High-order harmonic generation (HHG) by atoms in intense optical laser fields is a fascinating phenomenon and a versatile tool; it has spawned the field of attoscience, is used for spectroscopy, and serves as a light source in many optical laboratories [1]. Present-day theory of HHG largely gravitates around the single-active electron (SAE) approximation and the restriction to HHG from valence electrons [1–4]. Several extensions to the SAE view of HHG have been investigated previously. A two-electron scheme was considered that uses sequential double ionization by an optical laser with a subsequent nonsequential double recombination; in helium this leads to a second plateau with about 12 orders of magnitude lower yield than the primary HHG plateau [5]. Two-color HHG (optical plus XUV light) has been studied in a one-electron model [6] and with many-electron effects included by a frequency-dependent polarization [7]: the XUV radiation assists thereby in the ionization process leading to an overall increased yield [6] and the emergence of a new plateau [7], the latter, however, at a much lower yield. The above schemes suffer from tiny conversion efficiency beyond the conventional HHG cutoff (maximum photon energy).

We propose an efficient two-electron scheme for a HHG process manipulated by intense XUV light from the newly constructed free electron lasers (FEL)—e.g., the Free Electron Laser in Hamburg (FLASH). Our principal idea is sketched in Fig. 1. In the parlance of the three-step model [2,3], HHG proceeds as follows: (a) the atomic valence is tunnel ionized; (b) the liberated electron propagates freely in the electric field of the optical laser; (c) 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 fs for typical 800 nm optical 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 XUV excitation of an inner-shell electron into 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 XUV photons \( \omega_{X} \) is added shifting the HHG spectrum towards higher energies. 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 continuum electron returns.

The spatial one-electron states of relevance to the problem are the valence state \( |a \rangle \) and the core state \( |c \rangle \) of the closed-shell atom. In strong-field approximation, continuum electrons are described by free-electron states \( |\vec{k}\rangle \) for all \( \vec{k} \in \mathbb{R}^3 \) [8]. The associated level energies are \( E_a, E_c, \) and \( \frac{\vec{k}^2}{2m} \). We need to consider three different classes of two-electron basis states to describe the two-electron dynamics: first, the ground state of the two-electron system is given by the Hartree product \( |a \rangle \otimes |c \rangle \); second, the valence-ionized states with one electron in the continuum and one electron in the core...
state are $|\vec{k}\rangle \otimes |c\rangle$; third, the core-ionized states with one electron in the continuum and one electron in the valence state are $|\vec{k}\rangle \otimes |a\rangle$. We apply the three assumptions of Lewenstein et al. \cite{Lewenstein} in a somewhat modified way by considering also phenomenological decay widths of the above three state: $\Gamma_0$ and $\Gamma_c$ to account for losses due to ionization by the optical and xuv light for $|a\rangle \otimes |c\rangle$ and $|\vec{k}\rangle \otimes |c\rangle$, respectively, and $\Gamma_i$ to represent losses from ionization by the optical and xuv light and Auger decay of core holes for $|\vec{k}\rangle \otimes |a\rangle$ with radiative decay of the core hole being safely neglected. Further, the xuv light induces Rabi flopping in the two-level system of $|\vec{k}\rangle \otimes |a\rangle$ and $|\vec{k}\rangle \otimes |c\rangle$.

The two-electron Hamiltonian of the atom in two-color light (optical laser and xuv) reads $H = H_A + H_L + H_0$; it consists of three parts: the atomic electronic structure $H_A$, the interaction with the optical laser $H_L$, and the interaction with the xuv light $H_0$. We construct $H$ mostly from tensorial products of the corresponding one-particle Hamiltonians $h_A, h_L$, and $h_0$. The interaction with the optical and xuv light is treated in dipole approximation in length form \cite{Lewenstein}.

We make the following ansatz for the two-electron wavepacket (in atomic units)

$$|\Psi, t\rangle = a(t) e^{-\frac{i}{\hbar} \sum_{\alpha \beta}(E_{\alpha} + E_{\beta} - \omega_X) t i P_{\alpha \beta} t} (|a\rangle \otimes |c\rangle)$$

$$+ \int \frac{d^3k}{\mathbb{R}^3} [b_a(\vec{k}, t) e^{-\frac{i}{\hbar} \sum_{\alpha \beta}(E_{\alpha} + E_{\beta} - \omega_X) t i P_{\alpha \beta} t} |\vec{k}\rangle \otimes |c\rangle] + b_c(\vec{k}, t) e^{-\frac{i}{\hbar} \sum_{\alpha \beta}(E_{\alpha} + E_{\beta} + \omega_X) t i P_{\alpha \beta} t} |\vec{k}\rangle \otimes |a\rangle d^3k,$$

where we introduce a global phase factor based on $P_{\alpha \beta} = -E_{\alpha} + \frac{1}{2}$. The detuning of the xuv photon energy from the energy difference of the two ionic levels is $\delta = E_{\alpha} - E_{\beta} - \omega_X$. The index on the amplitudes $b_a(\vec{k}, t)$ and $b_c(\vec{k}, t)$ indicates which orbital contains the hole.

We insert $|\Psi, t\rangle$ into the time-dependent Schrödinger equation and project onto the three classes of basis states which yields equations of motion (EOMs) for the involved coefficients. We obtain the following EOM for the ground-state population

$$\frac{d}{dt} a(t) = -\frac{\Gamma_0}{2} a(t) - i \int \frac{d^3k}{\mathbb{R}^3} b_a(\vec{k}, t) \langle a | \hat{h}_L | \vec{k}\rangle d^3k.$$

The other two EOMs are written as a vector equation, defining the amplitudes $\vec{b}(\vec{k}, t) = (b_a(\vec{k}, t), b_c(\vec{k}, t))^T$, the Rabi frequency $R_{\alpha X}$ \cite{Lewenstein} for continuous-wave (CW) xuv light and the Rabi matrix

$$R = \begin{pmatrix} -\delta - i \Gamma_a & R_{0X} \\ R_{0X} & -\delta - i \Gamma_c \end{pmatrix}.$$

This yields for a CW optical laser electric field $E_L(t)$ oscillating with angular frequency $\omega_L$:

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

$$\times \frac{\partial}{\partial \vec{k}} \vec{b}(\vec{k}, t) - i a(t) E_L(t) \langle \vec{k} | \hat{h}_L | a\rangle \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

We change to the basis of xuv-dressed states using the eigenvectors $U$ and eigenvalues $\lambda_+, \lambda_-$ of $R$.

To determine the HHG spectrum, we solve Eq. (2) by neglecting the second term on the right-hand side as in Ref. \cite{Lewenstein}—its influence is included in $\Gamma_0, \Gamma_a$, and $\Gamma_c$ —and a constant xuv flux starting at $t = 0$ and ending at $t = T_P$. The HHG spectrum is given by the Fourier transform of $(\langle \Psi_0 | t \hat{D} | \Psi_c, t \rangle$, where $\hat{D}$ is the two-electron dipole dipole operator \cite{Lewenstein}, $| \Psi_0 | t$ is the ground-state part of the wavepacket (1) and $| \Psi_c, t \rangle$ is the continuum part, i.e.,

$$\hat{D}(\Omega) = -i \sum_{\{a,c\}} \sum_{\{+, -\}} U_{ij} w_j \int_0^{\infty} \left( \frac{2\pi}{\tau} \right)^{\frac{1}{2}} e^{-i\Omega \tau}$$

$$\times \sum_{N=-\infty}^{\infty} i^N J_N \left( \frac{\Omega}{\omega_c} | C(\tau) \right) e^{iN \omega_c \tau} \times \sum_{M=-\infty}^{\infty} b_{M, N, i}(\tau) h_{M, 0, i}(\Omega, \tau) d\tau.$$

Here, $\vec{w} = U^{-1} \left( \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right)$, the ponderomotive potential of the optical laser is $U_P$, $F_0(\tau)$, and $C(\tau)$ are defined as in Ref. \cite{Lewenstein} augmented by $\omega_L$ and with $I_P$ replaced by $\frac{\mathbb{1}}{F_0} + T_P$. Further, $J_N$ are Bessel functions and $b_{M, N, i}(\tau)$ are the coefficients defined in Eq. (17) of Ref. \cite{Lewenstein} for valence-(1) and core-hole recombination. Further,

$$h_{M, N, i}(\Omega, \tau) = e^{\frac{\pi}{\Omega} \tau} \left( 1 - e^{-\frac{i}{\tau} (\Omega_{M, N, i} - \Omega) T_P} \right) \sum_{M, N, i}.$$

Neglecting the factor $e^{\frac{\pi}{\Omega} \tau}$ for now, we see that the $h_{M, N, i}(\Omega, \tau)$ peak at $\Omega = \Omega_{M, N, i} = (2(M + N) + \delta_{i, a}) \omega_L + \delta_{i, c} \omega_X$. In other words, for $i = a$, the harmonics are shifted by $\omega_X$ with respect to the harmonics for $i = a$ such that, in general, none of them coincides with harmonics from $i = a$. The harmonic photon number spectrum (HPNS) for a single atom—the probability to find a photon with specified energy—along the $x$ axis is given by

$$\frac{d^2P}{d\Omega d\Omega_S} = 4 \pi \Omega g(\Omega) |\hat{D}(\Omega)|^2,$$

with the density of free-photon states $g(\Omega)$ \cite{Lewenstein} and the solid angle $\Omega_S$.

We apply our theory to krypton atoms. The energy levels are $E_a = -14.0 \text{ eV}$ for Kr $4p$ \cite{Lewenstein} and $E_c = -96.6 \text{ eV}$ for Kr $3d$ with a radial dipole transition matrix element of 0.206 Bohr \cite{Lewenstein}. The xuv light has the photon energy $\omega_X = E_a - E_c$. The optical laser intensity is set to $I_{0L} = 3 \times 10^{14} \text{ W/cm}^2$ at a wavelength of 800 nm. Both xuv and optical light have a pulse duration of $T_P = 3 \frac{\text{fs}}{c}$. The experimental value for the decay width of Kr $3d$ vacancies is $\Gamma_{\text{exp}} = 88 \text{ meV}$ \cite{Lewenstein}. The decay widths due to xuv ionization of the atom and the ion are obtained from the sum of the photoionization cross sections of the energetically accessible electrons \cite{Lewenstein, Lewenstein}; the ionization due to the optical laser is
The black solid lines show the contribution from recombination with a valence hole whereas the red dashed lines correspond to recombination with a core hole. The lines represent harmonic strengths obtained by integrating over peaks in the HPNS.

determined with Ref. [12] and is larger than the width for xuv ionization and Auger decay for the chosen parameters. We find for an xuv-intensity of $I_{\text{XUV}} = 10^{13} \text{ W/cm}^2$: $\Gamma_0 = 280 \text{ meV}$, $\Gamma_a = 1.5 \text{ meV}$, and $\Gamma_c = 88 \text{ meV}$, and for an xuv-intensity of $I_{\text{XUV}} = 10^{16} \text{ W/cm}^2$: $\Gamma_0 = 450 \text{ meV}$, $\Gamma_a = 170 \text{ meV}$, and $\Gamma_c = 300 \text{ meV}$.

In Fig. 2 we show the single-atom HPNS of HHG which is modified by xuv light. We find that the xuv excitation leads to two plateaus, one from valence- and one from core-hole recombination which overlap slightly. The width of the overlap can be tuned by changing the optical laser intensity and interference between both terms may occur. Even in the case of a moderate xuv intensity [Fig. 2a], the emission rate of HHG from core-hole recombination is substantial. This prediction can be interpreted in terms of an excitation (or even Rabi flopping) [9] of the remaining electron after tunnel ionization of an atom in the HHG process [Fig. 1b]. This electron sits in a two-level system where the electron is either in the valence or the core level. The strength of the HHG emission due to core-hole recombination is roughly proportional to the population of the upper state around 1 fs. For $10^{13} \text{ W/cm}^2$ the population is $\sim 0.001$ while it is $\sim 0.6$ for $10^{16} \text{ W/cm}^2$. Finally, we need to realize that the dipole matrix element for a recombination with a Kr 3d hole is not substantially different from the one with a Kr 4p hole thus explaining the similar yield of both contributions in Fig. 2b.

The xuv radiation from present-day FELs is generated with the self-amplification of spontaneous emission (SASE) principle; it is fully transversally coherent but exhibits only limited longitudinal coherence. We find that the fluctuating phase does not destroy the spectra [8]. Thus our interpretation of Fig. 2 is not invalidated when we relax the view assumed so far of entirely coherent xuv light with constant amplitude.

In conclusion, we predict HHG light from resonant excitation of transient ions in HHG that allows insights into the physics of core electrons and has various applications: it allows one to generate isolated attosecond x-ray pulses by ionizing atoms near the crests of a single-cycle optical laser pulse and selecting the highest photon energies by filtering [15]. This complements FEL-based strategies to generate attosecond x rays (Ref. [16] and References therein). Our scheme has the advantage that the attosecond pulses have a defined phase-relation to the optical laser and that it can be employed at any FEL with moderate cost and minimal impact on other experiments. Further, our scheme has the potential to become an in situ probe of the dynamics of cations in strong optical fields interacting with intense xuv light. Namely, the HHG spectra depend sensitively on the xuv pulse shape; a reconstruction with frequency resolved optical gating (FROG) [17] may be possible—thus offering the long-sought pulse characterization for SASE xuv light—but requires further theoretical investigation. Additionally, the emitted upshifted light due to core recombination bears the signature of the core orbital; thus it can be used for ultrafast time-dependent chemical imaging [18] involving inner shells which is not feasible so far. This allows one to extend such HHG-based methods to all orbitals that couple to the transient valance vacancy by suitably tuned xuv light. Our findings are not restricted to krypton but HHG spectra for resonant excitation of 1s electrons in neon were successfully computed and will be discussed in future work.

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