Multiphoton ionization of polarized atoms

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A theory is derived for the multiphoton ionization of polarized atoms. The angular distributions of the differential and total ionization probabilities are studied for various polarizations of the electromagnetic radiation. The circular dichroism is also studied. The multiphoton ionization of oriented *s*-state atoms near a resonance is studied separately. Some relevant experiments which might be carried out are discussed.

1. INTRODUCTION

The multiphoton ionization of atoms has been under study for a fairly long time now, both theoretically and experimentally.[1,2] Although subtler effects such as many-electron multiphoton ionization and above-threshold ionization have been studied in recent years (see the recent review in Ref. 3), the question of the multiphoton ionization of polarized atoms has not yet been taken up, to the best of our knowledge. This situation is generally not surprising, since even in such a classic effect as the atomic photoelectric effect it was only comparatively recently that research was undertaken on manifestations of the polarization of the target atom. Specifically, Klar and Kleinpoppen[4] derived general expressions for the angular distribution of the photoelectrons emitted from the polarized atoms. The circular dichroism in the angular distribution and in the total photoionization cross section was first studied theoretically in Ref. 5, although circular dichroism had been observed as early as 1970 in the photoionization of polarized alkali atoms.[6]

A preliminary polarization of the target atom opens up some new possibilities for experiments on multiphoton ionization. On the other hand, analysis of the experimental data makes it possible to determine the type of atomic polarization. Polarized atoms can be produced without difficulty by optical pumping, collisions, and other methods.[7] The ions formed through photoionization of unpolarized atoms[8,9] and atoms adsorbed on surfaces are also found to be polarized.

We recall that an atom which has a total angular momentum $j\neq 0$ is polarized if the states with different values of the projection m of the angular momentum onto some direction **n** are not uniformly populated. In this case the atom is in a mixed state consisting of an incoherent superposition of states with different values of m, and its density matrix is diagonal1) in m. This state is usually characterized not by the $2j$ independent populations which are the diagonal elements of the density matrix ρ^n_{mm} but by the degrees of polarization of order K, which are defined differently by different authors. According to Refs. 9 and 10, for example, we would have

$$P_K=\left[\frac{(2j+K+1)!\,(2j-K)!}{(2j)!\,(2j+1)!}\right]^{1/2}\overline{C^{jm}_{jmK0}},\tag{1}$$

where C^{jm}_{jmK0} is a Clebsch-Gordan coefficient, and the superior bar means an expectation value:

$$\overline{C^{jm}_{jmK0}}=\sum_{m=-j}^{j}\rho^n_{mm}C^{jm}_{jmK0}.$$

Here $P_0=1$, $P_1=\overline{m}/j$, and

$$P_2=3[\overline{m^2}-j(j+1)/3]/[j(2j-1)],\ldots,P_{K>2j}=0.$$

For the discussion below it is natural to specify the polarization state of the atom by means of irreducible components of the density matrix, i.e., multipoles of the state,[7]

$$\rho_{K0}{}^n=\sum_m(-1)^{j-m}(2K+1)^{1/2}\begin{pmatrix} j & j & K\\ m & -m & 0\end{pmatrix}\rho^n_{mm},\tag{2}$$

which are proportional to the degrees of polarization P_K given by (1),

$$P_K=\left[\frac{(2j+K+1)!\,(2j-K)!}{(2K+1)\,(2j)!\,(2j)!}\right]^{1/2}\rho^n_{K0},$$

and which are the same as the degrees of polarization introduced by Fano.[11] An atom is said to be "oriented" if $\rho^n_{10}\neq 0$ or "aligned" if $\rho^n_{20}\neq 0$.

Our purpose in the present paper is to take a detailed theoretical look at multiphoton ionization of polarized atoms. In Sec. 2 we derive general expressions for the probability for the multiphoton ionization of polarized atoms by partially polarized electromagnetic radiation. In Sec. 3 we analyze the general expressions and discuss the angular distribution and the circular dichroism. It is shown in Sec. 4 that atoms in s states may exhibit a polarization (orientation) during multiphoton ionization, in contrast with the situation in the photoelectric effect. In the final section, Sec. 5, we summarize the basic results and discuss some possible experimental studies which would be relevant.

2. GENERAL EXPRESSIONS FOR THE PROBABILITY FOR IONIZATION FROM AN $l\neq 0$ STATE

Let us derive an expression for the probability for the multiphoton ionization of a polarized atom by partially polarized electromagnetic radiation. To simplify the calculations below, we consider atoms which have a single electron outside a filled shell. In the nonrelativistic approximation, the ionization probability does not depend on the spin of the electron, so the polarization of the atom should not be manifested for s states in this approximation. The case of ionization from s state will be taken up separately in Sec. 4.

We direct the z axis of our laboratory coordinate system along the propagation direction of the electromagnetic radiation. The direction (**n**) of the polarization axis of the atom generally does not coincide with the wave vector of the photon. The density matrix of a polarized atom in the laboratory

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system, $\langle jm_j|\hat{\rho}|jm_j'\rangle$, is therefore nondiagonal. We expand it in irreducible components—the multipoles of the state, ρ_{KQ} (Ref. 7):

$$\langle jm_j|\hat{\rho}|jm_j'\rangle=\sum_{K,Q}(-1)^{j-m_j}(2K+1)^{1/2}\begin{pmatrix} j & j & K \\ m_j & -m_j' & -Q\end{pmatrix}\rho_{KQ}. \tag{3}$$

Using the law governing the transformation of multipoles of the state under rotations, we find

$$\rho_{KQ}=\sum_q \rho^n_{Kq}D^{(K)*}_{qQ}(0,\theta,\varphi),$$

where ρ^n_{Kq} are the multipoles in the atomic coordinate system, with z' axis running along the vector $\mathbf{n}$, and $D^{(K)}_{qQ}$ is the finite-rotation matrix. Since the density matrix of the atom is diagonal in the atomic coordinate system, we have $\rho^n_{Kq}=\rho_{K0}{}^n\delta_{q,0}$, and ρ^n_{K0} is given by (2). As a result, ρ_{KQ} can be expressed in terms of a spherical harmonic:

$$\rho_{KQ}=\rho^n_{K0}D^{(K)*}_{0Q}(0,\theta,\varphi)=\rho^n_{K0}[4\pi/(2K+1)]^{1/2}Y^*_{KQ}(\mathbf{n}).$$

Substituting the latter expression into (3), we can express the density matrix of an atom in the laboratory system in terms of the characteristics of its polarization state:

$$\langle jm_j|\hat{\rho}|jm_j'\rangle=\sum_{K,Q}(4\pi)^{1/2}(-1)^{j-m_j}\begin{pmatrix} j & j & K \\ m_j & -m_j' & -Q\end{pmatrix}Y^*_{KQ}(\mathbf{n})\rho^n_{K0}. \tag{4}$$

We write the polarization density matrix of the electromagnetic radiation in a basis of states with a definite helicity:[7]

$$\langle\lambda|\hat{\rho}^\gamma|\lambda'\rangle\equiv\rho^\gamma_{\lambda\lambda'}=\frac{1}{2}\begin{pmatrix} 1+\eta_2 & -\eta_3+i\eta_1 \\ -\eta_3-i\eta_1 & 1-\eta_2\end{pmatrix},$$

where the η_i are the Stokes parameters. The parameter values $\eta_1=\eta_3=0$, $\eta_2=\pm 1$ correspond to a right-hand (left-hand) circular polarization, while the values $\eta_1=\eta_2=\eta_3=0$ correspond to unpolarized radiation.

Working from the results of Ref. 7, we can derive the following expression for the differential probability for N-photon ionization per unit time of a polarized atom by partially polarized radiation of frequency ω, in the dipole approximation (we are using the atomic system of units):

$$\begin{aligned} dW^{(N)}/d\Omega_{\mathbf{p}}=2\pi(F2\pi\omega\alpha)^N&\sum_{\substack{m_j,m_j',\mu,\\ \lambda,\lambda'}}\langle\Psi^{(-)}_{\mathbf{p}\mu}|d_\lambda G_{E_i+(N-1)\omega}\\ &\ldots d_\lambda G_{E_i+\omega}d_\lambda|\Psi_{n_il_ijm_j}\rangle\langle jm_j|\hat{\rho}|jm_j'\rangle\\ &\times\langle\lambda|\hat{\rho}^\gamma|\lambda'\rangle\langle\Psi_{n_il_ijm_j'}|d_{\lambda'}{}^*G^+_{E_i+\omega}\\ &\ldots d_{\lambda'}{}^*G^+_{E_i+(N-1)\omega}d_{\lambda'}{}^*|\Psi^{(-)}_{\mathbf{p}\mu}\rangle.\end{aligned}\tag{5}$$

Here F is the photon flux density, α is the fine-structure constant, d_λ is the spherical component of the dipole moment, E_i is the energy of the initial state of the valence electron, and G_E is the Green's function of the valence electron.[2)] The function $\Psi^{(-)}_{p\mu}$, where $\mathbf{p}$ is the momentum, and μ is the projection of the electron spin in the final state, has as asymptotic behavior a superposition of a plane wave and an incoming spherical wave:

$$\Psi^{(-)}_{\mathbf{p}\mu}(r)=\sum_{l_f,m_f}i^{l_f}\exp(-i\delta_{l_f})Y^*_{l_fm_f}(\mathbf{n}_\mathbf{p})Y_{l_fm_f}\left(\frac{\mathbf{r}}{r}\right)\chi_\mu R_{E_fl_f}(r), \tag{6}$$

where δ_l is the partial phase shift in the scattering of the valence electron by the atomic core, $\mathbf{n}_\mathbf{p}=\mathbf{p}/p$, E_f is the energy of the electron in the final state, R_{El} are the radial wave functions of the continuum (normalized along the energy scale), and χ_μ is the spin wave function. The normalization of the function in (6) has been chosen in such a way that expression (5) for the probability is freed of factors corresponding to the density of final states. The function $\Psi_{n_il_ijm_j}$ describes the electron in an initial state with a definite main quantum number n_i, a definite orbital quantum number l_i, a total angular momentum $j=l_i\pm 1/2$, and a projection m_j of the total angular momentum:

$$\begin{aligned}\Psi_{n_il_ijm_j}(\mathbf{r})&=R_{n_il_i}(r)\,\Omega_{l_ijm_j}\left(\frac{\mathbf{r}}{r}\right)\\ &=R_{n_il_i}(r)\sum_{m_i,\mu}(-1)^{1/2-l_i-m_j}(2j+1)^{1/2}\\ &\times\begin{pmatrix} l_i & 1/2 & j \\ m_i & \mu & -m_j\end{pmatrix}Y_{l_im_i}\left(\frac{\mathbf{r}}{r}\right)\chi_\mu.\end{aligned}\tag{7}$$

We expand the Green's function G_E of the valence electron in spherical harmonics. Far from resonances, where we can ignore the fine structure of the levels of intermediate states, this expansion is

$$G_E(\mathbf{r},\mathbf{r}')=\sum_{l,m,\mu}g_l(E;r,r')Y_{lm}\left(\frac{\mathbf{r}}{r}\right)Y^*_{lm}\left(\frac{\mathbf{r}'}{r'}\right)\chi_\mu\chi_\mu^+, \tag{8}$$

where g_l is the radial Green's function.[1]

With the help of (6)–(8), we can integrate over the angular and spin variables in the composite matrix elements of order N in (5). Substituting (4) into (5), and carrying out a partial summation over angular-momentum projections, we then find our final expression for the differential probability for N-photon ionization:

$$\begin{aligned} dW^{(N)}/d\Omega_\mathbf{p}&=4\pi^{3/2}(F2\pi\omega\alpha)^N(2j+1)\sum_{\mathfrak{M}}\rho^n_{K0}\rho^\gamma_{\lambda\lambda'}(-1)^{j+1/2}\\ &\times\begin{Bmatrix} l_i & l_i & K \\ j & j & 1/2\end{Bmatrix}i^{l_f-l_f'}\exp[i(\delta_{l_f}-\delta_{l_f'})]\\ &\times\langle l_f\|n\|l_{N-1}\rangle\langle l_{N-1}\|n\|l_{N-2}\rangle\\ &\ldots\langle l_1\|n\|l_i\rangle\langle l_f'\|n\|l_{N-1}'\rangle\ldots\langle l_1'\|n\|l_i\rangle\\ &\times v_{E_fl_f,l_{N-1},\ldots,l_1,i}\,v^*_{E_fl_f',l_{N-1}',\ldots,l_1',i}\\ &\times S(l_i,K,l_f,l_f',l_{N-1},l_{N-2},\ldots,l_1,l_{N-1}',\ldots,l_1';m_f,m_f',\lambda,\lambda')\\ &\times Y_{l_fm_f}(\mathbf{n}_\mathbf{p})Y^*_{l_f'm_f'}(\mathbf{n}_\mathbf{p})Y^*_{K,m_f-m_f'+N(\lambda'-\lambda)}(\mathbf{n}),\end{aligned}\tag{9}$$

$$\mathfrak{M}=\{K,l_f,l_f',l_1,l_1',\ldots,\quad l_{N-1},l_{N-1}',m_f,m_f',\lambda,\lambda'\}.$$

Here $\langle l\|n\|l'\rangle$ is the reduced matrix element of the unit vector,[14] and

$$\begin{aligned} & v_{E_fl_f,\,l_{N-1},\,l_{N-2},\ldots,\,l_i,\,i} \\ &= \langle R_{E_fl_f}(r_N)\,|\,r_N g_{l_{N-1}}(E_i+(N-1)\,\omega;\,r_N,r_{N-1}) \\ &\qquad \ldots\; r_2 g_{l_1}(E_i+\omega;\,r_2,r_1)\,r_1\,|\,R_{n_il_i}(r_1)\rangle \end{aligned}$$

is the composite radial dipole matrix element of Nth order. Semiempirical methods for calculating this matrix element (the quantum-defect method and the model-potential method) have been worked out in detail.[1] In addition, we have

$$\begin{aligned} & S(l_i,K,l_f,l_f',l_{N-1},\ldots,l_1,l'_{N-1},\ldots,l_1';m_f,m_f',\lambda,\lambda') \\ &= \sum_{\mathfrak{m}}(-1)^{\mathscr{L}}\begin{pmatrix} l_f & 1 & l_{N-1}\\ -m_f & \lambda & m_{N-1}\end{pmatrix}\begin{pmatrix} l_{N-1} & 1 & l_{N-2}\\ -m_{N-1} & \lambda & m_{N-2}\end{pmatrix} \\ &\ldots\begin{pmatrix} l_1 & 1 & l_i\\ -m_1 & \lambda & m_i\end{pmatrix}\begin{pmatrix} l_f' & 1 & l'_{N-1}\\ -m_f' & \lambda' & m'_{N-1}\end{pmatrix} \\ &\times\begin{pmatrix} l'_{N-1} & 1 & l'_{N-2}\\ -m'_{N-1} & \lambda' & m'_{N-2}\end{pmatrix} \\ &\qquad\ldots\begin{pmatrix} l_1' & 1 & l_i\\ -m_1' & \lambda' & m_i'\end{pmatrix}\begin{pmatrix} l_i & l_i & K\\ -m_i & m_i' & Q\end{pmatrix}, \qquad (10) \\ &\qquad \mathfrak{m}=\{m_i,m_i',m_1,m_1',m_2,m_2',\ldots,m_{N-1},m'_{N-1}\}. \\ &\mathscr{L}=\sum_{i=1}^{N-1}(l_i-m_i+l_i'-m_i')+l_f-m_f+l_f'-m_f'-m_i. \end{aligned}$$

The sum over angular momentum projections in (10) is only a formal operation, since all the summation indices are fixed by the selection rules. The quantity S in (10) is proportional to a generalized Clebsch-Gordan coefficient.[15,16] From the selection rules we also find

$$Q=m_i-m_i'=m_f-m_f'+N(\lambda'-\lambda).$$

The latter relation was taken into account explicitly in the writing of the index of the spherical harmonic $Y_{KQ}(\mathbf{n})$ in (9).

The familiar expansion (Ref. 14, for example) for the product of two spherical harmonics of $\mathbf{n}_\mathrm{p}$ can be used in (9). In the case of one-photon ionization, we find the result derived by Cherepkov and Kuznetsov[5] after an expansion like (3) of the photon density matrix $\rho^{\gamma}_{\lambda\lambda'}$ in multipoles of the state, after a summation over the photon polarization index λ, and after the use of the generalized Wigner-Eckart theorem.[16] In the case under consideration here, of N-photon ionization with $N\geqslant 2$, however, some nonstandard sums over the index λ appear in (9), ruling out transformations of this sort.

To find the total probability for N-photon ionization, integrated over the electron emission direction,

$$W^{(N)}=\int\frac{dW^{(N)}}{d\Omega_\mathrm{p}}\,d\Omega_\mathrm{p}$$

it is sufficient (by virtue of the orthonormality of the spherical harmonics) to set $l_f=l_f'$, $m_f=m_f'$ in (9) and to omit the product $Y_{l_fm_f}Y^*_{l_f'm_f'}$:

$$\begin{aligned} W^{(N)} &= 4\pi^{3/2}(F2\pi\omega\alpha)^N(2j+1)\sum_{\mathfrak{M}'}\rho^n_{K0}\rho^{\gamma}_{\lambda\lambda'}(-1)^{j+1/2} \\ &\quad\times\begin{Bmatrix} l_i & l_i & K\\ j & j & 1/2\end{Bmatrix}\langle l_f\|n\|l_{N-1}\rangle\langle l_{N-1}\|n\|l_{N-2}\rangle\ldots\langle l_1\|n\|l_i\rangle \\ &\times\langle l_f\|n\|l'_{N-1}\rangle\ldots\langle l_1'\|n\|l_i\rangle v_{E_fl_f,\,l_{N-1},\ldots,\,l_1,\,i}\,v^*_{E_fl_f,\,l'_{N-1},\ldots,\,l'_1,\,i} \\ &\times S(l_i,K,l_f,l_f,l_{N-1},l_{N-2},\ldots,l_1,l'_{N-1},\ldots,l_1';m_f,m_f,\lambda,\lambda') \\ &\times Y^*_{K,\,N(\lambda'-\lambda)}(\mathbf{n}), \qquad (11) \\ &\mathfrak{M}'=\{K,l_f,l_1,l_1',\ldots,l_{N-1},l'_{N-1},m_f,\lambda,\lambda'\}. \end{aligned}$$

3. ANGULAR DISTRIBUTION OF THE IONIZATION PROBABILITY FOR VARIOUS POLARIZATIONS OF THE RADIATION; CIRCULAR DICHROISM

If the atoms in a system are polarized, there is a preferred direction: the polarization axis $\mathbf{n}$. The differential probability (9), and the total probability (11), for the ionization of polarized atoms thus contain an $\mathbf{n}$ dependence. This dependence disappears only in the case of unpolarized atoms, in which the multipoles of the state in (2) are given by $\rho^n_{K0}=(2j+1)^{-1/2}\delta_{K,0}$ (Ref. 7), and the total ionization probability becomes isotropic.

In the general case of a partial polarization of the ionizing radiation (we are including in this general case the particular case of purely elliptical polarization), the directions in the plane perpendicular to the wave propagation direction are obviously not equivalent. This fact is reflected in the expressions derived above: In the case $\lambda\neq\lambda'$, the product of three spherical harmonics in (9) and thus the differential probability for multiphoton ionization of polarized atoms depend on the orientation of the vectors $\mathbf{n}_\mathrm{p}$ (the direction in which the photoelectron is moving) and $\mathbf{n}$ (the polarization axis of the atom) with respect to the laboratory coordinate system. Correspondingly, the total ionization probability in (11) depends on the orientation of the polarization axis of the atom with respect to the laboratory coordinate system.

In contrast, the directions in the plane perpendicular to the wave propagation direction are equivalent if the radiation is an incoherent superposition of left-hand and right-hand circularly polarized waves. The polarization density matrix of the photon is diagonal in this case:

$$\rho^{\gamma}_{\lambda\lambda'}=\frac{1}{2}\begin{pmatrix}1+\eta_2 & 0\\ 0 & 1-\eta_2\end{pmatrix}.$$

Included, in particular, here are the case of a purely right-hand or purely left-hand circular polarization ($\eta_2=\pm 1$) and the case of unpolarized radiation ($\eta_2=0$). Since $\rho^{\gamma}_{\lambda\lambda'}$, is diagonal, the differential ionization probability in (9) depends on the difference between the azimuthal angles of the vectors $\mathbf{n}_\mathrm{p}$ and $\mathbf{n}$ in this case, through

$$\exp[i(m_f-m_f')(\varphi_\mathrm{p}-\varphi)],$$

reflecting the equivalence of all directions in the xy plane of the laboratory coordinate system. The total ionization probability in (11) depends only on the angle between the polarization direction of the atom, $\mathbf{n}$, and the propagation direction of the electromagnetic wave.

A similar situation arises in the case of a linear polarization of the ionizing radiation. In our dipole approximation, all directions in the plane perpendicular to the electric field of the wave should be equivalent. Corresponding expressions for the probabilities for ionization of the atom can be derived from the expressions for the probabilities for ionization by circularly polarized radiation, by setting $\lambda=0$ in those expressions and by assuming that the z axis of the laboratory system is directed along the polarization vector of the wave.

Expressions for the probability for multiphoton ionization of polarized atoms by right-hand (left-hand) circularly polarized electromagnetic radiation can be found from (9) and (11) by setting

$$\rho_{\lambda\lambda'}^{\gamma}=\delta_{\lambda,\pm1}\delta_{\lambda',\pm1}$$

in those expressions. Expression (9) in this case yields different values for the differential probability for the multiphoton ionization of polarized atoms in the cases of left-hand and right-hand circular polarizations of the radiation (this is circular dichroism in the angular distribution of the photoelectrons). In the total ionization probability, in contrast, one does not observe circular dichroism, regardless of the polarization of the target atom. If, for example, states with opposite projections of the total angular momentum are equally populated, the state of the polarized atom does not change under reflection in a plane perpendicular to the polarization axis **n**, i.e., upon reversal of the axis. In this case, the only multipoles of the state ρ_{K0}^{n} in (2) which are nonzero are those which have even values of K (Ref. 7). For brevity below, we will call such polarization states "aligned," although in the standard terminology an atom would be regarded as aligned if the condition $\rho_{20}^{n}\neq0$ held. When the atoms become aligned, the ionization probability evidently does not change if the polarization axis **n** is reversed [see (9)]. For aligned atoms, there should be no circular dichroism in the total ionization probability, because of parity conservation: Under the operation of mirror reflection, the angle between the polarization axis of the atoms and the radiation propagation direction does not change, nor does the state of the aligned atoms. Right-hand polarized radiation, on the other hand, becomes left-hand polarized radiation.

The absence of a circular dichroism from the total probability for the multiphoton ionization of aligned atoms follows in a purely formal way from expression (11) when one makes use of the symmetry properties of the $3j$ symbols in (10).

We might also note that for an arbitrary polarization of an atom the total probability for ionization by right-hand (left-hand) circularly polarized radiation propagating at an angle θ from the **n** axis is equal to the probability for ionization by left-hand (right-hand) circularly polarized radiation propagating at an angle $\pi-\theta$ from this axis. This result follows directly from (11) by virtue of the symmetry of the $3j$ symbols; it also follows from general considerations based on parity conservation.

4. IONIZATION OF POLARIZED ATOMS FROM *S* STATES

The polarization of an atom with a single s electron outside a filled shell means that this atom is oriented, since in this case we have $\rho_{10}^{n}\neq0$. According to (2), for a total angular momentum $j=1/2$ we have a multipole $\rho_{00}^{n}=2^{-1/2}$, while we have $\rho_{K0}^{n}=0$ for $K>1$. The polarized state of the atom is thus characterized by only one multipole, ρ_{10}^{n}.

As was pointed out at the beginning of Sec. 2, the polarization of atoms in s states should not be manifested in the nonrelativistic approximation, in which the ionization probability is independent of the electron spin. This situation corresponds to the disappearance of the terms with $K\neq0$ from expressions (9) and (11) in the case $l_i=0$, as a result of the selection rules in terms of the angular momentum in the $6j$ and $3j$ symbols [see (10)].

In this case, the orientation of the atom thus generally contributes a small effect $\sim\alpha^2$. In contrast with the photoelectric effect, however, in the case of multiphoton ionization atoms in s states should exhibit orientation near a resonance. The reason is that if the magnitude of the deviation from resonance with intermediate levels E_{nlj} approaches the fine-structure splitting of these levels, this fine structure of the levels (a relativistic effect) of the intermediate states cannot be ignored. If the deviation from resonance satisfies $\Delta\sim\alpha^2$ (where Δ is expressed in atomic units), the effect should be of order unity, i.e., the same as in the ionization of polarized atoms from a state with $l_i\neq0$.

A resonant case of this sort can easily be arranged in experiments on multiphoton ionization. The reason is that only the ionization width Γ of an intermediate resonant level can reach values on the order of α^2. The orientation of an s-state atom, however, will be manifested weakly only for $\Gamma\gg\alpha^2$, i.e., only in very strong fields (in the least favorable case, in which there can be a one-photon ionization from an intermediate state, the electric field of the wave is $\gtrsim0.1$ a.u.).

Let us take a more detailed look at the two-photon ionization of oriented atoms from s states. The intermediate resonance in this case is a one-photon resonance: $\Delta=E_{n1j}-E_{n_i01/2}-\omega$. To incorporate the fine structure of the levels of intermediate states, we should write the Green's function of the valence electron, which appears in the general expression for the ionization probability (5), in the following form,[1] instead of as in (8):

$$G_E(\mathbf{r},\mathbf{r}')=\sum_{l,j,m_j} g_{lj}(E;r,r')\,\Omega_{ljm_j}\left(\frac{\mathbf{r}}{r}\right)\Omega^{+}_{ljm_j}\left(\frac{\mathbf{r}'}{r'}\right). \qquad (12)$$

Here Ω_{ljm_j} corresponds to a state with a definite orbital angular momentum l, a total angular momentum $j=l\pm1/2$, and a projection m_j of the total angular momentum. It is constructed by the standard rule (7) for combining angular momenta. It is sufficient to restrict the discussion below for the Green's function in (12) to the resonance approximation.

Substituting (6), (7), and (12), along with (4) with $j=1/2$, into (5), we find an expression for the probability for two-photon ionization, in which our remaining task is to calculate the sum of $3j$ symbols.

Here is the final expression for the total probability for two-photon ionization of oriented atoms in s states by right-hand (left-hand) circularly polarized radiation:

$$W_{\pm}^{(2)}=\frac{2\pi}{27}(F2\pi\omega\alpha)^2\Big[f_{1/2}^{2}+\frac{2}{5}f_{1/2}f_{3/2}+\frac{11}{5}f_{3/2}^{2}$$
$$\mp2^{1/2}\rho_{10}^{n}\cos\theta\left(f_{1/2}^{2}+\frac{2}{5}f_{1/2}f_{3/2}-\frac{7}{5}f_{3/2}^{2}\right)\Big], \qquad (13)$$

where θ is the angle between the polarization axis of the atom and the radiation propagation direction, and

$$f_j=\frac{\langle R_{E_f2}|r|R_{n1}\rangle\langle R_{n1}|r|R_{n_i0}\rangle}{E_{n1j}-E_{n_i01/2}-\omega} \qquad (14)$$

is the radial component of the second-order matrix element in the resonance approximation.

The circular dichroism in the total ionization probability and also the symmetry during ionization by right-hand and left-hand polarized radiation, which was mentioned at the end of Sec. 3, follow explicitly from expression (13).

As we move away from the resonance, it becomes legitimate to ignore the fine structure of the levels of intermediate states; i.e., we can set $f_{1/2} \approx f_{3/2} \equiv f$ [see (14)]. As a result, the term in parentheses multiplying ρ_{10}^{n} in (13) vanishes, and (as expected) the atoms do not exhibit orientation. In this case expression (13) yields the same result as is found from (11) with $N = 2$ and $l_i = 0$: The probability for two-photon ionization of unpolarized atoms from the s state by circularly polarized radiation is[1]

$$W^{(2)} = \frac{4\pi}{15}(F2\pi\omega\alpha)^2 f^2.$$

5. CONCLUSION

We have carried out a detailed theoretical study of the multiphoton ionization of polarized atoms. We have derived general expressions for the differential probability [expression (9)] and for the total probability [expression (11)] for the multiphoton ionization of polarized atoms with a single electron outside a filled shell. It has also been shown that the polarization (or orientation) of an s-state atom is manifested in resonant multiphoton ionization (Sec. 4).

Various methods are available for polarizing atoms. For example, in the case of axisymmetric excitation the atom is in a state which is an incoherent mixture of states with different projections of the angular momentum onto the symmetry axis (the type of polarization which we have been discussing here.[7] In laser experiments, the simplest approach would apparently be to study the multiphoton ionization of atoms excited beforehand by another laser. During excitation by unpolarized radiation or by linearly polarized radiation, the atoms would be aligned, so no circular dichroism would be observed in the total ionization probability (Sec. 3). During excitation by (for example) circularly polarized radiation, the atoms would be oriented.

In experimental studies of multiphoton ionization, relative cross sections can be found much more accurately than absolute cross sections. In addition, while all that can be compared with theoretical predictions in the case of unpolarized atoms is the ratio of the total ion yields for different polarizations of the radiation, in the case of a preliminary polarization of the target it becomes possible to compare relative probabilities for various angles between the polarization axis of the atom and the radiation propagation direction (i.e., by varying the experimental geometry), without changing the polarization of the radiation. In a similar way, one could make use of the circular dichroism in the total probability for multiphoton ionization. Wider opportunities open up in a study of the angular distribution of photoelectrons. Various experiments might be planned on the basis of the general analysis in Sec. 3 above.

Finally, a study of polarization effects accompanying multiphoton ionization would make it possible to solve the inverse problem: determining the polarization state of the excited atoms.

It is our hope that studies of this sort will attract the interest of experimentalists.

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1) One might also look at the more general polarization case in which the density matrix is not diagonal in m (the case of a coherent superposition of states). As will become clear in the discussion below, the angular distribution in the final expressions changes in this case: A spherical harmonic of **n** should be replaced by a linear combination of Wigner functions (finite-rotation matrices).

2) We are using the one-electron approximation, which has been worked out thoroughly for the case of alkali atoms.[1] In principle, electron-electron correlations could be dealt with by *ab initio* methods[12] or semiempirical methods.[13]

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