# Light scattering by polarized atoms

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A theory of light scattering by polarized systems is developed. Expressions, extending the well-known results of Placzek, are derived for the differential and total cross sections for scattering of arbitrarily polarized radiation by polarized systems. It is shown that up to second-order multipoles (orientation and alignment) of the state of a polarized system can appear in the total cross section, and multipoles of up to fourth order, inclusive, can appear in the differential cross section. The characteristics of the atomic scattering are examined. For atoms with a single electron outside a closed shell the radial and angular parts are completely separated in the reduced matrix elements of the light-scattering tensor. The example of *s*-*s* scattering, when orientation of the atom can be manifested only near resonance, is worked out in detail.

## 1. INTRODUCTION

In Placzek's theory of light scattering (see Ref. 1) the scattering system (atom or molecule) is assumed to be freely oriented, i.e., unpolarized (states with different projections of the angular momentum are equally populated). As far as we know, light scattering by polarized systems has never been studied. Only the Compton effect on polarized electrons has been considered.[1] But systems with polarized atoms have now been studied for quite a long time.[2]

Polarized atoms can be easily produced, during different excitation processes, with the help of optical pumping[2,3] and other methods, which give a nonuniform population of states with different values of the projection of the angular momentum on some direction. Although experiments on light scattering by polarized atomic (molecular) gases are more complicated, it seems to us that they should be of interest to investigators. A polarized system becomes asymmetric, which results in a significant change in the angular distribution of the scattered radiation. For a definite type of polarization the target also becomes optically active, which is manifested as circular dichroism in the total cross section of the process. Thus the polarization state of an atom can be in principle determined from the scattering of light.

We note that photoprocesses such as emission and absorption of light[3] and the atomic photoelectric effect[4,5] have been investigated in detail for polarized atoms. The theory of multiphoton ionization of polarized atoms is developed in our recent paper.[6]

In the present paper our aim is to fill the above gap. We develop below a theory of light scattering by polarized atoms. The next section is of a methodological character: we describe a polarized atom and show how to simplify usefully the solution of the problem. In Sec. 3 expressions are derived and analyzed for the differential and total light-scattering cross sections of polarized systems. In Sec. 4 the specific nature of atomic scattering is discussed, expressions are obtained for the reduced matrix elements of the scattering tensor for atoms with a single electron outside a closed shell, and the interesting example of *s*-*s* scattering, when the polarization (orientation) of an atom can be observed only near resonance is examined.

## 2. SPECIFICATION OF THE INITIAL STATE OF A POLARIZED ATOM. THE LIGHT-SCATTERING TENSOR

An atom[1)] with angular momentum $j\neq 0$ is polarized when states with different values of the projection $m$ of the angular momentum on some direction **n** are not populated equally. We assume below that the state of a polarized atom is an incoherent mixture of states with different projections of the angular momentum on the axis **n**, so that the density matrix of the atom is diagonal with respect to $m$ in an atomic coordinate system (ACS) whose $z_a$ axis is oriented along the vector **n**. It is well known that such polarization states arise if the excitation of the atom was axially symmetric with respect to **n**.[3]

We shall specify the state of a polarized atom not by the $2j$ independent occupation numbers of magnetic sublevels—the diagonal elements $\rho^n_{mm}$ of the density matrix in the ACS—but by the irreducible components of the density matrix, which are called the multipole states:[3]

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

Obviously, the multipole $\rho^n_K$ (1) of the state is proportional to the average value of the zeroth component of an irreducible tensor quantity of rank $K$, characterizing the polarized atom. An unpolarized atom corresponds to equal populations of magnetic sublevels, and

$$\rho^n_K=(2j+1)^{-1/2}\delta_{K,0}. \tag{2}$$

In the general case, however, there are $2j+1$ different state multipoles:

$$\rho^n_0=(2j+1)^{-1/2},$$

$$\rho^n_1=3^{1/2}[j(j+1)(2j+1)]^{-1/2}\overline{m},$$

$$\rho_2^n=5^{1/2}[j(j+1)(2j-1)(2j+1)(2j+3)]^{-1/2}$$
$$\times[3\overline{m^2}-j(j+1)],\ldots,$$

$$\rho^n_{K>2j}=0,$$

where the overbar indicates statistical averaging:

$$\bar{f}=\sum_m f_m\rho^n_{mm}.$$

An atom is said to be oriented if $\rho_1^n\neq0$ and aligned if $\rho_2^n\neq0$.

For analysis of the results obtained below, we note that the states of a polarized atom can be separated into mirror-symmetric and mirror-asymmetric. In mirror-symmetric states the magnetic sublevels with opposite projections of the angular momentum are equally populated, i.e., $\rho^n_{mm}=\rho^n_{-m,-m}$. The populations and multipoles (1) of the state transform as follows under the inversion operation, when the polarization axis **n** is inverted;:

$$\rho^n_{mm}\to\rho^n_{-m,-m},\quad \rho^n_K\to(-1)^K\rho^n_K.$$

In mirror-symmetric states all state multipoles of odd rank $K$ are thus zero. For mirror-symmetric states of polarization to arise, the excitation of an atom must obviously be not only axisymmetric but also mirror-symmetric (for example, excitation by unpolarized or linearly polarized radiation).

Using the law of transformation of multipoles of the state under rotations, the density matrix of a polarized atom in an arbitrary coordinate system can be represented in the form (a more detailed discussion is given in Ref. 6)

$$\langle jm|\hat{\rho}|jm'\rangle=(4\pi)^{1/2}\sum_{K,Q}(-1)^{j-m}$$
$$\times\begin{pmatrix} j & j & K\\ m & -m' & -Q\end{pmatrix}Y^*_{KQ}(\mathbf{n})\rho^n_K,\quad(3)$$

where $Y^{(n)}_{KQ}$ are spherical harmonics.[2]

With the help of the Kramers–Heisenberg formula[1] and the results of Ref. 3, the initial expression for the cross section for the scattering of a photon with frequency $\omega$ and polarization vector **e** by a polarized atom can be represented in the following form (the atomic system of units is employed in this paper):

$$d\sigma/d\Omega'=\omega\omega'^3\alpha^4\sum_{m_1,m_1',m_2}\langle\nu_2j_2m_2|c_{ik}|\nu_1j_1m_1\rangle e_i'^*e_k$$
$$\times\langle j_1m_1|\hat{\rho}|j_1m_1'\rangle$$
$$\times\langle\nu_2j_2m_2|c_{i'k'}|\nu_1j_1m_1'\rangle^*e'_{i'}e^*_{k'}.\quad(4)$$

Here $\omega'$ and $\mathbf{e}'$ are the frequency and polarization vector of the scattered photon (both Rayleigh and Raman scattering are considered), $\alpha$ is the fine structure constant, the indices 1 and 2 designate the initial and final states of the atom, and $\nu$ denotes all atomic quantum numbers other than the angular momentum $j$ and its projection $m$. In Eq. (4) repeated Cartesian tensor indices $i$, $k$, $i'$, and $k'$ are summed over. The matrix element of the scattering tensor $c_{ik}$ is determined as follows:

$$\langle2|C_{ik}|1\rangle=\sum_n\left(\frac{\langle2|d_i|n\rangle\langle n|d_k|1\rangle}{E_n-E_1-\omega-i0}\right.$$
$$\left.+\frac{\langle2|d_k|n\rangle\langle n|d_i|1\rangle}{E_n-E_1+\omega'-i0}\right),\quad(5)$$

where **d** is the dipole-moment operator of the atom, $E_n$ is the energy of the corresponding atomic state, $E_1+\omega=E_2+\omega'$, and the summation extends over all possible states of the atom, including the states of the continuous spectrum.

In Ref. 1 the matrix element (5) of the operator $c_{ik}$ is called the scattering tensor. In the present paper it is terminologically more convenient to call the scattering tensor the operator $c_{ik}$ itself. If we now introduce the resolvent of the Hamiltonian for the atom

$$\hat{G}_E=\sum_n\frac{|n\rangle\langle n|}{E_n-E-i0},$$

whose matrix elements are the atomic Green's function, then the scattering tensor, according to Eq. (5), must be written in the form

$$c_{ik}=d_i\hat{G}_{E_1+\omega}d_k+d_k\hat{G}_{E_1-\omega'}d_i.\quad(6)$$

The scalar product of the tensors $c_{ik}$ and $e_i'^*e_k$ in Eq. (4) can be expressed as a sum of the scalar products of the irreducible parts of these tensors. We employ the following notation for the irreducible parts of the tensor $e_i'^*e_k$:[7]

$$\{\mathbf{e}'^*\otimes\mathbf{e}\}_{kq}=\sum_{q_1,q_2}C^{kq}_{1q_11q_2}e'^*_{q_1}e_{q_2},\quad k=0,1,2,\quad(7)$$

where $C^{kq}_{1q_11q_2}$ are Clebsch–Gordan coefficients. We define the irreducible component of the scattering tensor (6) as follows:

$$t^c_{kq}=\sum_{q_1,q_2}C^{kq}_{1q_11q_2}(d_{q_1}\hat{G}_{E_1+\omega}d_{q_2}+d_{q_2}\hat{G}_{E_1-\omega'}d_{q_1}).\quad(8)$$

In Eqs. (7) and (8) the components of vectors are taken to be the spherical components:

$$a_0=a_z,\quad a_{\pm1}=\mp2^{-1/2}(a_x\pm ia_y).\quad(9)$$

We express in terms of spherical components the scalar product of the considered tensors;

$$c_{ik}e_i'^*e_k=\sum_{q_1,q_2}(-1)^{q_1+q_2}c_{q_1q_2}e'^*_{-q_1}e_{-q_2}.$$

Next we substitute here the expansion of $c_{q_1q_2}$ in irreducible parts [inversion of Eq. (7)]:

$$c_{q_1q_2}=\sum_{k,q}C^{kq}_{1q_11q_2}t^c_{kq}$$

and, using the symmetry property of the Clebsch–Gordan coefficients, we arrive at the desired expression:

$$c_{ik}e_i'^{*}e_k=\sum_{k,q}(-1)^{k-q}t^{c}_{kq}\{\mathbf{e}'^{*}\otimes\mathbf{e}\}_{k,-q}. \qquad (10)$$

In the matrix elements of the irreducible parts of the scattering tensor (8) the dependence on the magnetic quantum numbers can be separated with the help of the Wigner–Eckart theorem and we can introduce the reduced matrix elements of the scattering tensor $\langle \nu_2 j_2 \| t^c_k \| \nu_1 j_1\rangle$, where $k=0,1,2$:

$$\langle \nu_2 j_2 m_2 | t^c_{kq} | \nu_1 j_1 m_1\rangle=(-1)^{j_2-m_2}\begin{pmatrix} j_2 & k & j_1 \\ -m_2 & q & m_1\end{pmatrix}\times\langle \nu_2 j_2 \| t^c_k \| \nu_1 j_1\rangle. \qquad (11)$$

Then, using expression (3) for the density matrix of the atom, the summation in Eq. (4) over the projections of the angular momenta is easily performed and the geometric and dynamical parts are separated.

In the next section we present the final expression for the cross section in the most general case of partial polarization of the scattered radiation. The state of partial polarization of light is given by the polarization density matrix with the matrix elements $\rho^{\gamma}_{\lambda\lambda'}$. We employ below the laboratory coordinate system (LCS), whose $z$ axis (it is also the quantization axis of all angular momenta) is oriented along the direction of propagation of the incident radiation. Then the polarization density matrix of the photon in the basis of states with definite helicity (the basis vectors are unit vectors with right- and left-hand circular polarization) is expressed in the standard manner in terms of the Stokes parameters $\eta_i$:[3]

$$\begin{pmatrix}\rho^{\gamma}_{+1,+1} & \rho^{\gamma}_{+1,-1}\\ \rho^{\gamma}_{-1,+1} & \rho^{\gamma}_{-1,-1}\end{pmatrix}=\frac{1}{2}\begin{pmatrix}1+\eta_2 & -\eta_3+i\eta_1\\ -\eta_3-i\eta_1 & 1-\eta_2\end{pmatrix}. \qquad (12)$$

We recall that the parameter $\eta_2$ determines the degree of circular polarization, $\eta_3$ determines the degree of linear polarization with respect to the $x$ and $y$ axes of the LCS, and $\eta_1$ determines the degree of linear polarization with respect to two mutually perpendicular axes making an angle of 45° with the $x$ and $y$ coordinate axes. The Stokes parameters $\eta_1=\eta_3=0$ and $\eta_2=\pm 1$ correspond to right (left)-hand circular polarization, and $\eta_1=\eta_2=\eta_3=0$ correspond to unpolarized light.

The initial expression for the scattering cross section for partially polarized light is obtained by averaging Eq. (4) over two statistically independent states of elliptic polarization (eigenvectors of the density matrix), whose incoherent superposition is partially polarized light, and then switching to the basis of states with definite helicity. This operation is equivalent to the formal substitution

$$e_k e^{*}_{k'}\rightarrow\sum_{\lambda,\lambda'}\rho^{\gamma}_{\lambda\lambda'}e_{\lambda,k}e^{*}_{\lambda',k'} \qquad (13)$$

in Eq. (4). Here the unit vectors $\mathbf{e}_{\pm 1}$ describing the right- (left-) hand circular polarization of the photon are expressed in terms of the first two unit basis vectors of the LCS:

$$\mathbf{e}_{\pm 1}=\mp 2^{-1/2}(\mathbf{e}_x\pm i\mathbf{e}_y).$$

The spherical components (9) of these vectors in the LCS are

$$e_{\lambda,q}=(-1)^{\lambda}\delta_{q,-\lambda}. \qquad (14)$$

## 3. CROSS SECTION FOR LIGHT SCATTERING BY POLARIZED SYSTEMS

The irreducible-tensor technique described in the preceding section makes it possible to separate easily in the expression for the light-scattering cross section the angular and dynamical parts (the latter appear in the reduced matrix elements of the scattering tensor) in the case of an arbitrary polarized system. In this section, for definiteness, we refer to atoms.

Substituting into Eq. (4) the formulas (3), (10), and (11), making the substitution (13), and summing over the magnetic quantum numbers, we arrive at the following expression for the cross section for scattering, by a polarized atom, of partially polarized light described in the LCS by the polarization density matrix (12):

$$\frac{d\sigma}{d\Omega'}=(4\pi)^{1/2}\omega\omega'^{3}\alpha^{4}\sum_{\substack{K,Q,k,k',\lambda,\lambda'\\(k,k'=0,1,2)}}\rho^{n}_{K}Y^{*}_{KQ}(\mathbf{n})\times(-1)^{j_1+j_2+k+k'}\begin{Bmatrix}k & k' & K\\ j_1 & j_1 & j_2\end{Bmatrix}\times\langle \nu_2 j_2\|t^c_k\|\nu_1 j_1\rangle\langle \nu_2 j_2\|t^c_{k'}\|\nu_1 j_1\rangle^{*}\times\rho^{\gamma}_{\lambda\lambda'}\sum_{q,q'}(-1)^{q}\begin{pmatrix}k & k' & K\\ -q & q' & Q\end{pmatrix}\times\{\mathbf{e}'^{*}\otimes\mathbf{e}_{\lambda}\}_{kq}\{\mathbf{e}'^{*}\otimes\mathbf{e}_{\lambda'}\}^{*}_{k'q'}. \qquad (15)$$

Since the irreducible tensor (7) satisfies the relation

$$\{\mathbf{e}'^{*}\otimes\mathbf{e}\}^{*}_{kq}=(-1)^{k-q}\{\mathbf{e}'\otimes\mathbf{e}^{*}\}_{k,-q},$$

the inner sum over $q$ and $q'$ in Eq. (15) can be written in the form of an irreducible tensor consisting of four polarization vectors:[7]

$$\sum_{q,q'}(-1)^{q}\begin{pmatrix}k & k' & K\\ -q & q' & Q\end{pmatrix}\{\mathbf{e}'^{*}\otimes\mathbf{e}_{\lambda}\}_{kq}\{\mathbf{e}'^{*}\otimes\mathbf{e}_{\lambda'}\}^{*}_{k'q'}=(-1)^{K-k'}(2K+1)^{-1/2}\{\{\mathbf{e}'^{*}\otimes\mathbf{e}_{\lambda}\}_{k}\otimes\{\mathbf{e}'\otimes\mathbf{e}^{*}_{\lambda'}\}_{k'}\}_{KQ}. \qquad (16)$$

We note that the case of pure polarization of the scattered light is obtained in Eq. (15) by choosing the appropriate Stokes parameters in the polarization density matrix (12). Scattering of right (left)-hand circularly polarized radiation corresponds thus to

$$\rho^{\gamma}_{\lambda\lambda'}=\delta_{\lambda,\pm 1}\delta_{\lambda',\pm 1}. \qquad (17)$$

The expression for the cross section for the scattering of linearly polarized radiation is simplest if the LCS is redefined by orienting the $z$ axis along the polarization vector $\mathbf{e}_0$. In this case the cross section is obtained from the corresponding expression for the scattering cross section for circularly polarized radiation, in which the polarization indices $\lambda$ and $\lambda'$ are formally set equal to zero. It should be kept in mind that in the case of pure polarization, given by the vector

$$\mathbf{e}=-\sum_{\lambda=\pm1}e_{-\lambda}\mathbf{e}_\lambda,$$

the elements of the polarization density matrix can also be represented in the form

$$\rho^{\gamma}_{\lambda\lambda'}=e_{-\lambda}(e_{-\lambda'})^*.$$

For this reason, the scattering cross section can be written [in essence, starting from Eq. (4)] in terms of the polarization vector $\mathbf{e}$, dropping in Eq. (15) $\rho^{\gamma}_{\lambda\lambda'}$ and the summation over the polarization indices $\lambda$ and $\lambda'$, and removing the polarization indices of the vectors. In this form the expression for the scattering cross section will be valid in any coordinate system, in particular, in the ACS, where

$$Y_{KQ}(\mathbf{n})=Y_{KQ}(0,\varphi)=[(2K+1)/(4\pi)]^{1/2}\delta_{Q,0}.$$

However, the LCS is apparently more convenient for finding the explicit form of the angular distribution of the scattered radiation.

The explicit dependence of the scattering cross section on the polar and azimuthal angles $\theta'$ and $\varphi'$, which determine the direction of motion of the scattered photon, can be derived quite simply. The irreducible tensors (7), each consisting of two polarization vectors, must be written in terms of the spherical components of these vectors (expressions ready for use are given, for example, in Ref. 7). The spherical components of the vectors $\mathbf{e}_\lambda$ in the LCS are given by Eq. (14). In the case when the scattered photon is circularly polarized the spherical components of the polarization vectors $\mathbf{e}'_{\pm1}$ are also determined by Eq. (14), but in the coordinate system $x'y'z'$ of the scattered photon with the $z'$ axis oriented in the direction of motion of the photon. These components are transformed into the LCS by the standard method in terms of Wigner's functions (see, for example, Ref. 8). The result is

$$e'_{\pm1,1}=-\tfrac{1}{2}(1\mp\cos\theta')e^{i\varphi'},$$

$$e'_{\pm1,0}=\pm2^{1/2}\sin\theta'; \qquad (18)$$

$$e'_{\pm1,-1}=-\tfrac{1}{2}(1\pm\cos\theta')e^{-i\varphi'}.$$

In the general case of elliptically polarized scattered light the vector $e'$ can be represented in the form

$$\mathbf{e}'=\mathbf{e}'_x\cos\beta+\mathbf{e}'_ye^{i\delta}\sin\beta,$$

where $\mathbf{e}'_{x,y}$ are Cartesian unit vectors in the system $x'y'z'$ and $\delta$ and $\beta$ are real parameters. The parameter $\delta$ is the phase difference between two waves linearly polarized along the $x'$ and $y'$ axes. The case $\delta=0$ corresponds to a wave linearly polarized at an angle $\beta$ to the $x'$ axis. Transforming to a spiral basis, we write the vector $\mathbf{e}'$ in the form

$$\mathbf{e}'=2^{1/2}(ie^{i\delta}\sin\beta-\cos\beta)\mathbf{e}'_1+2^{1/2}(ie^{i\delta}\sin\beta+\cos\beta)\mathbf{e}'_{-1} \qquad (19)$$

and with the help of Eq. (18) we easily find its spherical components in the LCS. The spherical components of the vector that is the complex conjugate of $\mathbf{e}'$ can be found according to Eq. (9) from the formula

$$e'^*_q=(-1)^q(e'_{-q})^*.$$

Evidently, when the scattered radiation is linearly polarized the scattering cross section (in the dipole approximation) should depend only on the direction of the polarization vector $\mathbf{e}'_0$. For this reason, for given $\mathbf{e}'_0$ the scattering cross section will be the same in all directions perpendicular to the polarization vector.

We note that having determined the differential scattering cross section for right- and left-hand circularly polarized scattered photons and also for linear polarization [$\delta=0$ in Eq. (19)] at angles $\beta=0$, $\pi/2$, $\pi/4$, and $3\pi/4$ to the $x'$ axis we can find the Stokes parameters and the polarization density matrix of the scattered light.

In the case of unpolarized atoms the multipoles of the state $\rho^n_K$ are determined by Eq. (2), where we must set $j=j_1$. From the selection rules in $6j$ and $3j$ symbols contained in Eq. (15) it follows that in this case $k=k'$. Thus the cross section separates into a sum of three independent parts, whose intensity is determined by the squared moduli of the reduced matrix elements of the scattering tensor of ranks $k=0$, 1, and 2, respectively. The components of the irreducible tensors $t^c_k$ can be expressed in terms of the scalar ($k=0$), antisymmetric ($k=1$), and symmetric ($k=2$) tensors into which the scattering tensor separates.[1] Thus we arrive at the well-known result obtained by Placzek: The light-scattering cross section of freely oriented (unpolarized) systems can be expressed as a sum of scalar, antisymmetric, and symmetric scatterings. Calculating the $6j$ symbol in Eq. (15) [it also gives the selection rule $\Delta(j_1,j_2,k)$] and writing the irreducible tensor product of the four polarization vectors (16) with $k=0$ in terms of the scalar products of these vectors (see, for example, Ref. 7), we represent in the standard form [Ref. 1, Eq. (60.7)] the cross section for the scattering of light with definite polarization $\mathbf{e}$ by unpolarized atoms:

$$\frac{d\sigma}{d\Omega'}=\omega\omega'^3\alpha^4\left\{\frac{1}{3}\beta_0|\mathbf{e}'^*\mathbf{e}|^2+\frac{1}{6}\beta_1(1-|\mathbf{e}'\mathbf{e}|^2)+\frac{1}{10}\beta_2\left(1+|\mathbf{e}'\mathbf{e}|^2-\frac{2}{3}|\mathbf{e}'^*\mathbf{e}|^2\right)\right\},$$

where

$$\beta_k\equiv(2j_1+1)^{-1}|\langle\nu_2j_2\|t^c_k\|\nu_1j_1\rangle|^2. \qquad (20)$$

The parameters $\beta_k$, introduced above in Eq. (20), are essentially identical to the quantities $G^0$, $G^a$, and $G^s$,[1] determining the intensity of the scalar, antisymmetric, and symmetric scatterings:[3)]

$$G^0=\frac{1}{3}\beta_0,\quad G^a=\beta_1,\quad G^s=\beta_2. \qquad (21)$$

We now discuss some peculiarities of light scattering by polarized atoms. First, it is obvious that in this case the scattering cross section does not separate into a sum of three independent parts: Eq. (15) will contain terms which in turn contain the product the reduced matrix elements of the irreducible parts of a scattering tensor $k$ of different ranks. The angular distribution of the scattered light and the dependence of the angular distribution on the polarization of the incident and scattered radiations will change significantly. In addition, the scattering cross section (15) depends, as it should, on the orientation of the polarization axis $\mathbf{n}$ of the atom.

It is interesting to note that, as follows from Eq. (15), only the atomic state multipoles $\rho_K^n$ of rank $K \leqslant 4$ can appear in the differential light-scattering cross section of a polarized atom (see the selection rules in $6j$ and $3j$ symbols with $K,K'=0,1,2$). In this connection we recall that in the case of dipole emission and absorption of light by a polarized atom only the state multipole $\rho_K^n$ with $K \leqslant 2$ (orientation and alignment) can appear.[3]

The total light-scattering cross section integrated over all directions of motion of the scattered photon can be easily obtained from Eq. (15). For this we note that

$$\int e_q'^*(e_{q'}'^*)^* d\Omega' = \frac{4\pi}{3}\delta_{q,q'}, \tag{22}$$

where $q,q'=0, \pm 1$. Substituting into Eq. (15) the irreducible tensors constructed from two polarization vectors in the form (7), we take Eq. (14) into account and integrate the differential cross section over $\Omega'$, using the formula (22). We transform next the sum of the product of three $3j$ symbols over the projections of the angular momenta in the usual manner (see, for example, Ref. 8) into the product of $3j$ and $6j$ symbols and write the final expression for the total cross section in the following form:

$$\begin{aligned}\sigma = {} & \frac{(4\pi)^{3/2}}{3}\omega\omega'^3\alpha^4 \sum_{K,Q,k,k',\lambda,\lambda'} \rho_K^n Y_{KQ}^*(\mathbf{n})[(2k+1) \\ & \times(2k'+1)]^{1/2}(-1)^{j_1+j_2+\lambda'+1}\begin{Bmatrix} k & k' & K \\ j_1 & j_1 & j_2 \end{Bmatrix} \\ & \times \begin{Bmatrix} 1 & 1 & K \\ k' & k & 1 \end{Bmatrix} \langle \nu_2 j_2 \| t_k^c \| \nu_1 j_1 \rangle \\ & \times \langle \nu_2 j_2 \| t_{k'}^c \| \nu_1 j_1 \rangle^* \rho_{\lambda\lambda'}^\gamma \begin{pmatrix} 1 & 1 & K \\ -\lambda & \lambda' & -Q \end{pmatrix}. \end{aligned} \tag{23}$$

In the case of unpolarized atoms we substitute into Eq. (23) the state multipoles $\rho_K^n$ in the form (2) $(j=j_1)$ and after calculating the sum over the photon polarization indices

$$\begin{aligned}(-1)^{\lambda'+1}\sum_{\lambda,\lambda'}\rho_{\lambda\lambda'}^\gamma \begin{pmatrix} 1 & 1 & 0 \\ -\lambda & \lambda' & 0 \end{pmatrix} = 3^{-1/2}\sum_\lambda \rho_{\lambda\lambda}^\gamma \\ = 3^{-1/2},\end{aligned}$$

and the $6j$ symbols we obtain the following expression for the total light-scattering cross section:

$$\sigma = \frac{4\pi}{9}\omega\omega'^3\alpha^4 \sum_{k=0,1,2}\beta_k, \tag{24}$$

where the parameters $\beta_k$ are determined by Eq. (20). After summing the cross section (24) over two polarizations of the scattered photon (i.e., multiplying by 2) we obtain Eq. (60.8) of Ref. 1 [see Eq. (21)]. The total cross section of light scattering by an unpolarized atom (spherically symmetric system) (24) is naturally independent of the direction of incidence of the initial photon or of its polarization. Therefore the averaging of the cross section over the directions of incidence and polarizations, which is discussed in Ref. 1, is superfluous.

The total cross section for light scattering by polarized atoms (23) depends on both the direction of the incident radiation (on the orientation of the polarization axis $\mathbf{n}$ of the atom in the LCS) and the type of polarization of the radiation. The cross section does not reduce to a simple sum of amplitudes of the scalar, antisymmetric, and symmetric scattering amplitudes, as in the case of unpolarized atoms [see Eq. (24)]. It is also interesting to note that only the orientation and alignment of the polarized atom, i.e., the multipoles $\rho_{1,2}^n$ of the state [see the selection rules in the $6j$ and $3j$ symbols in Eq. (23)], can be manifested in the total scattering cross section. We recall in this connection that state multipoles of rank up to 4, inclusive, can be observed in the differential scattering cross section.

We now discuss in somewhat greater detail the cases of circular and linear polarization of the incident radiation. As follows from what was said above, the total scattering cross section for these cases is obtained if the polarization density matrix of the photon in the form Eq. (17) is substituted into Eq. (23):

$$\begin{aligned}\sigma_\lambda = {} & \frac{(4\pi)^{3/2}}{3}\omega\omega'^3\alpha^4 \sum_{K,k,k'} \rho_K^n Y_{K0}(\mathbf{n})[(2k+1)(2k' \\ & +1)]^{1/2}(-1)^{j_1+j_2+\lambda+1}\begin{Bmatrix} k & k' & K \\ j_1 & j_1 & j_2 \end{Bmatrix} \\ & \times \begin{Bmatrix} 1 & 1 & K \\ k' & k & 1 \end{Bmatrix} \langle \nu_2 j_2 \| t_k^c \| \nu_1 j_1 \rangle \\ & \times \langle \nu_2 j_2 \| t_{k'}^c \| \nu_1 j_1 \rangle^* \begin{pmatrix} 1 & 1 & K \\ -\lambda & \lambda & 0 \end{pmatrix}. \end{aligned} \tag{25}$$

Here $\lambda = \pm 1$ corresponds to right (left)-hand circular polarization of the incident photon. The case of linear polarization corresponds to $\lambda=0$, and then it is also necessary to assume that the $z$ axis of the LCS is oriented along the polarization vector $\mathbf{e}_0$.

The total scattering cross section (25) depends only on the angle $\theta$ between the polarization axis $\mathbf{n}$ of the atom and the direction of propagation of the incident radiation (the direction of $\mathbf{e}_0$ in the case of linear polarization). A dependence on only the angle $\theta$ remains also when the photon polarization density matrix $\rho_{\lambda\lambda'}^\gamma$ in Eq. (23) is diagonal, i.e., when the incident radiation is an incoherent mixture of left- and right-hand circularly polarized waves (in particular, this includes also the case of unpolarized light). In all these cases the directions in the $xy$ plane of the LCS are equivalent.

If the atom is oriented, i.e., $\rho_1^n \neq 0$, then, as follows from Eq. (25), $\sigma_1 \neq \sigma_{-1}$. Thus oriented atoms scatter right- and left-hand circularly polarized light differently. This circular dichroism effect in the total light-scattering cross section is consistent with conservation of parity in electromagnetic interactions, since an oriented atom is in a mirror-asymmetric polarized state (see Sec. 2). Conversely, if an atom is only aligned, i.e., $\rho_2^n \neq 0$ but $\rho_1^n = 0$, then circular dichroism is not observed in the total scattering cross section (25). The absence of circular dichroism in the total light-scattering cross section of unoriented atoms is a consequence of the parity conservation (cf. the analogous discussion in Refs. 6 and 11 for multiphoton ionization of polarized atoms). From these same considerations, which are based on parity conservation, it follows that in the case of arbitrary polarization of an atom the total scattering cross section should not change when the direction of propagation of the incident radiation is reversed and simultaneously the circular polarization changes from right(left)-hand to left(right)-hand polarization. This symmetry of the total cross section (25) can be seen directly.

In the case of scattering of linearly polarized light the atom orientation set by the pseudotensor $\rho_1^n$ cannot be manifested in the total cross section $\sigma_0$. This also follows directly from Eq. (25) (cf. the analogous situation for multiphoton ionization by linearly polarized radiation, when odd-rank multipoles of the state are not manifested in the total cross section[11]).

## 4. ATOM WITH ONE ELECTRON OUTSIDE A CLOSED SHELL

We assume that the atom is polarized in a state with a definite total angular momentum $j_1$ of the electron shell. For an atom with one electron outside a closed shell $j_1 = l_1 \pm 1/2$ and $l_1$ are, respectively, the total and orbital angular momenta of the valence electron. The quantum numbers which specify the state of the atom in Eqs. (4) and (11) are $(\nu, j, m) = (n, l, j, m)$, where $n$ is the principal quantum number of the valence electron.

We employ below the single-electron approximation, which gives good results in calculations of the probabilities of multiphoton transitions in alkali-like atoms in the optical frequency range.[12,13] For group-III atoms the single-electron approximation can be used reliably to study transitions between the excited states of the valence electron. In the single-electron approximation $\hat{G}_E$ in formula (6) for the scattering tensor must be interpreted as the Green's function of the valence electron.

Using the Wigner–Eckart theorem to separate the dependences on the magnetic quantum numbers in the matrix elements of the dipole moment $d_q$ of the valence electron, and then summing over the magnetic quantum numbers, we obtain for the matrix element of the irreducible component of the scattering tensor (8) an expression of the form (11). Then the reduced matrix elements of the scattering tensor will be determined by the following formula:

$$\begin{aligned}\langle n_2 l_2 j_2 \| t_k^c \| n_1 l_1 j_1 \rangle &= [(2j_2+1)(2j_1+1)(2k+1)]^{1/2} \\ &\times (-1)^{l_2-k-1} \sum_{l,j} (-1)^{j-j_2+l} \\ &\times (2j+1) \begin{Bmatrix} k & j_1 & j_2 \\ j & 1 & 1 \end{Bmatrix} \\ &\times \begin{Bmatrix} j_2 & 1 & j \\ l & 1/2 & l_2 \end{Bmatrix} \begin{Bmatrix} j_1 & 1 & j \\ l & 1/2 & l_1 \end{Bmatrix} \\ &\times \langle l_2 \| \hat{n} \| l \rangle \langle l \| \hat{n} \| l_1 \rangle [v_{n_2 l_2, lj, n_1 l_1}(E_1 \\ &+ \omega) + (-1)^k v_{n_2 l_2, lj, n_1 l_1}(E_1 - \omega')]. \end{aligned} \tag{26}$$

Here

$$\langle l' \| \hat{n} \| l \rangle = (-1)^{l' + l_{\max}} (l_{\max})^{1/2},$$

$$l_{\max} = \max(l, l'), \quad l' = l + 1$$

is the reduced matrix element of the unit vector,[14]

$$v_{n_2 l_2, lj, n_1 l_1}(E) = \langle R_{n_2 l_2}(r) \,|\, r g_{lj}(E; r, r') r' \,|\, R_{n_1 l_1}(r') \rangle \tag{27}$$

is a radial composite second-order matrix element, where $R_{nl}$ is the radial wave function, and $g_{lj}$ is the radial Green's function of the valence electron. Semiempirical methods—the quantum-defect method and the model-potential method[12,13]—have been developed for finding the radial Green's function of the valence electron and for calculating composite matrix elements.

Equation (26) is valid both near and far from resonance. Far from resonance, when the detuning from intermediate levels significantly exceeds their fine-structure splitting, which, generally speaking, is of order $\alpha^2$, the fine structure of the intermediate levels can be neglected and $g_{lj} \approx g_l$. For this reason, dropping the total angular momentum index $j$ in the radial composite matrix element (27) and transforming the sum over $j$ of the product of three $6j$ symbols in Eq. (26) with the help of the well-known addition rule (see, for example, Ref. 8), we obtain the following expression for the reduced matrix elements of the scattering tensor:

$$\begin{aligned}\langle n_2 l_2 j_2 \| t_k^c \| n_1 l_1 j_1 \rangle &= (-1)^{j_1 - l_1 + 1/2} \begin{Bmatrix} j_2 & j_1 & k \\ l_1 & l_2 & 1/2 \end{Bmatrix} \\ &\times [(2j_2+1)(2j_1+1)(2k \\ &+1)]^{1/2} \sum_l \begin{Bmatrix} k & l_1 & l_2 \\ l & 1 & 1 \end{Bmatrix} \langle l_2 \| \hat{n} \| l \rangle \\ &\times \langle l \| \hat{n} \| l_1 \rangle [v_{n_2 l_2, l, n_1 l_1}(E_1 + \omega) \\ &+ (-1)^k v_{n_2 l_2, l, n_1 l_1}(E_1 - \omega')]. \end{aligned} \tag{28}$$

In connection with the use of the expressions (26) or (28) for the reduced matrix elements of the scattering tensor, it should be kept in mind that as resonance is approached not only does the cross section increase, but the character of the light scattering by polarized atoms itself changes. We illustrate this with the help of a simple example. Let the initial state of the atom be an *s* state, i.e., $l_1=0$ (for example, the ground state of an alkali-metal atom). From the selection rules with respect to orbital angular momenta and parity, contained in the reduced matrix elements of the unit vector, it follows that the final state of the atom can be either *s* or *d*. For *s*-*d* scattering, far from resonance, there arises only symmetric scattering [$k=2$ for $l_2=2$, as follows from $\Delta(l_1,l_2,k)$ in the $6j$ symbol (28)], while $j_2=3/2$ near resonance at $k=1$ and 2 [see Eq. (26)] and, as discussed in detail in Sec. 3, interference of symmetric and antisymmetric scatterings will therefore be observed in the light-scattering cross section of the polarized atom. For $j_2=5/2$ only the symmetric scattering remains in the resonance region, just as far from resonance.

The case of *s*-*s* scattering (coherent or Raman) is even more interesting. Here $j_1=1/2$ and the polarization of the atom reduces simply to nonuniform population of two of its magnetic sublevels, i.e., orientation ($\rho_1^n \neq 0$; $\rho_K^n \equiv 0$ for $j_1=1/2$ by definition (1) if $K>1$). If $l_1=l_2=0$, only scalar scattering remains far from resonance, i.e., $k=0$ [see Eq. (28)]. In final analysis, the coefficient in front of the multipole $\rho_1^n$ of the state in the expressions for the differential (15) and total (23) light-scattering cross sections, which is proportional to the corresponding $6j$ symbol, vanishes and the polarization (orientation) of the atom is not manifested at all. This result can be easily understood on the basis of simple physical considerations. The polarization of an atom with an *s* electron outside a closed shell reduces to orientation of the spin of a valence electron. For *s*-*s* scattering, when the levels in the initial and final states of the atom have no fine structure and the fine structure of the intermediate levels far from resonance can be neglected, the relativistic effects are negligibly small ($\sim\alpha^2$). But in the nonrelativistic limit the light scattering cannot depend on the initial projection of the electron spin, so that no atom should not be observed. Analysis of the nonrelativistic expression (28) for the reduced matrix elements of the scattering tensor leads to the same conclusion.

Conversely, at frequencies such that the resonance with the intermediate levels $E_{nlj}$ has a detuning that approaches their fine-structure splitting, the fine structure of the intermediate levels (relativistic effect) cannot be neglected. For detunings $\Delta \lesssim \alpha^2$ the manifestation of orientation in *s*-*s* scattering should be of the order of unity (compare with resonance multiphoton ionization of atoms oriented in the *s* state[6]). It can be stated that in this case there arises the additional parameter $\alpha^2/\Delta$, so that near resonance the relativistic effect increases sharply. We now consider this case in greater detail.

Calculating the $6j$ symbols in Eq. (26), we obtain the following expression for the nonzero reduced matrix elements of the scattering tensor:

$$\left\langle n_2 0 \frac{1}{2} \left\| t_k^c \right\| n_1 0 \frac{1}{2} \right\rangle = \begin{cases} -\frac{1}{3}\sqrt{\frac{2}{3}}\,(f_{1/2}^{(0)}+2\,f_{3/2}^{(0)}), & k=0, \\ \frac{2}{3\sqrt{3}}\,(f_{3/2}^{(1)}-f_{1/2}^{(1)}), & k=1. \end{cases} \tag{29}$$

Here $f_j^{(k)}$ is the combination of radial compound matrix elements (27):

$$f_j^{(k)} = v_{n_2 0,1j,n_1 0}(E_1+\omega) + (-1)^k v_{n_2 0,1j,n_1 0}(E_1-\omega').$$

If the energy $\omega$ does not exceed the ionization threshold of the atom from the initial state, then $f_j^{(k)}$ can be assumed to be real. In the resonance region of interest to us we can, in addition, confine ourselves in the calculation of the radial compound matrix element to the resonance (pole) approximation. Far from resonance, at a detuning $\Delta \gg \alpha^2$, the radial matrix elements with two values of the intermediate angular momentum are approximately equal and, therefore, $f_{1/2}^{(k)} \approx f_{3/2}^{(k)} \equiv f^{(k)}$. More accurately,

$$|f_{3/2}^{(k)}-f_{1/2}^{(k)}| \sim |f^{(k)}|\,\alpha^2/\Delta. \tag{30}$$

As a result, only the reduced matrix element $\langle \| t_0^c \| \rangle$ [it can also be found from Eq. (28)], which determines the scalar scattering of light, remains nonzero.

Substituting the obtained reduced matrix elements of the scattering tensor (29) into Eqs. (15) and (23), we can find the differential and total light-scattering cross sections. We present the final expression for the total cross section for scattering of circularly polarized radiation propagating at an angle $\theta$ to the polarization axis **n** of an atom [see Eq. (25)]:

$$\begin{aligned} \sigma_\lambda = \frac{4\pi}{243}\,\omega\omega'^3\alpha^4 \{ & |f_{1/2}^{(0)}+2\,f_{3/2}^{(0)}|^2 + 2|f_{3/2}^{(1)}-f_{1/2}^{(1)}|^2 \\ & + \sqrt{2}\lambda\rho_1^n \cos\theta \cdot \mathrm{Re}[(f_{3/2}^{(1)}-f_{1/2}^{(1)})(2\,f_{1/2}^{(0)}+4f_{3/2}^{(0)} \\ & + f_{1/2}^{(1)}-f_{3/2}^{(1)})^*]\}. \end{aligned} \tag{31}$$

Here $\lambda=\pm1$ corresponds to right(left)-hand circular polarization of the incident radiation. Equation (31) describes also scattering of linearly polarized radiation (with $\lambda=0$), but in this case, as noted in Sec. 3, the orientation of the atom is not manifested in the total cross section.

In order that the expression (31) be valid for quite small detunings, comparable to the natural linewidths, the widths of the corresponding intermediate levels must be introduced in the standard manner[1] into the denominators of the composite matrix elements.

From Eq. (31) follow explicitly the circular dichroism effect in the total light scattering cross section of an oriented atom as well as the symmetry associated with transition from right- to left-hand circular polarization accompanied by reversal of the direction of propagation of the radiation (see end of Sec. 3).

Far from resonance, when $\Delta \gg \alpha^2$, the term with the multipole $\rho_1^n$ of the state in Eq. (31) can be neglected [see Eq. (30)] and orientation of the atom will practically not be manifested.

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[1)] The results of Secs. 2 and 3 are valid for any quantum system (atom, molecule, and nucleus) that is polarized in a state with definite angular momentum *j*.

[2)] In the case of nonaxisymmetric excitation the state of a polarized atom is a coherent superposition of states with different values of *m*. The density matrix of the atom is nondiagonal with respect to *m*, even in the ACS. In addition, in Eq. (3) and the formulas for the cross sections of the elementary process the spherical harmonic of **n** is replaced by a linear combination of Wigner functions, which depend on the three Euler angles determining the orientation of the ACS.

[3)] The quantities $\beta_k$ are proportional to the squared moduli of the so-called invariant atomic parameters introduced in Refs. 9 and 10.

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