Interference of one- and two-photon processes in the ionization of atoms and molecules


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We derive general phenomenological expressions for the angular distribution of electrons emitted when atoms or molecules are ionized by a light field containing the fundamental frequency \( \omega \) and the second harmonic \( 2\omega \). The polar asymmetry in the angular distribution appears because of interference of the one-photon process in the second harmonic \( 2\omega \) and the two-photon process in the field of frequency \( \omega \). We find the absolute phase of the interference term for alkali atoms in the quantum-defect approximation.

1. INTRODUCTION

Osterberg and Margulis\(^1\) recorded a grating of the quadratic polarizability tensor \( \chi^{(2)}(z) \) generated in a quartz fiber by the picosecond radiation of a neodymium-glass laser, \( E(\omega, z) \) (\( \lambda = 1.06 \mu \text{m} \)), and its second harmonic \( E(2\omega, z) \) (\( \lambda = 0.53 \mu \text{m} \)). In a number of later papers devoted to this process attempts were made to explain the writing mechanism (grating formation).\(^2\) One hypothesis was that the grating is induced by the cubic electronic polarizability\(^3\) of the static electric field \( E^z(z) \) and the spatial grating written in the medium, i.e., \( \delta \beta = \chi^{(3)}(z) \). It was assumed that by some mechanism the static electric field grating is induced in the medium and that this field is proportional to the product of the square of the fundamental-frequency field and the second-harmonic field: \( E^z(z) = E^*(\omega)E^*(2\omega) \). It was also assumed that the interference between the two-photon ionization by the fundamental-frequency field and the two-photon ionization by the second-harmonic field leads to a polar asymmetry in the angular distribution of photoelectrons. This results in the appearance of a nonzero average current whose direction depends on the phase of the interference terms \( E^*(\omega)E^*(2\omega) \). As has recently been shown,\(^4\) the process may be of higher order (three- and four-photon ionization).

An earlier paper of two of the present authors (N.B.B. and B.Ya.Z.)\(^5\) calculated the differential (in the scattering angle) photoionization cross section for an atom using a simplified short-range potential model for the case where there is interference between one- and two-photon ionization. The experiments initiated by these calculations (Refs. 6 and 7) detected a polar asymmetry in photoionization depending on the phase of the interference terms \( E^*(\omega)E^*(2\omega) \). It was assumed that by some mechanism the static electric field grating is induced in the medium and that this field is proportional to the product of the square of the fundamental-frequency field and the second-harmonic field: \( E^z(z) = E^*(\omega)E^*(2\omega) \). It was also assumed that the interference between the two-photon ionization by the fundamental-frequency field and the two-photon ionization by the second-harmonic field leads to a polar asymmetry in the angular distribution of photoelectrons. This results in the appearance of a nonzero average current whose direction depends on the phase of the interference terms \( E^*(\omega)E^*(2\omega) \). As has recently been shown,\(^4\) the process may be of higher order (three- and four-photon ionization).

The polar asymmetry of the photoelectrons excited to states in the continuum appears because of the interference of states of different parities (Fig. 1b). Under one-photon ionization the \( p \)-state of an electron is excited. In the absence of any potential the electronic wave function of the \( p \)-state has the form

\[
\psi_j(r) = \frac{\sin kr}{r} \cos \theta, \tag{1}
\]

where \( \delta k \) is the absolute value of the momentum vector. The ground-state wave function \( \psi_0(r) \) is real; hence, the electric dipole matrix element \( \langle \psi_j | \hat{\mathbf{d}} | \psi_0 \rangle \) of the transition to state (1) is real, too.

The parity and angular momentum selection rules allow for a two-photon transition to the \( d \)- and \( s \)-states. For the sake of simplicity we consider the transition to the \( s \)-state. When there is no potential, the wave function of an \( s \)-state of the tinuous spectrum assumes the form

\[
\psi_j(r) = \frac{\sin kr}{r} \sin \theta, \tag{2}
\]

In the absence of an intermediate resonance of effective radial matrix element for a two-photon transition (see below), \( \langle \psi_j | \hat{\mathbf{d}} | \psi_0 \rangle \), is also real. As a result the wave function of the excited state is proportional to the following expression:

\[
\psi_j|\hat{\mathbf{d}}|\psi_0 = \frac{\sin kr}{r} \cos \theta \sin \theta, \tag{3}
\]

To calculate the probability of electron emission in the expressions \( \cos kr \) and \( \sin kr \), only the terms with \( \exp ikr \), which correspond to outgoing waves, must be retained. The probability of photoionization in the \( \theta \) direction is

\[
W(\theta) = \left| \langle \psi_j | \hat{\mathbf{d}} | \psi_0 \rangle E(2\omega) \cos \theta \right|^2. \tag{4}
\]

Clearly, the interference term responsible for polar asymmetry

\[
W(\theta) - W(-\theta) = i \cos \theta E(2\omega) E^*(\omega) \times \langle \psi_j | \hat{\mathbf{d}} | \psi_0 \rangle + \text{c.c.}, \tag{5}
\]

210 Sov. Phys. JETP 75 (2), August 1992 0038-5646/92/080210-05$05.00 © 1992 American Institute of Physics 210
The polar asymmetry is expressed in the following manner:

\[ \text{scattering phase } \delta \text{ by the atomic potential, all of which is reflected in Eq. (7).} \]

As the electron moves away from the atom, it acquires a phase of \( 2 \) for the p-wave and, in addition, an additional phase factor \( i \) would lead to a reversal of sign in the interference term (5).

If one allows for the effect of an attractive potential on free-electron motion, the wave functions of the continuous spectrum are modified somewhat. At great distances from the atom, the wave functions of an electron near an atom do not change the phase of the "outgoing plane wave" \( \psi_{out}(r) \)

\[ \psi_{out}(r) = (\text{see, e.g., Ref. 13), which exhibits the following asymptotic behavior as } r \rightarrow \infty: \]

\[ \psi_{out}(r) = e^{i k r} \]

with \( n' = r/\alpha \). The potential of an atom or molecule is usual-

has an additional phase factor \( i = \exp(\text{exp}(i/2)) \). Note that one of the matrix elements may prove to be negative, which would lead to a reversal of sign in the interference term (5).

The present paper is devoted to studying the angular distribution of the emitted electrons. In the event of third-harmonic generation, the virtual channels and their interference produces polar asymmetry effects in the angular spectrum, effects that cannot exist on bound-bound transitions in atoms and molecules, which is possible. States with different parities are excited in different channels, and their interference produces polar asymmetry effects in the angular spectrum, effects that cannot exist on bound-bound transitions in atoms and molecules.

\[ W(n) - W(-n) = \exp \left[ i \left( \delta_0 - \delta_2 \right) \right] X \cos \theta \exp(i \Delta E) E(2\omega) E^*(\omega) + c.c. \]

Exciting the s- and p-states of the continuous spectrum of an electron near an atom does not change the phase of the wave function. As the electron moves away from the atom, it acquires a phase of \( 2/\alpha \) for the p-wave and, in addition, a phase \( \delta_2 \) depending on perturbation of electron motion by the atomic potential, all of which is reflected in Eq. (7).

The interferometric molecules. To illustrate, in Fig. 2 we depict the time dependence of \( E_n(t) \) at \( E = 1 \, e_1 \) and \( B = 1 \, e_2 \). Despite the fact that the time average of the field is zero, \( \langle E \rangle = 0 \), the polar asymmetry in the \( E_n(t) \) dependence can clearly be seen.

2. A PHENOMENOLOGICAL APPROACH

The probability of one- and two-photon ionization with emission of an electron in the given direction \( n = k/\alpha \) can be calculated within the framework of the perturbation theory in the optical \( E \) and \( B \) fields. We denote the wave function of the initial state by \( |f \rangle \), or for the wave function of the final electronic state \( |f' \rangle \) we must take what is known as the "outgoing plane wave" \( \psi_{out}(r) \) (sec, e.g., Ref. 13), which exhibits the following asymptotic behavior as \( r \rightarrow \infty: \)

\[ \psi_{out}(r) = e^{i k r} \]

where \( \alpha = r/\alpha \). The potential of an atom or molecule is usual-

\[ E(t) = \cos \omega t + \cos 2\omega t \]

although it satisfies \( \langle E \rangle = 0 \), the field has polar asymmetry characterized by the quantity \( \langle E^2 \rangle = 0.75 \).

FIG. 1. (a) An electron in the bound s-state may be emitted either to the p-state of the continuous spectrum via one-photon ionization by 2h\( \omega \) quanta or to the p- and d-states via two-photon ionization by \( 4h\omega \) quanta. (b) The interference of the electron s-wave \( |E(\omega)\rangle \) and p-wave \( |E(2\omega)\rangle \) of the states of the continuous spectrum leads to asymmetry in the angular distribution of the emitted electrons.

211 Sov. Phys. JETP 79 (2), August 1992

Anderson et al.
ly invariant under time reversal \( t \rightarrow -t \), and then
\[ h(-n') = h(n,n'), \]
where \( h(n,n') \) is the ordinary quantum-mechanical amplitude for scattering on an atom or molecule of a particle with initial direction specified by the vector \( n \) and final direction by \( n' \).

In the absence of intermediate resonances, the effective interaction Hamiltonian can be written as
\[ P = -i \int d^4x \left\{ \frac{e}{2m} \left[ \bar{\psi} \gamma^\mu \left( \partial_\mu + ig A_\mu \right) \psi \right] + \bar{\psi} \gamma^\mu \left( \partial_\mu + ig A_\mu \right) \psi \right\}, \]
where the components of the dipole moment operator \( \bar{d}_i \) and of the symmetric tensor \( M_{\alpha\beta} \) are specified by the respective matrix elements \( \langle \bar{d}_i | \bar{d}_j \rangle = \delta_{ij} \delta_{\alpha\beta} \delta_{\mu\nu} \).

The main property of the vectors \( u \) and \( p \) introduced by Eqs. (12)-(15) is their orthogonality to the vector \( n \), that is,
\[ u_n = 0 \quad \text{and} \quad p_n = 0. \]
The probability of an electron being emitted into the solid angle \( \Omega \), is proportional to
\[ W(n) = \frac{1}{\sqrt{\Omega}} \int \langle \bar{d}_i | \bar{d}_j \rangle | E \rangle | E \rangle. \]

Averaging this expression over the isotropic distribution of the initial states of an electron in an atom or molecule is isotropic. The symmetry of the problem for electron emission in a given direction \( n \) manifests itself most fully if we expand the vector \( d \) and the symmetric tensor \( M_{\alpha\beta} \) in irreducible components along \( n \) and at right angles to \( n \):
\[ d = d_n + u, \quad M_{\alpha\beta} = M_{\alpha\beta n} + u_{\alpha\beta n}. \]
The four nonnegative constants \( C_{\alpha \beta} \) and \( C_{\alpha \beta \gamma} \) are determined by the following formulas:
\[ W(n) = \left( T_{\alpha\beta n} \right)^2 \Omega = \left( T_{\alpha\beta n} \right)^2 \Omega. \]

And, finally, the terms that describe the interference of one- and two-photon ionization are
\[ W(1) = G_{\alpha \beta n} + G_{\alpha \beta n} (n, e \beta = -1 \beta), \]
\[ W(2) = G_{\alpha \beta n} (n, e \beta = -1 \beta), \]
\[ G_{\alpha \beta n} = G_{\alpha \beta n} (n, e \beta = -1 \beta), \]
\[ G_{\alpha \beta n} = G_{\alpha \beta n} (n, e \beta = -1 \beta). \]

All the formulas (12)-(25) employ the summation convention for repeated tensor indices. Thus, we conclude that for an isotropic distribution of the orientations of the initial states the photoionization probability \( W(n) \) is characterized by two real constants \( A_1 \) and \( A_2 \) (one-photon ionization), one complex-valued constant \( C_1 \), and four real constants \( C_{\alpha \beta} \), \( C_{\alpha \beta \gamma} \), and \( C_{\alpha \beta \gamma \delta} \) (two-photon ionization), and also three complex-valued constants \( G_{\alpha \beta n} \), \( G_{\alpha \beta n} (n, e \beta = -1 \beta) \), and \( G_{\alpha \beta n} (n, e \beta = -1 \beta) \) (interference terms). It is easy to show that all the real constants are nonnegative and all the complex-valued constants satisfy the following inequalities
\[ |C_{\alpha \beta}|^2 \leq C_{\alpha \beta} \leq C_{\alpha \beta}, \]
\[ |G_{\alpha \beta n}|^2 \leq C_{\alpha \beta n}, \]
\[ |G_{\alpha \beta n} (n, e \beta = -1 \beta)|^2 \leq C_{\alpha \beta n} (n, e \beta = -1 \beta). \]
The interested reader can obtain the final expressions for...
by three independent “amplitude” factors $A^1$, $C^1$, and $C^{2'}$ and two phase differences $-i\epsilon, \epsilon, \exp(i\delta_3 - i\delta_3)$ and $-i\epsilon, \epsilon, \exp(i\delta_3 - i\delta_3)$. This is much simpler than the general phenomenological expression, which depends on eleven “probabilities” and four phase factors.

An important corollary of the fact that the ground s-state and the final state $\phi_0(r)$ (with fixed energy and direction n) are nondegenerate is that the 100% “contrast” of the interference terms. This means the following: (1) In the absence of the first harmonic, that is, when we have $E(\omega) = 0$, for the monochromatic wave $E(2\omega) \neq 0$ one can select a polarization of B such that $(B_0) = 0$ and $W(n) = 0$ although $(BB^*) \neq 0$. (2) For the monochromatic field $E(\omega) = 0$ (at $B = 0$) one can select a polarization such that $W(n) = 0$ although $(EE^*) \neq 0$. (3) For the bichromatic field with arbitrary polarizations of B and E one can select an intensity ratio and a phase shift such that $W(n) = 0$ holds for $(EE^*) \neq 0$ and $(BB^*) \neq 0$. (4) The same can be done for a fixed intensity ratio by tuning the polarization of the field. An expression of this type was obtained in Ref. 5 within the framework of the short-range potential model. In this model, which can be employed to describe a negative ion, $\delta_{l} = \delta_{l} = 0$ and $\delta_{l} \neq 0$. We will not give any explicit expressions for the phenomenologically derived constants $\delta_{l}, \epsilon, \epsilon, \epsilon, \epsilon, \epsilon$, and $\delta_{l}C^{2'}$ (see Ref. 5).

4. THE SCATTERING PHASE IN THE QUANTUM-DEFECT APPROXIMATION

In spectroscopy a well-known formula empirically established by Rydberg gives the asymptotic behavior of the energies of highly excited states of atoms or ions:

$$E_{\nu} = \frac{Z^2}{2(n-\mu_i)^2}$$

where $Z$ is the atomic number of the atomic core, and $\mu_i$ is the so-called quantum defect. This formula (Eq. 29) is usually explained within the framework of the WKB approximation or by employing the Bohr-Sommerfeld rule for quantization of the radial electron motion in the presence of the Coulomb and centrifugal potential, $-Z^2/r + \ell(\ell + 1)/2r^2$. For highly excited levels the departure from a purely Coulombic potential can be allowed for by introducing an effective phase shift $-\nu_i$, in the WKB wave function. It is natural to assume that the effect of the departure from the Coulomb potential on the phase of the wave function is the same for both positive and negative values of the electron energy, assuming $|E| < Z^2Ry/2$. Hence, if the kinetic energy $T$ of an electron moving in a spherically symmetric potential of the atomic core is much less than $Z^2Ry/2$, the quantum-mechanical scattering phase can be expressed in terms of the quantum defect. All the details and limitations of quantum-defect theory can be found in numerous monographs and reviews, for instance, in Refs. 16 and 17. Here we give only the final expression for the scattering phase:

$$\delta_i = \nu_i + \arg \left \{ \left ( \frac{Z^2}{2\ell} \right ) \right \}$$

In our case the kinetic energy is equal to $2\nu - |E|$, with $|E|$ the binding energy in the initial s-state. Using the well-known formula for the Euler gamma function, $\Gamma(x + p + 1) = (x + p)! \Gamma(x + p)$, we arrive at the following expressions for the phase differences of interest;
Table I lists the data on $\mu$ for alkali atoms and hydrogen obtained by spectroscopic measurements.

Thus, for alkali atoms near the ionization threshold, the absolute value of the phase of interference term and the energy dependence of the phase yield to an exact calculation that allows for the long-range Coulomb potential.

5. CONCLUSION

We have established the most general form of angular distribution of electrons when atoms or molecules are illuminated by a bichromatic field $E(ω_1)$ and $E(2ω)$ with allowance for one-photon ionization by field $E(2ω)$ and two-photon ionization by field $E(ω)$. We hope that the effects of polar asymmetry in $E(2ω)E^{*}(ω)$ in alkali atoms will soon be observed.

Table I. The size of the quantum defect $\mu$ in alkali atoms for states with different $l$ and $j$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$j$</th>
<th>$I$</th>
<th>$N_0$</th>
<th>$L_z$</th>
<th>$K$</th>
<th>$H_0$</th>
<th>$Q_0$</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>$1/2$</td>
<td>0</td>
<td>0.40</td>
<td>1.35</td>
<td>2.15</td>
<td>3.15</td>
<td>4.08</td>
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<tr>
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<td>$3/2$</td>
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<td>0.042</td>
<td>0.807</td>
<td>1.74</td>
<td>2.628</td>
<td>3.186</td>
</tr>
<tr>
<td>2</td>
<td>$5/2$</td>
<td>0</td>
<td>0.0035</td>
<td>0.014</td>
<td>0.26</td>
<td>1.34</td>
<td>2.426</td>
</tr>
</tbody>
</table>

\[\delta_0 - \delta = \alpha (\mu_0 - \mu) - \tan^{-1} \left( \frac{Z^2 \beta}{2F} \right) \]  
\[\delta_0 - \delta = \alpha (\mu_0 - \mu) + \tan^{-1} \left( \frac{Z^2 \beta}{2F} \right) \]  

Table I lists the data on $\mu$ for alkali atoms and hydrogen obtained by spectroscopic measurements.

Thus, for alkali atoms near the ionization threshold, the absolute value of the phase of interference term and the energy dependence of the phase yield to an exact calculation that allows for the long-range Coulomb potential.

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We have established the most general form of angular distribution of electrons when atoms or molecules are illuminated by a bichromatic field $E(ω_1)$ and $E(2ω)$ with allowance for one-photon ionization by field $E(2ω)$ and two-photon ionization by field $E(ω)$. We hope that the effects of polar asymmetry in $E(2ω)E^{*}(ω)$ in alkali atoms will soon be observed.

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