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

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(Submitted 9 December 1991)
Zh. Eksp. Teor. Fiz. **102**, 397–405 (August 1992)

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 ω and the second harmonic 2ω. The polar asymmetry in the angular distribution appears because of interference of the one-photon process in the second harmonic 2ω and the two-photon process in the field of frequency ω. 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, $E(\omega,z)$ ($\lambda = 1.06$ μm), and its second harmonic $E(2\omega,z)$ ($\lambda = 0.53\,\mu$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 $\mathbf{E}^{\rm st}(z)$ and the spatial grating written in the medium, i.e., $\delta\chi^{(2)} = \chi^{(3)}\mathbf{E}^{\rm st}(z)$. 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: $\mathbf{E}^{\rm st}(z) \propto E^2(\omega)E^*(2\omega)$. 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 $E^2(\omega)E^*(2\omega)$. 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 shift between the fundamental frequency field (ω) and its second harmonic (2ω). Unfortunately, the experiments were conducted not for free atoms but for the cathode of a photomultiplier. In agreement with theoretical predictions, these experiments established that different phase shifts between the average of the cube of the field strength, $E^2(\omega)E(2\omega)$ and the photoionization cross section correspond to different polarizations of the light waves.

From the viewpoint of atomic theory the appearance of a phase shift is related to the quantum mechanical scattering phase.[5-7] We discuss this fact for the simple case of an atom undergoing from the s-state (Fig. 1).

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

$$\psi_p(r) = \left(\frac{\cos kr}{r} - \frac{\sin kr}{kr^2}\right)\cos\theta, \tag{1}$$

where $\hbar k$ is the absolute value of the momentum vector. The ground-state wave function $\psi_0(r)$ is real; hence, the electric dipole matrix element $\langle\psi_p|\hat{d}|\psi_0\rangle$ 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 continuous spectrum assumes the form

$$\psi_s(r) = \frac{\sin kr}{r}. \tag{2}$$

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

$$\langle\psi_s|\hat{M}|\psi_0\rangle E^2(\omega)\frac{\sin(kr)}{r} + \langle\psi_p|\hat{d}|\psi_0\rangle E(2\omega)\cos\theta\,\frac{\cos(kr)}{r} + O(r^{-2}). \tag{3}$$

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 θ direction is

$$W(\theta) \propto |-i\langle\psi_s|\hat{M}|\psi_0\rangle E^2(\omega) + \langle\psi_p|\hat{d}|\psi_0\rangle E(2\omega)\cos\theta|^2. \tag{4}$$

Clearly, the interference term responsible for polar asymmetry

$$W(\mathbf{n}) - W(-\mathbf{n}) \propto i\cos\theta E(2\omega)E^{*2}(\omega) \times\langle\psi_0|\hat{M}|\psi_s\rangle\langle\psi_p|\hat{d}|\psi_0\rangle + \text{c.c.}, \tag{5}$$

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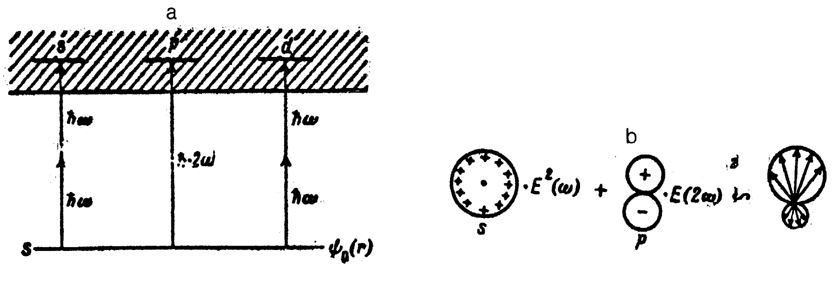

FIG. 1. (a) An electron in the bound s-state may be emitted either to the p-state of the continuous spectrum via one-photon ionization by $2\hbar\omega$ quanta or to the s- and d-states via two-photon ionization by $\hbar\omega$ quanta. (b) The interference of the electron s-wave $\propto E^2(\omega)$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

has an additional phase factor $i = \exp(i\pi/2)$. 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).

If one allows for the effect of an attractive potential on free-electron motion, the wave functions (1) and (2) of the continuous spectrum are modified somewhat. At great distances from the atom ($r \to \infty$), however, this modification reduces to a shift in the phase of the arguments of $\sin(kr)$ and $\cos(kr)$ by what is known as the quantum mechanical scattering phase δ:

$$\psi_s(r) \approx \frac{\sin(kr+\delta_s)}{r},$$

$$\psi_p(r) \approx \frac{\cos(kr+\delta_p)}{r}\cos\theta. \tag{6}$$

The polar asymmetry is expressed in the following manner:

$$W(\mathbf{n})-W(-\mathbf{n}) \propto i\exp[i(\delta_p-\delta_s)] \times\cos\theta\langle\hat{M}\rangle\langle\hat{d}\rangle E(2\omega)E^{*2}(\omega)+\text{c.c.} \tag{7}$$

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 $\pi/2$ for the p-wave and, in addition, phases δ_s and δ_p owing to perturbation of electron motion by the atomic potential, all of which is reflected in Eq. (7).

The present paper is devoted to studying the angular distribution of electrons for randomly oriented atoms or molecules ionized by the combined action of mutually coherent fields $\mathbf{E}(\omega)\exp(-i\omega t)$ and $\mathbf{E}(2\omega)\exp(-2i\omega t)$ of arbitrary polarization. Special attention is paid to the phase of the interference term and its polarization dependence.

The interference of processes taking place in several channels with the participation of various fields and satisfying the condition on the sum of frequencies, $\Sigma n_i\omega_i = \text{const}$, has been extensively discussed in the literature.[8-12] For instance, Man'kin and Afanas'ev[8] considered the interference of the virtual channels $\mathscr{E}_2 - \mathscr{E}_1 = \hbar\omega + \hbar\omega$ and $\mathscr{E}_2 - \mathscr{E}_1 = \hbar\cdot 3\omega - \hbar\omega$ in the event of third-harmonic generation in gases near a two-photon absorption resonance. Krasnikov *et al.*[9] experimentally studied the interference $\mathscr{E}_2 - \mathscr{E}_1 = \hbar\omega_1 + \hbar\omega_2$ and $\mathscr{E}_2 - \mathscr{E}_1 = \hbar\omega_3 - \hbar\omega_4$ processes on a bound-bound transition in sodium vapor. The present paper considers bound-free transitions. In the continuous spectrum there is degeneracy with respect to angular momentum and parity at a given energy. Hence, interference of processes when the numbers of participating photons are odd and even (in our case, one- and two-photon absorption) 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 spherically symmetric molecules.

In what follows we use the notation $\mathbf{E}(\omega) = \mathbf{E}$ and $\mathbf{E}(2\omega) = \mathbf{B}$, so that the instantaneous value of the real electric field vector can be written as

$$\mathbf{E}_{\text{real}}(t) = (\mathbf{E}e^{-i\omega t} + \text{c.c.})/2 + (\mathbf{B}e^{-2i\omega t} + \text{c.c.})/2. \tag{8}$$

To illustrate, in Fig. 2 we depict the time dependence of $E_x(t)$ at $\mathbf{E} = 1\cdot\mathbf{e}_x$ and $\mathbf{B} = 1\cdot\mathbf{e}_x$. Despite the fact that the time average of the field is zero, $\langle E\rangle = 0$, the polar asymmetry in the $E_x(t)$ 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 $\mathbf{n} = \mathbf{k}/k$ can be calculated within the framework of the perturbation theory in the optical $\mathbf{E}$ and $\mathbf{B}$ fields. We denote the wave function of the initial state by $|I\rangle$ or $\psi_0(r)$, and for the wave function of the final electronic state $|F\rangle$ we must take what is known as the "outgoing plane wave" $\psi_{\mathbf{n}}^{(-)}(\mathbf{r})$ (see, e.g., Ref. 13), which exhibits the following asymptotic behavior as $r \to \infty$:

$$\psi_{\mathbf{n}}^{(-)}(\mathbf{r}) = \sim e^{ik\mathbf{nr}} + h(\mathbf{n},\mathbf{n}')e^{-ikr}/r, \tag{9}$$

with $\mathbf{n}' = \mathbf{r}/r$. The potential of an atom or molecule is usual-

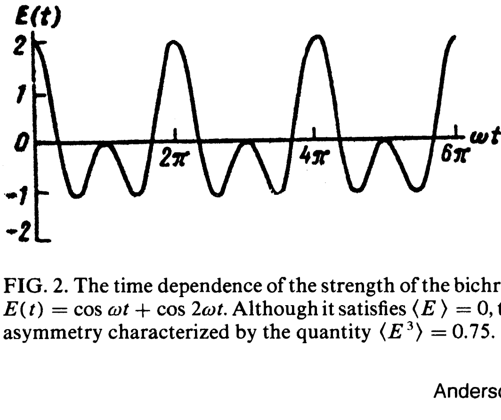

FIG. 2. The time dependence of the strength of the bichromatic light field $E(t) = \cos\omega t + \cos 2\omega t$. Although it satisfies $\langle E\rangle = 0$, the field has polar asymmetry characterized by the quantity $\langle E^3\rangle = 0.75$.

ly invariant under time reversal $t\to -t$, and then $h(-\mathbf{n},\mathbf{n}')=f(\mathbf{n},\mathbf{n}')$, where $f(\mathbf{n},\mathbf{n}')$ is the ordinary quantum-mechanical amplitude for scattering on an atom or molecule of a particle whose initial direction is specified by the vector $\mathbf{n}$ and final direction by $\mathbf{n}'$.

In the absence of intermediate resonances, the effective interaction Hamiltonian can be written as

$$\hat{V}=[-\hat{d}_i(t)B_ie^{-2i\omega t}+\hat{M}_{ik}(t)E_iE_ke^{-2i\omega t}+\text{H.c.}]/2\,, \tag{10}$$

where the components of the dipole moment operator $\hat{d}_i$ and of the symmetric tensor $\hat{M}_{ik}$ are specified by the respective matrix elements[13]

$$\langle F|\hat{M}_{ik}|I\rangle=\langle F|\hat{M}_{ik}'+\hat{M}_{ki}'|I\rangle/2,$$
$$\langle F|\hat{M}_{ik}'|I\rangle=\sum_j\langle F|\hat{d}_i|j\rangle(\mathscr{E}_j-\mathscr{E}_I-\hbar\omega)^{-1}\langle j|\hat{d}_k|I\rangle. \tag{11}$$

Here we assume that the distribution of the orientation 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 $\mathbf{n}$ manifests itself most fully if we expand the vector $\mathbf{d}$ and the symmetric tensor M_{ik} in irreducible components along $\mathbf{n}$ and at right angles to $\mathbf{n}$:

$$\mathbf{d}=\mathbf{n}d_0+\mathbf{u}, \tag{12}$$
$$M_{ik}=M_0\delta_{ik}+M_2(n_in_k-\delta_{ik}/3)+n_ip_k+n_kp_i+Q_{ik}, \tag{13}$$

where

$$d_0=(\mathbf{dn}),\quad \mathbf{u}=\mathbf{d}-\mathbf{n}d_0, \tag{14}$$

$$M_0={}^1/_3M_{jj},\quad M_2={}^3/_2(M_0-n_jM_{jl}n_l),$$
$$p_i=M_{ij}n_j-n_i(n_sM_{st}n_t). \tag{15}$$

The main property of the vectors $\mathbf{u}$ and $\mathbf{p}$ introduced by Eqs. (12)–(15) is their orthogonality to the vector $\mathbf{n}$, that is, $\mathbf{un}=0$ and $\mathbf{pn}=0$. The Q_{ik} have nonzero components only in a plane perpendicular to $\mathbf{n}$ and, in addition, $\operatorname{Tr}\hat{Q}\equiv Q_{jj}=0$. An expansion similar to (12)–(15) was used earlier in studying the molecular scattering of light.[14,15] The probability of an electron being emitted into the solid angle Δ_0 is proportional to

$$|\langle F|\hat{d}_i|I\rangle B_i+\langle F|\hat{M}_{ik}|I\rangle E_iE_k|^2. \tag{16}$$

Averaging this expression over the isotropic distribution of the orientations of the initial states yields

$$W(\mathbf{n})=T^{(11)}_{ik}B_iB_k^*+T^{(22)}_{iklm}E_iE_kE_l^*E_m^*$$
$$+(T^{(12)}_{ikl}B_iE_k^*E_l^*+\text{c.c.}). \tag{17}$$

The tensor quantities $\hat{T}$ are the result of summing expression (16) over all the final states of the ionized atom (or molecule) and averaging over all the initial states and orientations. For instance, to within an unimportant numerical factor,

$$T^{(11)}_{ik}=\overline{\langle F|\hat{d}_i|I\rangle^*\langle F|\hat{d}_k|I\rangle}, \tag{18}$$

where the horizontal line indicates the above-mentioned procedure of summation and averaging. The problem possesses the symmetry of a small group, the group of rotations about the $\mathbf{n}$ axis and reflections in the plane containing $\mathbf{n}$. Hence, as the result of averaging, the products of the components of $\mathbf{n}(\mathbf{dn})$ and $\mathbf{u}=\mathbf{d}-\mathbf{n}(\mathbf{dn})$ vanish and we get

$$T^{(11)}_{ik}=A_{\parallel}n_in_k+A_{\perp}\rho_{ik}, \tag{19}$$
$$\rho_{ik}=\delta_{ik}-n_in_k. \tag{20}$$

Here the nonzero coefficients appear as a result of averaging:

$$A_{\parallel}=\overline{|\langle F|(\hat{\mathbf{d}}\mathbf{n})|I\rangle|^2}, \tag{21a}$$
$$A_{\perp}={}^1/_2\langle F|\hat{u}_k|I\rangle\langle F|\hat{u}_k|I\rangle^*. \tag{21b}$$

Formula (19) describes the dichroism, so to say, of one-photon absorption of light with emission of an electron in the given direction $\mathbf{n}$.

The expression for the probability of two-photon ionization may be derived along similar lines:

$$T^{(22)}_{iklm}=C_0\delta_{ik}\delta_{lm}+C_2(n_in_k-{}^1/_3\delta_{ik})(n_ln_m-{}^1/_3\delta_{lm})$$
$$+C_{02}\delta_{ik}(n_ln_m-{}^1/_3\delta_{lm})+C_{02}^*(n_in_k-{}^1/_3\delta_{ik})\delta_{lm}$$
$$+C_p(n_in_m\rho_{kl}+n_in_l\rho_{km}+n_kn_m\rho_{il}+n_kn_l\rho_{im})$$
$$+C_Q(\rho_{il}\rho_{km}+\rho_{im}\rho_{kl}-\rho_{ik}\rho_{lm}). \tag{22}$$

The four nonnegative constants C_0, C_2, C_p, and C_Q and the complex-valued constant C_{02} are determined by the following formulas:

$$C_0=\overline{|\langle F|M_0|I\rangle|^2},\quad C_2=\overline{|\langle F|M_2|I\rangle|^2},$$
$$C_{02}=\overline{\langle F|M_0|I\rangle\langle F|M_2|I\rangle^*},\quad C_p={}^1/_2\overline{\langle F|p_j|I\rangle\langle F|p_j|I\rangle^*},$$
$$C_Q={}^1/_4\overline{\langle F|Q_{ik}|I\rangle\langle F|Q_{ik}|I\rangle^*}. \tag{23}$$

And, finally, the terms that describe the interference of one- and two-photon ionization are

$$T^{(12)}_{ikl}=G_{00}n_i\delta_{kl}+G_{01}n_i(n_kn_l-{}^1/_3\delta_{kl})+G_{up}(\rho_{ik}n_l+\rho_{il}n_k)\,. \tag{24}$$

where

$$G_{00}=\overline{\langle F|d_0|I\rangle\langle F|M_0|I\rangle^*},\quad G_{01}=\overline{\langle F|d_0|I\rangle\langle F|M_2|I\rangle^*},$$
$$G_{up}={}^1/_2\overline{\langle F|u_j|I\rangle\langle F|p_j|I\rangle^*}. \tag{25}$$

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 $W(\mathbf{n})$ is characterized by two real constants $A_{\parallel}$ and $A_{\perp}$ (one-photon ionization), one complex-valued constant C_{01} and four real constants C_0, C_1, C_p, and C_Q (two-photon ionization), and also three complex-valued constants G_{00}, G_{01}, and G_{up} (interference terms). It is easy to show that all the real constants are nonnegative and all the complex-valued constants satisfy the following inequalities

$$|C_{02}|^2\leqslant C_0C_2,\quad |G_{00}|^2\leqslant C_0A_{\parallel},$$
$$|G_{02}|^2\leqslant C_2A_{\perp},\quad |G_{up}|^2\leqslant C_pA_{\perp}. \tag{26}$$

The interested reader can obtain the final expressions for

$W(\mathbf{n})$ by multiplying the tensors $T_{ik}^{(11)}$, $T_{iklm}^{(22)}$, and $T_{ikl}^{(12)}$ by the appropriate products of fields, $B_i B_k^*$, $E_i E_k E_l^* E_m^*$, and $B_i E_k^* E_l^*$. The representation of tensor T adopted here has roughly the same justification as in the problem of molecular scattering of light.[14,15] It is after averaging over orientations that the products of irreducible representations of the small group of rotations about $\mathbf{n}$ provide the only nonzero result. This result is obtained below in the framework of the standard theory of angular momentum for the most interesting case where the initial state of the atom is spherically symmetric (s-state) and the final state of the atomic core has zero angular momentum.

3. IONIZATION OF AN ATOM FOR SPHERICALLY SYMMETRIC AND NONDEGENERATE INITIAL AND FINAL STATES

The general expression for the ionization probability $W(\mathbf{n})$ simplifies considerably when the initial state of the atom and the final state of the atomic core after ionization have zero angular momenta. We denote the initial state of an electron in an atom by $|I\rangle$ or $\psi_0(|r|)$. Then the wave functions of the final state, $|F\rangle$, describing the motion of the electron in the spherically symmetric potential of the ionized atomic core can be represented in the form[13]

$$\psi_{\mathbf{n}}^{(-)}(r)=\frac{1}{2k}\sum_{l=0}^{\infty} i^l(2l+1)\exp(-i\delta_l)R_{kl}(r)P_l\left(\mathbf{n}\frac{\mathbf{r}}{r}\right), \tag{27}$$

where $R_{kl}(r)$ are the radial wave functions, and $P_l \equiv P_l(\cos\theta)$ are Legendre polynomials. If we assume $\mathbf{n}$ to be the quantization axis, states with different values of l but zero values of the projection $m_{\mathbf{n}}$ contribute to $\psi_{\mathbf{n}}^{(-)}(\mathbf{r})$. The amplitudes (12)–(15) obey the following selection rules. The dipole moment $\hat{\mathbf{d}}$ is a vector, so that $\Delta l = +1$, and $\Delta m_{\mathbf{n}} = 0$ for $(\hat{\mathbf{d}}\mathbf{n})$ and $\Delta m_{\mathbf{n}} = \pm 1$ for $\hat{\mathbf{u}} = \hat{\mathbf{d}} - \mathbf{n}(\hat{\mathbf{d}}\mathbf{n})$. Hence, $\hat{d}_0 = (\hat{\mathbf{d}}\mathbf{n})$ and the term with $l=1$ in (27) provide a nonzero contribution to the one-photon transition from the ground s-state to the continuum states (27). The selection rules for the scalar part $M_0\delta_{ik}$ of the symmetric tensor M_{ik} are, obviously, $\Delta l = 0$ and $\Delta m = 0$; hence, owing to a M_0 a nonzero matrix element emerges only during a transition to the final s-state (27). The remaining part of tensor M_{ik}, that is, the symmetric traceless part, yields transitions to a continuum state with $l=2$ if the initial state is the s-state. The selection rules in the quantum number m are $\Delta m = 0$ for $M_2(n_i n_k - \delta_{ik}/3)$, $\Delta m = \pm 1$ for $p_i n_k$, and $\Delta m = \pm 2$ for Q_{ik}. Hence, of the traceless part of M_{ik} only M_2 yields a transition to the final state (27).

The resulting expression for the photoionization probability has the form

$$\frac{dW(\mathbf{n})}{d\Omega} = \Big|\varepsilon_p(\mathbf{Bn})A_{\parallel}^{1/2} i\exp(i\delta_p)+\varepsilon_s(\mathbf{EE})C_0^{1/2}\exp(i\delta_s) + \varepsilon_d\Big[(\mathbf{En})^2-\frac{1}{3}(\mathbf{EE})\Big]C_2^{1/2}\exp(i\delta_d)\Big|^2. \tag{28}$$

Here we have introduced the factor ε, that assumes the value $+1$ or -1 depending on the sign of the radial matrix element M_0. The factors ε_p and ε_d have similar meaning. Since $|\varepsilon_s \exp(i\delta_s)| = 1$, the right-hand side of (28) is determined by three independent "amplitude" factors $A_{\parallel}^{1/2}$, $C_0^{1/2}$, and $C_2^{1/2}$ and two phase differences $-i\varepsilon_s\varepsilon_p\exp(i\delta_s - i\delta_p)$ and $-\varepsilon_s\varepsilon_d\exp(i\delta_s - i\delta_d)$. 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 $\psi_{\mathbf{n}}(\mathbf{r})$ (with fixed energy and direction $\mathbf{n}$) are nondegenerate and is the 100% "contrast" of the interference terms. This means the following: (1) In the absence of the first harmonic, that is, when we have $\mathbf{E}(\omega) = 0$, for the monochromatic wave $\mathbf{E}(2\omega) \equiv \mathbf{B}$ one can select a polarization of $\mathbf{B}$ such that $(\mathbf{Bn}) = 0$ and $W(\mathbf{n}) = 0$ although $(\mathbf{BB}^*) \neq 0$. (2) For the monochromatic field $\mathbf{E}(\omega) \equiv \mathbf{E}$ (at $\mathbf{B} = 0$) one can select a polarization such that $W(\mathbf{n}) = 0$ although $(\mathbf{EE}^*) \neq 0$. (3) For the bichromatic field with arbitrary polarizations of $\mathbf{B}$ and $\mathbf{E}$ one can select an intensity ratio and a phase shift such that $W(\mathbf{n}) = 0$ holds for $(\mathbf{EE}^*) \neq 0$ and $(\mathbf{BB}^*) \neq 0$. (4) The same can be done for a fixed intensity ratio by varying the polarizations and/or phases of the fields. 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, $\delta_p = \delta_d = 0$ and $\delta_s \neq 0$. We will not give any explicit expressions for the phenomenologically derived constants δ_s, $\varepsilon_p A_{\parallel}^{1/2}$, $\varepsilon_s C_0^{1/2}$, and $\varepsilon_d C_2^{1/2}$ (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:

$$E_{n,l} \approx -\frac{Z^2\,\mathrm{Ry}}{2(n-\mu_l)^2}, \tag{29}$$

where Z is the atomic number of the atomic core, and μ_l 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, $-Ze^2/r + \hbar^2(l+1/2)^2/2mr^2$. For highly excited levels the departure from a purely Coulombic potential can be allowed for by introducing an effective phase shift $-\pi\mu_l$ 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 $|E| \ll Z^2\mathrm{Ry}/2$. Hence, if the kinetic energy T of an electron moving in a spherically symmetric potential of the atomic core is much less than $Z^2\mathrm{Ry}/2$, 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:

$$\delta_l=\pi\mu_l+\arg\left[\Gamma\left(l+1-i\left(\frac{Z^2\,\mathrm{Ry}}{2T}\right)^{1/2}\right)\right]. \tag{30}$$

In our case the kinetic energy is equal to $2\hbar\omega - |\mathscr{E}_I|$, with $|\mathscr{E}_I|$ the binding energy in the initial s-state. Using the well-known formula for the Euler gamma function, $\Gamma(x+iy+1) = (x+iy)\Gamma(x+iy)$, we arrive at the following expressions for the phase differences of interest;

TABLE I. The size of the quantum defect μ in alkali atoms for states with different l and j.

l	j	H	Na	Li	K	Rb	Cs
0	$^1/_2$	0	0,40	1,35	2,18	3,13	4,06
1	$^1/_2$ $^3/_2$	0	0,047	0,857 0,856	1,718 1,715	2,659 2,646	3,596 3,564
2	$^3/_2$ $^5/_2$	0	0,0037	0,014	0,26	1,34	2,475 2,466

$$\delta_p-\delta_s=\pi(\mu_p-\mu_s)-\tan^{-1}\left[\left(\frac{Z^2\,\mathrm{Ry}}{2T}\right)^{1/2}\right], \tag{31a}$$

$$\delta_p-\delta_d=\pi(\mu_p-\mu_d)+\tan^{-1}\left[\left(\frac{Z^2\,\mathrm{Ry}}{2T}\right)^{1/2}\right]. \tag{31b}$$

Table I lists the data on μ 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 $\mathbf{E}(\omega)$ and $\mathbf{E}(2\omega)$ with allowance for one-photon ionization by field $\mathbf{E}(2\omega)$ and two-photon ionization by field $\mathbf{E}(\omega)$. We hope that the effects of polar asymmetry in $E(2\omega)E^2(\omega)$ in alkali atoms will soon be observed.

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Translated by Eugene Yankovsky