Photoelectron angular distribution in bichromatic atomic ionization

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Abstract. Theoretical aspects of photoelectron angular distributions are discussed with reference to bichromatic ionization by an FEL beam. Specifically, we consider an asymmetry in the angular distribution due to interference between the ionization paths from the fundamental and the second harmonic. The case of circularly polarized radiation is analyzed in detail in the vicinity of an intermediate resonance in the two-photon ionization paths. Similarities and differences to interference phenomena due to non-dipole effects are also discussed.

1. Introduction
The recent commissioning of free electron lasers (FELs), producing very high-brilliant femtosecond radiation pulses in the extreme ultraviolet (XUV) regime, has opened new avenues in the studies of such a developed field as the photoelectron angular distribution (PAD) in atomic photoionization. These studies are of fundamental importance for our understanding of the interaction between intense high-frequency electromagnetic fields and quantum systems. Keeping in mind applications to photoprocesses with FELs and, in particular, with the new seeded FERMI machine [1], which generates coherent pulses of arbitrary polarization and high photon-energy resolution, we concentrate the present discussion on the coherent control in two-pathway ionization by the fundamental near an intermediate atomic resonance (two-photon ionization) and its second harmonic (one-photon ionization) (Fig. 1a). The PADs, produced by bichromatic $\omega + 2 \omega$ photoionization has been studied in the optical range (see [2] for the list of references). To realize a bichromatic field in the XUV regime, an admixture of the second harmonic, which is routinely generated at FELs, can be used.

The seemingly independent phenomena of $\omega + 2 \omega$ ionization in the dipole limit and single-photon ionization with accounting for the lowest-order non-dipole correction (Fig. 1b) are united by the fact that in both cases quantum interference, which mixes parity-changing and parity-conserving transitions, plays a crucial role. This mixing breaks one of the symmetry planes in the PADs. One purpose of the present contribution is to discuss the similarities and differences between the ionization by a bichromatic field (Fig. 1a) and one-photon ionization with accounting for both dipole $E1$ and quadrupole $E2$ electric transitions (Fig. 1b) in the context of PADs (section 2), as well as the symmetry breaking of PADs and its phase control in the bichromatic

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ionization in the region of intermediate resonance (section 3). To simplify the discussion, we restrict ourselves to ionization of an $s$ electron.

2. $\omega-2\omega$ and $E1-E2$ interference: Similarities and differences
   The process depicted in Fig. 1(a) occurs in a bichromatic field, which we take in the form
   \[ E(t) = E_1(t) \cos \omega t + E_2(t) \cos(2 \omega t + \phi), \]  
   (1)
   where $E_1(t)$ and $E_2(t)$ are the electric fields of the fundamental and the second harmonic, respectively, and $\phi$ is the relative phase between the harmonics. We assume that the pulses contain many optical cycles, so that the individual carrier-envelope phases of the harmonics are not important for the dynamics of the process. The two terms in (1) give rise to corresponding terms in the amplitude.

   Figure 2 shows schemes of transitions for the two processes displayed in Figs. 1(a) and 1(b), respectively. In both cases the final degenerate states of the continuum are characterized by both parities. Thus the $E1-E2$ and the $\omega-2\omega$ interferences manifest themselves in the
Figure 3. (Color online). Visual representation of the $\omega - 2\omega$ interference (upper row, the amplitude of the fundamental is 0.3 of the second harmonic) and the $E1 - E2$ interference (lower row, the $E2$ amplitude is half of the $E1$ amplitude) on the PADs. The left-most polar plots represent the angular structure of the single-photon ionization amplitude in the dipole approximation. The next (small) 3D plot represents the angular structure of the two-photon amplitude (upper row) and the $E2$ single-photon ionization amplitude (lower row). Their square absolute sum yields the 3D plots near the center of each row, respectively. The very right column shows the PADs without accounting for the interference terms. The coordinate system, as described in the text, is shown in the right bottom corner.

PADs, but they vanish in the angle-integrated cross section. The difference between the two processes when considering PADs originates from the difference in the tensorial structure of their respective transition operators, despite their identical ranks and parity properties. In particular, let us consider linearly polarized radiation and choose the $X$ and $Z$ axes of the coordinate system parallel to the photon beam and to the direction of the electric vector, respectively. Then the structure of the transition amplitude from an initial state $i$ to a final (continuum) state $f$, $T_{if}^{E1,E2}$, accounting for the electric dipole and quadrupole terms, and the structure of the ionization amplitude, $T_{if}^{\omega,2\omega}$, accounting for the two terms in Eq. (1), are of the respective forms

$$T_{if}^{E1,E2} = c_{E1} \langle z \rangle_{if} + c_{E2} \langle xz \rangle_{if},$$  
$$T_{if}^{\omega,2\omega} = c_{\omega} \langle z \rangle_{if} + c_{2\omega} \langle z^2 \rangle_{if}.$$  

(2)

(3)

Here the $c_{\alpha}$ are some complex rotationally invariant coefficients and $\langle g(x,y,z) \rangle_{if}$ denotes a transition matrix element of an operator with the Cartesian coordinate structure described.
by a function $g(x, y, z)$. Figure 3 illustrates a typical influence of the two-photon ionization (upper row) and the non-dipole corrections (lower row) on the PADs. In fact, single-photon ionization due to a “small admixture” of the second harmonic in the radiation beam is so strong (a first-order process) in the majority of cases that it dominates the two-photon ionization by the fundamental (a second-order process). Correspondingly, its contribution is seen to be much larger in the upper row of Fig. 3.

The $\omega - 2\omega$ interference, therefore, reveals itself, for linearly polarized radiation, as a “right-left asymmetry”, while the $E1 - E2$ interference appears as a “forward-backward asymmetry”. Both effects have been experimentally observed: the first one only in the optical range, with corresponding theoretical developments (e.g. [3]), and the second one routinely in the XUV range (not speaking about hard X-rays) (e.g. [4]), with many theoretical calculations of the non-dipole effects in the PADs (e.g. [5]).

3. $\omega - 2\omega$ interference in the region of an intermediate resonance

To increase the probability of the two-photon ionization path one can use an intermediate discrete atomic state [6]. To our knowledge, the behavior of the PAD near such a resonance had not been analyzed until to our recent work [2], where the case of linearly polarized radiation was considered. Within lowest-order perturbation theory in the dipole approximation, the PAD in this case may be presented in the form

$$\left( \frac{dW}{d\Omega} \right)_{lin} = \frac{W_{lin}^{0}}{4\pi} \left[ 1 + \frac{4}{7} \beta_{k}^{lin} P_{k}(\cos \theta) \right],$$

where $\theta$ is the electron emission direction with respect to the electric field, $P_{k}(x)$ are the Legendre polynomials, and $W_{lin}^{0}$ is the angle-integrated ionization probability for linearly polarized radiation. The anisotropy parameters $\beta_{k}^{lin}$ are expressed in terms of the amplitudes corresponding to the three pathways (see Fig. 2a): $s - p$ (first order), $s - s$ and $s - d$ (second order), which we denote by $U^{(1)}$, $U_{s}^{(2)}$ and $U_{d}^{(2)}$, respectively:

$$\beta_{2}^{lin} = 2 \left( W_{lin}^{0} \right)^{-1} \left[ \sqrt{\frac{5}{2}} \Re \left( U_{d}^{(2)} U_{s}^{(2)*} \right) + 7 \eta^{2} \left| U_{s}^{(1)} \right|^{2} + \frac{5}{7} \left| U_{d}^{(2)} \right|^{2} \right],$$

$$\beta_{4}^{lin} = \frac{18}{7} \left( W_{lin}^{0} \right)^{-1} \left| U_{d}^{(2)} \right|^{2},$$

$$\beta_{1}^{lin} = 2 \sqrt{\frac{3}{5}} \eta \left( W_{lin}^{0} \right)^{-1} \Re \left[ \left( U_{s}^{(2)} + \frac{2}{\sqrt{5}} U_{d}^{(2)} \right) U_{s}^{(1)*} \right],$$

$$\beta_{3}^{lin} = 6 \sqrt{\frac{3}{5}} \eta \left( W_{lin}^{0} \right)^{-1} \Re \left( U_{d}^{(2)} U_{s}^{(1)*} \right).$$

Here

$$W_{lin}^{0} = \eta^{2} \left| U_{s}^{(1)} \right|^{2} + \left| U_{s}^{(2)} \right|^{2} + \left| U_{d}^{(2)} \right|^{2},$$

$\Re[F]$ denotes the real part of the complex quantity $F$, and we assume an electric field of the form (1) with $E_{2}(t) = \eta E_{1}(t) (\eta > 0)$. The transition amplitudes may be presented in the form [2]

$$U^{(1)} = -i D_{Ep,s}^{(1)} T^{(1)}, \quad U_{l}^{(2)} = - \sum_{E_{n}} D_{El,s}^{(2)}(E_{n}) T_{El}^{(2)}(E_{n}) \quad (l = 0, 2),$$

where $D_{Ep,s}^{(1)}$ and $D_{El,s}^{(2)}(E_{n})$ are the radial dipole matrix elements of the first and second order between the initial $s$ state and the final states with energy $E$ and orbital angular momentum $l$ (see Eqs. (7) and (8) of [2]); the summation is performed over intermediate $p$ states with energies $E_{n}$.
The factors $T^{(1)}$ and $T^{(2)}_{En}$ are independent of the atomic wavefunctions, but they depend on the details of the laser pulse.

Terms with odd-rank Legendre polynomials in (4) are responsible for the left-right asymmetry in the PADs, as illustrated by the upper row of Fig. 3. This asymmetry in the region of the resonance was discussed in [2]. Compact parameterizations for the anisotropy parameters $\beta_{kn}$ and the left-right asymmetry $A(0^\circ) = (\beta_{12} + \beta_{34}) (1 + \beta_{23} + \beta_{45})^{-1}$ were derived in the vicinity of an isolated intermediate state (resonance) for pulses with many optical cycles.

Here we proceed further and consider the $\omega + 2\omega$ photoionization by circularly polarized radiation. A formalism for the PADs in bichromatic fields of arbitrary polarization may be developed by standard methods [7] and will be published elsewhere. The PAD for ionization of an $s$ electron by a circularly polarized bichromatic field takes the form

\[
\frac{dW}{d\Omega} = \frac{W_{0}^{\text{circ}}}{4\pi} \left[ 1 + \sum_{k=2,4} \beta_{k}^{\text{circ}} P_{k} (\cos \theta) + |\gamma_{34}| \sin^{3} \theta \cos (\mu \varphi + \psi) \right],
\]

where the angle $\theta$, in contrast to Eq. (4), is counted relative to the direction of the radiation beam. Furthermore, $\mu = 1$ or $\mu = 3$ for equal or opposite helicity of the fundamental and the second harmonic, respectively. There is no forward-backward asymmetry in the PAD (11), which exists in the PADs of single-photon ionization beyond the dipole approximation. Expressions for the anisotropy parameters are of the form

\[
\beta_{2}^{\text{circ}} = - \left( W_{0}^{\text{circ}} \right)^{-1} \left[ \eta^{2} \left| U^{(1)} \right|^{2} + \frac{10}{7} \left| U_{d}^{(2)} \right|^{2} \right],
\]

\[
\beta_{4}^{\text{circ}} = \frac{3}{7} \left( W_{0}^{\text{circ}} \right)^{-1} \left| U_{d}^{(2)} \right|^{2},
\]

\[
\gamma_{31} = -3 \gamma_{33} = -3 \frac{\sqrt{5}}{2} \eta \left| U_{0}^{\text{circ}} \right|^{-1} \left( U_{d}^{(2)} U^{(1)*} \right),
\]

\[
\psi = \arg \left( U_{d}^{(2)} U^{(1)*} \right),
\]

and

\[
W_{0}^{\text{circ}} = \eta^{2} \left| U^{(1)} \right|^{2} + \left| U_{d}^{(2)} \right|^{2}.
\]

Since no $s$ wave is produced by a circularly polarized fundamental, the left path of the two-photon process is absent in Fig. 2(a). The second-order amplitude $U_{d}^{(2)}$ for circularly polarized radiation differs by the constant factor $\sqrt{3}$ from the corresponding amplitude for the linearly polarized case. Note that the parameterization (11) is valid for pulses with finite time duration.

Another, not widely known phenomenon, is the breaking of the axial symmetry of the PAD in $\omega + 2\omega$ ionization, even for infinitely long pulses [8]. This symmetry breaking is described in our case by the third term in (11) and depends on the interference between the first-order and the second-order ionization amplitudes, $U_{d}^{(1)}$ and $U_{d}^{(2)}$. It includes the relative phase between the harmonics as well as the relative phase between the $d$ and $p$ electron waves in the continuum. The origin of the axial symmetry breaking for a field with the fundamental and the second harmonics is illustrated in Fig. 4. We take the $X$ axis along the electric field of the fundamental, as it is generated by an FEL. When integrating (averaging) over the relative phase of the harmonics, the asymmetry vanishes. It also vanishes when the relative phase of the harmonics is held fixed, but the direction of the electric field vector of the fundamental (i.e., the initial phase of the fundamental), generated by the FEL, is chaotic. The latter corresponds to integrating the PAD (11) over the azimuthal angle $\varphi$. When the above stability conditions with respect to the
phases are fulfilled, the third term in (11) should contribute to the observed PAD. Then the PAD (11) is characterized by a symmetry plane instead of an axis, and $\psi$ or $\psi/3$ is the angle of this plane with respect to the $X$ axis for equal ($\mu = 1$) or opposite ($\mu = 3$) helicities of the harmonics. Another parameter, which may characterize the PAD in this case, is a “polar asymmetry” along the line of intersection between the plane perpendicular to the radiation beam and the symmetry plane of the PAD. This polar asymmetry is given by

$$
A = \left| \frac{\left( \frac{dW}{d\Omega} \right)_{\text{circ}} (\vartheta = 90^\circ, \varphi = -\psi) - \left( \frac{dW}{d\Omega} \right)_{\text{circ}} (\vartheta = 90^\circ, \varphi = \pi - \psi)}{\left( \frac{dW}{d\Omega} \right)_{\text{circ}} (\vartheta = 90^\circ, \varphi = -\psi) + \left( \frac{dW}{d\Omega} \right)_{\text{circ}} (\vartheta = 90^\circ, \varphi = \pi - \psi)} \right| \left. \frac{1 - \beta_2^\text{circ}}{2 + 3\beta_4^\text{circ}/8} \right| \gamma_{3\mu}.
$$

(17)

It is instructive to compare Eqs. (12)–(16) with the expressions for the parameters $\beta_{1,2}^\text{lin}$ (5)–(9). For circularly polarized radiation, terms describing the interference between the first- and second-order amplitudes contain both real and imaginary parts of their product, while for linearly polarized radiation only the real part of this product contributes to the PAD. The additional information for the circularly polarized radiation is due to the breaking of the axial symmetry. Generally, for an infinitely long “pulse”, breaking of the axial symmetry can occur when the frequencies of the two circularly polarized beams are related to each other by a simple fraction, in analogy with the condition for Lissajous figures. Note that the axial symmetry is not destroyed by the $E1 - E2$ interference for the circular polarized beams.

To demonstrate the behavior of the PAD in the vicinity of an intermediate resonance, we performed numerical calculations for the $\omega + 2\omega$ ionization of the hydrogen atom near the $1s - 2p$ transition ($E_{2p} = 0.375$ a.u.) within perturbation theory for a pulse duration of 40 optical cycles with a $\sin^2$ envelope. These pulse parameters correspond to our previous calculations for linearly polarized radiation [2]. We took $\eta = 0.225$ and the intensity of the fundamental $I = 10^{12}$ W/cm$^2$. As shown in [2], for this intensity and pulse duration, lowest-order perturbation theory still can
provide an adequate qualitative description of the process. The results of the calculations are shown in Figs. 5 and 6, respectively.

As seen from Fig. 5(a), the symmetry plane of the PAD quickly rotates by $\pi$ when the photon energy passes through the resonance. The value of $\psi$ does not depend on the mutual helicity of the fundamental and the second harmonic. Recall, however, that the plane of symmetry is characterized by the angle $\psi$ for equal helicities of the harmonics and by $\psi/3$ for the opposite helicities. The polar asymmetry shown in Fig. 5(b) does not depend on the relative phase $\phi$ between the harmonics, provided the rotating-wave approximation (RWA) is valid, i.e., for laser pulses longer than about $10^{-20}$ optical cycles. We did not apply the RWA in our calculations, but the results for different values of $\phi$ are indistinguishable within the thickness of the line. The polar asymmetry assumes its maximum value near the resonance, and then drops away from the resonance.

The two parameters, $\psi$ and $A$, are not sufficient to completely characterize the PADs. To visualize them, Fig. 6 shows 3D plots of the PADs in the vicinity of the resonance, together with their cuts through the plane perpendicular to the radiation beam. The PADs change rapidly with the photon energy near the resonance and exhibit very different shapes for equal and opposite helicities of the harmonics. Therefore, a pronounced circular dichroism in the angular distribution, which is the difference between the above two PADs, occurs in $\omega + 2\omega$ photoionization.

4. Conclusions
Keeping in mind applications to photoionization with new FELs, we theoretically studied interference effects in two-pathway ionization by the fundamental $\omega$ and its second harmonic $2\omega$ (bichromatic $\omega + 2\omega$ photoionization). This interference manifests itself in the PADs. The difference between $\omega - 2\omega$ interference and $E1 - E2$ interference in one-photon ionization in the PADs is related to the different tensorial structure of the corresponding transition operators, despite their identical ranks and parity properties. Within perturbation theory, a parameterization was derived for the PAD in bichromatic $\omega + 2\omega$ photoionization by circularly polarized radiation. The axial symmetry of the PAD breaks down, but symmetry is kept with respect to a plane containing the radiation beam. The axial-symmetry-breaking term contains
two dynamical parameters, which we defined as the angle of the symmetry plane and the polar asymmetry. The results were exemplified by numerical predictions for ionization of atomic hydrogen within second-order perturbation theory in the vicinity of the $1s-2p$ transition. The PAD, its polar asymmetry, and the angle of the symmetry plane change rapidly as function of the photon energy when scanning the resonance. For pulses with many optical cycles, the polar asymmetry is independent of the helicities of the fundamental and the second harmonic, as well as the phase between the harmonics, while the angle of the symmetry plane is related to the relative phase between the harmonics and depends on the mutual sign of their helicity. Further studies of bichromatic photoionization by circularly polarized radiation, beyond perturbation theory by directly solving the time-dependent Schrödinger equation, are desirable in order to extend the range of intensities of the radiation for which reliable predictions can be made.

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