PHOTOELECTRON ANGULAR DISTRIBUTIONS

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1. Introduction

The ejection of electrons from materials under the action of electromagnetic radiation has long been a rich source for experimental study. The earliest investigations of this problem were concerned with the electrons omitted from a metal surface that is irradiated with ultraviolet light, the so-called photoelectric effect. The results of these experiments led Einstein\,\(^1\) to the hypothesis that photoelectric emission was a quantum effect in which a quantum of radiation energy \(h\nu\) was absorbed by an electron in the metal. The subsequent experimental confirmation of this interpretation played an important role in laying the foundation for quantum mechanics, as well as providing an independent determination of Planck's constant, \(h\).

Study of the atomic photoeffect is more usually called photoionization, and in the case of negative atomic ions, photodetachment. Until recently, most atomic studies were limited to the ejection of inner shell electrons by X-rays and \(\gamma\)-rays. Provided relativistic effects could be neglected, exact differential cross section calculation for K- and L-shell electrons by hydrogenic atoms have been worked out by Sommerfeld and his students.\,\(^2\) Their results are summarized in an excellent review by Hall\,\(^3\) as well as in Bethe and Salpeter's book Quantum Mechanics of One- and Two-Electron Atoms.\,\(^4\) With the advent of intense monochromatic light sources, in conjunction with the development of extremely sensitive electron energy analysers, it has become possible to study the photoejection of valence electrons, and by this means, to measure such important quantities as ionization potentials, electron affinities, cross sections for photoejection, relative transition probabilities to excited states, etc.\,\(^5\) This new field

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\(^2\)Alfred P. Sloan Fellow.
has been given the name **photoelectron spectroscopy**. However for photoelectron spectroscopy to realize its full potential, experiments must be designed which take into account the form of the angular distribution of the ejected electrons since a knowledge of the photoelectron distribution is ordinarily one of the prerequisites for accurate work. Accordingly, it seems worthwhile to review the calculation of photoelectron angular distributions for one-electron systems and to extend these results to many-electron systems.

II. The One-Electron Problem

Consider the ejection of an electron from a hydrogen-like atom due to a radiative transition from the bound state \( \psi_i \) to the continuum state \( \psi_f \). The differential cross section will be proportional to the square of the transition matrix element summed over all final states and averaged over all initial states:

\[
I(\theta) \propto \left| \langle \psi_f | \mathcal{T} | \psi_i \rangle \right|^2 \text{ averaged over orientations} \quad (\text{II.1})
\]

where \( \mathcal{T} \) is the operator for the interaction between the atom and the electromagnetic field. Let the radiation be polarized along the Z direction. To good approximation we need only consider the leading dipole term of the interaction operator:

\[
\mathcal{T} = \mathbf{r} \cdot \mathbf{E} = r \mathbf{C}_0^1 (\theta, \phi) \quad (\text{II.2})
\]

where \( r \) is the position coordinate of the electron and \( \theta, \phi \) are polar angles measured from the Z axis. Throughout this paper, we neglect retardation effects arising from the momentum of the photon.\(^4\)

The bound state of the atom is in a definite state of angular momentum and may be represented by

\[
| \psi_i \rangle = R_{n', \ell', m'} (r) | \ell' m' \rangle \quad (\text{II.3})
\]

where \( R_{n', \ell', m'} (r) \) gives the radial behavior of the wavefunction. The continuum state of the atom is not in a definite state of angular momentum. It must have the correct asymptotic form of a plane wave plus incoming spherical waves.\(^6\) If \( k \) is a unit vector along the ejection direction of the outgoing electron, we may write

\[
| \psi_f \rangle = k \mathcal{Y}^*(k) \sum_{\ell, m} (\ell) e^{-i\ell \phi} \mathcal{Y}_{\ell, m} (\hat{k}) \mathcal{Y}_{\ell', m'} (\hat{r}) \mathcal{G}_{k_\ell m_\ell} (r) \quad (\text{II.4})
\]
where \( G_{kl}(r) \) is the radial wavefunction divided by \( kr \) and \( \delta_r \) is the phase shift of the \( t^{th} \) partial scattered wave.\(^7\) We will find it convenient to rewrite (II.4) in the form

\[
\psi_{-1} = \sum_{t,m} a(t,m) Y_{t,m}^{*}(\hat{k}) G_{kt}(\hat{k}) \quad (II.5)
\]

where

\[
a(t,m) = 4\pi \langle i | t \rangle e^{-i\delta_r} Y_{t,m}^{*}(\hat{k}). \quad (II.6)
\]

The transition matrix element is evaluated as follows:

\[
\langle \psi_+ | r C_0^1 | \psi_+ \rangle = \sum_{t,m} a(t,m) \sigma_{t} \langle t,m | C_0^1 | t',m' \rangle \quad (II.7)
\]

where \( \sigma_{t} \) is the dipole integral

\[
\sigma_{t} = \int_0^r R_{nt'} G_{kt} dr. \quad (II.8)
\]

Eq. (II.7) may be further simplified using the identities\(^8\)

\[
\langle t,m | C_0^1 | t',m' \rangle = (-1)^{t'-m} (t || C^1 || t') \left( \begin{array}{c} 1 \ 1 \ 1 \\
 -m \ 0 \ m' \end{array} \right) \quad (II.9a)
\]

and

\[
(t || C^1 || t') = (-1)^{g} t_\geq \quad (II.9b)
\]

where \( g = (t' - t + 1)/2 \) and \( t_\geq \) is the greater of \( t \) and \( t' \). Hence

\[
\langle \psi_+ | r C_0^1 | \psi_+ \rangle = \sum_{t,m} a(t,m) (-1)^{t'-m+g} t_\geq \sigma_{t} \left( \begin{array}{c} t \ 1 \ t' \\
 -m \ 0 \ m' \end{array} \right) \quad (II.10)
\]

Note that in Eq. (II.10) \( m \) must equal \( m' \); otherwise, the expression vanishes.

The differential cross section is now obtained by squaring Eq. (II.10) and averaging over all the initial states \( m' \). We assume that the magnetic sublevels \( m' \) are equally populated.\(^9\)

Thus,
\[ I(\ell) = \frac{1}{2\ell' + 1} \sum_{m'} \mathcal{A}(\ell_{1}, m') a^* (\ell_{2}, m') \]

\[ (-1)^{\ell' + \ell_{1} + \ell_{2}} \mathcal{Y}_{\ell_{1}}^{*} \mathcal{Y}_{\ell_{2}}^{*} \mathcal{Y}_{\ell'} \mathcal{Y}_{\ell'} \]

\[ \left( \begin{array}{cc} \ell_{1} & \ell' \\ -m' & 0 \end{array} \right) \left( \begin{array}{cc} \ell_{2} & \ell' \\ -m' & 0 \end{array} \right) . \]  (II.11)

Eq. (II.11) is really composed of four terms since \( \ell_{1} = \ell' + 1 \) and \( \ell_{2} = \ell' + 1 \) only. We now drop the primes on \( \ell \) and \( m \) since no confusion can result. With the help of explicit algebraic expression for the 3-j symbols,

\[ \left( \begin{array}{cc} \ell' + 1 & \ell' \\ -m & 0 \end{array} \right) = (-1)^{\ell' - m - 1} \left( \begin{array}{cc} \ell' + 1 & \ell' \\ -m & 0 \end{array} \right) \frac{(\ell' + 1)(\ell' + 2)(\ell' + 3)}{L} \frac{1}{(\ell' + 1)\ell' + 1} \]  (II.12a)

and

\[ \left( \begin{array}{cc} \ell' - 1 & \ell' \\ -m & 0 \end{array} \right) = (-1)^{\ell' - m} \left( \begin{array}{cc} \ell' - 1 & \ell' \\ -m & 0 \end{array} \right) \frac{\ell' - m}{(\ell' + 1)(\ell' - 1)} \]  (II.12b)

Eq. (II.11) becomes

\[ I(\ell) = \frac{16\pi^{0}}{2\ell + 1} \sum_{m} \left[ \mathcal{Y}_{\ell - 1, m}^{*} \left( \begin{array}{cc} \ell' & \ell' \\ \ell' + 1, m \end{array} \right) \right]^{2} \]

\[ + \mathcal{Y}_{\ell' + 1, m}^{*} \left( \begin{array}{cc} \ell' - 1 & \ell' \\ \ell' + 1, m \end{array} \right) \left[ \mathcal{Y}_{\ell' + 1, m}^{*} \mathcal{Y}_{\ell' - 1, m}^{*} \right]^{2} \]

\[ + \mathcal{Y}_{\ell' + 1, m}^{*} \left( \begin{array}{cc} \ell' - 1 & \ell' \\ \ell' + 1, m \end{array} \right) \left[ \mathcal{Y}_{\ell' + 1, m}^{*} \mathcal{Y}_{\ell' + 1, m}^{*} \right]^{2} \]

\[ + \mathcal{Y}_{\ell' + 1, m}^{*} \left( \begin{array}{cc} \ell_{+1} & \ell_{+1} \\ \ell_{+1}, m \end{array} \right) \left( \begin{array}{cc} \ell_{+1} & \ell_{+1} \\ \ell_{+1}, m \end{array} \right) \]  (II.13)
Recall that
\[ \cos^2 Y_{l,m} = \sum_{m} \left[ \frac{(t+1)^2 - m^2}{(2t+1)(2t+3)} \right] Y_{l+1,m}^* Y_{l-1,m} + \sum_{m} \left[ \frac{t^2 - m^2}{(2t+1)(2t-1)} \right] Y_{l+1,m}^* Y_{l-1,m} \]  
(II.14)

By squaring both sides of Eq. (II.14) and summing over \( m \) we obtain the result
\[ \sum_{m} \left[ \frac{(t+1)^2 - m^2}{(2t+1)(2t+3)} \right] \frac{t^2 - m^2}{(2t+1)(2t-1)} Y_{l+1,m}^* Y_{l-1,m} = \frac{(t+1)(2-3 \sin^2 \theta)}{8\pi(2t+1)} \]  
(II.15)

where we have used the identities
\[ \sum_{m} |Y_{l,m}|^2 = \frac{2t+1}{4\pi} \]  
(II.16a)
\[ \sum_{m} m^2 |Y_{l,m}|^2 = \frac{t(t+1)(2t+1)}{8\pi} \sin^2 \theta \]  
(II.16b)

and
\[ \sum_{m} m^4 |Y_{l,m}|^2 = \frac{2(t+1)}{9\pi} \epsilon \frac{t(t+1)}{\epsilon} \sin^2 \theta \sin^2 (t+1)(2t+1)(t+2) \sin^2 \theta \]  
(II.16c)

Combining Eqs. (II.13), (II.15) and (II.16) allows us to write the expressions for the photoelectron angular distribution in the form \( I(\theta) = a + b \cos^2 \theta \), i.e.,
\[ I(\theta) = \frac{2\pi}{(2t+1)^2} \left[ \epsilon \frac{t(t+1)}{\epsilon} \left( \sigma_{t-1} + \sigma_{t+1} + 2\sigma_{t+1} \cos \delta_{t+1} - \delta_{t-1} \right) \right] + \left[ \epsilon \frac{t(t-1)}{\epsilon} \sigma_{t-1} + (t+1)(t+2) \sigma_{t+1} - \delta(t+1) - \delta(t-1) \cos \delta_{t+1} - \delta_{t-1} \right] \cos^2 \theta \]  
(II.17)

If we let \( \sigma_{\text{total}} \) represent the total cross section, Eq. (II.17) may be put into the general form
\[ I(\beta) = \frac{I_{\text{total}}}{4\pi} \frac{1 + 8 P_2(\cos \beta)}{1 + 8 P_2(\cos \beta)} \] (II.18)

where \( P_2(\cos \beta) = (3 \cos^2 \beta - 1)/2 \) and \( \beta \) is an asymmetry parameter. For photoejection from the initial state with orbital angular momentum \( \ell \), \( \beta \) is given by the formula\(^1\)

\[ \beta = \frac{\frac{\ell(-1)}{2} + \ell(1) + \ell(2)}{(2\ell + 1)} \frac{\cos(\ell + 1) - \cos(\ell - 1)}{\cos(\ell + 1) + \cos(\ell - 1)} \] (II.19)

and the value of \( \beta \) ranges from \( \beta = 2 \) to \( \beta = -1 \). For the limiting case \( \beta = 2 \), the angular distribution has a \( \cos^2 \beta \) distribution peaked about the polarization vector of the light; for the limiting case \( \beta = -1 \), the angular distribution has a \( \sin^2 \beta \) distribution peaked in a plane at right angles to the polarization vector of the light; and for the case \( \beta = 0 \), the angular distribution is isotropic.

Examination of the form of Eq. (II.19) reveals that the photoejection of an \( s \)-type electron (\( \ell = 0 \)) must result in a cosine-squared distribution (\( \beta = 2 \)), whereas for a non-\( s \)-type electron (\( \ell \neq 0 \)), two competing outgoing channels are always present, and the form of the anisotropy will depend on the interference between the \( \ell + 1 \) and \( \ell - 1 \) partial waves. This, in turn, is most sensitive to the phase shift difference \( \delta_{\ell+1} - \delta_{\ell-1} \), although it also depends on the relative magnitudes of the dipole integrals \( \sigma_{\ell+1} \) and \( \sigma_{\ell-1} \). We conclude that a study of the angular distribution of photoelectrons can provide information about quantities characterizing the bound and continuum states of the atom which would be difficult to obtain otherwise, and hence, can serve as a sensitive probe of the electronic structure of the atom.

III. The Many-Electron Problem

We now focus our attention on the photoejection of electrons from atoms having more than one electron. The question we put to ourselves is what effect on the form of the angular distribution does the multiplet and fine structure of the atom have? We start by assuming that the initial and final states can be described in a satisfactory manner using Russell-Saunders coupling, in which the total orbital and spin angular momenta are considered to be well-defined quantities for both states.

The calculation of the photoelectron differential cross section proceeds then in a similar manner to the one-electron problem except that a many-electron wavefunction must be constructed which satisfies the Pauli exclusion principle, i.e., it must be antisymmetric with respect to the interchange of the electron space and spin coordinates.
We shall assume as a first approximation that the initial and final states can be represented by a Slater determinant of spin-orbitals. Thus the radial wavefunctions and phase shifts are to be calculated in the usual central field approximation. Later on we will consider the general case in which a linear combination of configurations is used in order to take into account correlation (non-central field).

We now construct the properly antisymmetrized initial and final state wavefunctions. If \( \sigma_j \) denotes the spin coordinate of the \( j \)th electron, the spin-orbital of the ejected electron in the continuum state may be written as

\[
\psi_{l,msm_s} = \delta(\sigma | m_2) Y_{l,m} G_{\sigma^l}(r) \ .
\]  

(III.1)

Let \( L^s, M_s^s, S^t, M_t^t \) describe in LS coupling notation the final atomic state formed when the photoelectron departs. Then, in terms of the one-electron states for the free electron, \( \psi_{l,msm_s} \), the final state wavefunction of the \( N \)-electron atom can be represented as

\[
f_f = \frac{1}{\sqrt{N!}} \sum_{P} (\sigma^P) \sum_{l,m} (-1)^P a(r,m) ^{L^s,M_s^s} \psi_{l,msm_s} \]  

(III.2)

where \( P \) is the permutation operator. Note that \( f_f \) refers to a given \( m_l \), \( M_s^s \) and \( M_t^t \) and we will perform a sum over these quantum numbers to obtain the differential cross section. We wish to rewrite Eq. (III.2) by coupling together \( L^s \) and \( \sigma \), and \( S^t \) and \( s \) to form the resultants \( L' \) and \( S' \), respectively. With the help of the identities

\[
| j_1 m_1 \rangle | j_2 m_2 \rangle = \sum_{j_3,m_3} (-1)^{j_3-j_1-m_3} \begin{pmatrix} j_3 \cr j_1 \end{pmatrix} \begin{pmatrix} j_2 \cr j_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \cr m_1 & m_2 & -m_3 \end{pmatrix} | j_3 m_3 \rangle 
\]  

(III.3a)

and

\[
| j_3 m_3 \rangle = \sum_{j_1 m_1} (-1)^{j_3-j_1-m_3} \begin{pmatrix} j_3 \cr j_1 \end{pmatrix} \begin{pmatrix} j_2 \cr j_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \cr m_1 & m_2 & -m_3 \end{pmatrix} | j_1 m_1 \rangle | j_2 m_2 \rangle 
\]  

(III.3b)

where \( [j] = 2j+1 \), Eq. (III.2) becomes
\[ t = \frac{1}{\sqrt{NT}} \sum_{s',m} \sum_{L'} \sum_{S'} (-1)^P a(t,m) [\langle L'|S'| S' \rangle (-1)^{S'-S_m+P-L''-M'_L} \langle S'' - S_m + P - L'' - M'_L \rangle] \]

\[
\begin{pmatrix}
\begin{pmatrix}
S'' & S_m & -M'_L \\
M'_S & -M'_L & -M'_L
\end{pmatrix}
\end{pmatrix}
\begin{pmatrix}
\begin{pmatrix}
L'' & L'' \\
L'_S & M'_L & M'_L
\end{pmatrix}
\end{pmatrix}
\phi(L'' S'' s''; L' M'_S S' M'_L).
\]

(III.4)

The initial state wavefunction may be similarly represented in LS coupling notation by

\[
\phi_i = \frac{1}{\sqrt{N'_T}} \sum_{s, m, S} (-1)^P \phi(L_m, S_m).
\]

(III.5)

The dipole transition operator has the form \( \sum_j \vec{r}_j \cdot \vec{z} = \sum_j \vec{r}_j C_0^1 \),

where \( r_j \) is the position coordinate of the \( j \)th electron. Since the dipole transition operator is a sum of one-electron operators, we may therefore find the matrix elements between antisymmetrized states in the usual way:

\[
\langle \psi | \sum_j \vec{r}_j C_0^1 | \psi' \rangle = \sum_j \sum_{l', m, L'} a(t, m) [\langle L' | l' \rangle (-1)^{S'' - S_m + P - L'' - M'_L} \langle L_m, S_m | M'_L \rangle] \phi(L_m, S_m) \phi(L'_S, L'_L, M'_S, M'_L).
\]

(III.6)

where we have used the Wigner-Eckart theorem for

\[
\langle \phi(L_m, S_m, M'_L) | \phi C_0^1 | \phi(L'_S, L'_L, M'_S, M'_L) \rangle = \delta(M'_S, M'_L) \delta(S, S') (-1)^{P - M'_L} \langle L'_S | l' \rangle \phi(L'_S, L'_L, M'_S, M'_L) \phi(L_m, S_m).
\]

(III.7)

The \( \pm \) sign in Eq. (III.6) is determined by the parity of the number of permutations required to order the configurations in standard form. Note that \( M'_L = M'_L \); otherwise, Eq. (III.7) vanishes.
We may now distinguish between two interesting cases in the evaluation of the reduced matrix element \( \langle LS||rC^1||L'S \rangle \):

(a) the ejected electron is a non-equivalent electron, corresponding to the transition core \( \ell' \rightarrow \text{core } \ell \)

and

(b) the ejected electron is one of \( n \) equivalent electrons, corresponding to the transition

\[ \ell, n \rightarrow \ell', n-1' \]

In either case we have \(^{12}\)

\[ \langle LS||rC^1||L'S \rangle = (-1)^{L' + L + 1 + \ell + \ell}' \left[ \begin{array}{c} L \cr \ell \cr \ell' \cr L' \end{array} \right] \left[ \begin{array}{c} L ' \cr \ell ' \cr \ell '' \cr L '' \end{array} \right] \sigma(t', \ell, L, L') \]

where

\[ \sigma(t', \ell, L, L') = \int_0^m r R_{n', \ell} G_{k, l} \, dr \] \(^{12}\)

for a non-equivalent electron photo-transition or

\[ \sigma(t', \ell, L, L') = \frac{1}{n} \langle \ell', n-1', S', L' \rangle \int_0^m r R_{n', \ell} G_{k, l} \, dr \] \(^{12}\)

for an equivalent electron photo-transition. \(^{13}\) In Eq. (III.9b) \( \langle \ell', n-1', S', L' \rangle \) is the appropriate coefficient of fractional parentage. \(^{14}\)

Substituting Eqs. (III.8) and (III.9) into Eq. (III.6) gives

\[ \langle \frac{1}{n} \sum_j \sum_i F_j G_i \frac{1}{j} \rangle = \sum_j \sum_i a(t', m, S, L', L; -1) \left[ \begin{array}{c} L \cr \ell \cr \ell' \cr L' \end{array} \right] \langle S'\, S \rangle \langle M'_S \, m - M'_S \rangle \langle M''_L \, m - M''_L \rangle \left[ \begin{array}{c} L \cr 1 \cr L' \end{array} \right] \left[ \begin{array}{c} L \cr \ell \cr L' \end{array} \right] \left[ \begin{array}{c} L \cr \ell \cr L' \end{array} \right] \]

We use the identity
\[
\begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
j_1 & j_2 & j_3 \\
n_1 & n_2 & n_3
\end{pmatrix}
= \sum_{n_1, n_2, n_3} (-1)^{j_1 + j_2 + j_3 + n_1 + n_2 + n_3}
\begin{pmatrix}
j_1 & j_2 & j_3 \\
n_1 & n_2 & n_3
\end{pmatrix}
\begin{pmatrix}
j_1' & j_2' & j_3' \\
n_1' & n_2' & n_3'
\end{pmatrix}
\quad \text{(III.11)}
\]

to obtain in place of Eq. (III.10)
\[
\langle \frac{1}{j} \left| \sum_i C_i^j | \frac{1}{j} \rangle \rangle = \sum_{j, j', \ell, \ell', L, L', n_1, n_2, n_3} \sum_{\lambda, \lambda'} \sum_{\lambda''} \alpha(\ell, m) \beta(\ell', \ell, L, L') \gamma[S] \delta[L]
\sum_{s-S''} s_{-S''-M_S-g+1+L''\lambda''+n_1+n_2+n_3}
\]
\[
\begin{pmatrix}
S'' & S' & S \\
M_S' & -M_S & M_S
\end{pmatrix}
\begin{pmatrix}
L'' & \lambda'' & L'' \\
M_L'' & -M_L & M_L
\end{pmatrix}
\begin{pmatrix}
L & \lambda & L \\
M_L & -M_L & M_L
\end{pmatrix}
\begin{pmatrix}
j_1 & j_2 & j_3' \\
n_1 & n_2 & n_3'
\end{pmatrix}
\begin{pmatrix}
j_1' & j_2' & j_3' \\
n_1' & n_2' & n_3'
\end{pmatrix}
\quad \text{(III.12)}
\]

From the orthogonality properties of the 3-j symbols
\[
\sum_{j_3 \ell_3} \{j_3\} \begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1' & m_2' & m_3
\end{pmatrix}
= \delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{j_3 j_3'}
\quad \text{(III.13a)}
\]

and
\[
\sum_{m_1 m_2 m_3} \begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1 & m_2 & m_3
\end{pmatrix}
= \frac{\delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{j_3 j_3'} \delta_{m_1 m_1' \delta_{m_2 m_2' \delta_{m_3 m_3'}}}}{[j_3]}
\quad \text{(III.13b)}
\]

Eq. (III.12) may be simplified to read
\[ \langle \hat{t}_1 | \sum_j r_j C_0^j | \hat{t}_f \rangle = \pm \sum_{\ell, m} \sum_{n_3} a(\ell, m) \sigma(\ell', \ell, L, L')[L] [S]^{\frac{1}{2}} \]

\[ = \pm \sum_{S', m' - M_S} [s - S' - M_S + g + \ell + \ell' + L + n_3]
\]

\[ = (-1)^{t + \ell'} \left( \begin{array}{c} \ell' \ \ell \ \ell' \ m' \ \ell' \ n_3 \\ L \ L' \ L'' \ \ell \ \ell' \ \ell' \ m' \ \ell' \ n_3 \end{array} \right) . \]

Equation (III.14)

To obtain the final differential cross section we must average over the initial states \( M_l \) and \( M_S \), and since we are not distinguishing between final states we must sum over \( M_l' \) and \( M_S' \), i.e.

\[ I(\theta) = \frac{1}{[S]\ell L} \sum_{M_S, M_l} \sum_{M_S', M_l'} \sum_{l, m} \sum_{t, m_1} \sum_{\ell, m_2} \sum_{t', m_2} \sum_{\ell', m_3} \sum_{n_3} a(t_1, m_1) a^*(t_2, m_2, t_1, t_2, \ell, \ell', -1, n_3 + n_3') \]

\[ \sigma(\ell, \ell', L, L')[\ell, L', L''][S]^{\frac{1}{2}} \]

\[ \times \left( \begin{array}{c} \ell' \ \ell \ \ell' \ m' \ \ell' \ n_3 \\ L \ L' \ L'' \ \ell \ \ell' \ \ell' \ m' \ \ell' \ n_3 \end{array} \right) . \]

Equation (III.15)

We carry through this procedure:

\[ I(\theta) = \sum_{M_S} \sum_{M_l} \sum_{M_S'} \sum_{M_l'} \sum_{l, m} \sum_{t, m_1} \sum_{\ell, m_2} \sum_{t', m_2} \sum_{\ell', m_3} \sum_{n_3} a(t_1, m_1) a^*(t_2, m_2, t_1, t_2, \ell, \ell', -1, n_3 + n_3') \]

\[ \sigma(\ell, \ell', L, L')[\ell, L', L''][S]^{\frac{1}{2}} \]

\[ \times \left( \begin{array}{c} \ell' \ \ell \ \ell' \ m' \ \ell' \ n_3 \\ L \ L' \ L'' \ \ell \ \ell' \ \ell' \ m' \ \ell' \ n_3 \end{array} \right) . \]

Equation (III.16)

Applying Eq. (III.13) liberally to Eq. (III.16) we obtain
\[ I(\vec{r}) = \sum_{m'_{1},m'_{2}} \sum_{m'_{1},m'_{2}} a(t_{1},m') \, \sigma \, \langle t_{1},m'_{1} | t_{2},m'_{2} \rangle \, \langle t_{1}, \frac{1}{2}, 0 | t_{2}, \frac{1}{2}, -1 \rangle \, \langle t_{1}, \frac{1}{2}, 0 | t_{2}, \frac{1}{2}, 1 \rangle \, \sigma_{11}^{+} \sigma_{22}^{+} \sigma_{11}^{-} \sigma_{22}^{-} \]

\[ \sigma(t',s'_{1},t_{1},L_{1},L_{1}'') \, \sigma(t',s'_{2},t_{2},L_{2},L_{2}'') \, \left( \begin{array}{ccc} t_{1} & 1 & s'_{1} \\ -m_{1} & 0 & m_{1} \end{array} \right) \, \left( \begin{array}{ccc} t_{2} & 1 & s'_{2} \\ -m_{2} & 0 & m_{2} \end{array} \right) \, \sigma_{11}^{+} \sigma_{22}^{+} \sigma_{11}^{-} \sigma_{22}^{-} \]  

\[ (III.17) \]

We recognize Eq. (III.17) as being practically identical to Eq. (II.11). Hence, we have shown, to the accuracy of the approximations we have made, that the angular distribution of photoelectrons resulting from a \( t' \rightarrow t \) electron jump in a many-electron atom whose states are described by LS coupling is equivalent to the angular distribution for a \( t' \rightarrow t \) electron jump in a one-electron atom. If we include the effects of configuration interaction, this simple picture is no longer exactly so. Instead we must superimpose different one-electron angular distributions weighted by the square of the configuration mixing coefficients. An example serves to clarify this. Suppose we considered the photoionization of the Mg atom ground state: \( 1s^{2} \, 2s^{2} \, 2p^{6} \, 3s^{2} \, 3p_{0} \). If we can ignore configuration interaction, the ejection of the 3s electron must lead to a "pure" \( \cos \theta \) distribution. However, if we include the effects of configuration mixing, then configurations like \( 1s^{2} \, 2s^{2} \, 2p^{6} \, 3p_{1} \) and \( 1s^{2} \, 2s^{2} \, 2p^{6} \, 3p_{2} \) are mixed in, and the angular distribution need no longer a pure \( \cos \theta \) distribution. The detailed form of the angular distribution will depend on the exact extent of the configuration mixing. In any case, however, the angular distribution must have the same general form as Eq. (II.18).

The same conclusions obtain if we consider photoelectron transitions between different fine structure levels of the atom which are characterized by \( J \), the total angular momentum of the system. Let \( L' \, S' \, J' \, M' \) be the correct coupled description of the final atom state after the free electron has departed. Then using Eqs. (III.3a) and (III.3b) we may uncouple \( L' \, S' \, J' \, M' \) and recouple it to \( \tau \, m \, s \, m_{s} \) to form a resultant uncoupled state \( \psi \, L' \, S' \, J' \, \tau \, m \, s \, m_{s} \) for the final state wavefunction. Thus

\[ \langle L' \, S' \, J' \, \tau \, m \, s \, m_{s} | a(t',m) \rangle = \sum_{M_{L},M_{S}} (-1)^{P} a(t',m) \, a(t'+,m) \, \langle L' \, S' \, J' | M' \, M_{L}, M_{S} \rangle \, \langle M_{L} \, M_{S} \, -M' | L' \, S' \, J' \, \tau \, m \, s \rangle \]
\[ \frac{1}{\sqrt{N!}} \sum_{l,m} \sum_{M_L^-} \sum_{M_S^-} \frac{1}{\sqrt{M_{l^-}! M_{s^-}!}} (-1)^P \frac{\Gamma_{J'J}(l',m')}{\Gamma_{J'}(l',m')} \frac{1}{\sqrt{M_{l^-}! M_{s^-}!}} (-1)^P \frac{\Gamma_{J}^+(l',m')}{\Gamma_{J}^+(l',m')} \]

\[ \left( \begin{array}{c} L' \; S' \; J' \\ M_L^- \; M_S^- \; m' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^+ \; M_S^+ \; m'' \\
 \end{array} \right) \]

\[ \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^+ \; M_S^+ \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^+ \; M_S^+ \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; J'' \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; M_S^- \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; M_S^- \; m'' \\
 \end{array} \right).
\]

Similarly the initial state \(|SJM\rangle\) can also be re-expressed in an uncoupled representation as

\[ \frac{1}{\sqrt{M_L^+! M_S^+!}} \sum_{P} \frac{1}{\sqrt{M_L^-! M_S^-!}} (-1)^P \frac{\Gamma_{J}^+(l',m')}{\Gamma_{J}^+(l',m')} \]

\[ \left( \begin{array}{c} L \; S \; J \\ M_L^- \; M_S^- \; m \\
 \end{array} \right) \left( \begin{array}{c} L \; S \; J \\ M_L^+ \; M_S^+ \; m \\
 \end{array} \right) \left( \begin{array}{c} L \; S \; J \\ M_L^- \; M_S^- \; m \\
 \end{array} \right) \left( \begin{array}{c} L \; S \; J \\ M_L^+ \; M_S^+ \; m \\
 \end{array} \right).
\]

(III.19)

The evaluation of the transition dipole matrix element proceeds in a straightforward manner

\[ \left\langle \psi_f \left| \frac{1}{\sqrt{M_L^+! M_S^+!}} \sum_{j} \frac{1}{\sqrt{M_L^-! M_S^-!}} (-1)^P \frac{\Gamma_{J}^+(l',m')}{\Gamma_{J}^+(l',m')} \right| \psi_i \right\rangle_{\text{coupled}} = \]

\[ \sum_{M_L^-} \sum_{M_S^-} \frac{1}{\sqrt{M_L^-! M_S^-!}} (-1)^P \frac{\Gamma_{J}^+(l',m')}{\Gamma_{J}^+(l',m')} \left( \begin{array}{c} L' \; S' \; J' \\ M_L^- \; M_S^- \; m' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^+ \; M_S^+ \; m'' \\
 \end{array} \right) \]

\[ \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^+ \; M_S^+ \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; M_S^- \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; M_S^- \; m'' \\
 \end{array} \right) \left( \begin{array}{c} L'' \; S'' \; J'' \\ M_L^- \; M_S^- \; m'' \\
 \end{array} \right). \]

(III.20)

where \( \left\langle \psi_f \left| \frac{1}{\sqrt{M_L^+! M_S^+!}} \sum_{j} \frac{1}{\sqrt{M_L^-! M_S^-!}} (-1)^P \frac{\Gamma_{J}^+(l',m')}{\Gamma_{J}^+(l',m')} \right| \psi_i \right\rangle_{\text{uncoupled}} \) is the matrix element we previously encountered and evaluated in Eq. (III.14). Thus,
\[ \langle \psi' | \sum_j r_j C_j^0 | \psi \rangle_{\text{coupled}}^{\pm} \sum_{t', m} \sum_{M_L', M_S'} \sum_{M_L, M_S} a(t', m) t^{\pm} \]

\[ \sigma(e', e, L', J') (L' L S J) (L S') (M_L' M_S') (M_L M_S) \]

\[ \langle \psi' | \sum_j r_j C_j^0 | \psi \rangle_{\text{coupled}}^{\pm} \]

\[ I(e) = \frac{1}{(2)^{r+1}} \sum_{m_s} \sum_{M''} \sum_{M'} \left| \langle \psi' | \sum_j r_j C_j^0 | \psi \rangle_{\text{coupled}}^{\pm} \right|^2 . \]  

The differential cross section is obtained once again by squaring Eq. (III.21) and summing over the final states \( m_{S''} \) and \( M'' \) and averaging over the initial states \( M'' \).

When the operations indicated are carried out, it is again possible to show that Eq. (III.22) collapses to Eq. (III.17) except for multiplicative factors which are the same for all terms, i.e., the angular distribution of photoelectrons from individual fine structure levels for a \( t' - t \) transition is the same as the \( t' - t \) angular distribution in a one-electron atom. \cite{15} We conclude therefore that the internal structure of a many-electron atom does not alter the form of the angular distribution of photoelectrons from the general expression given in Eq. (II.18). These results might have been expected since the internal states do not cause the existence of outgoing channels which interfere with each other. We have shown that these intuitive ideas are borne out by the calculations of this section. \cite{16}

**IV. Some Generalizations**

The results of the last sections have many possible applications and we shall content ourselves here to outlining briefly some of the possible extensions:

**A. Higher-Order Multipoles**

So far we have restricted ourselves to considering the effects of dipole transitions. Actually we should write the interaction operator in a multipole expansion of irreducible tensor operators: \cite{8}

\[ T = \sum_{k, q} (-1)^{q} C_{-q}^{k} r^{k} C_{q}^{k} \]  

(IV.1)
and recalculate the differential cross section using this more accurate expression. The extension of our results to high-order terms in Eq. (IV.1) is well known; a multipole of order \( \ell \) causes the angular distribution to have a \( P_\ell (\cos \theta) \) dependence. Moreover, there are interference terms arising between the various multipoles, and these cause the angular distribution to depend on \( \varphi \) as well as \( \theta \), i.e., the angular distribution is no longer independent of the direction of light propagation. Since the ratio of the magnitude of the magnetic dipole and electric quadrupole to the electric dipole term is approximately the same as the velocity of the recoiling photoelectron divided by the speed of light, it is obvious that for photoelectron spectroscopy the contribution from the higher order multipoles is normally overshadowed by the dipole term, and hence for many practical purposes may be neglected.

B. Electron and Heavy Particle Impact Ionization

We have emphasized the dipole pattern of the electron distribution which results from photoejection. In the energy range in which the Born approximation is valid, we can expect the same conclusions to hold. Here we replace the electric vector of the light beam \( \vec{E} \) by the momentum transfer vector \( \vec{K} \). The differential cross section of the ejected electron is found by taking the matrix elements of \( e^{i\vec{K} \cdot \vec{R}} \) \((\vec{R} = \vec{r} - \vec{r}')\) between properly antisymmetrized initial and final state wavefunctions. Once again \( \vec{K} \cdot \vec{R} \) is the leading interaction term and the angular distribution measured with respect to \( \vec{K} \) will be the same as in photoionization or in photodetachment. In the laboratory we do not measure the angular distribution about \( \vec{K} \) but rather about the initial particle beam direction \( \vec{k}_0 \). The proper weighting and transformation to laboratory coordinates has been worked out elsewhere. Since the average orientation of \( \vec{K} \) with respect to \( \vec{k}_0 \) changes with the energy of the particle beam, the angular distribution may also be expected to show an energy-dependent behavior.

C. Polarization of Atomic Emission Accompanying Photoelectron Ejection

As intense deep UV light sources are developed the possibility is created of leaving the final state of the atom "sans electron" in an excited state from which the atom radiates. The question arises what will be the population of the different magnetic sublevels of the excited state and hence what will be the polarization of the atomic emission. Let us consider an atom whose initial and final states can be described in Russell-Saunders coupling notation \( L\Omega \) and \( S\Omega \). The probability of finding the atom in a certain \( M^z \) state after the photoelectron is depleted is found by squaring the matrix element
The angular distribution is not only complicated by the sinusoidally time-varying electric field of the light beam which Stark modulates and mixes the atomic sublevels, but also by the fact that we cannot distinguish between an n-photon ionization process in which n photons are observed and, say, an (n+2)-photon process in which n+1 photons are absorbed and one is emitted at the same frequency.

Let us restrict our attention to two-photon ionization processes. The differential cross section may be obtained by a straightforward application of second-order perturbation theory. The result is

\[ I(\phi) = \sum_j \left| \frac{\langle \phi | r C_0(\epsilon_j) | \epsilon_j \rangle \langle \epsilon_j | r C_0 | \phi \rangle}{E_{\epsilon_j} - E_j + \hbar \omega} \right|^2 \]  

(IV.2)

where the light is polarized along the Z axis, \( E_\epsilon \) and \( E_j \) are the energies of the initial and intermediate states, and the sum in Eq. (IV.2) is to be performed over all intermediate states of the atom. Eq. (IV.2) is only valid for a non-resonance process i.e. the photon energy \( \hbar \omega \) does not lie within a natural width of any intermediate state. \[ j \]
We have seen in the case of a one-photon process that we need only consider a single jumping electron \( \ell \rightarrow \ell' \). The same holds for multi-photon processes, and we evaluate Eq. (IV.2) accordingly. Let the initial state be represented by \( \phi_i = \sum_{\ell,m} a(\ell,m) \psi_{\ell,m} \) and the final state by \( \phi_f = \sum_{\ell',m'} a(\ell',m') \psi_{\ell',m'} \). Then, we have from Eq. (II.10)

\[
I(\theta) = \sum_{\ell} \sum_{j} a(\ell,j)(-1)^{\ell - m + j} \langle \sigma_{\ell/j} \rangle \left[ \begin{array}{c} \ell \ 1 \\
-\ell \
\end{array} \right] \left[ \begin{array}{c} m \\
0 
\end{array} \right] \left( \begin{array}{c} \ell \ 1 \\
0 
\end{array} \right) / (E_i - E_j - h\nu)^2. \tag{IV.3}
\]

Eq. (IV.3) is quite formidable, involving the interference of the \( \ell + 2 \), \( \ell \) and \( \ell - 2 \) outgoing channels. The angular distribution has the general form \( |a_{\ell+2} \psi_{\ell+2,m} + a_{\ell} \psi_{\ell,m} + a_{\ell-2} \psi_{\ell-2,m}|^2 \). However, in the practical cases where the contribution of one of the intermediate states \( j \) dominates, the problem is at once much simplified. In this approximation the angular distribution depends only on the dipole radial integrals \( \sigma_{\ell/j} \) and phase shifts \( \sigma_{\ell/j} \). With the help of Eq. (II.11) we rewrite Eq. (IV.3) as

\[
I(\theta) = \sum_{\ell} \sum_{j} \left( -1 \right)^{\ell} a(\ell,j) a(\ell,j') \left[ \begin{array}{c} \ell \ 1 \\
-\ell \
\end{array} \right] \left[ \begin{array}{c} m \\
0 
\end{array} \right] \left( \begin{array}{c} \ell \ 1 \\
0 
\end{array} \right) / (E_i - E_j - h\nu)^2. \tag{IV.4}
\]

From the identities (II.13), (II.14), (II.15), and (II.16a-c), it is clear that the angular distribution of a two-photon non-resonant process has the general form

\[
I(\theta) = a + b \cos^2 \theta + c \cos^4 \theta, \tag{IV.5}
\]

provided we can ignore all intermediate states but one. Eq. (IV.5) also is a special result if the electron ejected in the two-photon
process is an $n$-type ($n'=0$) electron. Three-photon and higher-order photon processes can be calculated by a simple extension of Eq. (IV.2). For sufficiently intense light pulses, it should be expected that the perturbation treatment of the radiation interaction problem will ultimately fail.

E. Molecular Photoionization and Photodetachment

We have discussed up to this point the angular distribution of photoelectrons arising from the photoionization of atoms or the photodetachment of negative atomic ions, and we have found that the differential cross section (for a one-photon dipole transition) is given by the relation $\Gamma(\delta) = a + b \cos^2 \delta$. At first glance it might appear that a more complex angular distribution should result for molecular photoionization or photodetachment since the spherical symmetry of the problem is destroyed by the non-central force field of the nuclei in which the bound electrons move. However, we wish to show that the same general form for the angular distribution results as in the atomic case if we properly average over all orientations of the molecule.

In order to emphasize the similarity between the atomic and the molecular case, we choose to make an expansion of the molecular electronic wavefunctions in terms of atomic wavefunctions (the so-called one-center expansion) where we have chosen, say, the midpoint of the molecule as the origin. For simplicity we shall consider a one-electron transition in a diatomic molecule. As in the atomic case, the ejected electron can be represented by

$$\gamma_{\ell} = \sum_{\ell, m} c_{\ell m} G_{\ell \ell} (r) Y_{\ell m} (\theta, \phi) Y^*_{\ell m} (\theta, \phi) .$$  \hspace{1cm} (IV.6)

Similarly, the initial state can also be represented by an expansion in terms of spherical harmonics

$$\psi_{\ell} = \sum_{\ell', m'} c'_{\ell' m'} R_{\ell \ell'} (r) Y_{\ell' m'} (\theta', \phi')$$  \hspace{1cm} (IV.7)

where $\theta', \phi'$ are polar angles measured about the internuclear axis. Of course $\psi_{\ell}$ can be determined as accurately as desired by including more and more terms in the expansion. It should be noted, however, that the expansion in Eq. (IV.7) must be modified to have the proper symmetry of the molecule. For example, if we were treating the $H_2$ ground state $^1\Sigma_g^+$, the expansion would have no terms with $m \neq 0$, since it represents a $\Sigma$ state. Moreover, only even values of $l$ are permitted due to the gerade symmetry. Thus for the ground state of $H_2$
\begin{equation}
\psi = c_{00}^2 R_0(t) Y_{00}^{(\theta', \phi')} + c_{20}^2 R_2(t) Y_{20}^{(\theta', \phi')} + \cdots \quad (IV.8)
\end{equation}

It might be wondered whether such a treatment converges rapidly to give an accurate description of the molecular state. For the H₂ ground state, recent variational calculations have shown\(^{21}\) that the coefficient \(c_{00}^2\) in Eq. (IV.8) is greater than 0.9.

Eq. (IV.7) appears to have a quite simple form since the electrons are described with respect to the internuclear axis of the molecule. However, we must transform the wavefunction to the laboratory frame. This is achieved by the use of the Wigner rotation matrices:\(^8\)

\begin{equation}
Y_{l', m'} = \sum_{m''} D_{m'' m}^{l'} (\alpha \beta \gamma) Y_{l'' m''} \quad (IV.9)
\end{equation}

where the Euler angles \(\alpha \beta \gamma\) define the transformation necessary to bring the internuclear axis frame in coincidence with the laboratory frame. The calculation of the differential cross section proceeds as for the atomic case, with the exception that we must average over all possible molecular orientations, i.e. we must integrate over \(\alpha, \beta\) and \(\gamma\). Due to the orthogonality relation

\begin{equation}
\int_0^{2\pi} \int_0^{\pi} \sin \theta \, d\theta \, d\phi \, D_{m'' m}^{j'} (\alpha \beta \gamma) D_{m''' m}^{j''} (\alpha \beta \gamma) = \delta_{m'' m}^{j'} \delta_{j'' j} \delta_{m''' m} \quad (IV.10)
\end{equation}

all cross terms disappear from the differential cross section, and we again obtain the result that \(I(\theta) = a + b \cos^2 \theta\) for molecular photodetachment and molecular photoionization. However a final word of caution regarding molecules is in order. Direct molecular photoionization is normally accompanied by molecular autoionization, so that any comparison between calculated and measured molecular photoelectron distributions must take this competing process into account.

References
1. A. Einstein, Ann. Physik (4) 17, 132 (1905); 20, 199 (1906).
6. This choice for the form of the continuum wavefunction ensures that the plane-wave and spherical-wave parts of Eq. (II.4) interfere in such a way that $\mathcal{M}_j^J$ corresponds to an outgoing radial flux. For further discussion see G. Breit and H. A. Bethe, Phys. Rev. 93, 888 (1954).

7. For a Coulomb potential Eq. (II.4) must be modified so that $G_{ij}^J(t)$ has the correct asymptotic limit and $\tau_j$ is replaced by $\tau_j + \sigma_j$, where $\sigma_j = \arg \Gamma(-i\tau/k)$. Here $Z$ is the nuclear charge and $k$ the wave number of the ejected electron. See N. F. Mott and N. W. Maser, The Theory of Atomic Collisions (Clarendon Press, Oxford, 1965), Eq. (46).

8. We make heavy usage of angular momentum coupling theory. See (a) A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton University Press, Princeton, New Jersey, 1957) and (b) M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., The 3-j and 6-j Symbols (The Technology Press, Cambridge, Massachusetts, 1959).

9. If this is not so, each magnetic sublevel should be weighted in the sum according to its population (more properly, a density matrix treatment is necessary). The resultant angular distribution is quite complex in general.

10. This formula first appeared in Ref. 5 but with a typographical error of a factor of 3 in the denominator.


12. B. G. Wybourne, Spectroscopic Properties of Rare Earths (Inter-science Publishers, New York, 1965), Eqs. (3-13) and (3-16).

13. Note that we have assumed that the $R_{n'_f}$, radial wavefunctions are orthogonal to each other. If they are not, then we must multiply by

$$\prod_{\text{electrons}} \int_0^\infty R_{n'_f}^{(i)}(r) \ast R_{n'_f}^{(f)}(r) \, dr,$$

where $i$ and $f$ refer to the initial and final states. This is a constant multiplier in the same way as the fractional parentage coefficient, and hence will not affect the form of the angular distribution.

15. Thus, in the absence of "differential" configuration interaction and intermediate coupling, we would predict that the angular distribution arising from different fine structure levels of the same term value would have the same form. J. Berkowitz and H. Ehrhardt, Phys. Letters 21, 531 (1966); J. Berkowitz, H. Ehrhardt and T. Tekaat, Z. Physik 200, 69 (1967) have measured the photoelectron angular distribution for ejected electrons which leave the argon atom in the states \( \text{Ar II}^2P_{1/2} \) and \( \text{Ar II}^2P_{3/2} \). They find that the two angular distributions are quite similar.

16. These results were stated previously without proof in Ref. 5.


19. For two-photon resonant absorption the angular distribution should be like a one-photon process.

20. W. Zernik, Phys. Rev. 135, 51 (1964) has carried out an exact calculation of the angular distribution for the two-photon ionization of the hydrogen 2s metastable state by the light from a ruby laser.