Study of high-order harmonic generation in xenon based on time-dependent density-functional theory

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Abstract

The high-order harmonic generation (HHG) in xenon is studied by using the time-dependent density-functional theory. The dynamics of all electrons on the outer 4th and 5th atomic shells is considered with subsequent separation of contributions of different atomic orbitals to the HHG amplitude. It is shown that giant enhancement of HHG yield in a spectral region near 100 eV is caused by perturbation of the electron–electron interaction potential induced by recolliding photoelectron wavepacket originated from the 5\textit{p}\textsubscript{0} orbital. This perturbation leads to the collective oscillations of all orbitals on the 4th shell closely localized in space and strongly interacting with each other. The resulting HHG yield is enhanced by more than an order of magnitude compared with the response of the single 5\textit{p}\textsubscript{0} orbital. The high accuracy of the numerical results is confirmed by comparing the calculated HHG spectra and photoionization cross-sections with experimental results and an analytical parameterization of the HHG yield.

1. Introduction

High-order harmonic generation (HHG) is one of the most well-known phenomena of strong-field physics, which is of interest for numerous applications [1, 2]. HHG serves as a unique tool for producing subfemtosecond and attosecond highly coherent light pulses in the extreme ultraviolet (XUV) range. The high intensity of generated XUV pulses and their precise synchronization with the laser field allows pump-probe studies of ultrafast phenomena in quantum systems from atoms and molecules to periodic solid structures (see [3, 4] and references therein). Moreover, XUV pulses obtained within HHG can be used for far-field imaging with nanometer resolution [5], frequency-stabilized seeding for free-electron lasers [6] and controlling magnetic dynamics [7].

The physical mechanism of HHG is qualitatively explained in the framework of a three-step scenario [8]. At the first step, atom or molecule is ionized by an intense field, at the second step, liberated electron is accelerated, and at the third step, electron returns back and recombines with the emission of high-energy photon in a wide energy range. While at the second step, the decisive factor is the interaction of moving electron with the laser field, the type and state of the target affect the ionization probability and the recombination cross section [9–20]. Thus, the multielectron dynamics associated with the motion of various electrons in an atom or molecule can significantly affect both the form of HHG spectra and the optimal generation regimes [12, 14, 21–29].

A typical example of the large influence of multielectron effects at the recombination stage is the giant enhancement of HHG yield in xenon, associated with the interaction of the photoelectron, originating from the external 5\textit{p}\textsubscript{0} orbital, with the inner electrons of the atom [14, 23–26, 30, 31]. This enhancement was first predicted in [30] based on the analytical parametrization of the HHG spectra within the so-called...
electron wave packet (EWP), which describes the ionization and propagation of photoelectron in the continuum, and a differential photorecombination cross section (PRCS), which is related to a differential photoionization cross section (PICS) according to the principle of the detailed balance [32]. PICS from the outer 5p subshell of Xe atom has a broad maximum near photon energy of 100 eV due to the giant resonance in the PICS from the inner 4d subshell and interchannel coupling via electron–electron interaction [33, 34]. Experimental measurements of HHG spectra in Xe using near-IR driving wavelengths confirm the existence of a giant (more than an order of magnitude) harmonic yield enhancement near 100 eV, which qualitatively agrees with the result of analytical parameterization [10, 14, 26, 30, 31]. The giant enhancement in the HHG spectrum of Xe atom was numerically studied in references [24, 26] by applying time-dependent configuration-interaction singles approach and in reference [25] by using time-dependent R-matrix theory. In these studies, the dynamical interaction between orbitals on the outer 5th shell and 4d subshell was taken into account, while the other orbitals were freezeed. Although the calculated HHG spectra’s coincidence with results of analytical parametrization and experiment is not perfect, obtained HHG spectra contain a broad maximum in the vicinity of 100 eV, which disappears if the interaction between the orbitals is excluded from calculations. Moreover, all five 4d_{m} orbitals (m = 0, ±1, ±2) on 4d subshell contribute to the HHG, and it is not sufficient to take into account only the 4d_{0} orbital aligned in the direction of the laser polarization [24]. However, due to the rapid increase in the required computational resources with the number of active orbitals, the role of other orbitals on the 4th shell in HHG has not been studied previously.

An alternative approach that may be applicable to investigate the enhancement of HHG yield in Xe is the time-dependent density-functional theory (TDDFT) [35, 36]. The heart of the TDDFT are the time-dependent Kohn–Sham (TDKS) equations for atomic orbitals, which include the interaction of electrons with the laser pulse, nucleus, and electron–electron exchange–correlation interaction. This approach describes with high accuracy giant resonance in the PICSs of various Xe and Xe-like ions [37–40]. However, this approach has not been used previously to study HHG in Xe due to the high complexity of calculations. The main difficulties are caused by a high probability of recolliding electron to move over long distances and acquire high energies, the very sharp increase of the potential energy in the vicinity of the ion, the divergences arising at partial freezing of individual shells of an atom.

Recently, we developed the numerical code for TDKS equations solution in a spherical coordinate system that is based on the careful discretization of the numerical grid, careful selection of calculation region size, and parallelization between the nodes of a computing cluster [20]. This code allows to simulate HHG in argon taking into account all electrons and demonstrate that a significant multielectron effect in HHG at high laser-pulse intensity is the laser-induced polarization of the atom itself [20]. In this work, we use this numerical code to carry out numerical simulation of the HHG in Xe, taking into account the dynamics of all subshells on the 4th and 5th atomic shells. We show that at the enhancement region and at higher frequencies HHG is influenced not only by the 4d subshell, but also the other, 4p and 4s subshells on the 4th shell. The results are explained based on the dynamics of electron–electron potential induced by the recombining 5p_{0} wave packet and the interaction between electrons on the 4th shell. We also perform the analysis of the Xe atom interaction with monochromatic XUV field and demonstrate a high linear response of 4p and 4s subshells.

The paper is organized as follows. In section 2, we discuss the TDKS equations and details of the numerical method. Section 3 is devoted to study the dynamics of orbitals of Xe atom in monochromatic XUV field. In section 4 we calculate HHG spectrum in the infrared field and compare it with the results of experiment and the analytical parametrization of the HHG spectrum, which provides high accuracy of EWP calculation at frequencies below the cutoff frequency [41]. Contributions of different orbitals and subshells to the total dipole acceleration are studied in section 4.1. Our main results are summarized in section 5. In the appendix we present the details of the analytical parametrization of the HHG spectrum. Atomic units (a.u.) are used throughout the paper unless specified otherwise.

2. General formulation

2.1. Initial electronic structure of xenon atom

The initial condition for the TDKS equations corresponds to the unperturbed Xe atom in the ground state. It is found within stationary density functional theory, which expresses the state of a multielectron atom in terms of stationary Kohn–Sham (KS) orbitals, \( \psi_{j}^{(0)}(\mathbf{r}) \). The unperturbed KS orbitals satisfy the system of stationary KS equations:

\[
\hat{H}_0 \psi_{j}^{(0)} = E_j \psi_{j}^{(0)}, \quad j = 1, 2, \ldots, N/2, \tag{2.1}
\]
binding energy. For the definiteness we assume that KS orbital index \( n \), angular momentum \( l \) and its magnetic projection \( m \) on the quantization axis \( \hat{z} \):

\[
\psi_{nlm}^{(0)}(r) = r^{-1}\Psi_{nlm}^{(0)}(r)Y_{lm}(\theta, \varphi),
\]

where \( \Psi_{nlm}^{(0)}(r) \) is the radial part of KS orbital, \( Y_{lm}(\theta, \varphi) \) is the spherical harmonic, angles \( \theta \) and \( \varphi \) are polar and azimuthal angles of the spherical coordinate system. Principal quantum number \( n \), angular momentum \( l \) and its magnetic projection \( m \) correspond to the same binding energy. For the definiteness we assume that KS orbital index \( j \) increases with \( n, l \) and \( m \), i.e.

\[
j = \begin{cases} 
\frac{n(n - 1)(2n - 1)}{6} + m + l + l^2 + 1 & n \leq 4, \ l < \min(n, 3), \\
m + l + l^2 + 24 & n = 5, \ l < 2.
\end{cases}
\]

The corresponding ground state configuration, taking into account the presence of two electrons with different spins in each state \((n, l, m)\), is written as \([Ar]3d^{10}4s^24p^64d^{10}5s^25p^6\), where \([Ar] = 1s^22s^22p^63s^23p^6\) is the electronic configuration of Ar atom.

The radial parts of KS orbitals \( \Psi_{nlm}^{(0)}(r) \) are found within the imaginary time propagation method [43] (see the numerical scheme of time propagation in section 2.2). In order to resolve oscillations of wave functions with the scale \( \sim 1/N \) near the nucleus, we use a nonuniform spatial grid, which has a higher density of nodes near the nucleus. The radial nodes of the spatial grid are specified as

\[
r_n = k\Delta r + (\Delta r/\Delta r - 1)r_0 \tanh (k\Delta r/r_0),
\]

where \( k \) is the wave number and \( \Delta r \) is the node spacing.

Table 1. Absolute values of orbital binding energies of Xe. (A) Our DFT calculation with LB94 exchange–correlation potential [42]. (B) Experiment [44,45].

| Orbital | Energy (eV) |
|--------|-------------|
|        | (A) DFT     | (B) Experiment |
| 1s     | 33 068.8    | 34 561         |
| 2s     | 5032.4      | 5453           |
| 2p     | 4741.3      | 5107 (3p \text{\,3/2}) | 4786 (3p \text{\,1/2}) |
| 3s     | 1039.8      | 1148.7         |
| 3p     | 915.2       | 1002.1 (3p \text{\,3/2}) | 940.6 (3p \text{\,1/2}) |
| 3d     | 682.6       | 689 (3d \text{\,3/2}) | 676.4 (3d \text{\,1/2}) |
| 4s     | 189.4       | 213.2          |
| 4p     | 145.5       | 146.7 (4p \text{\,3/2}) | 145.5 (4p \text{\,1/2}) |
| 4d     | 69.9        | 69.5 (4d \text{\,3/2}) | 67.5 (4d \text{\,1/2}) |
| 5s     | 23          | 23.3           |
| 5p     | 12.8        | 13.4 (5p \text{\,3/2}) | 12.1 (5p \text{\,1/2}) |
where $k$ is an integer, $\delta r = 10^{-4}$ a.u. is tiny step of the radial grid, which is realized near the nucleus; 
$\Delta r = 0.1$ a.u. is the radial step for large distances; $r_0 = 20$ a.u. is the scale for changing spatial step from $\delta r$ to $\Delta r$. The size of radial grid was limited by 200 a.u.

The binding energies of KS orbitals are derived from (2.1). They are listed in table 1 along with experimental binding energies, which resolve spin–orbit splitting of $p$ and $d$ energy levels [44, 45]. The deviation of the numerical and experimental binding energies do not exceed 11%. In particular, for the outer $5s$ and $4p$ subshells, the accuracy of agreement with the experiment is 5%, for $5s$, $4p$, and $4d$ subshells, it is 1%, and for the $4s$ orbital, it is 11%. Thus, the used LB94 exchange–correlation approximation is generally well suited for describing the electronic configuration of the Xe atom.

### 2.2. Time-dependent Kohn–Sham equations

We consider the interaction of a linearly polarized laser pulse with an atomic target in the dipole approximation. For this case, TDKS equations are

$$
\frac{\partial}{\partial t} \psi_j(r, t) = \hat{H} \psi_j(r, t),
$$

(2.7)

$$
\hat{H} = -\frac{\nabla^2}{2} - \frac{N}{r} + r \cdot F(t) + V_{ee}[\rho(r, t)],
$$

(2.8)

where $F(t) = \hat{z}F(t)$ is the electric field of a short laser pulse, $\psi_j(r, t)$ is the wave function of the TDKS orbital determining the time-dependent electron density

$$
\rho(r, t) = 2\sum_{j=1}^{N/2} |\psi_j(r, t)|^2.
$$

(2.9)

The TDKS equations are solved with initial condition

$$
\psi_j(r, t = 0) = \psi_j^{(0)}(r),
$$

(2.10)

which we have discussed in the previous subsection.

Interaction of an intense laser pulse with an atomic target induces a time-dependent dipole moment $D(t)$. For linearly polarized field, the dipole moment is directed along $z$ axis, $D(t) = \hat{z}D(t)$ and is expressed in terms of density distribution:

$$
D(t) = \int \rho(r, t) \, dr = \sum_j D_j(t),
$$

(2.11)

$$
D_j(t) = 2 \int \hat{z}|\psi_j(r, t)|^2 \, dr.
$$

(2.12)

The properties of the radiation generated by atom subjected into intense laser field are determined by the dipole acceleration $a(t)$:

$$
a(t) = \frac{d^2D(t)}{dt^2} = \sum_j a_j(t),
$$

(2.13)

$$
a_j(t) = \frac{d^2D_j(t)}{dt^2} = -2F(t) - 2 \int |\psi_j|^2 \frac{\partial}{\partial z} \left( V_{ee} - \frac{N}{r} \right) \, dr,
$$

(2.14)

where $a_j(t)$ is the partial dipole acceleration of the KS orbital having index $j$. The spectral density of the dipole acceleration is given by squared Fourier transform of $a(t)$,

$$
R[a](\omega) = \left| \int_{-\infty}^{\infty} a(t)e^{i\omega t} \, dt \right|^2.
$$

(2.15)

The general formulation of the density functional method allows one to study the contributions of different KS orbitals, subshells, and whole shells of an atom to the total dipole acceleration; thereby, TDKS equations provide access to the inner details of the atomic response in the external field. Corresponding contributions from shell or subshell, respectively, are given by proper summation in $j$:

$$
\hat{a}_n(t) = \sum_j a_j(t), \quad \hat{a}_{nl}(t) = \sum_{n,l} a_{j}(t),
$$

(2.16)
where the range of \( j \) determines the contribution for whole shell \( n \) or either subshell \((n, l)\). The spectral density of partial contributions of KS orbitals, subshells, and shells are calculated using equation (2.15) as \( R[A_j](\omega), R[\tilde{A}_e](\omega) \), and \( R[\tilde{A}_b](\omega) \), respectively.

The algorithm for the numerical solution of TDKS equation (2.7) is the same as that used by us in reference [20]. Taking into account that for linearly polarized laser pulse the magnetic quantum number is conserved for each KS orbital, the KS orbitals are expanded in spherical harmonics [43, 46]:

\[
\psi_j(r, t) = r^{-\frac{1}{2}} \sum_{l=0}^{l_{\text{max}}} a_j^{l0} Y_{l0}(\theta, \varphi). 
\]  
(2.17)

Each term corresponds to the orbital momentum \( l \), and \( \psi_j(r, t) \) is the radial part satisfying the initial condition \( \psi_j(r, 0) = \delta_{l0}\psi_{l0}^0(r) \). Here, \( \delta_{l0} \) is the Kronecker symbol, and \( n, l, m \) are quantum numbers that define KS orbital number \( j \) by (2.6). Since \( |\psi_j(r, t)|^2 \) does not depend on the azimuthal angle, the electron–electron interaction potential can be expanded in the Legendre polynomial, \( P_l(\cos \theta) \), series. For considered laser pulse parameters, this expansion may be limited by the first three terms:

\[
V_{ee}\{\rho(r, t)\} \approx \sum_{k=0}^{2} V_{ee}^{(k)}(r, t) P_k(\cos \theta). 
\]  
(2.18)

Using expansion (2.17) and approximation (2.18) we reduce equation (2.7) to the system of coupled equations:

\[
i \frac{\partial}{\partial t} \Psi_j(r, t) = \left( \hat{R}_j + \hat{W}_j \right) \Psi_j(r, t), 
\]  
(2.19)

where \( \Psi_j \) is the column-vector whose \( l \)th element is \( \psi_j(r, t) \). Elements of the diagonal matrix \( \hat{R}_j \) are

\[
\left[ \hat{R}_j \right]_{pp} = \frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} - \frac{N}{r} + V_{ee}(0) + \frac{l(l+1) - 3m^2}{(2l+1)(2l+3)} V_{ee}^{(2)}, 
\]  
(2.20)

and elements of the pentadiagonal matrix \( \hat{W}_j \) are determined by

\[
\left[ \hat{W}_j \right]_{kl} = \begin{cases} 
\delta_{l-2m} V_{ee}^{(2)}, & k = l - 2 \\
\delta_{l-1m} \left[ rF(t) + V_{ee}^{(1)} \right], & k = l - 1 \\
\delta_{lm} \left[ rF(t) + V_{ee}^{(1)} \right], & k = l \\
\delta_{l+1m} V_{ee}^{(2)}, & k = l + 1 \\
0, & \text{otherwise}
\end{cases} \]  
(2.21)

where

\[
ce_{lm} = \sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}}, \\
d_{lm} = \frac{3}{2} c_{lm} \sqrt{\frac{(l+2)^2 - m^2}{(2l+3)(2l+5)}}. 
\]  
(2.22)

The propagation of \( \Psi_j(r, t) \) over time step \( \Delta t \) is performed using three-split-operator symmetric decomposition [47]:

\[
\Psi_j(r, t + \Delta t) \approx e^{-i\Delta t \hat{W}_j/2} e^{-i\Delta t \hat{R}_j(t)/2} e^{-i\Delta t \hat{W}_j(t)/2} \Psi_j(r, t). 
\]  
(2.23)

First and third exponential operators are applied through the diagonalization of matrix \( \hat{W}_j \) within unitary transformation \( \hat{W}_j = \hat{S}_j \hat{W}_{j, \text{diag}} \hat{S}_j \), where \( \hat{W}_{j, \text{diag}} \) is the diagonal matrix and unitary matrix \( \hat{S}_j \) is known analytically:

\[
e^{-i\Delta t \hat{W}_j/2} = \hat{S}_j e^{-i\Delta t \hat{W}_{j, \text{diag}}/2} \hat{S}_j^\dagger. 
\]  
(2.24)

The second exponential operator is approximated by Crank–Nicholson method:

\[
e^{-i\Delta t \hat{R}_j} \approx (1 + i\hat{R}_j \Delta t/2)^{-1}(1 - i\hat{R}_j \Delta t/2). 
\]  
(2.25)

The second derivative in \( \hat{R}_j \) is calculated by using the Numerov approximation [46].

The maximum orbital momentum in expansion of wave functions in spherical harmonics is \( l_{\text{max}} = 64 \) for calculations in section 3 and \( l_{\text{max}} = 512 \) for calculations in section 4. The orbitals on 1–3 shells are frozen, i.e. \( \psi_j(r, t) \equiv e^{-i\theta_j^0(t)} e^{-i\theta_j^0(0)}(r) \) for \( j \leq 14 \). Freezing of internal orbitals makes it possible to use a relatively large time step \( \Delta t = 0.02 \) a.u. without losing accuracy in numerical calculations. The absorbing layer is modeled by multi-hump imaginary potentials [48] with total absorption layer width \( r_{\text{abs}} = 50 \) a.u., providing a wide range of effectively absorbed de Broglie wavelengths.
3. Interaction with monochromatic XUV field

In this section, we consider the interaction of Xe atom with a perturbative monochromatic XUV field. Within the numerical solution of TDKS equation (2.7), we calculate the total (angle-integrated) PICS and study the response of individual subshells from the 4th and 5th shells.

The XUV field \( F(t) \) is parameterized as \( F(t) = F_0 f(t) \cos(\omega_0 t), \) where \( \omega_0 \) is the carrier frequency, and \( f(t) \) is trapezoidal envelope with duration \( \tau_p = 5 \) fs for flat top part and \( \tau_0 = 0.5 \) fs for tuning on/off part. The intensity of the XUV pulse is fixed, \( I = 2 \times 10^{12} \) W cm\(^{-2} \), while frequency \( \omega_0 \) is considered in the range 20–220 eV. For such parameters we can neglect the contribution from the two-photon ionization.

The PICS \( \sigma_{nl}^{\omega_0}(\omega_0) \) is found based on the sum of the averaged ionization probabilities per unit time from individual KS orbitals:

\[
\sigma_{nl}^{\omega_0}(\omega_0) = \frac{\omega_0}{T} \sum_{\text{subshell } (n,l)} \bar{w}_j(\omega_0),
\]

(3.1)

\[
\bar{w}_j(\omega_0) = \frac{2}{\tau_p} \left( 1 - \int_{t<\tau_0} |\psi_j(t = t_f)|^2 dt \right),
\]

(3.2)

where, \( t_f = \tau_p + 2\tau_0 \) is the ending time of the XUV pulse, \( r_0 = 10 \) a.u. determines the radius of the sphere, whose edge separates bounded \( (r < r_0) \) and free electrons \( (r > r_0). \) The used value of \( r_0 \) was chosen based on the stability of \( \sigma_{nl}^{\omega_0} \) when changing \( r_0 \) near 10 a.u. for all considered \( n, l \) in a wide range of \( \omega_0. \)

Figure 1(a) shows PICS \( \sigma_{nl}^{\omega_0}(\omega_0) \) for all subshells on 4th and 5th shells. PICSs for 5p, 5s, and 4d subshells contain wide maxima near \( \omega_0 \approx 100 \) eV. The corresponding maximum in 4d PICS is more than an order of magnitude higher than that for 5p and 5s subshells. Note that the calculated PICSs are in excellent agreement with the experimental PICS from reference [49], which confirms the high accuracy of the TDKS equation (2.7) with used electron–electron interaction potential for studying phenomena caused by electron–electron interactions in Xe atom. PICSs for 4s and 4p subshells are negligible in the region of the giant resonance 60 eV < \( \omega < 130 \) eV due to insufficient photon energy for ionization (the threshold of the photoelectric effect for 4p subshell is \( |E_{4p}| = 145.5 \) eV, for 4s \(|E_{4s}| = 189.4 \) eV, see table 1).

In the central mean-field model, the shape resonance in the 4d PICS originates from a sharp resonance–like increase in the matrix element of the transition from the 4d state to the continuum \( \epsilon f \) state. This results from the double-well structure of the effective potential created by the ion field and centrifugal force. The barrier between these two wells suppresses the overlapping of continuum \( \epsilon f \) and 4d bound state wave functions. This overlapping gradually increases with increasing \( \epsilon \) and is maximized for those energies, which are located near the maximum of this barrier [50–54]. As a result, the matrix element of the 4d \( \rightarrow \epsilon f \) transition increases sharply. The further increasing photoelectron energy in \( \epsilon f \)-channel leads to a decreasing transition matrix element due to the nodal structure of 4d orbital, thereby forming the shape of the giant resonance in the 4d PICS.

Our TDKS calculations of PICSs with the frozen potential for electron–electron interaction \( \langle V_ee(r,t) \rangle \equiv V_ee[\rho_0(r)] \) show: (i) the maximum of PICS for 4d subshell is located at \( \omega_0 \approx 80 \) eV; (ii) PICSs for 5p and 5s subshells do not show up maxima (see dashed lines in figure 1(a)). The account of the time-dependent dynamics into potential \( V_ee(r,t) \) shifts the maximum of the 4d PICS and makes the shape of resonance wider. Moreover, due to the energy exchange with the external shell, PICSs for 5p and 5s subshells also get a strong maximum around 90 eV (see solid lines in figure 1(a)). All these issues are found in agreement with previous results in reference [40].

The broadening and shift of the giant resonance in 4d PICS is primarily the consequence of the ‘collectivization’ of ten 4d electrons via the interchannel coupling [33, 40, 51, 53, 54]. However, when the Xe atom is exposed to an external field at the frequency \( \omega_0 \gtrsim 100 \) eV, a linear response (i.e. induced dipole moment) is observed not only for 4d but also for 4p and 4s subshells. This can be seen from the calculation of spectral densities at the carrier frequency \( \omega_0 \) of the dipole acceleration for individual subshells, \( R[\bar{\sigma}_{nl}](\omega_0) \), and for the 4th shell, \( R[\bar{\sigma}_s](\omega_0) \), where \( n = 4 \). Freezing of the electron–electron potential leads to a decrease in the 4p and 4s orbitals response in the range \( \omega_0 = 100–130 \) eV by an order of magnitude or even higher (see figure 1(c)). Thus, the electron–electron interaction with the 4d subshell causes the enhancement of the response of 4p and 4s subshells. This strong interchannel coupling is realized due to similar spatial distribution of all orbitals on the 4th shell (see figure 2). Indeed, according to the perturbation theory for the TDKS equations [37, 55], the coupling matrix element between different KS orbitals is maximized for similar spatial distributions of their wavefunctions. Figure 2 shows that the wide maxima of the radial probability distributions of KS orbitals \(|\Psi_{nl0}(r)|^2 \) for 4d, 4p and 4s subshells are located at \( r \sim 0.68–0.75 \) a.u., and the characteristic scales of the decreasing from the maximum for 4d, 4p...
Figure 1. (a) Angle-integrated partial PICS $\sigma_{nl}(\omega_0)$ of Xe for 5p, 5s, 4d, 4p and 4s subshells. Solid lines are TDDFT results, dashed lines are TDDFT results with frozen electron–electron potential, and black crosses are experimental data for 4d, 5s, and 5p subshells from reference [49]. (b) and (c) Linear response of individual subshells at the 4th shell (thin lines) and the whole 4th shell (thick line) calculated as $R_{anl}(\omega_0)$ and $\tilde{R}_{an}(\omega_0)$ for $n = 4$, respectively, in monochromatic XUV field with frequency $\omega_0$ and intensity $I = 2 \times 10^{12}$ W cm$^{-2}$. The panels (b) and (c) corresponds to the TDDFT result with time-dependent and frozen electron–electron potential, respectively. The dashed vertical lines in panels (b) and (c) denote the transition energies between subshells with orbital angular momentum $l$ differing by one.

Figure 2. Radial probability distribution $|\Psi_{anl}^{\text{KS}}(r)|^2$ for stationary KS orbitals on 4th and 5th shells.

and 4s wave functions are approximately the same. This promotes a laser photon energy transfer from the 4d subshell to orbitals on 4p and 4s subshells through the electron–electron interaction. This physical channel, along with the interaction between electrons on the 4d subshell, can also be one of the reasons for the shift and expansion of the giant resonance in the PICS for the 4d subshell.
It should be noted that the calculated responses of individual subshells of the Xe atom in the XUV field contain narrow resonance maxima seen in figure 1(b). The corresponding frequencies equal to the difference in the binding energies of the given subshell and the other subshells having angular momentum differing by one. This resonance maxima originate from the transition between the initial state \((n', l', m)\) to the state \((n, l, m)\) of unperturbed Hamiltonian under the action of external XUV field with a resonant frequency \(\omega_0 = |E_{l'} - E_l|\), where \(E_l\) is the energy of the \((n, l, m)\) level and \(l' = l \pm 1\). As a result, the dipole moment of \(j\)th KS orbital, \(D_j(t)\), contains a cross-term that oscillates with this frequency.

However, the dipole moment of \(j\)th KS orbital, \(D_j(t)\), also contain oscillations at the same resonant frequency and the same amplitude but the opposite sign, which is due to the back transition \((n', l', m) \rightarrow (n, l, m)\) in the \(j\)th KS orbital \(\psi_j\). As a result, all the ‘artificial’ resonances of KS orbitals cancel each other in the total dipole moment. Indeed, as is seen from figure 1(b), the responses of \(4d\) and \(4p\) subshells have narrow resonance maxima at \(\omega_0 = |E_{4d} - E_{4p}| \approx 75.6\) eV, but there is no any enhancement in the total response of the 4th shell at this resonance frequency.

4. HHG in xenon

The nonlinear response of the xenon atom appears at high harmonics of the IR frequency when the atom is subjected to an external IR field. This section considers the HHG in Xe subjected to the two-cycle IR-field having intensity \(I = 1.9 \times 10^{14}\) W cm\(^{-2}\) and wavelength \(\lambda = 1.8\) μm. The selected parameters correspond to the experiment [14]. In the numerical calculations, we parameterize the electric component of the laser pulse in terms of vector potential:

\[
F(t) = -\frac{1}{c} \frac{\partial A}{\partial t}, \quad A(t) = -\frac{c F_0}{\omega_0} f(t) \sin(\omega_0 t),
\]

where \(\omega_0 = 2\pi c/\lambda\) is the carrier frequency, \(c\) is the speed of light, \(F_0\) is the strength of a laser pulse, whose magnitude determines the intensity of a laser pulse as \(I = F_0^2 I_0\), where \(F_0\) is normalized to the atomic electric-field unit and \(I_0 = 3.51 \times 10^{16}\) W cm\(^{-2}\). The envelope of the vector potential is \(f(t) = \sin^2(\pi t/\tau)\) for \(0 < t < \tau\) and \(f(t) = 0\) otherwise. The intensity full-width at half maximum duration \(\tau_p = \tau(2 \arccos(2^{-1/4})/\pi) = 12\) fs corresponds to two field periods at the carrier frequency.

In figure 3(a) we show a comparison of HHG spectra \(R[a](\omega)\) calculated within TDDFT (blue solid line), analytical parameterization (red solid line) suggested in references [10, 56, 57], and experimental result [14] (black line). The analytical parameterization of HHG yield consists in the separation of the atomic and laser parts (EWP):

\[
R(\omega) = W(\varepsilon) \sigma_{\text{rec}}(\varepsilon, 0),
\]

where \(W(\varepsilon)\) is the EWP, \(\sigma_{\text{rec}}(\varepsilon, 0)\) is the differential PRCS of electron with kinetic energy \(\varepsilon = \omega - E_p\), where \(E_p\) is the ionization potential (see more details in appendix A). All three HHG spectra are found in good agreement with each other. The spectral intensity (averaged over 2\(\omega_0\) range) contains a giant enhancement region with a maximum at \(\omega \approx 100\) eV. In the frequency range below the giant enhancement, the spectrum contains a minimum at \(\omega \approx 60\) eV and a narrow near-threshold enhancement region near \(\omega \approx 20\) eV. For harmonic energies above the giant resonance maximum, the numerical HHG spectrum has a pronounced minimum at \(\omega \approx 160\) eV and gradually increases with \(\omega\) up to the cutoff at \(\omega \approx 185\) eV. Experimental harmonic yield rapidly drops off at frequencies above the giant enhancement region, which can be caused by the propagation macroscopic effects associated with phase mismatch, defocusing, and others in the experiment [58–61]. Also, our calculations do not take into account the spatial intensity distribution of the laser pulse, which can be also one of the reasons for deviation of HHG spectrum from the experimental results.

To ensure that the high harmonic generation in Xe is provided within the standard three-step scenario (and impact ionization does not play an important role), we calculate the Gabor transform of the dipole acceleration found from TDDFT:

\[
S(\omega, t) = \int_{-\infty}^{\infty} a(t - t') e^{-i\omega t'} - (2 \ln 2) t'^2 / \tau_0^2 dt',
\]

where \(\tau_0 = 0.2\) fs. Figure 3(b) shows the time-frequency distribution \(|S(\omega, t)|^2\) and the classical dependences of the generation frequency for the trajectories with one and higher-order returns [63] (dotted

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6 Since the ionization is weak, the potential \(-N/\tau + V_m[\rho(t, t)]\) has the same stationary bound energies as the unperturbed potential.

7 For ease of understanding, figures 3 and 4 show the smoothed spectra obtained by averaging the spectrum using a smooth rectangular window function with a width \(\approx 2\omega_0\).
Figure 3. (a) HHG spectra for Xe atom subjected to the two-cycle linearly polarized laser pulse with peak intensity $I = 1.9 \times 10^{14}$ W cm$^{-2}$ and central wavelength $\lambda = 1.8$ $\mu$m. The blue dotted line is the TDDFT result, blue solid line is the smoothed TDDFT result, the red line is the (smoothed) analytical result for HHG yield (4.2) utilizing experimental PRCS [49, 62], black line denotes normalized experimental HHG spectrum from reference [14]. (b) Time-frequency spectrogram $|S(\omega, t)|^2$ (in arbitrary units) of the dipole acceleration $a(t)$ calculated using TDDFT. Black lines denote the classical dependences of the emitted photon energy on the return time moment for first return (dotted lines) and higher-order returns (dashed lines).

and dashed lines, respectively) on the return time moment. The generation frequency was found as $\omega_c = E_{\text{kin}} + I_p$, where $I_p = 12.1$ eV is the ionization potential of Xe atom, $E_{\text{kin}}$ is the gained kinetic energy calculated using classical Newton equation (see appendix A). Over the entire frequency range $\omega > 20$ eV, high harmonics are generated along classical trajectories supporting three-step scenario of HHG. An increase in the spectral intensity is observed along all trajectories near $\omega \approx 100$ eV, which indicates the high amplitude of recombination in the region of giant HHG enhancement. In addition, the spectral intensity is locally increased in the vicinity of caustics corresponding to the merging of ‘short’ and ‘long’ closed electrons trajectories (classified in terms of return time) [64]. In the vicinity of the caustic, the partial amplitude of HHG is described by Airy function, which forms a wide peak [30, 65, 66]. Caustic generated by electrons with first return at $21$ fs $< t_r < 23$ fs leads to the formation of an intermediate ‘plateau’ in the HHG spectrum ending at $\omega \approx 130$ eV. High-order returns at $18$ fs $< t_r < 23$ fs result in local maximum in HHG spectrum at $\omega \approx 90$ eV. Spectral caustics corresponding to the highest possible return energy lead to an increase in the spectral intensity in the cutoff region at 185 eV, and this increase is enhanced by the smooth growth of the differential PRCS in this frequency range.

4.1. Individual response of orbitals on two active shells

The TDDFT formalism allows one to separate the contributions of different KS orbitals to the total dipole acceleration, thereby providing a detailed study of their collective contribution to the enhancement of the HHG yield. In figure 4 we present the Fourier spectra of contributions $a_n(t)$ for individual orbitals, of contributions $\pi_{n}(t)$ for subshells 4$d$, 4$p$, and 4$s$, and contribution for 4th shell determined by $\hat{a}_n(t)$ for $n = 4$.

4.1.1. 5$p_0$ orbital

Let us consider the response of the outer-valence 5$p_0$ orbital, which is oriented in space along the electric field and interacts most actively with the linearly-polarized IR laser pulse. As seen from figure 4(a), the partial dipole acceleration spectrum of 5$p_0$ KS orbital contains a high-frequency flat plateau with the same cutoff as the full HHG spectrum. At low frequencies, $\omega \sim 15–30$ eV, the response of 5$p_0$ orbital contains a near-threshold enhancement associated with a sharp increasing of the transition matrix element from the continuum state to the 5$p_0$ state with decreasing frequency of emitted photons [11, 51, 53, 67, 68]. The response of the 5$p_0$ KS orbital is well described by the three-step scenario for the HHG [1, 8], i.e. the electron from the 5$p_0$ KS orbital is ionized by a laser pulse, then it is accelerated by a laser field in the continuum and, finally, electron recombines to the initial state with the emission of a photon with energy
equal to the sum of gained kinetic energy and ionization potential. The only peculiarity is that response of 5p₀ KS orbital contains a narrow peak at \( \omega = E_{5p} - E_{4d} \approx 57.1 \) eV caused by the transition between 5p₀ and 4d₀ levels led by the electron–electron interaction. In the full HHG spectrum, this resonant peak is compensated by the corresponding resonance term in the response of 5s orbitals (orange, gray, and light blue lines, respectively). The only peculiarity is that response of 5p₀, 5p₁, and 5s orbitals (orange, gray, and light blue lines, respectively). The blue lines in (a) and (b) show the total smoothed HHG yield; the black line in (a) is the total smoothed HHG yield calculated with frozen electron–electron potential.

\[ \psi_{\text{res}}(r, t) = \psi_{\text{res}}(r, t) + \psi_{\text{rec}}(r, t), \]

where \( \psi_{\text{rec}}(r, t) \) is the so-called adiabatic part, which can be well approximated by the field-free wave function, \( \psi_{\text{free}}(r, t) \approx \psi_{\text{free}}(r)e^{-iE_{\text{free}}t} \), and \( \psi_{\text{rec}}(r, t) \) is the rescattering part of the wave function. Although this rescattering part is exponential small, it induces both the time-dependent moment given by the 5p₀ orbital, \( D_{5p_0}(t) \approx \int \psi_{\text{rec}}^* \psi_{\text{rec}} \, dr + \text{c.c.} \), and variation in the electron density \( \rho(r, t) \) from the corresponding field-free

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Footnote 8: For 5p₀ KS orbital, survival probability is 88.4%, while in frozen-core model, i.e. excluding polarizability, just 19.3%.
distribution,
\[ \rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta \rho(\mathbf{r}, t), \]  
\[ \delta \rho(\mathbf{r}, t) \approx \psi_{\text{res}}^* \psi_{\text{res}} + \text{c.c.} \]  
(4.5)
(4.6)

The small changes in the density \( \rho(\mathbf{r}, t) \) lead to a variation of electron–electron interaction, \( \delta V_{ee} \):
\[ V_{ee}[\rho] \approx V_{ee}[\rho_0] + \delta V_{ee}, \quad \delta V_{ee} = \int \frac{\delta \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + V_{ee}^{(0)} \delta \rho, \]  
(4.7)
where \( V_{ee}^{(0)} \equiv \langle \partial V_{ee}/\partial \rho \rangle|_{\rho=\rho_0}. \) The term \( \delta V_{ee} \) can be considered as a perturbation which acts as a broadband excitation source inducing the time-dependent moment \( D_j(t) \) of KS orbitals. Moreover, the rescattering part of \( 5p_0 \) KS orbital can affect on all orbitals including those with \( m \neq 0 \). The account of \( \delta V_{ee} \) within perturbation theory leads to variation \( \psi_j(\mathbf{r}, t) \) of the KS orbitals with index \( j \neq 3p_0 \):
\[ \psi_j(\mathbf{r}, t) \approx \psi_j^{(0)}(\mathbf{r}) e^{-iE_j t} + \delta \psi_j(\mathbf{r}, t), \]  
(4.8)
\[ \delta \psi_j = \sum_q \delta c_j^q(t) \psi_j^{(0)}(\mathbf{r}) e^{-iE_j'}, \]  
(4.9)

where the sum is carried out over all possible states \( q \) of the unperturbed Hamiltonian (2.1) forming a complete orthogonal system of wavefunctions \( \psi_q^{(0)}(\mathbf{r}) \), and
\[ \delta c_j^q(t) = \delta c_j^{q,\to}(t) + \delta c_j^{q,\leftarrow}(t), \]
\[ \delta c_j^{q,\to}(t) = -i \int_0^t d\tau' e^{i\Delta E_c^{q,\to}(\tau')} \int \int \frac{[\psi_q^{(0)}(\mathbf{r}) \psi_j^{(0)}(\mathbf{r})]^* \psi_{\text{res}}(\mathbf{r}, \tau', t') \psi_j^{(0)}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \, d\mathbf{r}, \]
\[ \delta c_j^{q,\leftarrow}(t) = -i \int_0^t d\tau' e^{i\Delta E_c^{q,\leftarrow}(\tau')} \int \int \frac{[\psi_q^{(0)}(\mathbf{r}) \psi_j^{(0)}(\mathbf{r})]^* \psi_{\text{res}}(\mathbf{r}, t', \tau') \psi_j^{(0)}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \, d\mathbf{r}, \]
\[ \Delta E_c^{q,\pm}(t) = E_q - E_j \pm E_{3p_0}. \]  
(4.10)

Using the variation in \( \psi_j \), the time-dependent dipole moment of \( j \)th KS orbital (2.12) can be written as
\[ D_j(t) \approx \sum_q d_q [\delta c_j^{q,\to}(t) + \delta c_j^{q,\leftarrow}(t)] e^{i(E_j - E_{3p_0})t} + \text{c.c.}, \]  
(4.11)

where \( d_q = \int [\psi_q^{(0)}(\mathbf{r})]^* \mathbf{z} \psi_{j}^{(0)}(\mathbf{r}) \, d\mathbf{r} \) is the transition dipole matrix element. Among all possible intermediate states \( q \), only those with the same quantum numbers \( m \) and differing by one orbital angular momentum \( \ell \) compared to the \( j \)th state contribute to the sum (4.11).

The high response of KS orbitals for \( j \neq 3p_0 \) can be interpreted as a collective dynamics of the valence \( 5p_0 \) electron and a core electrons (see also references [14, 24, 31]). Indeed, in the first step, the valence electron \( (5p_0 \) electron) tunnels through the barrier and gets some extra kinetic energy \( E_k \) into the laser-perturbed continuum, which shares with a core electron on \( j \)th orbital. The correlation between these two electrons induces changing in electron–electron interaction and leads to the ‘relaxation’ of these two electrons into \( 5p_0 \) orbital and intermediate \( ef \) states with a hole in \( j \)th state. The subsequent transition from \( q \)th state to \( j \)th state returns the atom to the initial ground state with a harmonic emission of frequency \( \omega = E_k - E_{3p_0} \) in agreement with the energy conservation law.

Excitation of oscillations of the 4th shell due to the recoiling photoelectron leads to the formation of a giant HHG yield in the frequency range \( \omega = 60 – 130 \text{ eV} \), which at \( \omega = 100 \text{ eV} \) is more than one order of magnitude higher compared to the contribution of \( 5p_0 \) KS orbital. In this frequency range, the 4d subshell contains a giant resonance in PICS, so that 4d orbitals have large coupling matrix elements with the rescattering continuum wavepacket, \( 5p_0 \) state and intermediate \( ef \) states in the continuum, and also high dipole matrix elements of transition \( ef \to 4d \). Different orbitals from 4d subshell near the giant enhancement have the same high response (see figure 4(c) and reference [24]), which is due to the interaction of laser-perturbed \( 5p_0 \) KS orbital with all \( m \) orbitals and with the ‘collectivization’ of electrons.
in the 4d subshell [33, 40, 54]. However, as seen from figure 4(b), a large response in the region of giant HHG enhancement is also observed for deeper-lying 4p and 4s subshells. We note that it was previously accepted that only 4d subshell participates in HHG enhancement. Moreover, as can be seen from figures 4(c) and (d), the responses of individual KS orbitals in the 4th shell have a comparable response at \( \omega > 100 \) eV. Coherent summation of responses from different subshells on 4th shell leads to a noticeable (more than two times) increase in HHG yield compared to the contribution of only 4d subshell in the frequency range \( \omega \sim 80–140 \) eV. Above the giant enhancement region, at \( \omega > 170 \) eV, the response of the 4p subshell exceeds the response of the 4d subshell despite fewer electrons on the 4p subshell. The reason for the broadband high-frequency response of 4p and 4s orbitals is related, from the one hand, to the action of the \( \delta V_{ee} \) perturbation induced by the rescattering wavepacket from 5p\(_0\) orbital. From the other hand, as shown in section 3, 4p and 4s subshells can oscillate due to the coupling with the 4d orbital. In the case of HHG, this means that the recollision-induced perturbations \( \delta \psi_j (4.9) \) in the wavefunctions of 4d KS orbitals induce a secondary perturbation in the electron–electron potential, which acts on all other KS orbitals, including 4p and 4s orbitals. Note that the effect of this secondary disturbance is also noticeable in the response of orbitals from 5th shell at \( \omega = 70–130 \) eV (see figure 4(a)). In this frequency range signal amplification is observed for 5p\(_{±1}\) orbitals. In general, the contribution of the 5p\(_{±1}\) and 5s orbitals to HHG is significantly lower than that for the 4th shell and 5p\(_0\) orbital because of the small matrix element of the transition to the high-energy continuum states. At the same time, induced time-dependent electron–electron potential \( \delta V_{ee} \) leads to a broadband response of the 5s and 5p\(_{±1}\) KS orbitals on the outer shell for the frequency range \( \omega \sim 15–30 \) eV. A large low-frequency response of orbitals on the outer shell also exists in other noble-gas atoms, e.g. for Ar atom see references [20, 22]. The responses of orbitals on the outer shell are in phase and provide visible contribution (comparable with that for of 5p\(_0\) KS orbital) to the total HHG yield for \( \omega \sim 15–30 \) eV.

5. Summary and conclusions

To conclude, in this work, we have used the time-dependent density functional theory to study the HHG by Xe atom in an intense infrared pulse. In contrast to the previous numerical studies of this phenomenon, the dynamics of the whole 4th and 5th shells of the Xe atom is taken into account, leading to a good agreement with the experiment and the analytical parameterization of HHG yield in terms of the EWP and exact (experimental) PRCS to the 5p\(_0\) state. It was demonstrated that as for argon atom [20], in the low-frequency range of generated spectral harmonics (\( \omega \sim 15–30 \) eV), a comparable contribution to HHG is given by all orbitals from the outer shell. The origin of such unusual collective contribution is the broadband component in electron–electron harmonics induced by the recolliding 5p\(_0\) wave packet, which collisionally disturbs outer shell orbitals, thereby induces the time-dependent dynamics in these orbitals. In the giant enhancement region (\( \omega \sim 60–130 \) eV), the 5th shell’s response is much smaller than that of the 4th shell, which is easily excited by the electron–electron potential due to the giant resonance in 4d transition to the continuum. Moreover, in addition to 4d subshell, deeper-lying 4p and 4s subshells also participate in the HHG, giving substantial contribution at higher frequencies. The reason for the substantial response of the 4p and 4s subshells at the giant resonance is the dynamic interaction between the orbitals on the 4th shell, associated with the close localization of their wave functions in space. The results of numerical simulations demonstrate that a similar response of 4p and 4s subshells is presented by interaction of Xe atom with an external linearly-polarized XUV field. Therefore, correlation interaction between all orbitals on the 4th shell can contribute to both the formation of the HHG spectra by infrared field and PICSs from 4d, 5p, and 5s subshells of Xe atom.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
Appendix A. Analytical factorization of HHG yield

The HHG yield in an intense low-frequency linearly-polarized laser field can be factorized into two factors [30, 56, 57, 66, 75]. The first universal factor, $W(\mathcal{E})$, known as EWP, describes tunneling and propagation of an active electron in a laser field along closed classical trajectories with returning energy $\mathcal{E} = \omega - I_p$, where $\omega$ is harmonic frequency. The second factor is field-free differential PRCS for the zero angle between returning electron momentum and polarization vector of emitted photon, $\sigma_{\text{rec}}(\mathcal{E}, 0)$,

$$R(\omega) = W(\mathcal{E})\sigma_{\text{rec}}(\mathcal{E}, 0). \quad (A.1)$$

Differential PRCS $\sigma_{\text{rec}}(\mathcal{E}, \theta)$ is related to the differential PICS, $\sigma_{\text{ion}}(\mathcal{E}, \theta)$, by the principle of detailed balance [32]:

$$\sigma_{\text{rec}}(\mathcal{E}, \theta) = \sigma_{\text{ion}}(\mathcal{E}, \theta) \frac{\omega^2}{2\mathcal{E}^2}, \quad (A.2)$$

where $\theta$ is an angle between photon polarization vector and electron momentum.

Although factorization (A.1) was theoretically justified within the single-active electron approximation (SAEA) [56, 66, 75], it provides a qualitative agreement with HHG experimental results [11, 12, 14–16]. For practical calculations, the form of EWP can be found numerically within SAEA calculation for a reference atom [56, 57], or either within analytical expressions [41, 76]. In this work, EWP was calculated analytically within adiabatic approximation for HHG [41]. Within adiabatic approximation, the EWP is determined by the set of real times $\{t_j^{(0)}, t_j^{(0)}\}$, corresponding to the moments of ionization ($t_j^{(0)}$) and recombination ($t_j^{(0)}$). These times obey a system of transcendental equations:

$$K_j' = 0, \quad \frac{K_j^2}{2} = \omega - I_p - \Delta \mathcal{E}_j, \quad (A.3)$$

where $K_j'$ and $K_j$ are instantaneous electron momenta at the moment of ionization and recombination

$$K_j' = K(t_j^{(0)}; t_j^{(0)}, t_j^{(0)}), \quad K_j = K(t_j^{(0)}; t_j^{(0)}, t_j^{(0)}),$$

and $K(t; t_j^{(0)}, t_j^{(0)})$ is instantaneous (at the moment $t$) momentum of an electron moving along a closed trajectory in the time interval $(t_j^{(0)}, t_j^{(0)})$ in the laser field with vector potential $A(t) = -\hat{z} \int \mathbf{F}(t')dt'$,

$$K(t; t_j^{(0)}, t_j^{(0)}) = A(t) - \frac{1}{t_j^{(0)} - t_j^{(0)}} \int_{t_j^{(0)}}^{t_j^{(0)}} A(\xi) d\xi. \quad (A.4)$$

The term $\Delta \mathcal{E}_j$ is the quantum correction [72]

$$\Delta \mathcal{E}_j = \frac{I_p}{\Delta t_j} \frac{F_j' \cdot K_j}{F_j^2}, \quad (A.5)$$

where $\Delta t_j = t_j^{(0)} - t_j^{(0)}$ and $F_j' \equiv F(t_j^{(0)})$. Detailed analysis of the system (A.3) for the case of linearly-polarized laser field can be found in [77].

The EWP $W(\mathcal{E})$ is proportional to the square of a sum over the partial amplitudes, corresponding to closed electron trajectories,

$$W(\mathcal{E}) = \frac{\pi}{2} \omega \sqrt{2\mathcal{E}} \left| \sum_j [a_j^{(\text{tun})} a_j^{(\text{prop})}]^2 \right|, \quad (A.6)$$

where each partial amplitude can be factorized in terms of tunneling, $a_j^{(\text{tun})}$, and propagation, $a_j^{(\text{prop})}$, factors. The tunneling factor, $a_j^{(\text{tun})}$, is given by

$$a_j^{(\text{tun})} = \frac{Q_j \mathcal{C}_1 e^{-\kappa \omega / (\mathcal{F}_j)}}{\sqrt{2\mathcal{F}_j}}, \quad (A.7)$$

where $\mathcal{F}_j = \sqrt{F_j^2}$, $\kappa = \sqrt{2I_p}$ and $\mathcal{C}_1$ is dimensionless asymptotic coefficient of the initial bound state for the neutral atom,

$$\psi_{\kappa, \omega, \theta, \phi} |_{\kappa r > 1} \rightarrow \mathcal{C}_1 \sqrt{\kappa r}^{-1} (\kappa r)^{1/4} e^{-\kappa r} Y_{1, m} (\theta, \phi).$$
The Coulomb factor, $Q_j$, in equation (A.7) for the case of linearly polarized laser field reduces to a ‘static’ factor [78],

$$Q_j = Q_j^{\text{(stat)}} = \left( \frac{2\pi^3}{3} \right)^{1/2}. \tag{A.8}$$

The propagation factor, $\sigma_j^{\text{(prop)}}$, is given by

$$\sigma_j^{\text{(prop)}}(\Omega_k) = \frac{e^{-i S(t_j^a, t_j^b) + i\omega t_j^b}}{\Delta t_j^{1/2} \sqrt{K_j \cdot K_j}}, \tag{A.9}$$

where $K_j \equiv \partial K(t_j^a, t_j^b, t_j^c)/\partial t_j^b$, and $S(t_j^a, t_j^b)$ is the classical action of an electron

$$S(t_j^a, t_j^b) = J_x \Delta t_j + \int_{t_j^a}^{t_j^b} K_j^2(\xi; t_j^a, t_j^b) d\xi. \tag{A.10}$$

The angular distribution of PICS follows from parametrization

$$\sigma_{\text{ion}}(\omega, \beta) = \frac{\sigma_{\text{ion}}(\omega)}{4\pi} \left[ 1 + \beta(\omega) P_2(\cos \theta) \right]. \tag{A.11}$$

Here, $\sigma_{\text{ion}}(\omega)$ is the angle-integrated partial cross section for $5p$ subshell, $\beta(\omega)$ is the photoelectron asymmetry parameter, $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is a Legendre polynomial and $\theta$ is the angle between the photoelectron momentum direction and the photon polarization direction, $\omega$ is the photon energy. The values of $\sigma_{\text{ion}}(\omega)$ and $\beta(\omega)$ are taken from the results of experimental measurements in references [49, 62].

**References**

[1] Krausz F and Ivanov M 2009 Rev. Mod. Phys. 81 163
[2] Popmintchev T, Chen M-C, Arpin P, Murnane M M and Kapteyn H C 2010 Nat. Photon. 4 822
[3] Plaja L, Torres R and Zait A 2013 Attosecond Physics: Attosecond Measurements and Control of Physical Systems (Berlin: Springer)
[4] Schultz T and Vrakking M 2014 Phys. Rev. Lett. 112 110801
[5] Fan T et al 2011 Phys. Rev. Lett. 105 093903
[6] Smirnova O, Mairesse Y, Patchkovskii S, Dudovich N, Villeneuve D, Corkum P, Ivanov M Y, Corkum P and Ivanov M Y 2009 Nature 460 972–7
[7] Ion(13) is the angle-integrated partial cross section for $5p$ subshell, $\beta(\omega)$ is the photoelectron asymmetry parameter, $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is a Legendre polynomial and $\theta$ is the angle between the photoelectron momentum direction and the photon polarization direction, $\omega$ is the photon energy. The values of $\sigma_{\text{ion}}(\omega)$ and $\beta(\omega)$ are taken from the results of experimental measurements in references [49, 62].
