shape of the HHG spectrum. Therefore, we assume the simplest scenario for the ionization step: Following ionization, the many-electron wave packet is in a superposition of the nondegenerate N-electron ground state $|\Psi_0^N\rangle$ and continuum states associated with the various eigenstates of the $(N-1)$-electron system. The cationic eigenstates of relevance here are characterized by $S = 1/2$. In addition to the neutral ground state only the (doubly degenerate) cationic ground state, $|\Psi_{0\sigma}^{N-1}\rangle$, is populated ($\sigma$ denotes the sign of the spin projection number). This assumption can be motivated by the fact that the probability of exciting two electrons at once is negligible. However, the ionization step may require more detailed attention, especially for complex molecules [8].

Thus, we make the ansatz

$$|\Psi\rangle = |\Psi_0^N\rangle + \sum_{\boldsymbol{k}} b_{\boldsymbol{k}}(t)\frac{1}{\sqrt{2}}\{c^\dagger_{\boldsymbol{k}+}|\Psi_{0-}^{N-1}\rangle + c^\dagger_{\boldsymbol{k}-}|\Psi_{0+}^{N-1}\rangle\}, \tag{2}$$

which is the many-electron analogue of Eq. (3) of Ref. [2]. Depletion of the N-electron ground state is neglected for simplicity and can be easily reintroduced when needed. The operator $c^\dagger_{\boldsymbol{k}\sigma}$ creates an electron in a plane-wave state characterized by the momentum vector $\mathbf{k}$ and the spin projection $\sigma \times 1/2$. [Box normalization is implied throughout. See, for example, Ref. [9] for the phase convention underlying the construction of the $S = 0$ continuum state in Eq. (2).]

Let $\hat{D}$ stand for the dipole operator in the many-particle Fock space. The TSM recombination amplitude analogous to Eq. (1) is now given by

$$a^{\mathrm{rec}}(\mathbf{k}) = \frac{1}{\sqrt{2}} \sum_{\sigma} a^{\mathrm{rec}}_{\sigma}(\mathbf{k}), \tag{3}$$

where

$$a^{\mathrm{rec}}_{\sigma}(\mathbf{k}) = \langle \Psi_0^N | \hat{D} c^{\dagger}_{\mathbf{k}\sigma} | \Psi^{N-1}_{0\bar{\sigma}} \rangle. \tag{4}$$

Here, $\bar{\sigma} = -\sigma$. The dipole operator in the second quantization takes the form [10]:

$$\hat{D} = \sum_{\mathbf{k}'\sigma'} \sum_{\mathbf{k}''\sigma''} d_{\mathbf{k}'\sigma',\mathbf{k}''\sigma''} c^{\dagger}_{\mathbf{k}'\sigma'} c_{\mathbf{k}''\sigma''}. \tag{5}$$

Upon inserting Eq. (5) in Eq. (4) and exploiting the anticommutation relations [10] satisfied by the $c_{\mathbf{k}'\sigma'}$ and $c^{\dagger}_{\mathbf{k}'\sigma'}$ operators, we arrive at the following expression for the recombination amplitude:

$$a^{\mathrm{rec}}_{\sigma}(\mathbf{k}) = \langle \varphi^{(D)}_{0\sigma} | d | \mathbf{k}\sigma \rangle + \langle \Psi_0^N | c^{\dagger}_{\mathbf{k}\sigma} \hat{D} | \Psi^{N-1}_{0\bar{\sigma}} \rangle. \tag{6}$$

$|\varphi^{(D)}_{0\sigma}\rangle$ is the Dyson (spin) orbital [11–13] deriving from $|\Psi^{N-1}_{0\bar{\sigma}}\rangle$:

$$\begin{aligned} \varphi^{(D)}_{0\sigma}(\mathbf{x}) &= \langle \Psi^{N-1}_{0\bar{\sigma}} | \hat{\Psi}(\mathbf{x}) | \Psi_0^N \rangle \\ &= \sum_{\mathbf{k}'\sigma'} \langle \mathbf{x} | \mathbf{k}'\sigma' \rangle \langle \Psi^{N-1}_{0\bar{\sigma}} | c_{\mathbf{k}'\sigma'} | \Psi_0^N \rangle. \end{aligned} \tag{7}$$

$\hat{\Psi}(\mathbf{x})$ is the field operator [10], which removes an electron at position $\mathbf{x}$. The relation

$$\hat{\Psi}(\mathbf{x}) = \sum_{\mathbf{k}'\sigma'} \langle \mathbf{x} | \mathbf{k}'\sigma' \rangle c_{\mathbf{k}'\sigma'} \tag{8}$$

has been used. The first term in Eq. (6) equals the Fourier transform of the dipole operator times the Dyson orbital $|\varphi^{(D)}_{0\sigma}\rangle$. (Dyson orbitals, which are independent of a specific one-particle model, are common in ionization problems [11–13].) In what follows we analyze the two terms in Eq. (6).

The recombination of a high-energy electron with the cation is the inverse process of photoionization high above threshold. In this limit, it is known [14] that the ionization cross section can be expressed in terms of the one-particle Green's function [10]. If and only if the perturbative analysis of the one-particle Green's function is based on the canonical Hartree-Fock model [9] corresponding to the neutral ground state of the molecule, all self-energy diagrams in first order with respect to the residual electron-electron interaction vanish [15]. This is the basis of Koopmans' theorem [16]. Motivated by this observation, we base our analysis of Eq. (6) on Hartree-Fock orbitals.

Let

$$\hat{F} = \sum_{p} \varepsilon_p c^{\dagger}_p c_p \tag{9}$$

denote the Hartree-Fock one-body operator. Its eigenstates $|\varphi_p\rangle$ in the one-electron Hilbert space are spin orbitals forming a complete orthonormal set. The eigenvalues ε_p are orbital energies. Orbitals and energies may be assumed real. We use indices $i, j, k, l, \ldots$ for orbitals that are occupied in the N-electron Hartree-Fock ground state

$$|\Phi_0^N\rangle = \prod_{i=1}^{N} c^{\dagger}_i |\mathrm{vacuum}\rangle. \tag{10}$$

Unoccupied orbitals are symbolized by indices $a, b, c, d, \ldots$, whereas for general orbitals indices $p, q, r, s, \ldots$ are employed.

Applying Møller-Plesset [17] partitioning, the exact electronic Hamiltonian $\hat{H}$ is then given by

$$\hat{H} = \hat{F} + \hat{V} - \hat{V}^{(HF)}, \tag{11}$$

where

$$\hat{V} = \frac{1}{2} \sum_{pqrs} v_{pqrs} c^{\dagger}_p c^{\dagger}_q c_s c_r \tag{12}$$

is the Coulomb two-body operator and

$$\hat{V}^{(HF)} = \sum_{pq} \left\{ \sum_{i} v_{pi[qi]} \right\} c^{\dagger}_p c_q \tag{13}$$

represents the interaction with the Hartree-Fock mean field. Here we made use of the definition $v_{pq[rs]} = v_{pqrs} - v_{pqsr}$ (v_{pqrs} is a standard electron-electron Coulomb matrix element).

Using the canonical Hartree-Fock orbitals, the two matrix elements contributing to the recombination amplitude in Eq. (6) can be written as

$$\langle \varphi^{(D)}_0 | d | \mathbf{k} \rangle = \sum_{p} \langle \Psi_0^N | c^{\dagger}_p | \Psi_0^{N-1} \rangle \langle \varphi_p | d | \mathbf{k} \rangle, \tag{14}$$

$$\langle \Psi_0^N | c^{\dagger}_{\mathbf{k}} \hat{D} | \Psi_0^{N-1} \rangle = \sum_{p} \langle \Psi_0^N | c^{\dagger}_p \hat{D} | \Psi_0^{N-1} \rangle \langle \varphi_p | \mathbf{k} \rangle. \tag{15}$$

(In order to keep the notation from becoming too cluttered, the spin index in $|\varphi^{(D)}_{0\sigma}\rangle$, $|\mathbf{k}\sigma\rangle$, and $|\Psi^{N-1}_{0\bar{\sigma}}\rangle$ is suppressed from now on.) The exact eigenstates $|\Psi_0^N\rangle$ and $|\Psi_0^{N-1}\rangle$ can be expressed in terms of determinants deriving from the Hartree-Fock ground state. Employing perturbation theory to first order in the interaction

$$\hat{H}_1 = \hat{V} - \hat{V}^{(HF)}, \tag{16}$$

one obtains

$$\begin{aligned} |\Psi_0^N\rangle = |\Phi_0^N\rangle &+ \sum_{a<b} \sum_{i<j} \frac{v_{ab[ij]}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} c^{\dagger}_a c^{\dagger}_b c_j c_i |\Phi_0^N\rangle \\ &+ O(H_1^2) \end{aligned} \tag{17}$$

and

$$|\Psi_0^{N-1}\rangle = c_0|\Phi_0^N\rangle + \sum_a \sum_{i<j} \frac{v_{a0[ij]}}{\varepsilon_i + \varepsilon_j - \varepsilon_0 - \varepsilon_a} c_a^\dagger c_j c_i |\Phi_0^N\rangle + \sum_{a<b} \sum_{i<j} \frac{v_{ab[ij]}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} c_a^\dagger c_b^\dagger c_j c_i c_0 |\Phi_0^N\rangle + O(H_1^2). \tag{18}$$

Note that due to the use of the Hartree-Fock model, single excitations of $|\Phi_0^N\rangle$ do not contribute to the exact ground state of the neutral system. Also observe that we assumed that there is one specific orbital $|\varphi_0\rangle$—the highest occupied molecular orbital (HOMO)—that characterizes the cationic ground state to leading order. This is meaningful, since the Hartree-Fock one-hole configurations do not couple among each other.

Substituting Eqs. (17) and (18) into Eq. (14), it follows that

$$\langle \varphi_0^{(D)}|d|\boldsymbol{k}\rangle = \langle \varphi_0|d|\boldsymbol{k}\rangle + O(H_1^2). \tag{19}$$

Thus, up to second order in many-body perturbation theory, the recombination amplitude does not distinguish between Dyson orbital and Hartree-Fock orbital. For the second matrix element in Eq. (6) we find, using Eq. (15),

$$\langle \Psi_0^N|c_{\boldsymbol{k}}^\dagger \hat{D}|\Psi_0^{N-1}\rangle = \sum_i \{d_{ii}\langle \varphi_0|\boldsymbol{k}\rangle - d_{0i}\langle \varphi_i|\boldsymbol{k}\rangle\} + \sum_i \langle \varphi_i|\boldsymbol{k}\rangle \sum_a \sum_j d_{ja} \frac{v_{a0[ij]}}{\varepsilon_i + \varepsilon_j - \varepsilon_0 - \varepsilon_a} + \sum_a \langle \varphi_a|\boldsymbol{k}\rangle \sum_b \sum_i d_{bi} \frac{v_{ab[0i]}}{\varepsilon_0 + \varepsilon_i - \varepsilon_a - \varepsilon_b} + O(H_1^2). \tag{20}$$

From this result we draw the following conclusions. First, the matrix element $\langle \Psi_0^N|c_{\boldsymbol{k}}^\dagger \hat{D}|\Psi_0^{N-1}\rangle$, which forms an integral part of the recombination amplitude [Eq. (6)], does not vanish in zeroth order. There are exchange terms that depend on all occupied orbitals that are connected to $|\varphi_0\rangle$ via an electric dipole transition. In addition, if a polar molecule is considered that is not just aligned but oriented relative to the laser polarization axis, then there are correction terms associated with static dipole moments d_{ii}. Therefore, while Eq. (19) shows that at the one-particle level HHG is, in principle, sensitive to the Hartree-Fock HOMO, there is no obvious way to accurately reconstruct it without *a priori* knowledge of the occupied orbitals. The strength of HHG-based orbital imaging rests in the fact that it gives access to the phase of (a combination of) orbitals rather than the probability density alone. Second, as a consequence of electron correlation—in both the cation and the neutral molecule—there are first-order corrections [terms in Eq. (20) depending on the electron-electron repulsion matrix elements $v_{pq[rs]}$]. In a perturbation-theoretic sense, these corrections are greater than the second-order difference between a Dyson orbital and a Hartree-Fock orbital.

At last, it is useful to estimate some of the terms in Eq. (20) for a specific example. For this purpose, we choose atomic argon. Instead of the canonical Hartree-Fock orbitals we employ orbitals calculated utilizing the Hartree-Slater code by Herman and Skillman [18,19]. The Hartree-Slater one-electron potential $V_{\mathrm{HS}}(r)$ is local and central, and the occupied Hartree-Fock orbitals in a closed-shell atomic system such as argon are fairly well reproduced. Using the Hartree-Slater potential and orbitals allows comparing the TSM HHG spectrum with the numerical solution of the time-dependent Schrödinger equation (TDSE). The corresponding Hamiltonian is

$$H(t) = H_0 - E(t)z; \qquad H_0 = \frac{\boldsymbol{p}^2}{2} + V_{\mathrm{HS}}(r), \tag{21}$$

where $E(t)$ is the laser electric field.

Equation (21) describes a single-electron system. Yet, surprisingly, the corresponding TSM recombination amplitude contains exchange terms identical to the zeroth-order terms in Eq. (20). To show this we introduce the evolution operator $U(t)$ associated with $H(t)$, with the initial condition $U(0) = 1$. The electron that is most likely to participate in the HHG process is the $3p_z$ electron, because it is most easily tunnel-ionized.

Let $|\varphi_0\rangle$ denote the $3p_z$ orbital of H_0, and let $|\varphi_i\rangle$ $(i \neq 0)$ denote the (spatial) orbitals of H_0 with lower energy. By the unitarity of the time evolution, $U(t)|\varphi_0\rangle$ always remains orthogonal to $U(t)|\varphi_i\rangle$. However, the intensity of the laser field in an HHG experiment is dictated by the requirement that the tunnel-ionization rate of $|\varphi_0\rangle$ is slow compared to the laser cycle. Therefore, the states $|\varphi_i\rangle$ are barely affected by the field. In other words, $U(t)|\varphi_i\rangle \approx |\varphi_i\rangle$ up to a phase. From this argument it follows that $U(t)|\varphi_0\rangle$ remains nearly orthogonal to all $|\varphi_i\rangle$. If this were not the case, one would have to artificially project the $|\varphi_i\rangle$ out of $U(t)|\varphi_0\rangle$ to enforce the exclusion principle.

The above observation suggests that the approximation of the continuum electron by a plane wave within the standard TSM can be improved by projecting the $|\varphi_i\rangle$ out of it. This leads to the recombination amplitude

$$a_{\mathrm{HS}}^{\mathrm{rec}}(\boldsymbol{k}) = \langle \varphi_0|d|\boldsymbol{k}\rangle - \sum_i d_{0i}\langle \varphi_i|\boldsymbol{k}\rangle. \tag{22}$$

The exchange correction in this expression is identical (in the atomic case) to the zeroth-order correction derived using the many-body approach [see Eqs. (6), (19), and (20)]. Higher order terms in the residual electron-electron interaction are not reproducible by one-particle arguments.

Although Eq. (21) is a very simplified model of an argon atom, the fact that the exchange (projection) terms still show up in the TSM allows testing the TSM by comparison with the numerical solution of the TDSE. In particular, one

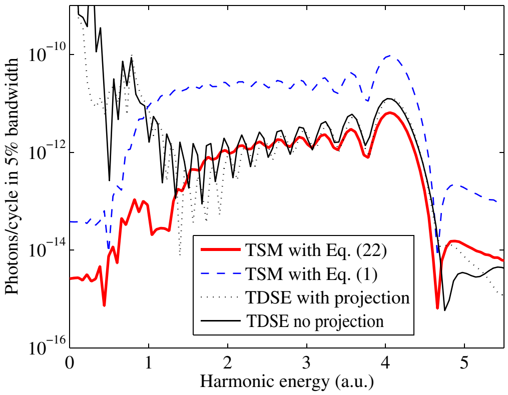

FIG. 1 (color online). HHG spectrum for the Hamiltonian (21) with V_{HS} corresponding to argon. $E(t) = E_0 \sin\omega t$, where $\omega = 0.057$ a.u. corresponding to a 800 nm laser, and $E_0 = 0.12$ a.u. The spectrum was extracted after one laser cycle. The dotted line and the thin solid line were obtained from a numerical solution of the TDSE with and without projecting out the states below $3p$ at every step. The dashed and the thick lines were obtained using the TSM, with Eqs. (1) and (22), respectively.

can see which expression, (1) or (22), better approximates the HHG spectrum.

The comparison is displayed in Fig. 1. One can see that the spectrum obtained by integrating the TDSE barely depends on whether the occupied orbitals are projected out (dotted line) or not (thin solid line) at each step of the integration. However, the TSM spectrum with Eq. (1) significantly differs from the one with Eq. (22), and the latter agrees much better with the TDSE result. The ionization rate used in Fig. 1 was computed for the argon V_{HS} using a suitably adapted version of the technique described in Ref. [20]. The acceleration form of the dipole operator $[d = -\partial_z V_{\mathrm{HS}}(r)]$ was used, since it gives more accurate TSM spectra than other forms [21].

The TSM provides a clear physical picture of the processes underlying HHG. It not only allows one to calculate HHG spectra in a computationally efficient fashion, it also highlights HHG as a potentially powerful diagnostic tool in atomic and molecular physics. The many-body formulation of the TSM developed in this work lays the foundation for connecting HHG and the properties of many-electron systems.

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