High-order harmonic generation with resonant core excitation by ultraintense x rays

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High-order harmonic generation (HHG) is combined with resonant x-ray excitation of a core electron into the transient valence vacancy that is created in the course of the HHG process. To describe this setting, I develop a two-active-electron quantum theory for a single atom assuming no Coulomb interaction among the electrons; one electron performs a typical HHG three-step process whereas, another electron is excited (or even Rabi flops) due to the intense x rays from the core into the valence hole and after the first electron has left the atom. Depending on the probability to find a vacancy in the valence and the core, the returning continuum electron recombinates with the valence and the core emitting HHG radiation that is characteristic for the combined process. After presenting the theory of x-ray boosted HHG for continuous-wave light fields, I develop a description for x-ray pulses with a time varying amplitude and phase. My prediction offers novel prospects for nonlinear x-ray physics, attosecond x rays, and HHG-based time-dependent chemical imaging involving core orbitals.

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I. INTRODUCTION

Since the surprise discovery of high-order harmonic generation (HHG) by atoms in intense optical laser fields [1, 2], HHG has spawned the field of attoscience, for spectroscopy, and serves as a light source in many optical laboratories [3–7]. Initially, there has been a period of learning about the fundamental physics of HHG which lead to a phenomenological description of HHG by a single atom in terms of a three-step model [8, 9] and quantum theories [10, 11]. Soon it was realized that the high harmonic (HH) light from a dense gas is not well-described by the HH spectrum of a single atom and, additionally, one needs to account for propagation effects of the optical laser and the HH radiation in the macroscopic medium [12, 13]. Nowadays, more and more applications based on HHG have come into focus [see, e.g., Refs. 3, 6, and 7]. To name a few, in atoms, there is the phase measurement of resonant two-photon ionization in helium [24] and intense x-ray generation [25]; for molecules, there is tomographic imaging of orbitals and related methods for structure determination [25–31], and the control of electron localization in photodissociation [31]. Finally, for condensed matter, an attosecond spectroscopy has been developed [32].

Present-day theory of HHG [3, 6, 7] mostly gravitates around HHG from valence electrons and the single-active electron (SAE) approximation [32–34]. Within the SAE approximation and the three-step model of HHG [8, 9], the optical laser tunnel ionizes a valence electron and accelerates it in the continuum. When the optical laser field changes direction, the liberated electron is driven back to rescatter with the parent ion. This may cause the electron to recombine with the ion whereby the excess energy due to the atomic potential and due to the energy gained from the optical laser field is released in terms of a high harmonic of the optical frequency. In HHG each rescattering generates attosecond bursts of radiation. HHG from an ultrashort optical laser pulse leads to an attosecond pulse train [35] in which the individual attosecond pulses are separated by a half cycle period of the optical laser from which a single attosecond burst can be isolated by filtering out the harmonics close to the HHG cutoff (maximum photon energy for a given optical laser intensity) [36]. By optimizing the quantum path of the continuum electron, the HHG cutoff can be increased by a factor of 2.5 [37].

HHG beyond the SAE model with only a single atomic valence state has been studied in a few works. In Refs. 38–41, HHG from a coherent superposition of the ground state and an excited state of an atom was investigated. A shift of the HH spectrum was found amounting to the energy difference between the two states involved with the shifted plateau having a similar height as the one they get for HHG from an electron either in the higher state or the lower energy state alone. Recently, it was both experimentally observed and theoretically explained in [42, 43] that molecular states below the highest occupied molecular orbitals have significant impact on the HHG emission; the authors of [44] investigate in strong-field approximation [11, 45, 46] the influence of quantum interference on HHG spectra of molecules with two optically active electrons from different states. Multiple cutoffs from plasmon-like excitations in ions were predicted in Ref. 44. The role of multielectron effects regarding the recombination probability of the recolliding electron was discussed in Ref. 27 and 48. A two-electron scheme was considered that uses sequential double ionization by an optical laser with a subsequent nonsequential double recombination; in helium it leads to a second plateau with about 12 orders of magnitude lower yield than the pri-
Frequently, the SAE approximation and valence-electron HHG is also applied to two-color HHG where a optical laser is combined with VUV/XUV light from another HHG process. The VUV radiation assists, thereby, in the ionization process leading to an overall increased yield. This principle is evolved further by using attosecond XUV pulses to assist in the HHG process which increases the HHG yield for a certain frequency range by enhancing the contribution from specific quantum orbits. However, there are only few exceptions, e.g., Refs. 27, 48, 60–63, in which many-electron effects are treated for two-color HHG. In Refs. 60 and 61 the influence of other electrons is included implicitly by using a frequency-dependent polarizability for the atoms; the XUV light is found to cause new plateaus to emerge at higher energies, however, with a much lower HHG yield.

Alternatively to HHG sources for XUV light and, particularly, x rays, there are synchrotrons and—most relevant for this work—the newly constructed free electron lasers (FEL) that provide exciting novel opportunities for strong-field physics. For example, the Free Electron Laser in Hamburg (FLASH) offers XUV to soft x-ray radiation that is ideal for studying the valence and shallow core of atoms or the Linac Coherent Light Source (LCLS) which delivers soft and hard x rays suitable for x-ray diffraction with atomic resolution and examining core electrons of most elements in the periodic table. Existing FELs produce light of unprecedented intensity which can be used—among many other applications—to manipulate optical strong-field processes. They operate according to the self-amplification of spontaneous emission (SASE) FEL which produce chaotic light that can be modeled by the partial coherence method (PCM).

The combination of optical light and x rays has proven very beneficial in the past, e.g., to control the interaction of the x rays with optical light in various ways involving atoms and molecules (please see Refs. 77–83 and Refs. therein). Recently, x-ray and optical wave mixing—specifically sum-frequency generation of x rays and optical light—was demonstrated at LCLS by Glover et al. with a conversion efficiency of $3 \times 10^{-7}$ which offers a novel way to probe matter. Such x-ray and optical wave mixing was proposed theoretically by many years ago in the 1970s but only recently it has been observed experimentally due to the construction of FELs with unprecedented x-ray intensity. The experiment of Glover et al. is a very encouraging motivation of theoretical research on x-ray boosted HHG. Within the SAE, HHG from core electrons of neon that are ionized by x rays was studied theoretically. A single-atom efficiency comparable with conventional HHG was found and attosecond pulses were isolated from the x-ray-boosted HHG spectra.

In this work, I would like to develop in detail the theory of HHG by an optical laser with an additional resonant excitation (or even Rabi flopping) in intense x rays. Specifically, I will focus on the case of continuous-wave (CW) light, first, and a CW optical laser in combination with arbitrary x-ray pulses, second. The principal idea is sketched in Fig. 1. In the parlance of the three-step model, the x-ray-boosted HHG process proceeds as follows: first, the atomic valence is tunnel ionized; second, the liberated electron propagates freely in the electric field of the optical laser; third, the direction of the optical laser field is reversed and the electron is driven back to the ion and eventually recombines with it emitting HHG radiation. The excursion time of the electron from the ion is approximately $1\text{fs}$ for typical 800 nm laser light. During this time, one can manipulate the ion such that the returning electron sees the altered ion as depicted in Fig. 1. Then, the emitted HHG radiation bears the signature of the change. Perfectly suited for this modification during the propagation step is x-ray excitation of an inner-shell electron to the valence shell. The recombination of the returning electron with the core hole leads to a large increase of the energy of the emitted HHG light as the energy of the x-ray photons is added to the unmodified HHG spectrum. A prerequisite for this to work certainly is that the core hole is not too short lived, i.e., it should not decay before the electron returns. In Ref. 62 we examined HHG in krypton atoms where tunnel ionization leads to 4p vacancies. The XUV light is tuned to the $3d \rightarrow 4p$ resonance in the cation which leads to a second high-yield HHG plateau that is shifted to higher energies by the XUV photon energy. Similarly, we studied x-ray-boosted HHG for neon 2p vacancies where x rays were tuned to the $1s \rightarrow 2p$ resonance in the cation. If the x rays are very intense, even Rabi flopping of the core electron is possible. Such Rabi oscillations have been investigated in neon atoms (without optical laser).

Our scheme offers new prospects for HHG involving core electrons. However, if one is only interested in an extension of the HHG cutoff into the kiloelectronvolt regime, one may use conventional HHG that is laboratory size and valence-electron-based. In this case, the optical laser intensity needs to be high $\sim 10^{15}$ W/cm$^2$ and its wavelength should be in the midinfrared instead of the NIR. The longer wavelength, however, reduces HHG efficiency due to longer continuum propagation and thus enlarged spreading of the wave packet. Additionally, such a high optical laser intensity increases the ionization rate substantially leading to large electron background that causes phase mismatching. A good HHG yield can, nonetheless, be obtained by a judicious choice of the gas pressure.

The paper is structured as follows. The theory of HHG in the presence of a CW optical laser and X-ray x rays is developed in Sec. II A. I discuss the wavefunction ansatz [Sec. II A], the Hamiltonian [Sec. II B], the equations of motion (EOMs) [Sec. II C], the time-dependent dipole transition matrix element [Sec. II D], and the HHG spectrum [Sec. II E].
arbitrary x-ray pulses is derived in Sec. III. I present the Hamiltonian, the wave function ansatz, and the EOMs [Sec. III A], decouple and integrate the EOMs [Sec. III B], and calculated the time-dependent electric dipole moment and the HHG spectrum [Sec. III C]. Finally, conclusions are drawn in Sec. IV. In the Appendix, I discuss the harmonic photon number spectrum (HPNS). All equations are formulated in atomic units \([104]\).

II. HIGH HARMONIC GENERATION WITH CONTINUOUS WAVE X RAYS

I consider the HHG process for an atom in the two-color light of an optical laser and intense x-rays. The optical laser-only problem was treated by Lewenstein et al. \([11]\) for a valence electron in SAE \([33, 34]\). Here I consider also a core electron in addition to the valence electron [Fig. 1]. The combined treatment of HHG and x-rays, which induce Rabi flopping \([73, 89–98]\) in the residual ion, represents a genuine two-active-electron problem.

A. Symmetry and basis states

The theory is developed here for a closed-shell atom with a spin-singlet ground state. I set out from a non-relativistic, independent-electron solution of the atomic electronic structure of Hartree-Fock-Slater type \([105, 106]\) with spherical averaging of the one-electron potential leading to a central potential as described by Herman and Skillman \([77, 107]\). Thus, for an isolated atom without light fields, atomic orbitals with the same principle and angular quantum numbers are degenerate with respect to the magnetic quantum number \([108]\). As no spin-dependent terms are considered in the Hamiltonian for the atom in the optical and x-ray light, all quantities can be expressed in terms of spatial atomic orbitals. Observables, however, need to be multiplied by a factor of 2 in order to account for the two electrons per spatial orbital.

The essential states relevant to describe HHG in two-color light are deduced as follows. I assume that the polarization vectors of the optical laser \(\vec{e}_l\) and the x rays \(\vec{e}_X\) are linearly polarized along the z axis \(\vec{e}_z\), i.e., \(\vec{e}_l = \vec{e}_X = \vec{e}_z\) holds. In this case, the magnetic quantum number is conserved in the interactions in the absence of spin-orbit coupling which influences strong-field ionization of heavier atoms \([78, 109–111]\). However, strong optical fields align the atomic orbitals along the linear optical laser polarization axis. I will not treat spin-orbit coupling in what follows and assume that the magnetic quantum number is a good quantum number. Hence, one-electron states of relevance to the problem are the valence states \(|a; m\rangle\) with magnetic quantum numbers \(m \in \mathcal{M}_a\) with \(\mathcal{M}_a = \{−l_a, \ldots, l_a\}\) for principal \(n_a\) quantum number and angular momentum \(l_a\) quantum numbers. The core states for principal \(n_c\) and angular momentum \(l_c\) quantum numbers are \(|c; m\rangle\) with \(m \in \mathcal{M}_c\) for \(\mathcal{M}_c = \{−l_c, \ldots, l_c\}\). Continuum states are approximated as free-electron states, i.e., plane waves [see Eq. \(\text{(1)}\)], and are denoted by \(|\vec{k}\rangle\) for all \(\vec{k} \in \mathbb{R}^3\) \([108]\). Specifically, I use momentum-normalized free-electron wave functions

\[
|\vec{r}\rangle|\vec{k}\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}},
\]

with the position operator \(|\vec{r}\rangle\). Taking \(|\vec{k}\rangle\) for the continuum electrons implies that one makes the strong-field approximation (SFA) \([11, 45, 46]\), i.e., I neglect the impact of the Coulomb potential on continuum electrons. Only electrons with \(m \in \mathcal{M}\) for \(\mathcal{M} = \mathcal{M}_a \cap \mathcal{M}_c\) are amenable to a core excitation by the x rays in electric dipole approximation. The HHG process from states \(|a; m\rangle\) with \(m \in \mathcal{M}_a\), \(\mathcal{M}_c\), is described within the SAE approximation \([33, 34]\) following Lewenstein et al. \([11]\) because no core electrons couple to these valence vacancies in electric dipole approximation. Hence there are \(N/2 = \#\mathcal{M}_a + \#\mathcal{M}\) relevant states in the system occupied by \(N\) electrons. As tunnel ionization of valence electrons takes predominantly place along the linear optical laser polarization axis \([99, 100]\), mostly the valence state along the polarization axis is depleted which has a magnetic quantum number \(m = 0\) which then couples via x rays to core electrons with \(m = 0\). Furthermore, the matrix element that is responsible for HHG in the Lewenstein model, \(\langle \vec{k} | e \vec{e}_L | a; m\rangle\) with the electric dipole operator \(e\), vanishes for \(m \neq 0\) and \(s\) and \(p\) valence states from a central potential \([112]\). There may, however, be a weak influence of the valence states with \(m \neq 0\), if non-plane-wave continuum states are used and electron correlations are considered \([113]\). Consequently, I use only \(m = 0\) orbitals in the valence and the core in what follows and I drop the magnetic quantum number in the notation throughout \([62, 63]\).

To describe the quantum dynamics of resonant x-ray excitation in the course of HHG, one needs to consider two active electrons: one in the valence or continuum and one in the core or valence. The spatial one-
electron states are occupied by two electrons each with opposite spin. To facilitate a core excitation, the spin of the valence vacancy and the core electron need to be the same as the interaction with the x rays is spin independent. Whether the electron with spin up or spin down in the valence is ionized does not change the result in either case and thus it is sufficient to consider only one case \[104\]. In other words, one needs to consider an effective two-electron system formed by one electron from the valence and one electron from the core with the same spin, i.e., the system has triplet spin. The total two-electron state can be factored into a spin part and an spatial part. Due to the Pauli exclusion principle for indistinguishable electrons and the fact that the spin part is symmetric with respect to electron exchange, the spatial part is antisymmetric \[92, 104\]. I use three different classes of spatial two-electron basis states. First, the ground state of the two-electron system is given by the Slater determinant

\[ |a c\rangle = \frac{1}{\sqrt{2}} \left[ |a\rangle \otimes |c\rangle - |c\rangle \otimes |a\rangle \right]. \tag{2} \]

This is a normalized linear combination of tensorial products of the two respective one-electron states which is antisymmetric with respect to electron exchange which includes statistical electron correlations between electrons in them \[92, 104\]. As core states are energetically well-separated from valence states, electron correlations between core and valence states are small and neglecting them has a minor influence on excitation and ionization energies which is referred to as core-valence separation \[114, 115\]. Second, the valence-ionized states with one electron in the continuum for all \(\vec{k} \in \mathbb{R}^3\) and one electron in the core state are

\[ |\vec{k} c\rangle = \frac{1}{\sqrt{2}} \left[ |\vec{k}\rangle \otimes |c\rangle - |c\rangle \otimes |\vec{k}\rangle \right]. \tag{3} \]

Third, the core-ionized states with one electron in the continuum and one electron in the valence state are

\[ |\vec{k} a\rangle = \frac{1}{\sqrt{2}} \left[ |\vec{k}\rangle \otimes |a\rangle - |a\rangle \otimes |\vec{k}\rangle \right]. \tag{4} \]

The three classes of basis states \((2), (3), \text{ and } (4)\) are mutually orthonormal.

I apply the three assumptions of Lewenstein et al. \[11\] in a somewhat modified way:

(a) The system is completely described by the three classes of states: the ground state \(|a c\rangle\), the valence-excited states \(|\vec{k} c\rangle\), and the core-excited states \(|\vec{k} a\rangle\).

(b) The depopulation of the ground state by optical laser-induced tunnel ionization and valence ionization by x rays is represented by a decay rate \(\Gamma_0\).

(c) The continuum electron is described as a free particle; the influence of the Coulomb potential of the residual ion can be omitted. Specifically, also the overlap between the free-electron wavefunctions and the ground-state state is neglected.

Further, I need to add the following clauses for the interaction of the x rays with the ion:

(d) The effect of the x rays—with energies in resonance with the level spacing—is confined to the two-level system consisting of \(|\vec{k} c\rangle\) and \(|\vec{k} a\rangle\) in the ion where one electron is excited from \(c \rightarrow a\) or, for ultraintense x rays, Rabi flops \[73, 89, 98\] between the two levels. The other bound electrons and the continuum electron are not influenced by the x rays apart from (b) and (e).

(e) Core hole decay and valence ionization by the optical laser and the x rays are taken into account in terms of phenomenological decay rates \(\Gamma_0\) and \(\Gamma_c\) for \(|\vec{k} c\rangle\) and \(|\vec{k} a\rangle\), respectively, which are independent of \(\vec{k}\).

Point (d) is justified by the fact that the x rays oscillate very rapidly and cause only a small ponderomotive potential \[112\]. Should the second electron be excited to the valence vacancy, tunnel ionization is still much smaller in (e) than for the neutral atom as the ionization potential of the ion is significantly larger than the ionization potential of the neutral atom. Thus, optical laser ionization of the second electron is strongly suppressed due to the exponential dependence of the tunnel rate on the ionization potential \[99, 100\]. I treat the interaction with the x rays incoherently via decay rates in point (e) in contrast to the coherent formulation of the resonant x-ray absorption in point (d).

The phenomenological decay rates of (d) are determined following Ref. \[88\]. I assume approximately monochromatic x rays, i.e., the photoabsorption cross sections \(\sigma_0\), \(\sigma_a\), and \(\sigma_c\) for one-photon absorption by the atom in the ground, valence-ionized, and core-ionized state, respectively, can be obtained with Refs. \[116\] and \[117\] and are approximately constant over the bandwidth of the x-ray pulse for a central angular frequency \(\omega_X\). Further, the x-ray intensity is represented by \(I_X(t)\) implying an x-ray photon flux of \(J_X(t) \approx \frac{I_X(t)}{\omega_X}\). With the optical-laser-induced decay widths \(\Gamma_{L,0}(t)\), \(\Gamma_{L,a}(t)\) and \(\Gamma_{L,c}(t)\) \[99, 100\], the instantaneous phenomenological decay widths of the atom in the three basis states are then given by

\[ \Gamma_i'(t) = \Gamma_{L,i}(t) + \theta(t) \sigma_i J_X(t) + \delta_{i,c} \gamma_c, \quad \text{for } i \in \{0, a, c\} \tag{5} \]

with the intrinsic decay width \(\gamma_c\) from Auger and radiative decay of the core-ionized state \[64, 118\] and the Heaviside step function \(\theta\) and \(\theta(0) = \frac{1}{2}\) \[119\]. The factor \(\theta(t)\) emphasizes that the x-ray pulse is zero for \(t < 0\). For CW light, I determine decay rates by
averaging Eq. (5) over an optical laser cycle

\[ \Gamma_t = \frac{1}{T_L} \int_0^{T_L} \Gamma'_t(t) \, dt'. \tag{6} \]

The degrees of destruction of the system by the optical laser, the x rays, and decay processes up to time \( t \) follow from Eq. (5) and are quantified by the factor 88:

\[ F_i(t) = \theta(t) \int_0^t \Gamma'_i(t') \, dt'. \tag{7} \]

B. Hamiltonian

The total two-electron Hamiltonian of the atom in two-color light (optical laser and x rays) reads

\[ \hat{H} = \hat{H}_A + \hat{H}_L + \hat{H}_X; \tag{8} \]

it consists of three parts: the atomic electronic structure \( \hat{H}_A \), the interaction with the optical laser \( \hat{H}_L \), and the interaction with the x rays \( \hat{H}_X \).

The one-electron Hamiltonian for the atomic electronic structure reads

\[ \hat{h}_A = |a\rangle \varepsilon_a \langle a| + |c\rangle \varepsilon_c \langle c| + \int \frac{1}{2} \langle \vec{k}\rangle \frac{\hbar^2}{2} \langle \vec{k}| \, d^3k, \tag{9} \]

with the energies \( \varepsilon_a, \varepsilon_c \), and \( \frac{\hbar^2}{2} \) of the one-electron states. The two-electron atomic electronic structure Hamiltonian follows as

\[ \hat{H}_A = \hat{h}_A \otimes \mathbb{1} + \mathbb{1} \otimes \hat{h}_A - i \langle a c| \frac{\Gamma_A}{2} \langle a c| \]
\[- i \int r \left| \langle \vec{k}\rangle \frac{\Gamma_A}{2} \langle \vec{k}|c\rangle + \langle \vec{k}\rangle \frac{\Gamma_A}{2} \langle \vec{k}|a\rangle \right| \, d^3k, \tag{10} \]

with the unity operator for the one-electron Hilbert space \( \mathbb{1} \).

The interaction of one electron with the optical laser field is described in electric dipole approximation in length form

\[ \hat{h}_L = E_L(t) \int_{\mathbb{R}^3} \left| \langle \vec{k}\rangle \langle \vec{k}| \hat{e}_L \cdot \vec{r} \langle a| \langle a| + h.c. \right| \, d^3k \tag{11} \]
\[ + E_L(t) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left| \langle \vec{k}\rangle \langle \vec{k}| \hat{e}_L \cdot \vec{r} \langle \vec{k}'\rangle \langle \vec{k}'| \right| \, d^3k \, d^3k', \tag{12} \]

using the electric field of the optical laser

\[ E_L(t) = E_{\text{OL}} \cos(\omega_L t), \tag{12} \]

with the peak amplitude \( E_{\text{OL}} \) and the optical laser angular frequency \( \omega_L \). The two-electron Hamiltonian for the interaction with the optical laser reads

\[ \hat{H}_L = \hat{h}_L \otimes \mathbb{1} + \mathbb{1} \otimes \hat{h}_L. \tag{13} \]

The optical laser couples only the valence electron to the continuum because the coupling of the core electron to the continuum is negligible. The influence of the optical laser on continuum electrons is represented by the last term on the right-hand side of Eq. (11).

The interaction of one electron with the x-ray radiation is described in electric dipole approximation in length form

\[ \hat{h}_X = E_X(t) \left| \langle c| \langle \vec{e}_X \cdot \vec{r} | a \rangle \langle a| + h.c. \right|, \tag{14} \]

for the x-ray electric field

\[ E_X(t) = E_{0X} \cos(\omega_X t) = \frac{E_{0X}}{2} [e^{i \omega_X t} + e^{-i \omega_X t}], \tag{15} \]

with the peak electric field \( E_{0X} \) and the x-ray angular frequency \( \omega_X \). The two-electron Hamiltonian for the x-ray interaction follows similarly as in Eq. (13) to

\[ \hat{H}_X = \hat{h}_X \otimes \mathbb{1} + \mathbb{1} \otimes \hat{h}_X. \tag{16} \]

C. Equations of motion

I make the following ansatz for the two-electron wavepacket

\[ |\Psi, t\rangle = a_0(t) e^{-i E_0 t} |a c\rangle + \int_{\mathbb{R}^3} b_a(\vec{k}, t) e^{-i E_0 t} |\vec{k} a\rangle + b_c(\vec{k}, t) e^{-i (E_0 + \omega_X) t} |\vec{k} a\rangle \, d^3k, \tag{17} \]

The index on the amplitudes \( b_a(\vec{k}, t) \) and \( b_c(\vec{k}, t) \) indicates which orbital contains the hole and \( \varepsilon_a + \varepsilon_c \). The phase factors in the ansatz (17) are chosen such that the equations of motion (EOMs) are simplified the most, that fast oscillations are separated, and thus the expansion coefficients vary comparatively slowly. I insert \( |\Psi, t\rangle \) into the time-dependent Schrödinger equation

\[ i \frac{\partial}{\partial t} |\Psi, t\rangle = \hat{H} |\Psi, t\rangle \tag{18} \]

with the Hamiltonian 88 and project onto the three classes of basis states which yields EOMs for the involved coefficients.

First, I obtain the EOM for the ground-state population by projecting onto the ground state \( |a c\rangle \) yielding

\[ \frac{d}{dt} a_0(t) = - \frac{E_{0X}}{2} a_0(t) - i \int_{\mathbb{R}^3} b_a(\vec{k}, t) \langle a| \hat{h}_L |\vec{k}\rangle \, d^3k. \tag{19} \]

The second term on the right-hand side can be neglected entirely for low ground-state destruction by the optical laser 11. For a higher destruction rate, the second term can be neglected as well, if the influence of the optical laser is included in \( \Gamma_0 \) 88.
Second, projecting onto $|\vec{k}c\rangle$ for all $\vec{k} \in \mathbb{R}^3$ gives the EOMs for the recombination of the continuum electron with the valence hole which is coupled to core electrons

$$\frac{\partial}{\partial t} b_a(\vec{k},t) = -\frac{i}{2} (\vec{k}^2 - \delta + 2 I_p - i \Gamma_c) b_a(\vec{k},t)$$

$$- i \int_{\mathbb{R}^3} b_a(\vec{k}' , t) \langle \vec{k}' | \hat{h}_{L} | \vec{k} \rangle \, d^3k'$$

$$- i b_a(\vec{k}, t) \langle c | \hat{h}_{X,RWA} | a \rangle$$

$$- i a_0(t) \langle \vec{k}' | \hat{h}_{L} | a \rangle \, .$$

(20)

Here, I make the rotating wave approximation $\hat{h}_X e^{-i\omega_X t} \approx \hat{h}_{X,RWA}$ [93]. Following Ref. 62, I introduce the energy $I_p = -\frac{1}{2}(\varepsilon_a + \varepsilon_c + \omega_c) = -\varepsilon_a + \frac{\hbar^2}{2m}$ and the detuning of the x-ray photon energy from the energy difference between the core and valence levels $\delta = \varepsilon_a - \varepsilon_c - \omega_X$. For zero detuning, $I_p$ corresponds to the valence IP of the atom, but is shifted to higher (lower) values, if $\omega_X$ is smaller (larger) than the level spacing.

Third, projecting onto $|\vec{k}a\rangle$ for all $\vec{k} \in \mathbb{R}^3$ gives the EOMs for the recombination of the continuum electron with the core hole

$$\frac{\partial}{\partial t} b_a(\vec{k},t) = -\frac{i}{2} (\vec{k}^2 + \delta + 2 I_p - i \Gamma_c) b_a(\vec{k},t)$$

$$- i \int_{\mathbb{R}^3} b_a(\vec{k}' , t) \langle \vec{k}' | \hat{h}_{L} | \vec{k} \rangle \, d^3k'$$

(21)

$$- i b_a(\vec{k}, t) \langle a | \hat{h}_{X,RWA} | c \rangle \, .$$

In order to evaluate the matrix elements in the EOMs that involve continuum electrons, I use the momentum-normalized free-electron wave functions of Eq. 11. Specifically, $\langle \vec{k} | \hat{h}_{L} | a \rangle = E_{L}(t) \varphi_{L,\vec{k},a}$ with $\varphi_{L,\vec{k},a} = \langle \vec{k} | \vec{e}_L \cdot \vec{r} | a \rangle$. The optical laser-induced continuum-valence transitions are caused by

$$\langle \vec{k} | \hat{h}_{L} | \vec{k}' \rangle = E_{L}(t) (-i) \frac{\partial}{\partial k_z} \delta^3(\vec{k}' - \vec{k}) ,$$

(22)

using the representation

$$\int_{-\infty}^{\infty} e^{i\Omega t} \, dt = 2\pi \delta(\Omega) \, ,$$

(23)

for the Dirac $\delta$ distribution [119]. Further,

$$\langle c | \hat{h}_{X,RWA} | a \rangle = \frac{E_{OX}}{2} \varphi_{X,c,a} = \frac{R_{OX}}{2}$$

(24)

for $\varphi_{X,c,a} = \langle c | \vec{e}_X \cdot \vec{r} | a \rangle$ and the Rabi angular frequency $R_{OX}$ [93]. I choose the spatial matrix element $\varphi_{X,c,a}$ and thus $R_{OX}$ to be real which is feasible due to the central potential used to determine atomic orbitals [77].

I rewrite Eqs. (20) and (21) as a vector equation defining the amplitudes

$$\vec{b}(\vec{k},t) = (b_a(\vec{k},t), b_c(\vec{k},t))^T$$

and the complex symmetric Rabi matrix

$$R = \begin{pmatrix} -\delta - i \Gamma_a & R_{OX} \\ R_{OX} & -\delta - i \Gamma_c \end{pmatrix} \, .$$

(26)

This yields the combined equations

$$\frac{\partial}{\partial t} \vec{b}(\vec{k},t) = -\frac{i}{2} (R + (\vec{k}^2 + 2 I_p) \mathbb{1}) \vec{b}(\vec{k},t)$$

$$+ E_L(t) \frac{\partial}{\partial k_z} \vec{b}(\vec{k},t)$$

$$- i a_0(t) E_L(t) \varphi_{L,\vec{k},a} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \, .$$

(27)

I determine the matrix of eigenvalues of $R$ as

$$A = \text{diag}(\lambda_+, \lambda_-)$$

(28)

with the eigenvalues

$$\lambda_{\pm} = -\frac{i}{2} (\Gamma_a + \Gamma_c) \pm \mu \, ,$$

(29)

and the complex Rabi frequency [93]:

$$\mu = \sqrt{\left[\delta + \frac{i}{2} (\Gamma_a - \Gamma_c)\right]^2 + R_{OX}^2} \, .$$

(30)

The matrix of eigenvectors of $R$ is $U$. With the eigenvectors and eigenvalues, I transform to the basis of x-ray-dressed states. I find the new amplitudes as

$$\vec{\beta}(\vec{k},t) \equiv \begin{pmatrix} \beta_+(\vec{k},t) \\ \beta_- (\vec{k},t) \end{pmatrix} = \begin{pmatrix} \mu \\ -i \Gamma_c \end{pmatrix} \, .$$

(31)

and the valence ionization fraction

$$\vec{w} = \begin{pmatrix} w_+ \\ w_- \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \, .$$

(32)

I recast Eq. (27) into

$$\frac{\partial}{\partial t} \vec{\beta}(\vec{k},t) = -\frac{i}{2} \left( \vec{A} + (\vec{k}^2 + 2 I_p) \mathbb{1} \right) \vec{\beta}(\vec{k},t)$$

$$+ E_L(t) \frac{\partial}{\partial k_z} \vec{\beta}(\vec{k},t)$$

$$- i a_0(t) E_L(t) \varphi_{L,\vec{k},a} \vec{w} \, ,$$

(33)

because $U$ depends neither on $\vec{k}$ nor on $t$.

Equation (33) is a system of two decoupled partial differential equations. To transform them into two ordinary differential equations, I introduce the vector potential [113, 120] of the optical laser:

$$\vec{A}_L(t) = - \int_{-\infty}^{t} E_L(t') \vec{e}_L e^{-\mu |t'|} \, dt'$$

$$= -\frac{E_{OL}}{\omega_L} \sin(\omega_L t) \vec{e}_L \, ,$$

(34)
The two-electron electric dipole operator \( \hat{\mathbf{e}} \) of the emitted light which is parallel to \( \hat{\mathbf{e}} \) can be integrated exactly \([119]\) yielding

\[
\frac{d}{dt} \tilde{\beta}(\vec{k}, t') = -\frac{i}{2} \left( A + \frac{1}{2} (\vec{k} - \vec{A}_L(t) + \vec{A}_L(t'))^2 \right) + 2|\vec{p}| \mathbf{1} \tilde{\beta}(\vec{k} - \vec{A}_L(t) + \vec{A}_L(t'), t') - i a_0(t) E_L(t') \varphi_{L, \vec{k} - \vec{A}_L(t) + \vec{A}_L(t')} e^{i \vec{q} \cdot \vec{k}}.
\]

This is an ordinary first-order differential equation which can be integrated exactly \([119]\) yielding

\[
\beta_{\pm}(\vec{k}, t) = -i w_{\pm} \int_0^t a_0(t') E_L(t') \varphi_{L, \vec{k} - \vec{A}_L(t) + \vec{A}_L(t')} e^{i \vec{q} \cdot \vec{k}} \times e^{-\frac{i}{2} \int_{t'}^t (\vec{k} - \vec{A}_L(t) + \vec{A}_L(t'))^2 dt''} \times e^{-i(\frac{\lambda}{2} + \xi r)(t-t')} \, dt' ,
\]

by letting \( t' = t \) because then \( \vec{k'} = \vec{k} \) and thus \( \beta_{\pm}(\vec{k}, t) = \beta_{\pm}(\vec{k'}, t') \). Next, one can transform back to the amplitudes of the bare states via \( \tilde{\beta}(\vec{k}, t) = U \tilde{\beta}(\vec{k}, t) \).

D. The time-dependent electric dipole transition matrix element

The emission of light in electric dipole approximation is governed by the electric dipole operator which reads for one-electron states

\[
\hat{d} = \int_{\mathbb{R}^3} \left[ |a\rangle \langle a| \hat{\mathbf{e}}_H \cdot \hat{r} |\vec{k}\rangle \langle \vec{k}| + |c\rangle \langle c| \hat{\mathbf{e}}_H \cdot \hat{r} |\vec{k}\rangle \langle \vec{k}| \right] d^3k + \text{h.c.} .
\]

It is defined such that it describes the recombination of a continuum electron with the valence and the core hole where I omit continuum-continuum transitions \([11, 13, 18]\). Here, \( \hat{\mathbf{e}}_H \) is the linear polarization vector of the emitted light which is parallel to \( \hat{\mathbf{e}}_L \). The one-electron electric dipole transition matrix elements are \( \varphi_{H, a \vec{k}} = \langle a| \hat{\mathbf{e}}_H \cdot \hat{r} |\vec{k}\rangle \) and \( \varphi_{H, c \vec{k}} = \langle c| \hat{\mathbf{e}}_H \cdot \hat{r} |\vec{k}\rangle \). The two-electron electric dipole operator \( \hat{D} \) is defined in analogy to Eq. \([13]\) by

\[
\hat{D} = \hat{d} \otimes \mathbf{1} + \mathbf{1} \otimes \hat{d} .
\]

High harmonic emission is determined by the dipole transition matrix element between the atomic ground state and the valence and core-excited states, respectively. Namely, it is expressed by \( \mathcal{D}(t) = \langle \Psi_0, t | \hat{D} | \Psi_v, t \rangle \) where \( \hat{D} \) is the two-electron electric dipole operator, \( |\Psi_0, t\rangle \) is the ground-state part of the wavepacket \([17]\) at time \( t \) and \( |\Psi_v, t\rangle \) is the continuum part \([13]\). Then, the time-dependent dipole transition matrix element follows from Eqs. \([17]\) and \([35]\) to

\[
\mathcal{D}(t) = \langle \Psi_0, t | \hat{D} | \Psi_v, t \rangle = a_0^*(t) \int_{\mathbb{R}^3} \varphi_{H, a \vec{k}}^* b_{a}(\vec{k}, t) + \varphi_{H, c \vec{k}} b_{c}(\vec{k}, t) e^{-i \omega \tau t} \, d^3k = 0 .
\]

The dipole components are

\[
\mathcal{D}_{ij}(t) = U_{ij} e^{-i \delta_{i, c} \omega \tau t} a_0^*(t) \int_{\mathbb{R}^3} \varphi_{H, \vec{k} + \vec{A}_L(t)} \bar{\beta}_j(\vec{k}, t) d^3k
\]

\[
= -i U_{ij} w_j e^{-i \delta_{i, c} \omega \tau t} a^*(t) \int_0^t a(t') \times \varphi_{H, \vec{k} + \vec{A}_L(t')} \bar{\beta}_j(\vec{k}, t) d^3k
\]

\[
\times \varphi_{H, \vec{k} + \vec{A}_L(t')} \bar{\beta}_j(\vec{k}, t) d^3\vec{k} ,
\]

by letting \( t' = t \) because then \( \vec{k'} = \vec{k} \) and thus \( \beta_{\pm} = \beta_{\pm}(\vec{k}, t') \). Next, one can transform back to the amplitudes of the bare states via \( \tilde{\beta}(\vec{k}, t) = U \tilde{\beta}(\vec{k}, t) \).

Equation \([40]\) can be understood easily term by term \([11]\). Here, \( w_j \varphi_{H, \vec{k} + \vec{A}_L(t')} \) is the fraction of valence ionization at time \( t' \) due to tunneling in the optical laser field; during propagation of the free electron from time \( t' \) to \( t \) in the optical laser field, the electron acquires the phase \( e^{-i S_j(\vec{p}, t', t)} \); the emission of HHG light at time \( t \) due to recombination of the continuum electron with the state \( i \in \{ a, c \} \) is governed by \( \varphi_{H, \vec{k} + \vec{A}_L(t')} ^* \); the shift of the HHG spectrum by \( \omega \tau \) for a recombination with the core is given by \( e^{-i \delta_{i, c} \omega \tau t} \); finally, \( U_{ij} \) is the transformation back to the bare-state basis. The action \([11]\) differs from the optical laser-only case \([11]\) by the summand \( \frac{d}{dt} (t-t') \) which represents the splitting of the core and valence states due to x-ray dressing.

To calculate \( \mathcal{D}(t) \) [Eq. \([29]\)], I make the saddle point approximation for the integration over the canonical momentum \( \vec{p} \) \([119]\). The stationary points of \( S_j(\vec{p}, t, t') \) [Eq. \([41]\)] are determined from \( \hat{\nabla}_p S_j(\vec{p}, t, t') = 0 \) and are given by the difference of the positions of the electron at time \( t \) and \( t' \) \([11]\). This suggests to introduce the new variable \( \tau = t-t' \), the excursion time of the continuum electron. At the stationary points, the canonical momentum satisfies

\[
\vec{p}_m(t, \tau) = \frac{E_{0L}}{\omega_L \tau} \hat{\mathbf{e}}_L \left[ \cos(\omega_L t) - \cos(\omega_L (t - \tau)) \right] ;
\]

\[\vec{p}_m(t, \tau) = \frac{E_{0L}}{\omega_L \tau} \hat{\mathbf{e}}_L \left[ \cos(\omega_L t) - \cos(\omega_L (t - \tau)) \right] ;\]
and the quasiclassical action is
\[ S_{st,j}(t, \tau) = \left( \frac{\lambda_j}{2} + I_P + U_P \right) \tau - 2 \frac{\omega_L}{\omega_L^*} \left( 1 - \cos(\omega_L \tau) \right) \] (43)
with the ponderomotive potential of the optical laser \( U_P = \frac{E_p^2}{2e} \) and [122]:
\[ C(\tau) = \sin(\omega_L \tau) - \frac{4}{\omega_L \tau} \sin^2 \left( \omega_L \frac{\tau}{2} \right) \] (44)
The multiple integral (40) is then replaced by a single integral over the excursion time
\[ \mathcal{D}_{ij}(t) = -i U_{ij} w_j e^{-i \delta_{j,\ell}^* \omega_{X} t} a_0^* (t) \int_{0}^{\infty} \sqrt{\frac{(2\pi)^2}{\tau}} \] (45)
\[ \times a_0(t - \tau) A_{st,i}(t, \tau) e^{-i S_{st,j}(t, \tau)} d\tau , \]
upon extending the integration over \( \tau \) to infinity and introducing the atomic terms at the stationary points of the quasiclassical action
\[ A_{st,i}(t, \tau) = E_L(t - \tau) \psi_{H,\mathbb{R}^0}^*(t, \tau) + A_L(t) \] (46)
\[ \times \psi_{H,\mathbb{R}^0}(t, \tau) + A_L(t) \] (47)
The factor \( \sqrt{\frac{(2\pi)^2}{\tau}} \) stems from the remaining integration in the saddle point approximation [119]. The dipole components without x rays are obtained from Eq. (45) by the replacements \( U_{ij} w_j e^{-i \delta_{j,\ell}^* \omega_{X} t} \rightarrow 1 \) and in Eq. (43) the replacement \( \lambda_\pm \rightarrow -\delta - i \Gamma_a \). Then the resulting equation becomes the same as Eq. (13) of Lewenstein et al. [11] apart from a few inessential sign changes, the decay width and the additional ground-state amplitudes here.
The atomic terms (46) are periodic with the optical laser oscillation \( T_L = \frac{2\pi}{\omega_L} \) and can thus be expanded in a Fourier series [119, 123]:
\[ A_{st,i}(t, \tau) = \sum_{M=-\infty}^{\infty} b_{M,i}(\tau) e^{-i (2M + \delta_{j,\ell}) \omega_L t} , \] (47)
with the coefficients
\[ b_{M,i}(\tau) = \frac{1}{T_L} \int_{0}^{T_L} A_{st,i}(t, \tau) e^{i (2M + \delta_{j,\ell}) \omega_L t} dt . \] (48)
The \( b_{M,i}(\tau) \) reflect the properties of the atomic states. The definition of the series and the coefficients incorporates the properties of the atomic states: the odd and even Fourier coefficients—restricted to an integration range from 0 to \( T_L/2 \)—can be examined by substituting \( t \rightarrow t + \frac{T_L}{2} \). Using the properties of Eqs. (12), (33), (42), and (40) under this replacement I find that the argument of the dipole matrix elements is negated.

To investigate the impact on the atomic dipole matrix elements, I express them with Eq. (1) and the spatial atomic orbital \( \varphi_i(\vec{r}) = \langle \vec{r} | i \rangle \) as follows
\[ \varphi_{j,\vec{k},i} = \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} e^{-i \vec{k} \cdot \vec{r}} \varphi_i(\vec{r}) d^3r . \] (49)
The central symmetry of the atomic potential implies that the orbitals are parity eigenstates [108] and a space inversion yields \( \varphi_{j,\vec{k},i} = \pm \varphi_{j,\vec{k},i} \) depending on the parity of \( |i\rangle \). Going back to Eq. (18), I find that for \( i = a \), the even Fourier coefficients vanish. As \( a \rightarrow c \) is a dipole transition, the states \( |a\rangle \) and \( |c\rangle \) have opposite parity. Therefore, for \( i = c \) the odd coefficients are zero. Following Ref. [112] Eq. (49) can be decomposed into a sum over radial integrals times spherical harmonics times Clebsch-Gordan coefficients.

E. High-order harmonic generation spectrum

1. Low ground-state depletion

First, I consider the HHG spectrum for low ground state depletion by tunnel ionization due to the optical laser and low valence ionization by the x rays, setting \( \Gamma_0 = 0 \). In this case, \( a_0(t) \approx 1 \) for all times \( t \) and Eq. (19) can be neglected altogether. As I assume a CW optical laser [12], the atomic terms [45] are periodic in \( t \) with period \( T_L \). This implies that the dipole components [Eq. (45) without the \( \omega_{X}\)-dependent term are also periodic with period \( T_L \) (in general \( \omega_{X} \) is not a harmonic of \( \omega_L \)). Consequently, \( e^{i \delta_{j,\ell} \omega_{X} t} \mathcal{D}_{ij}(t) \) can be expanded into a Fourier series in analogy to Eqs. (47) and (48). The even (odd) Fourier components are present when the even (odd) Fourier components of the Fourier series of the atomic terms are nonzero.

I simplify \( e^{i \delta_{j,\ell} \omega_{X} t} \mathcal{D}_{ij}(t) \) [Eq. (45)] by expanding the exponential of the quasiclassical action by decomposing the \( t \)-dependent part of \( e^{-i S_{st,j}(t, \tau)} \) in terms of the Jacobi-Anger expansion
\[ e^{-i \ell \cos \theta} = \sum_{m=-\infty}^{\infty} (-i)^m e^{-im \theta} J_m(z) , \] (50)
with the Bessel functions \( J_m(z) \) [119]. The general expression for the Fourier coefficients of the dipole compo-
lated by


de, where the integration over $t'$ leads to $\delta_{K-M,N}$ and I translated by $M \rightarrow K - M$. Further, I define

$$F_{0,j}(\tau) = \frac{\lambda_j}{2} \tau + F'_0(\tau)$$

 $$= \left( \frac{\lambda_j}{2} + I_p + U_p \right) \tau - 2 \frac{U_p}{\omega_L} \left( 1 - \cos(\omega_L \tau) \right).$$

Inspecting Eqs. (51) and (52), I find that there is a $e^{-i\frac{\lambda_j}{2} \tau}$ dependence of the integrand in Eq. (54). The eigenvalues of the Rabi matrix (29) have a negative imaginary component $-\frac{i}{2} (\Gamma_a + \Gamma_c)$ which causes $e^{-i\frac{\lambda_j}{2} \tau}$ to acquire an exponentially decaying factor. In other words, the longer the excursion time of a continuum electron, the stronger is its impact on the HHG spectrum suppressed. This effect adds another disadvantage to long trajectories versus short trajectories in addition to the spreading of the wave packet [17, 9, 11]. Along the same line, multiple returns of the continuum electron to the nucleus are diminished. For the case $i = a$, Eq. (51) becomes the Lewenstein et al. [11] result [Eq. (18)]—apart from constants—for a vanishing x-ray field, because then $U_{aj} = \delta_{j,+}$ and $w_j = \delta_{j,+}$.

The dipole moment $\tilde{D}(t)$ [Eq. (59)] is obtained from the Fourier coefficients of the components (51) as follows:

$$\tilde{D}(t) = \sum_{K=0}^{+\infty} \sum_{j \in \{\pm \}} \left[ \tilde{D}_{aj,2K+1} \ e^{-i(2K+1)\omega_L t} + \tilde{D}_{cj,2K} \ e^{-i2K\omega_L t} \right] \ e^{-i\omega_X t}.$$

The coefficients (51) for negative $K$ correspond to the inverse process where the HHG photon is emitted before the required number of optical laser photons is absorbed to satisfy energy conservation [13]. The energies of the emitted HHG photons are certainly the same as the photon energies emitted in the regular process. The inverse process is suppressed because the responsible Fourier coefficients have a highly oscillatory integrand and thus are very small; they are omitted in Eq. (53). I express $D(t)$ in frequency domain by a Fourier transformation

$$\tilde{D}(\Omega) = \int_{-\infty}^{\infty} D(t) \ e^{i\Omega t} \ dt$$

$$= 2\pi \sum_{K=0}^{+\infty} \sum_{m \in M} \left( \tilde{D}_{aj,2K+1} \delta((2K+1)\omega_L - \Omega) + \tilde{D}_{cj,2K} \delta(2K\omega_L + \omega_X - \Omega) \right).$$

using the representation (29) for the Dirac $\delta$ distribution [11].

The HHG spectrum is given by the frequency-resolved rate of the HHG photon emission [13, 14] where I consider here only emission along the $x$ axis with polarization vector $\vec{e}_x = \vec{e}_z$, I arrive with Appendix at

$$\frac{d\Gamma_H(\Omega)}{d\Omega} = 8\pi^2 \Omega \varrho(\Omega) W(\Omega),$$

with the density of free-photon states

$$\varrho(\Omega) = \frac{\Omega^2}{(2\pi)^3 c^3}$$

in the interval $[\Omega; \Omega+d\Omega]$ [23], the solid emission angle $\Omega_s$, the speed of light $c$ in vacuum and $W(\Omega)$ is

$W(\Omega) = W_1(\Omega)$

$$+ \sum_{H=0}^{+\infty} \delta((2H+1)\omega_L - \omega_X) W_{2,H}(\Omega) \quad (57a)$$

$W_1(\Omega) = \sum_{K=0}^{+\infty} \sum_{j,j' \in \{a,c\}} \left[ \tilde{D}_{aj,2K+1}^{*} \tilde{D}_{cj',2K+1} \delta_{j,j'} \right.$

$$\times \delta((2K+1)\omega_L - \omega_X - \Omega) \quad (57b)$$

$W_{2,H}(\Omega) = \sum_{K=0}^{+\infty} \sum_{j,j' \in \{\pm\}} \delta((2K+1)\omega_L - \Omega)$

$$\times \left[ \tilde{D}_{aj,2K+1}^{*} \tilde{D}_{cj',2(K-H) + c.c.} \right]. \quad (57c)$$

The HHG spectrum consist via Eq. (53) of discrete lines. The width of the lines in the HHG spectrum is zero—due to the $\delta$ distributions in Eq. (54)—despite the widths of the singly-ionized states $\Gamma_a$ and $\Gamma_c$. The $\Gamma_a$, $\Gamma_c$ enter Eq. (55) only via $U_{aj}$, $w_j$, and $\lambda_j$ which do not depend on $t$ and thus cause only a change of the height of the lines. The heights are the HH strengths which are determined by $W(\Omega)$. Without x rays I obtain

$$W(\Omega) = \sum_{K=0}^{+\infty} \left| \tilde{D}_{a+2K+1} \right|^2 \delta((2K+1)\omega_L - \Omega) \quad (58)$$

which becomes with Eq. (55) —apart from the factor of 2—identical to Eq. (16) in Ref. [14]. The experimental observable in HHG is the harmonic photon number spectrum (HPNS) [17]. The HPNS produced by a single
atom is obtained from $\Gamma_H(\Omega)$ by multiplication with the duration (square pulse) for which the HPNS is recorded. For realistic (Gaussian) optical laser pulses, one needs to take into account that the atomic terms can no longer be expanded into a Fourier series \(^{47}\) and thus the equations in this paper need to be reformulated.

There are several contributions to the HHG rate in Eq. \((65)\) which I analyze in the following. If $\omega_X = (2H + 1)\omega_L$ holds for an $H \in \mathbb{N}_0$, then I obtain $W(\Omega) = W_1(\Omega) + W_{2,H}(\Omega)$ from Eq. \((67)\); the HHG lines due to the recombinination with the core align with higher orders of the recombinination with the valence which leads to interference between both processes mediated by $W_{2,H}(\Omega)$. Otherwise, if $\omega_X$ is not an odd harmonic of $\omega_L$, then Eq. \((67)\) reduces to $W(\Omega) = W_1(\Omega)$ and the lines in the HHG spectrum belong to two distinct groups: first, $i = a$, HHG light due to recombinination with the valence vacancy gives rise to lines at the energies $(2K + 1)\omega_L$. The x rays induce interference effects in the recombinination via the two x-ray dressed states with $\omega_X$, HHG light due to recombinination with the valence vacancy. In the bare-states picture, this means that there are multiple pathways for the recombinination with the valence: once, direct recombinination and, alternatively, recombinination after an even number of Rabi cycles of the second electron. Second, $i = c$, HHG light due to recombinination with the x-ray dressed core vacancy leads to lines at the energies $2K(\omega_L + \omega_X)$. In other words, the HHG photon energies from a recombinination with the core are shifted by the photon energy $\omega_X$ of the x rays to higher energies. In the bare-states picture, an odd number of Rabi cycles was performed by the second electron.

2. X-ray induced ground-state depletion

Second, I consider the HHG spectrum with ground state depletion due to the optical laser and x rays by letting $\Gamma_0 > 0$. In doing so, I break the periodicity in time imposed by assuming CW optical laser and x rays. In other words, the x-ray dressed states of Eq. \((63)\) become an approximation to the x-ray dressed states of the nonperiodic system. In the ensuing Sec. III I will examine the HHG process for arbitrary x-ray pulses and overcome this limitation. This will facilitate to assess the results of this subsection and study the impact of a finite x-ray pulse.

To determine the time-dependent ground-state population, I need to solve Eq. \((19)\) where I neglect the second term on the right-hand side and include the destruction by tunnel-ionization in $\Gamma_0$. For a constant ionization rate $\Gamma_0$ starting at $t = 0$, the solution for the ground-state amplitude reads

$$a_0(t) = \theta(-t) + e^{-\frac{\Gamma_0}{T} t} \theta(t). \quad (59)$$

Clearly, $a(t)$ is not periodic in time. Additionally, the x-ray dressed states can only be used for $t \geq 0$. Before the x-ray pulse, the optical laser causes the usual HHG for valence electrons. The duration of the x-ray pulse is $T_P$. I will focus on the part with the x rays and disregard the additional contribution from $t < 0$ and $t > T_P$ to the valence-recombination part of the HHG spectra. Due to the lack of temporal periodicity, the HHG spectrum cannot be expanded into a Fourier series any longer and I need to calculate the Fourier transform of Eq. \((45)\) instead \cite{12, 13}:

$$\mathcal{D}_{ij}(\Omega) = \int_0^{T_P} \mathcal{D}_{ij}(t) e^{i\Omega t} dt$$

where I expanded the exponential of the quasiclassical action at the stationary point and translated by $M \rightarrow M - N$. I define the line shapes

$$h_{M,N,i}(\Omega, \tau) = \int_0^{T_P} e^{-i[(2(M+N)+\delta_i,a)\omega_L+\delta_i,c\omega_X-\Omega]t} \times a^*(t) a(t - \tau) dt. \quad (61)$$

Equation \((60)\) has a straightforward interpretation. Comparing it with the result without ground-state depletion \((54)\), I see that the $\delta$ distribution line shapes in the latter equation are replaced with finite-width line shapes in the former. Ground-state depletion thus “adds” a finite width to the Fourier coefficients.

Using the solution \((59)\) for the ground-state depletion, I find for the line shape \((61)\):

$$h_{M,N,i}(\Omega, \tau) = \frac{e^{-\frac{\Gamma_0}{T} \tau}}{\Gamma_0 + i(\Omega M,N,i - \Omega)} \times \frac{1}{(1 - e^{-\Gamma_0/(\Omega M,N,i - \Omega) T_P})}. \quad (62)$$

Neglecting the factor $e^{-\frac{\Gamma_0}{T} \tau}$, I see that $h_{M,N,i}(\Omega, \tau)$ peaks at $\Omega = (2(M+N)+\delta_i,a)\omega_L+\delta_i,c\omega_X$. In other words, the peaks are at the positions of the harmonics without ground-state depletion; for $i = c$, the harmonics are shifted by $\omega_X$ with respect to the harmonics for $i = a$.

The factor $e^{-\frac{\Gamma_0}{T} \tau}$ leads to a deformation and shifting of the peaks. Above all, $h_{M,N,i}(\Omega, \tau)$ has a finite width; its real part is proportional to a Lorentzian of a width of $4\Gamma_0$.

The HPNS for a single atom—the probability to find a photon with specified energy—along the $x$ axis follows from the Appendix and is given by

$$\frac{dP_H(\Omega)}{d\Omega d\Omega} = 4\pi \Omega \rho(\Omega)|\mathcal{D}(\Omega)|^2. \quad (63)$$
with \( \hat{D}(\Omega) = \sum_{i \in \{a,c\}, j \in \{+,,-\}} \hat{D}_{ij}(\Omega) \) [compare with Eq. (65)].

3. Cutoff law

The cutoff of the HHG spectrum with x-ray dressing is changed quite significantly with respect to the optical laser-only case. First, inspecting Eq. (39), I see that the terms for the recombination of the continuum electron with a core hole are shifted by \( \omega_X \) towards higher energy compared with the terms for the recombination with a valence hole. Neglecting the changes in the atomic terms \([13]\) between the two cases, I see that also the cutoff of the HHG spectrum resulting from the core hole increases by \( \omega_X \).

Second, the phenomenological semiclassical cutoff law of an optical laser-only HHG spectrum \([7,11]\) is given by

\[
\Omega_{\text{cut}} = 3.17 U_P + I_P ,
\]

with the valence ionization potential \( I_P \). X-ray dressing introduces, however, a changed situation. Namely, I observe that Eq. (39) contains two terms each for valence and core recombination with a changed situation. Namely, I observe that Eq. (39) contains two terms each for valence and core recombination with a shifted by \( \omega_X \) towards higher energy compared with the terms for the recombination with a valence hole. Neglecting the changes in the atomic terms \([13]\) between the two cases, I see that also the cutoff of the HHG spectrum resulting from the core hole increases by \( \omega_X \).

Consequently, there can be a few harmonics close to the cutoff that stem only from the term with the higher ionization potential.

III. HIGH-ORDER HARMONIC GENERATION WITH ARBITRARY X-RAY PULSES

I would like to examine HHG in the presence of a general x-ray pulse as they are obtained from x-ray free electron lasers which are frequently operate by the SASE principle \([58,70]\) using the PCM \([71,72]\). The formalism of the previous Sec. II relies on CW x rays [Eq. (14)] by going into a dressed-states picture [Eq. (33)] which is no longer practicable for arbitrary x-ray pulses. In this section, I pursue a derivation that circumvents the dressed-states picture. Expressions which have counterparts in Sec. II have the same symbol with a prime attached.

A. Hamiltonian, wave function ansatz, and equations of motion

In order to describe the interaction with arbitrary x-ray pulses, I need to replace the interaction with CW x rays \( \hat{h}_X \) [Eq. (14)] by

\[
\hat{h}_X = \theta(t) \left( \vec{e}_X \cdot \vec{r} \right) \frac{E_{\text{OX}}'}{2} \left[ e^{i (\omega_X t + \varphi_X(t))} + e^{-i (\omega_X t + \varphi_X(t))} \right] ,
\]

Here, \( E_{\text{OX}}' (t) \) is the time-dependent amplitude of the pulse starting at \( t = 0 \) and \( \varphi_X (t) \) is the time-dependent phase \([71,123]\). The two-electron Hamiltonian for the x-ray interaction \( \hat{H}_X' \) has the same form as Eq. (10) with \( \hat{h}_X \) replaced by \( \hat{h}_X' \).

The newly arisen dependence on the time-dependent phase of the x-ray field \([65]\) needs to be taken into account in the ansatz for the two-electron wavepacket \([17]\) which is modified by multiplying the phase factor of \( | \vec{k} \rangle \) additionally by \( e^{-i \varphi_X(t)} \). With this ansatz I obtain EOMs which are very similar to the ones obtained previously apart from the decay widths \( \Gamma_0' (t) \), \( \Gamma_0'' (t) \), and \( \Gamma_0'' (t) \) which are now time dependent. First, the ground-state population is formally identical to Eq. (19). Second, also the recombination of the continuum electron with the valence hole is formally identical to Eq. (20). Third, in the recombination of the continuum electron with the core hole, Eq. (21), the first term on the right hand side needs to be augmented by the summand \(-2 \varphi_X(t) \) with \( \varphi_X(t) = \frac{\omega_X}{2} (t) \). The modified Eqs. (20) and (21) are recast in terms of a matrix equation formally identical to Eq. (27) yielding

\[
\frac{\partial}{\partial t} \vec{b} (\vec{k}, t) = - \frac{1}{2} \left( R'(t) + (\vec{k}^2 + 2 I_P) \right) \vec{b} (\vec{k}, t) + E_{\text{LX}}(t) \frac{\partial}{\partial \vec{k}} \vec{b} (\vec{k}, t) - i a'(t) E_{\text{LX}}(t) \varphi_{L,\vec{k},a} \left( \begin{array}{c} 1 \\ 0 \end{array} \right) ,
\]

with \( \vec{b} (\vec{k}, t) = \left( b_{\delta a}(\vec{k}, t) \right) \) where the instantaneous Rabi matrix [compare with Eq. (20)] reads

\[
R'(t) = -i \text{diag}(\Gamma'_a(t), \Gamma'_c(t) - 2 i \varphi_X(t)) - \delta \sigma_z + R_{\text{OX}}' (t) \sigma_x ,
\]

with the Pauli matrices \( \sigma_x \) and \( \sigma_z \) \([92,108]\) and the instantaneous Rabi frequency \( R_{\text{OX}}' (t) = 2 \langle c | \hat{h}_{\text{OX},\text{RWA}} | a \rangle = E_{\text{OX}}'(t) \varphi_{\text{ox},c,a} \) for \( \hat{h}_{\text{OX}}' = E_{\text{OX}}'(t) e^{-i (\omega_X t + \varphi_X(t))} \approx \hat{h}_{\text{OX,RWA}} = (\vec{e}_X \cdot \vec{r}) \frac{E_{\text{OX}}'}{2} \) using the rotating wave approximation \([92]\).

B. Integration of the equations of motion

In order to solve the system of EOMs \([65]\), I need to realized that, in contrast to the EOMs for CW x rays [Eqs. (19) and (27)], the Rabi matrix \( R'(t) \) [Eq. (67)] is time dependent. A decoupling of the two recombination amplitudes, as in Eq. (41), is, therefore, no longer possible by going to an x-ray dressed-states picture because the eigenvector matrix of \( R'(t) \) does not commute with the time derivative. However, I can decouple the EOMs \([66]\) in a somewhat different way. I begin by removing the diagonal elements of \( R'(t) \) by the substitution

\[
b_a'' (\vec{k}, t) = b_a'' (\vec{k}, t) e^{\frac{i}{2} \delta t - \frac{\Gamma_a'(t)}{2} t} ,
\]

\[
b_a' (\vec{k}, t) = b_a' (\vec{k}, t) e^{\frac{i}{2} \delta t - \frac{\Gamma_a'(t)}{2} t - i \varphi_X(t)} ,
\]

In order to describe the interaction with arbitrary x-ray pulses, I need to replace the interaction with CW x rays \( \hat{h}_X \) [Eq. (14)] by

\[
\hat{h}_X = \theta(t) \left( \vec{e}_X \cdot \vec{r} \right) \frac{E_{\text{OX}}'}{2} \left[ e^{i (\omega_X t + \varphi_X(t))} + e^{-i (\omega_X t + \varphi_X(t))} \right] .
\]
with \( \vec{w}'(\vec{k}, t) = \left( \frac{\partial}{\partial \vec{k}} \hat{\Sigma}_v(\vec{k}, t) \right) \). Inserting the ansatz (68) into Eq. (66) leads to

\[
\frac{\partial}{\partial t} \vec{b}'(\vec{k}, t) = \left( -\frac{i}{2} R_{0X}(t) \vec{\Sigma}_x(t) - i \left( \frac{\vec{k}^2}{2} + I_p \right) \right) \vec{b}'(\vec{k}, t) + E_L(t) \frac{\partial}{\partial \vec{k}_z} \vec{b}'(\vec{k}, t) - i a'(t) E_L(t) \varphi_{L, \vec{k}_a} \left( e^{-\frac{i}{2} \delta t + \frac{I_p}{2}} 0 \right).
\]

(69)

The matrix

\[
\vec{\Sigma}_x(t) = \begin{pmatrix} 0 & e^{\Delta(t)} \\ e^{-\Delta(t)} & 0 \end{pmatrix}
\]

with the phase-amplitude difference

\[
\Delta(t) \equiv -i \delta t + i \varphi_X(t) + \frac{1}{2} \left( F_a(t) - F_e(t) \right)
\]

(70)

in Eq. (69) does not depend on momentum but does depend on time. Therefore, a diagonalization of \( \vec{\Sigma}_x(t) \) leads to time-independent eigenvalues

\[
\Lambda' \equiv \text{diag}(\lambda'_+, \lambda'_-) = \sigma_z,
\]

(72)

and time-dependent eigenvectors

\[
U' = \begin{pmatrix} e^{\Delta(t)} & -e^{-\Delta(t)} \\ e^{-\Delta(t)} & e^{\Delta(t)} \end{pmatrix}.
\]

(73)

I transform to the eigenbasis of \( \vec{\Sigma}_x(t) \)—in analogy to the dressed-state basis used before [Eq. (83)]—yielding

\[
\frac{\partial}{\partial t} \vec{b}'(\vec{k}, t) = \left( \hat{U}'^{-1}(t) U'(t) - \frac{i}{2} R_{0X}(t) \Lambda' \right) \vec{b}'(\vec{k}, t) - i \left( \frac{\vec{k}^2}{2} + I_p \right) \vec{b}'(\vec{k}, t) + E_L(t) \frac{\partial}{\partial \vec{k}_z} \vec{b}'(\vec{k}, t) - i a'(t) E_L(t) \varphi_{L, \vec{k}_a} \vec{w}'(\vec{k}, t).
\]

(74)

I added \( \hat{U}'^{-1}(t) U(t) \vec{b}'(\vec{k}, t) \) on both sides of Eq. (74) where the new amplitudes [compare with Eq. (81)] are

\[
\vec{b}'(\vec{k}, t) = \begin{pmatrix} \beta'_+(\vec{k}, t) \\ \beta'_-(\vec{k}, t) \end{pmatrix} = \hat{U}'^{-1}(t) \vec{b}'(\vec{k}, t).
\]

(75)

I use a dot over symbols to denote a time derivative \( \dot{\cdot} = \frac{d}{dt} \); the transformation rest reads

\[
\hat{U}'^{-1}(t) U'(t) = \frac{\dot{\Lambda}(t)}{2} (-1 + \sigma_z).
\]

(76)

using Eq. (74) and the valence ionization fraction

\[
\vec{w}'(t) = \begin{pmatrix} w'_v(t) \\ w'_c(t) \end{pmatrix} = U'^{-1}(t) \begin{pmatrix} e^{\frac{i}{2} \delta t + \frac{I_p(t)}{2}} \\ 0 \end{pmatrix}.
\]

(77)

In order to decouple the two differential equations (74), I need to approximate the transformation rest (76) by its diagonal elements \( \hat{U}'^{-1}(t) U'(t) \approx -\frac{\dot{\Lambda}(t)}{2} \mathbb{1} \). I refer to this as zeroth order and attach a superscript \( (0) \) to the involved coefficients. The resulting equations can be integrated exactly (119) analogous to Eqs. (85) and (86) yielding

\[
\beta'_0(\vec{k}, t) = -i \int_{t_0}^t \dot{a}'(0)(t') E_L(t') \varphi_{L, \vec{k} - \vec{A}_L(t') + \vec{A}_L(t')} \delta t' \times e^{-i S_{z,0}(\vec{k}, t')} w'_0(\vec{k}, t') d\tau.
\]

Here, the quasiclassical action [compare with Eq. (41)] is

\[
S_{z}(\vec{k}(t), t') = \frac{1}{2} \int_{t_0}^t \left( \dot{\vec{k}} - \vec{A}_L(t') + \vec{A}_L(t') \right)^2 d\tau'' + \frac{\lambda'_0}{2} \left( \Theta(t) - \Theta(t') \right) - \frac{1}{2} \left( \Delta(t) - \Delta(t') \right) + I_p(t - t')
\]

(79)

and pulse area (92) of the x rays is

\[
\Theta(t) = \theta(t) \int_{t_0}^t R_{0X}(t') d\tau.
\]

(80)

C. Time-dependent dipole moment and high-order harmonic generation spectrum

The time-dependent two-electron dipole transition matrix element follows from Eq. (83) by transforming \( \vec{b}'(\vec{k}, t) \) [Eq. (78)] back to the bare-state amplitudes \( \vec{b}'(\vec{k}, t) \) with the inverse of Eqs. (85) and (86):

\[
\mathcal{D}'(t) = \langle \Psi'_0, t | \hat{D} | \Psi'_c, t \rangle = \sum_{j \in \{a, c\}} \sum_{j \in \{+,-\}} \mathcal{D}'_{ij}(t),
\]

(81)

where I denote by \( \psi'_0, t \) the ground-state part of the modified wavepacket (17) and by \( \psi'_c, t \) the continuum part (15).

1. Zeroth order

I introduce the dipole components \( \mathcal{D}'_{ij}(t) \) using the zero-order coefficients

\[
\mathcal{D}'_{ij}^{(0)}(t) = U'_{ij}(t) e^{i \phi(t)} a'^{(0)*}(t) \int \psi_{H, i, \vec{k}} \beta'_i^{(0)}(\vec{k}, t) d^3k,
\]

(82)
and the time-dependent phase
\[ \phi_i(t) = (-1)^{\delta_{i,a}} \frac{\delta}{2} t - \delta_{i,c} \omega_X t + i \frac{F_i(t)}{2}. \] (83)

The dipole components are not periodic in time and thus the \( D_{ij}^{t}(t) \) cannot be expanded into a Fourier series. Instead, I need to take the Fourier transform of them. I introduce the canonical moment \( p = \vec{k} - \vec{A}_L(t) \) and the excursion time \( \tau \), expand the atomic terms into a Fourier series \([Eqs. (46), (47), \) and \( (48)\)\] and make the saddle point approximation \([119]\) which yields
\[ \tilde{D}_{ij}^{t}(0) = -i \int_0^\infty \sqrt{\frac{(2\pi)^3}{\tau^3}} e^{-i F_i'(0)} \times \sum_{N=0}^\infty i^N J_N \left( \frac{p}{\tau} \right) C(\tau) e^{i N \omega_L \tau} \]
\[ \times \sum_{M=-\infty}^\infty b_{M-N,i} h_{M,0,i,j}(0, \tau) d\tau, \]
where I expanded the exponential of the quasiclassical action at the stationary point, used \( F_i'(0) \) from Eq. \([52]\), \( C(\tau) \) from Eq. \([44]\), translated by \( M \rightarrow M - N \), and defined
\[ h_{M,0,i,j}(0, \tau) = \int_0^\infty e^{-i [2 (M+N) + \delta_{i,a} \omega_L + \delta_{i,c} \omega_X] t} \]
\[ \times e^{-i \frac{1}{2} \lambda_i (\theta(t) - \theta(t-\tau))} e^{i \phi_i(t)} \]
\[ \times e^{-i \frac{1}{2} \Delta(t) + \Delta(t-\tau)} a'(0)^*(t) \]
\[ \times a'(0)(t-\tau) U_{ij}(t) w_{ij}(t-\tau) dt. \] (85)

As in Sec. \([112]\) I disregard the contributions to the HHG spectrum from valence recombination in Eq. \([53]\) before the x-ray pulse sets in at \( t = 0 \), i.e., I assume an optical laser pulse which starts at zero time. As I assume a finite x-ray pulse, I restrict the integration \([53]\) to a optical laser pulse duration of \( T_P \) (square pulse). This result \([53]\) has a close resemblance to the dipole components for CW x rays with ground-state depletion \([60]\). However, the eigenvectors \( U'(t) \) transform from a different basis to bare states.

To find an expression for Eq. \([55]\), I need to solve the modified Eq. \([19]\) where I neglect the second term on the right-hand side because I assume a low tunnel ionization rate. For a x-ray induced ionization by an arbitrary pulse starting at \( t = 0 \), the solution for the ground-state amplitude reads
\[ a'(0)(t) = \theta(-t) + e^{-\frac{F_0(t)}{2}} \theta(t), \] (86)
similarly to Eq. \([59]\). This expression is inserted into Eq. \([85]\) to obtain the lineshape. I find with Eqs. \([72], \) \([73], [77], [80], \) and \([83]\):
\[ h_{M,0,i,j}(0, \tau) = \frac{(-1)^{\delta_{i,a}} \delta}{2} \int_0^\infty \frac{e^{-i F_0(t) + F_0(\tau-\tau)}}{2} \]
\[ \times e^{i [2 (M+N) + \delta_{i,a} \omega_L + \delta_{i,c} \omega_X - \Omega] t} \]
\[ \times e^{\frac{1}{2} \lambda_i (\theta(t) - \theta(t-\tau))} e^{i \phi_i(t)} \]
\[ \times e^{-\frac{1}{2} \Delta(t) + \Delta(t-\tau)} a'(0)^*(t) \]
\[ \times e^{-\frac{1}{2} \Delta(t) + \Delta(t-\tau)} a'(0)(t-\tau) U_{ij}(t) w_{ij}(t-\tau) dt. \]

Ignoring the impact of the other factors in the equation, the line shape peaks at \( \Omega = (2 (M+N) + \delta_{i,a} \omega_L + \delta_{i,c} \omega_X) \Omega \). The other factors differ substantially from the result \([52]\).

The reason for these contributions to occur is the only partial diagonalization of the instantaneous Rabi matrix \([67]\). The suppression of the lineshapes is caused by the destruction of the ground state at the time of tunnel ionization \( F_0(t-\tau) \) and at the time of recombination \( F_0(t) \) of the continuum electron with the ground-state part. Further, the term depending on \( F_0(t) \), \( F_c(t) \) represents the destruction of the intermediate hole state by x-ray absorption or Auger decay in between tunnel ionization and recombination. Inspecting Eq. \([29]\), I see that via Eq. \([7]\) this term and the term depending on the pulse area \([80]\) can be understood to result from \( \int_t \frac{\lambda \omega_X}{2} dt \) where I retain only the leading order in the expansion of the complex Rabi frequency \( \lambda \) with respect to \( R_{0X} \) which is taken to be large with respect to all other parameters in \( \mu \), i.e., \( \mu \approx R_{0X} \). Finally, the probability of the HHG photon emission along the \( x \) axis follows in zeroth order from Eq. \([63]\).

**2. First order**

I have obtained the solution of the coupled equations \([60]\) taking only the diagonal elements of the transformation rest \([76]\) into account. Higher order approximations to the amplitudes \( \tilde{B}(\vec{k}, t) \) can be obtained by iteration, i.e., the zero-order result obtained in Sec. \([111]\) is used in Eq. \([74]\) to specify the offdiagonal elements of Eq. \([70]\). For the first-order correction \( \tilde{B}^{(1)}(\vec{k}, t) \) to the wave function in the expansion
\[ \tilde{B}(\vec{k}, t) \approx \tilde{B}^{(0)}(\vec{k}, t) + \tilde{B}^{(1)}(\vec{k}, t), \] (88)
I find from Eq. (72):
\[
\frac{\partial}{\partial t} \beta^i(\kappa, t) = \left(-i \frac{\vec{k}^2}{2} + J_P - \frac{1}{2} \Delta(t) \right) \mathbb{I}
\]
\[
+ \frac{1}{2} R_{\alpha X}(t) \Delta^i \beta^i(\kappa, t)
\]
\[
+ E_L(t) \frac{\partial}{\partial k_z} \beta^i(\kappa, t)
\]
\[
- i a^{(0)}(t) E_L(t) \varphi_{L, \kappa} u''(t)
\]
\[
+ \frac{1}{2} \Delta(t) \sigma_x \beta^{(0)}(\kappa, t) .
\]
These equations are still decoupled and can be solved along the lines presented in this section [Eq. (78)] by inserting the expansion (88) which yields
\[
\beta^{(1)}(\vec{k}, t) = \int_0^t \frac{1}{2} \Delta(t') e^{-i S^i_{\perp}(\vec{k}, t', t')} \sigma_x \beta^{(0)}(\kappa, t') dt'.
\]
Next, the zero-order solution [Eq. (78)] is inserted into Eq. (90), the two actions are united and treated with the saddle point method [119]. Defining two excursion times \( t' = t - t' \) and \( \tau = t - t'' \) leads with the expansion of the atomic terms (87) to the first order correction of the line widths (85) in Eq. (84); the expression of the first-order correction of the dipole components reads
\[
\begin{align*}
\hat{\mathbf{D}}^{(1)}_{ij}(\Omega) &= -i \int_0^T \mathcal{U}'_{ij}(t) e^{i \phi(t')} a^{(0)\ast}(t) e^{-\frac{1}{2} \Delta(t)}
\times e^{\frac{1}{2} \lambda_i \Theta(t)} \sum_{M,N=-\infty}^{\infty} \mathcal{K}_{M,N,i,j}(t)
\times e^{-i[(2(M+N)\delta_{i,a}+\delta_{i,c})-\Omega]t} dt ,
\end{align*}
\]
with the integrals
\[
\mathcal{K}_{M,N,i,j}(t) = \int_0^t \frac{\Delta(t - \tau')}{2} e^{i \lambda_i \Theta(t - \tau')}
\times \left[ J_{M,N,i,j}(t) - J_{M,N,i,j}(\tau') \right] d\tau',
\]
and
\[
\begin{align*}
J_{M,N,i,j}(t) &= \int \sqrt{\frac{(2\pi)^3}{\tau^3}} b_{M-N,i}(\tau) e^{-i F_0(\tau)}
\times i^{M} J_N \left( \frac{b_{M-C}}{\lambda} C(\tau) \right) e^{i N \omega_L \tau}
\times a^{(0)}(t - \tau) w_{ij}(t - \tau)
\times e^{\frac{1}{2} \Delta(t - \tau')} e^{-\frac{1}{2} \lambda_i \Theta(t - \tau')} d\tau .
\end{align*}
\]
The first-order correction (91) differs significantly from the zero-order expression (88). Differences arise due to the additional integration over \( \tau' \). The dependence of \( \Delta(t - \tau') \) and \( \Theta(t - \tau') \) on \( \tau' \) accounts for the phase-amplitude change due to the offdiagonal matrix elements in Eq. (76). The form of the integral \( J_{M,N,i,j}(t) \) has a certain resemblance to the integration over \( \tau \) in Eq. (84); it represents the effective amplitude accumulated for all tunneling instances at \( t - \tau \) in the allowed interval \( [0; t] \). The integral \( \mathcal{K}_{M,N,i,j}(t) \) quantifies the impact of the change of the phase and amplitude via the offdiagonal elements onto the dipole components.

I obtain closed-form expressions for \( \hat{\mathbf{D}}^{(1)}_{ij}(\Omega) \) by using Eqs. (72), (73), (77), (80), (83), and (86) which yields
\[
\hat{\mathbf{D}}^{(1)}_{ij}(\Omega) = -i \int_0^T e^{\frac{1}{2} \varphi(t-\tau)} e^{\frac{1}{2} \lambda_i \Theta(t)}
\times e^{-i[(2(M+N)\delta_{i,a}+\delta_{i,c})-\Omega]t} dt,
\]
with the integrals
\[
\mathcal{K}_{M,N,i,j}(t) = \int_0^t \frac{1}{2} \left[ -i \delta + i \varphi(t - \tau') \right]
\times [J_{M,N,i,j}(t) - J_{M,N,i,j}(\tau') \right] d\tau',
\]
and
\[
\begin{align*}
J_{M,N,i,j}(t) &= \frac{(-1)^{k_j}}{2} \int_0^t \sqrt{\frac{(2\pi)^3}{\tau^3}} b_{M-N,i}(\tau) e^{-i F_0(\tau)}
\times i^{M} J_N \left( \frac{b_{M-C}}{\lambda} C(\tau) \right) e^{i N \omega_L \tau}
\times e^{\frac{1}{2} \Delta(t - \tau')} e^{-\frac{1}{2} \lambda_i \Theta(t - \tau')} d\tau .
\end{align*}
\]
The probability of the HHG photon emission along the x axis follows by inserting the sum of the zero- and first-order corrections into Eq. (89).

### IV. CONCLUSION

In this paper, I discuss theoretically the impact of x-ray excitation on the HHG spectrum. I derive equations for a two-electron model that is based on the one-electron model for HHG by Lewenstein et al. [11]. The first electron from the atomic valence tunnels through the potential barrier into the continuum where it propagates freely. Additionally, I consider a second electron from the atomic core which is driven by intense x rays that are tuned to the core–valence resonance in the ionic remnant which is formed by tunnel ionization. For high...
x-ray intensities, this electron Rabi flops between the valence hole and the core. The returning first electron thus sees a superposition of valence-hole and core-hole states and recombines with the valence or the core hole emitting HHG radiation that is characteristic of this superposition. I analyze the HHG spectrum and identify the parts due to recombination with the valence and the core. The latter light is shifted by the x-ray photon energy to higher energies.

In my treatment, I focused on the HHG spectrum of a single atom. However, in experiments, a macroscopic sample is used to study HHG. The propagation of the optical laser, xuv, and x-ray radiation through the gas transforms the spectrum significantly due to interferences effects caused by coherent emission of light by the sample. The phase matching \cite{22} shall be examined in future studies specifically under the objective of the impact of SASE x rays on the HHG process: estimates of the yield of x-ray-boosted HHG show that a considerable output can be achieved from a macroscopic medium \cite{88}.

The model of Lewenstein et al. \cite{11} describes excellently qualitatively HHG spectra but tends to overestimate the HHG yield significantly by roughly two orders of magnitude \cite{124}. These shortcomings of the model with respect to quantitative accuracy have been suggested to be mitigated by a few methods, using the Ehrenfest theorem \cite{124} for the recombination step, the eikonal-Volovk approximation (EVA) \cite{125}, and considering electron correlations \cite{27, 48}. In the case of a SAE, a numerical integration of the time-dependent Schrödinger equation \cite{126} is a route to obtain an accurate HH yield. However, in our case, a numerical integration of a two-electron Schrödinger equation would be required with substantially increased complexity \cite{126}.

My prediction offers novel prospects for nonlinear x-ray physics which is practicable unlike simultaneous multi-x-ray-photon absorption that exhibits tiny cross sections \cite{127}. Namely, the HHG process determines a time window in which x-ray interaction may occur. Rabi flopping is a highly nonlinear fundamental process and becomes experimentally feasible with x rays for the first time using FELs \cite{73, 94, 95, 96, 97}. The occurrence of Rabi oscillations may have a much clearer signature if combined with the HHG scheme compared with the case if only x rays are considered. HHG and x rays may also represent an optical gating to perform frequency resolved optical gating (FROG) \cite{128} with x-ray pulses thus offering the long-sought after pulse characterization for chaotic SASE FEL light \cite{124, 130} but requires further theoretical research. The novel scheme also makes single attosecond x-ray pulses \cite{131, 132} and attosecond x-ray pulse trains \cite{33} feasible using the same methods that are used with conventional HHG \cite{88}. Above all tomographic imaging of core orbitals with HHG comes into reach \cite{23, 24, 30}. Finally, HHG has been used to generate frequency combs in the xuv; potentially, such HHG spectra can be boosted by x rays in order to extend frequency-comb-based spectroscopy to the x-ray regime \cite{133, 134} provided that one has identically-shaped x-ray pulses which are carefully synchronized to the optical laser.

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Appendix: Harmonic photon number spectrum

1. Quantum-electrodynamic formulation

The recombination of the continuum electron with the hole in the cation leads to the emission of a HHG photon. This fluorescence cannot be treated with semiclassical fields; instead, quantum electrodynamics is required \cite{14, 16, 17, 77, 93, 135}. The quantized electric field of the HHG light is in dipole approximation

\[ \hat{E}_H = (-1) \sum_q \sqrt{\frac{2 \pi \Omega_q}{V}} \left[ \hat{c}_H^\dagger \hat{a}_q^\dagger - \hat{c}_H \hat{a}_q \right], \]  \hspace{1cm} (A.1)

with the photon energy \( \Omega_q \) of the \( q \)th mode, the normalization volume \( V \) used to quantize the electromagnetic field, the polarization vector \( \hat{e}_H \) along the \( z \) axis, and annihilation \( \hat{a}_q \) and creation \( \hat{a}_q^\dagger \) operators for photons in mode \( q \). The Hamiltonian for the HHG fluorescence \( \hat{H}_H \) is constructed based on Eq. (33) by replacing the polarization vector with \( \hat{E}_H \). The free HH field is

\[ \hat{H}_{EM} = \sum_q \Omega_q \hat{a}_q^\dagger \hat{a}_q, \]  \hspace{1cm} (A.2)

where I set the energy of the vacuum to zero. The quantum electrodynamic Hamiltonian for the description of fluorescence reads

\[ \hat{H}_{QED} = \hat{H}_A + \hat{H}_{EM} + \hat{H}_H, \]  \hspace{1cm} (A.3)

with the atomic Hamiltonian \( \hat{H}_A \) from Eq. (10).

The coefficients \( a(t), b_q(k, t) \), and \( b_q(k, t) \) from the EOMs of Sec. [ITC] were obtained with no HHG photons present and are assumed to be known here. To determine the amplitude of fluorescence, I need a similar wavepacket
to Eq. [17] which includes the photon number states of the HH field:

$$\ket{\Psi', t} = \sum_q c_q(t) e^{-i E_{q}t} \ket{a c} \otimes |1_q\rangle + |\Psi_c, t\rangle \otimes |0\rangle .$$  \hspace{1cm} (A.4)

Here, $|\Psi_c, t\rangle$ is the continuum part of Eq. [17], the vacuum state is $|0\rangle$ and $|1_q\rangle = \hat{a}_q^\dagger |0\rangle$.

2. No ground-state depletion

This new wavepacket is inserted into the time-dependent Schrödinger equation and projected on the state $\langle ac | \otimes \langle 1_q |$ where no ground-state depletion is assumed, i.e., $\Gamma_0 = 0$. This leads to an EOM for the amplitude to find a fluorescence photon similar to Eq. (19):

$$\frac{d}{dt} c_q(t) = \Omega_q c_q(t) - i \sqrt{\frac{2\pi \Omega_q}{V}} D(t) , \hspace{1cm} (A.5)$$

with the the time-dependent two-electron dipole transition matrix element [39]. The equation is integrated directly [119] yielding

$$c_q(t) = -\sqrt{\frac{2\pi \Omega_q}{V}} e^{-i \Omega_q t} \int_{-t}^{t} e^{i \Omega_q t'} D(t') \, dt' . \hspace{1cm} (A.6)$$

The expression for $D(t')$ can be replaced by a Fourier series expansion [54]. In the limit $t \to \infty$, the time integral in Eq. [A.6] becomes a Fourier transform [54]. I carry out the time integration for finite $t$ using

$$\int_{-t}^{t} e^{-i x t'} \, dt' = 2 t \sin c (x t) , \hspace{1cm} (A.7)$$

with the sinus cardinals for $z \in \mathbb{C}$:

$$\sin c z = \begin{cases} 1 & ; z = 0 \\
\sin z \overline{z} & ; z \neq 0 . \end{cases} \hspace{1cm} (A.8)$$

The amplitudes are

$$c_q(t) = -\sqrt{\frac{2\pi \Omega_q}{V}} e^{-i \Omega_q t} (2t) \sum_{j=1}^{\infty} \sum_{K=0}^{\infty} \left[ \hat{D}_{qj, 2K+1} \sin (2K+1) \omega_L t - \Omega_q t \right. \right.$$

$$\left. + \hat{D}_{qj, 2K} \sin (2K \omega_L t + \omega_K t - \Omega_q t) \right] . \hspace{1cm} (A.9)$$

The probability to measure a photon is given by $|c_q(t)|^2$. For large $t$, I transform it with the relation [108]:

$$\lim_{t \to \infty} t \sin c^2 (x t) = \pi \delta(x) . \hspace{1cm} (A.10)$$

The integral over $x$ of $t \sin c (x t) \sin ((x+y) t)$ for $y \neq 0$ vanishes in the limit $t \to \infty$. Therefore, the cross terms in the probability vanish and are dropped in the following.

The rate of photon emission is given by $\frac{\pi \Omega_q}{a(t)} |c_q(t)|^2$ Using the fact that free-photon states are spaced densely, I arrive at the rate in Eq. [55] upon integrating over $V$ times the density of free-photon states $g(\Omega)$ [Eq. [56]] and collecting the results in the energy dependent rate in Eq. [55]. The extra factor of 2 in Eq. [55] accounts for the two possible spin states in the valence orbital with $m = 0$. The HPNS per atom is obtained from the rate by multiplication with the optical laser pulse duration for a square pulse [see discussion after Eq. [55]].

3. Ground-state depletion by x-ray absorption

The situation of the previous subsection changes as soon as I consider ground-state depletion by setting $\Gamma_0 > 0$. In this case, the HHG emission is not periodic anymore. Instead of a rate, I, therefore, calculate the HPNS for a single atom directly, i.e., the probability for an atom to emit a HHG photon.

To describe the probability amplitude of HHG fluorescence photons, I make a product ansatz for the coefficient $c_q(t) = \frac{\xi_q(t)}{a(t)}$ in the wavepacket in Eq. [A.4] where $a(t)$ is the ground-state amplitude [59] [or Eq. (86) for $a'(t)$]. Replacing $\Gamma_0$ by $-\Gamma_0$ in $\hat{H}_A$ from Eq. [110] to account for loss of norm in $D(t)$, the division by $a(t)$ counters the increase of norm due to $-\Gamma_0$ such that $\xi_q(t)$ is not affected. This leads to an EOM in analogy to Eq. [A.5] which has the solution

$$\xi_q(t) = -\sqrt{\frac{2\pi \Omega_q}{V}} \int_{-t}^{t} e^{-i \int_0^t (\frac{\Gamma_0}{2} + \Omega_q) \, dt'} D(t') \, dt' . \hspace{1cm} (A.11)$$

The time integration over the decay width in the exponent yields two factors; the first factor simply is $a(t)^{-1}$ and cancels with the factor on the left-hand side. The second factor forms the dipole matrix element with the remainder of the integral such that I arrive at

$$\xi_q(t) \approx -\sqrt{\frac{2\pi \Omega_q}{V}} e^{-i \Omega_q t} \sum_{j} \hat{D}(\Omega_q) . \hspace{1cm} (A.12)$$

The integral in Eq. [A.11] becomes the Fourier transform of $D(t')$ in the limit $t \to \infty$. The HPNS from a single atom follows from Eq. [A.12] by taking the modulus squared, letting $t \to \infty$, and replacing the mode $q$ by $V \rho(\Omega)$ [Eq. [56]] yielding Eq. [63] [the extra factor of 2 stems from the two spin states]. In Sec. V of Ref. [11] an average HHG-emission rate is constructed from $|D(\Omega_q)|^2$ for nonvanishing ground-state depletion by multiplying its value at the positions of the harmonics with the area of the harmonic peaks.
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