ANGULAR DISTRIBUTIONS OF PHOTOELECTRONS: CONSEQUENCES OF SYMMETRY

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I. INTRODUCTION AND CONCLUSIONS

This article addresses itself to two questions which arise in the design of experimental facilities for measuring the angular distributions of electrons ejected from atoms or molecules by light: What angular distributions are possible? What is gained by using plane or circularly polarized light? These questions have partially been answered previously in the context of calculations involving specific models for the target atoms or molecules. Here they are answered by giving a simple systematic treatment based on symmetry. The only dynamical assumption is the rapid convergence of the multipole expansion of the absorbed light.

This sort of analysis has been common for many years in nuclear reaction theory, where it yields maximum-complexity theorems for angular distributions and polarizations. The results for electrons ejected from atoms or molecules by light are stronger for two reasons: the multipole absorp-

tion amplitudes decrease rapidly, and the transverse nature of light gives useful restrictions which are absent in the case of particle-induced reactions.

Sections II–V develop the mathematical machinery for describing the symmetry of the absorbed light: The photon is regarded as a particle of unit spin. Its polarization state is described by a density matrix in the multipole representation. That density matrix is expressed as a sum of standard matrices which have definite symmetry under rotation and which refer to particular terms in the multipole expansion.

Section VI gives the consequences of symmetry for any one group of electrons, selected by energy or any other scalar criterion, independently of other groups that may accompany it. It is shown that when the normalized angular distribution is written in the form

\[ I(\theta, \phi) = \sum_{L,M} b_{LM} Y_{LM}(\theta, \phi), \]

the \( b_{LM} \) for positive \( L \) correspond to particular products of multipole absorption amplitudes. Specifically, the \( b_{2M} \) depend only upon pure \( E1 \) and pure \( M1 \) absorption, the \( b_{1M} \) only upon \( E1\cdot M1 \) and \( E1\cdot E2 \) interference, and the \( b_{3M} \) only upon \( E1\cdot E2 \) interference. Circular polarization has no influence upon \( I(\theta, \phi) \). Plane polarization modifies the angular distribution in a predictable way, independently of the target atom or molecule. It increases the magnitude of the asymmetry and changes its shape, but plane polarization introduces no dynamical quantity which is not measured with unpolarized light. All these results depend only upon symmetry and the assumed decreasing amplitudes in the usual multipole expansion of the absorbed light.

Section VII presents a similar classification of the joint angular distribution of two ejected electrons. Here the results are less satisfactory, because they are much more complicated and to make sense of them would require additional restrictions from specific dynamical models. However, it is apparent from the general analysis that the dependence of two-electron angular distributions upon polarization is not determined by symmetry alone. In particular, circular polarization can reveal dynamical information which is unavailable with unpolarized or plane-polarized light, even in the pure electric-dipole approximation. Certain interference terms can be seen only with plane polarization, and others only with circular polarization.

It is assumed throughout this article that the target atoms or molecules are oriented at random. The same methods can be extended to see what information is gained by the use of polarized targets, but that is not done here.
II. POLARIZATION STATES OF A PHOTON

The consequences of symmetry for the angular distributions of photoelectrons depend only upon considerations of angular momentum and parity, and not at all upon a detailed description of the interaction of light with matter. It is therefore convenient to adopt the simple-minded view that a photon is a unit-spin particle, whose spin wave function $\chi$ may be written in the usual way:

$$\chi = \sum_{\mu} \alpha_\mu \chi_{1\mu}$$

$$S^2 \chi_{1\mu} = 2\chi_{1\mu} \quad \mu = 0, \pm 1. \quad (2.1)$$

$$S_z \chi_{1\mu} = \mu \chi_{1\mu}.$$

Here, $S$ is the spin angular momentum operator and $h = 1$. The interaction of light with matter happens to be such that photons are emitted into, or absorbed from, states wherein the component of $S$ in the direction of the momentum $k$ is necessarily $\pm 1$, never 0. For such states,

$$(k \cdot S)^2 \chi = k^2 \chi. \quad (2.2)$$

As the photon momentum direction will consistently be used to define the positive $z$-axis, that means

$$\alpha_0 = 0. \quad (2.3)$$

The usual polarization vector $e$, which represents the electromagnetic vector potential, has components $e_x, e_y, e_z$ given by

$$e_x = (1/\sqrt{2})(\alpha_{-1} - \alpha_1)$$

$$e_y = (i/\sqrt{2})(\alpha_{-1} + \alpha_1) \quad (2.4)$$

$$e_z = \alpha_0 = 0.$$

As $e$ is a polar vector, the spin wave function $\chi$ must be endowed with odd intrinsic parity. Under space inversion $P$, it transforms according to

$$P\chi_{1\mu} = -\chi_{1\mu}. \quad (2.5)$$

The photon wave functions for the pure circular- and pure plane-polarization states are given respectively by

left circular: \quad $\Phi_1 = \chi_{11} e^{ikz}$

right circular: \quad $\Phi_{-1} = \chi_{1-1} e^{ikz} \quad (2.6)$
All other pure polarization states of a plane wave are represented by linear combinations of any two of these four pure states. Impure polarization states are represented by statistical mixtures of pure states.

### III. MULTIPOLe DECOMPOSITION

For studying angular distributions, it is useful to introduce basis states which have definite parity and definite total angular momentum \( J \). To that end, the spatial part of the photon wave function is expressed as a sum of partial waves having definite orbital angular momentum \( \ell \).

\[
e^{ikz} = \sum_{l=0}^{\infty} i^l [4\pi(2l + 1)]^{1/2} j_l(kr) Y_{l0}(\theta, \phi).
\]  

(3.1)

Here, \( Y_{l0} \) is the usual spherical harmonic, \( j_l \) is the spherical Bessel function, and \( (r, \theta, \phi) \) are the usual polar variables. The angular-momentum analysis of the photon wave functions (2.6) is accomplished by introducing the vector coupling scheme

\[
\psi_{J\mu}^{(l)} \equiv \sum_{m} C(l, 1, j; m, \mu - m, \mu) Y_{lm}(\theta, \phi) \chi_{1, \mu - m}
\]  

(3.2)

where \( C(l, S, j; m_L, m_S, \mu) \) is the vector-coupling coefficient\(^2 \) for

\[
J = L + S, \quad \mu = m_L + m_S.
\]  

(3.3)

Inversion of (3.2) gives

\[
Y_{l0}(\theta, \phi) \chi_{1\mu} = \sum_{j = \lceil l - 1 \rceil}^{l + 1} C(l, 1, j; \mu, 0, \mu) \psi_{J\mu}^{(l)}.
\]  

(3.4)

The only cases of physical interest are \( \mu = \pm 1 \). For those, there is no term with \( j = 0 \). Substitution of (3.4) into (2.6) and grouping the terms according
to total angular momentum $j$ and parity $(-)^{j+1}$ gives, for $\mu = \pm 1$,

$$\Phi_{\mu} = \chi_{1\mu} e^{ikr} = \sum_{j=1}^{\infty} \{\mu |Mj, \mu\rangle + |Ej, \mu\rangle\}. \tag{3.5}$$

The basis states, which are called the magnetic and electric $2^j$-pole states, are defined by

$$|Mj, \mu\rangle \equiv -i'[2\pi(2j + 1)]^{1/2} j_j(kr)\psi_{j\mu}^{(j)} \tag{3.6M}$$

$$|Ej, \mu\rangle \equiv i^{-1}(2\pi)^{1/2}(j + 1)^{1/2} j_{j-1}(kr)\psi_{j\mu}^{(j-1)} - (j)^{1/2} j_{j+1}(kr)\psi_{j\mu}^{(j+1)}. \tag{3.6E}$$

Because of the odd intrinsic parity of the photon, they transform under space inversion according to

$$P |Mj, \mu\rangle = (-)^{j+1} |Mj, \mu\rangle$$

$$P |Ej, \mu\rangle = (-)^{j} |Ej, \mu\rangle, \tag{3.7}$$

and they obey* 

$$J^2 |Kj, \mu\rangle = j(j + 1) |Kj, \mu\rangle$$

$$J_z |Kj, \mu\rangle = \mu |Kj, \mu\rangle, \tag{3.8}$$

where $K$ stands for $M$ or $E$.

The plane-polarized photon wave functions may be expressed in the multipole basis by combining (3.5) with (2.7) to obtain

$$\Phi = \frac{-1}{\sqrt{2}} \sum_{j=1}^{\infty} \{ |Mj, 1\rangle + |Mj, -1\rangle + |Ej, 1\rangle - |Ej, -1\rangle \} \tag{3.9}$$

$$\Phi_y = \frac{-i}{\sqrt{2}} \sum_{j=1}^{\infty} \{ |Mj, 1\rangle - |Mj, -1\rangle + |Ej, 1\rangle + |Ej, -1\rangle \}.$$

All the kinematical information needed to see how angular distributions depend upon polarization is contained in (3.5) and (3.9). The specific dynamical assumptions involve only the invariant amplitudes for the absorption of the multipole states by particular atoms or molecules. Here, it is simply assumed that electric-dipole absorption dominates, and that

* The phase conventions used here are the standard ones; the multipole basis states transform under rotation as angular-momentum eigenstates, and under time reversal according to

$$T |Kj, \mu\rangle = (-)^{1/2} |Kj, -\mu\rangle.$$
the orders of magnitude of the amplitudes \((Kj)\) for absorption of other multipoles obey

\[
(Ej)/(E1) \sim (kR)^{j-1}
\]

\[
(Mj)/(Ej) \sim k/mc
\]  

(3.10)

where \(R\) is the radius of the target atom or molecule, and \(m\) is the mass of the electron. Then in practical situations it is usually sufficient to neglect all contributions to the angular distributions except those proportional to \((E1)^2, (E1)(M1),\) or \((E1)(E2)\).

**IV. THE PHOTON DENSITY MATRIX**

Even for a pure polarization state, the density matrix\(^4\) provides a more transparent approach to angular distributions than does the wave function. In particular, the density matrix for a randomly oriented target atom or molecule is spherically symmetric. Then the symmetry properties of the density matrix for the combined system, photon plus target, are just those of the density matrix for the photon alone.

The density matrix elements \(\langle K'j', \mu' | \rho | Kj, \mu \rangle\) for a photon in a pure polarization state \(\Phi\) are given by

\[
\langle K'j', \mu' | \rho | Kj, \mu \rangle = \langle K'j', \mu' | \Phi \rangle \cdot \langle \Phi | Kj, \mu \rangle,
\]

(4.1)

where \(K\) stands for \(M\) or \(E\). For a statistical mixture of pure states, the density matrices of the individual pure states are added with weights equal to their statistical weights in the mixture. The matrix (4.1) has infinitely many rows and columns, labeled by \((Kj, \mu)\) with \(-j \leq \mu \leq j\). However, only terms with \(\mu = \pm 1\) appear in the plane wave functions (3.5) and (3.9), or in fact in any plane wave function for the photon. Therefore, all rows and columns of \(\rho\) vanish identically, except those with \(\mu = \pm 1\) and \(\mu' = \pm 1\). Inspection of (3.5) and (3.9) shows that the coefficients \(\langle \Phi | Kj, \mu \rangle\) depend upon \(K\) and \(\mu\), but not upon \(j\). Consequently, the infinite-dimensional matrix \(\rho\) is really a repetition of four two-dimensional submatrices \(\rho(K', K)\), defined for \(\mu' = \pm 1, \mu = \pm 1\) by

\[
\langle \mu' | \rho(K', K) | \mu \rangle \equiv \langle K'j', \mu' | \rho | Kj, \mu \rangle.
\]

(4.2)

In the multipole representation, with nonvanishing columns labeled by \((Kj, \mu)\) and nonvanishing rows by \((K'j', \mu')\), the density matrix appears as

\* The estimates (3.10) are not quite correct because they are based on non relativistic theory. For instance, \((E2)\) has a relativistic term\(^3\) whose order of magnitude is given by \((k/mc)^2(E1)\).
For the states of pure circular polarization discussed above, the submatrices may be read off from (3.5) and (4.1).

\[
\rho_1(E, E) = \rho_1(M, M) = \rho_1(E, M) = \rho_1(M, E) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} (1 + \sigma_z)
\]

\[
\rho_{-1}(E, E) = \rho_{-1}(M, M) = -\rho_{-1}(E, M) = -\rho_{-1}(M, E) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}
\]

Here, \( \rho_{\pm 1} \) is the density matrix for the circular polarization state \( \Phi_{\pm 1} \) of (3.5), and the notation

\[
\begin{pmatrix} \mu' \mu \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}
\]

\[
\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
\]
is introduced for later convenience. In the same way, the density matrices for the plane polarized states are determined by (3.9) to be

\[
\begin{align*}
\rho_x(E, E) &= \rho_y(M, M) = \frac{1}{2}(1 - \sigma_+ - \sigma_-) \\
\rho_x(M, M) &= \rho_y(E, E) = \frac{1}{2}(1 + \sigma_+ + \sigma_-) \\
\rho_x(E, M) &= \rho_y(M, E) = \frac{1}{2}(\sigma_x + \sigma_+ - \sigma_-) \\
\rho_x(M, E) &= \rho_y(E, M) = \frac{1}{2}(\sigma_x - \sigma_+ + \sigma_-).
\end{align*}
\]  

(4.6)

For unpolarized light, the density matrix \(\rho_u\) is given by

\[
\begin{align*}
\rho_u &= \frac{1}{2}(\rho_1 + \rho_-) = \frac{1}{2}(\rho_x + \rho_y) \\
\rho_u(E, E) &= \rho_u(M, M) = \frac{1}{4}i \\
\rho_u(E, M) &= \rho_u(M, E) = \frac{1}{4}\sigma_x.
\end{align*}
\]  

(4.7)

(4.8)

The five special density matrices written out here are manifestly not independent, and in fact do not form a complete set. The reduction to a repetition of four two-dimensional matrices does go through in the same way for the general polarization state of a plane wave, and so does the tensor analysis which will follow.

V. EXPANSION IN STANDARD TENSORS

The symmetry of the photon density matrix is exposed by expressing it as a sum of irreducible tensor operators, that is of matrices \(T_{LM}\) which transform under rotation in the same way as the spherical harmonic functions \(Y_{LM}\). The standard tensors used here are defined by their matrix elements,

\[
\langle K'j', \mu' | T_{LM}(\kappa\lambda', \kappa\lambda) | Kj, \mu \rangle
\]

\[
\equiv \left[ \frac{2L + 1}{2j' + 1} \right]^{1/2} \delta_{K'j', \kappa\lambda'} \delta_{Kj, \kappa\lambda} C(j, L, j'; \mu, M, \mu'),
\]

(5.1)

which vanish except for \(|j' - j| \leq L \leq j' + j\). The vector-coupling coefficient \(C(j, L, j'; \mu, M, \mu')\) is required for an irreducible tensor by the Wigner-Eckart theorem. The remaining (scalar) factors are arbitrary. They have been chosen so that \(T_{LM}(K'j', Kj)\) has nonvanishing matrix elements between the multipole states \(Kj\) and \(K'j'\), and no others. The
Hermitian conjugates of the standard tensors can be found from the properties of the vector-coupling coefficients.

\[ T_{LM}(K'j', Kj)^\dagger = (-)^{j' - j + M} T_{-L, -M}(Kj, K'j') \]  

(5.2)

The standard tensors form an orthonormal set in the sense that their traces obey

\[ \text{Tr}\{T_{LM}(K'j', K'\lambda')^\dagger T_{LM}(Kj, K\lambda)\} = \sum_{K'j',\mu',\mu} \langle K''j'', \mu''| T_{LM}(K'j', K'\lambda')^\dagger T_{LM}(Kj, K\lambda) | K''j'', \mu''\rangle \]

\[ = \delta_{L, L'} \delta_{M, M'} \delta_{Kj, K'j'} \delta_{K\lambda, K'\lambda'} \]  

(5.3)

They form a complete basis for the expansion of any photon density matrix in the form

\[ \rho = \sum_{L, M} \sum_{K'j', Kj} a_{LM}(K'j', Kj) T_{LM}(K'j', Kj), \]  

(5.4)

where the tensor moments \( a_{LM} \) may be obtained by applying (5.3) to (5.4) to obtain

\[ a_{LM}(K'j', Kj) = \text{Tr} \{ \rho T_{LM}(K'j', Kj)^\dagger \}. \]  

(5.5)

In terms of the two-dimensional submatrices of \( \rho \), (5.5) becomes

\[ a_{LM}(K'j', Kj) = \text{Tr} \{ \rho(K'j', Kj) T_{LM}(K'j', Kj)^\dagger \} \]

\[ = (-)^{j' - j + M} \text{Tr} \{ \rho(K'j', Kj) T_{-L, -M}(Kj, K'j') \} \]  

\[ = (-)^{j' - j + M} \sum_{\mu', \mu} \langle \mu'| \rho(K'j', Kj) | \mu \rangle \times \langle Kj, \mu| T_{-L, -M}(Kj, K'j') | K'j', \mu' \rangle. \]  

(5.6)

(5.7)

As the density matrix is necessarily Hermitian, it follows from (5.2) and (5.4) that the complex conjugates of the tensor moments are given by

\[ a_{LM}(K'j', Kj)^* = (-)^{j' - j + M} a_{L, -M}(Kj, K'j'). \]  

(5.8)

In the sum (5.7), the matrix elements of \( \rho \) vanish outside the two-dimensional submatrix with \( \mu' = \pm 1, \mu = \pm 1 \). Therefore, only the same submatrices of the standard tensors \( T_{LM}(K'j', Kj) \) are needed for evaluation of the sum. Those submatrices have been evaluated, using (5.1), for small values of \( j \) and \( j' \). They are listed in Table I, with the notation (4.5). The values of \( L \) and \( M \) are restricted by (5.1) to \( |j' - j| \leq L \leq j' + j \) and \( M = \mu' - \mu = 0, \pm 2 \). The numerical values of the nonvanishing matrix elements are shown by (5.1) to be independent of \( K \) and \( K' \).
### TABLE I.
Values of All the Nonvanishing Standard Tensors $\langle K'j', \mu | T_{LM}(K', Kj) | Kj, \mu \rangle$ in the Subspace $\mu' = \pm 1, \mu = \pm 1$, for $j + j' \leq 3$. The Notations $I, \sigma_z, \sigma_+, \sigma_-$ are defined in Eq. (4.5).

<table>
<thead>
<tr>
<th>$L$</th>
<th>$M$</th>
<th>$j' = 1, \ j = 1$</th>
<th>$j' = 2, \ j = 1$</th>
<th>$j' = 1, \ j = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\frac{1}{6}$</td>
<td>$\frac{1}{6}$</td>
<td>$\frac{1}{6}$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{5}$</td>
<td>$\frac{1}{5}$</td>
<td>$\frac{1}{5}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>3</td>
<td>-2</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
</tbody>
</table>

### TABLE II.
Nonvanishing Tensor Moments of the Density Matrices for Unpolarized, Circular-Polarized, and Plane-Polarized Photons of $E1$, $M1$, and $E2$ Multipolarities. All Nonvanishing Tensor Moments for $j + j' \leq 3$ are Given. An Asterisk in the Last Column Indicates That the Tensor Moment Has Natural Parity i.e., Parity Equal to $(-)^L$.

<table>
<thead>
<tr>
<th>Tensor moments</th>
<th>Unpolarized</th>
<th>Circular</th>
<th>Plane</th>
<th>Natural parity?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{00}(E1,E1) = a_{00}(M1,M1)$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a_{00}(E1,E1) = a_{00}(M1,E1)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{10}(E1,E1) = a_{10}(M1,M1)$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a_{10}(E1,E1) = a_{10}(M1,E1)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{10}(E2,E1) = a_{10}(E1,E2)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{20}(E1,E1) = a_{20}(M1,M1)$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a_{20}(E1,E1) = a_{20}(M1,E1)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{22}(E1,E1) = a_{22}(M1,\ldots)$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a_{22}(E1,E1) = a_{22}(E1,E2)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{30}(E2,E1) = a_{30}(E1,E2)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$a_{32}(E2,E1) = a_{32}(E1,E2)$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$a_{32}(E2,E1) = a_{32}(E1,E2)$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td>$\frac{1}{3}^{1/2}$</td>
<td></td>
</tr>
</tbody>
</table>

10
The tensor moments $a_{LM}(K'j', Kj)$ can now be evaluated by using Eq. (5.5) and Table I. That has been done for the five polarization states whose density matrices are given in Section IV. The results for $j + j' \leq 3$ are listed in Table II.

From (3.7) and (4.1) it can be seen that the density matrix elements $\langle E_j', \mu' | \rho | E_j, \mu \rangle$ and $\langle M_j, \mu | \rho | M_j', \mu' \rangle$ have parity $(-)^{j+j'}$, while $\langle E_j', \mu' | \rho | E_j, \mu \rangle$ and $\langle M_j', \mu' | \rho | E_j, \mu \rangle$ have parity $(-)^{j-j'+1}$. The tensor moments $a_{LM}(K'j', Kj)$, which are linear combinations of density matrix elements with the same $(K'j', Kj)$, follow the same rule. The last column of Table II has an asterisk in cases of "natural parity," i.e., parity equal to $(-)^L$. The natural parity coefficients are the only ones which contribute to one-electron angular distribution, because for one electron, the parity of $Y_{LM}$ is the angular distribution is equal to $(-)^L$.

VI. ANGULAR DISTRIBUTION OF ONE ELECTRON

The normalized angular distribution of an electron ejected from an atom or a molecule is denoted by $I(\theta, \phi)$.

$$I(\theta, \phi) = \sum_{L,M} b_{LM} Y_{LM}(\theta, \phi)$$  \hspace{1cm} (6.1)

$$b_{00} = \frac{1}{(4\pi)^{1/2}}$$  \hspace{1cm} (6.2)

$$b_{L, -M} = (-)^M b_{LM}^*$$  \hspace{1cm} (6.3)

The angular distribution is a scalar linear function of the photon density matrix $\rho$; linear because a statistical mixture of photon states must give the same statistical mixture of the resulting angular distributions, and scalar because rotation (or space inversion) of the initial state must result in the same rotation (or space inversion) of the angular distribution. The most general scalar linear function is expressed by

$$b_{LM} = \sum_{K,j,K',j'} G_{L}(K'j', Kj) a_{LM}(K'j', Kj),$$  \hspace{1cm} (6.4)

where the scalar coefficients $G_{L}(K'j', Kj)$ depend upon the dynamics of the system, but not upon the photon density matrix $\rho$.

Assumption (6.4) relies upon all of the following conditions:

I. The target atoms or molecules are oriented at random, so that the density matrix for the target is invariant under rotation.

II. External fields, as in a crystal, may be neglected.
III. In the detection of the electron, all selection criteria other than the angles \((\theta, \phi)\) are invariant under rotation. Thus if several electrons are ejected, selection according to energy or time is permitted, but requiring a second electron to be ejected in a particular direction is not permitted.

The assumed invariance under space inversion implies that \(G_L(K'j', Kj)\) must vanish for cases of unnatural parity, because \(b_{LM}\) in (6.1) has parity \((-)^L\). The dynamical coefficients \(G_L(K'j', Kj)\) are subject to certain general restrictions. For instance, the Hermitian condition (5.8), combined with (6.3) gives

\[
G_L(K'j', Kj) = (-)^{j'-j}G_L(Kj, K'j')^*.
\] (6.5)

Obviously, the \(G_L(K'j', Kj)\) must also be restricted to give \(I(\theta, \phi) \geq 0\) for every photon density matrix \(\rho\).

If it is assumed that electric-dipole absorption is the dominant process and that all multipole contributions may be neglected except pure \(E1\), pure \(M1\), and the interference terms \(E1\cdot M1^*\) and \(E1\cdot E2\), then the tensor moments listed in Table II determine all the nonvanishing angular-distribution coefficients \(b_{LM}\), through (6.4). Those coefficients are displayed in Table III, for each of the five polarization states, using the notation

\[
B_1 = B_1^* = \text{Re} \left\{ \sqrt{2} G_1(M1, E1) + (6/5)^{1/2} G_1(E2, E1) \right\}
\]

\[
B_{2E} = B_{2E}^* = (1/6)^{1/2} G_2(E1, E1)
\]

\[
B_{2M} = B_{2M}^* = (1/6)^{1/2} G_2(M1, M1)
\]

\[
B_3 = B_3^* = (4/5)^{1/2} \text{Re} \left\{ G_3(E2, E1) \right\}.
\] (6.6)

Table III summarizes what can be said about the angular distribution of one electron, under the assumption that only the lowest multipole states contribute to the absorption of the light and with no additional dynamical assumptions. Pure electric-dipole radiation gives rise to a one-parameter angular distribution involving only \(y_0\) and \(y_2\). Polarization of the light gains no qualitatively new information, but plane polarization doubles the relative strength of the \(y_2\) contribution and rotates it. Specifically, for pure electric-dipole absorption,

\[
I_y(\theta, \phi) = I_{\pm 1}(\theta, \phi) = \frac{1}{4\pi} + B_{2E}(5/16\pi)^{1/2}[3 \cos^2 \theta - 1]
\] (6.7)

\[
I_x(\theta, \phi) = \frac{1}{4\pi} - 2B_{2E}(5/16\pi)^{1/2}[3 \cos^2 \theta_x - 1],
\] (6.8)
TABLE III.

Angular Distribution Coefficients. Defined by $I(\theta, \phi) = \sum h_{iM} Y_{iM}(\theta, \phi)$, for one electron. The Dynamical Coefficients $B$ Are Defined through Eqs. (6.4) and (6.6).

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Unpolarized</th>
<th>Circular</th>
<th>Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b_0$</td>
<td>$b_1$</td>
<td>$b_1$</td>
</tr>
<tr>
<td></td>
<td>$b_22 - b_{2, -2}$</td>
<td>$b_2$</td>
<td>$b_2$</td>
</tr>
<tr>
<td></td>
<td>$b_3$</td>
<td>$b_3$</td>
<td>$b_3$</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>$B_1$</td>
<td>$B_1$</td>
</tr>
<tr>
<td></td>
<td>$B_2M$</td>
<td>$B_2M$</td>
<td>$B_2M$</td>
</tr>
<tr>
<td></td>
<td>$B_3$</td>
<td>$B_3$</td>
<td>$B_3$</td>
</tr>
</tbody>
</table>

where $\theta_x$ is the polar angle with respect to the x-axis. The nonnegativity condition for pure electric-dipole absorption follows from* (6.8).

$$-1 \leq (20\pi)^{1/2} B_{2E} \leq \frac{1}{2}.$$  (6.9)

It can be seen in the examples of Table II, and it is true in general, that circular polarization has no effect upon the natural-parity coefficients, which are the only ones relevant to the angular distribution of one electron.

If all contributions are neglected other than those appearing in (6.6), then Table III shows that the coefficient of $Y_1$ measures a mixture of $E_1\cdot M_1$ and $E_1\cdot E_2$ interference, and the coefficient of $Y_3$ measures only the $E_1\cdot E_2$ interference. These terms have no first-order effect on the coefficient of $Y_2$, which measures the pure electric- or pure magnetic-dipole absorption. Polarization has no effect upon the $E_1\cdot M_1$ term. Plane polarization enhances the $E_1\cdot E_2$ term by a factor $[1 + 2 \times (5/6)]^{1/2} \approx 1.6$, and changes its shape. Specifically, the $Y_3$ term for unpolarized light is proportional to $\cos 0 [\cos^2 \theta - \frac{1}{2}]$, while for $xz$ plane polarization that factor becomes $2 \cos 0_x [\frac{1}{2} - \cos^2 \theta_x]$.

VII. TWO-ELECTRON ANGULAR DISTRIBUTIONS

The results of Section VI apply to the angular distribution $I(\theta, \phi)$ of any polar vector in the final state. That vector could, for instance, be the momentum of one electron selected for its energy, the total momentum of all electrons, or the difference between two momenta. Only the values of the dynamical $G$ coefficients depend upon which polar vector is chosen. (For

* It has not been proved here that (6.9) is the tightest possible restriction. In fact, it is.
an axial vector, such as $p_1 \times p_2$ for two electrons, the parity selection rules are changed.)

One way to express a two-electron angular distribution is

$$I(\theta_1, \phi_1, \theta_2, \phi_2) = \sum_{L, M, l_1, l_2} C_{LM}(l_1, l_2)V_{LM}(l_1, l_2).$$

(7.1)

$$V_{LM}(l_1, l_2) \equiv \sum_m C(l_1, l_2, L; m, M - m_1, M) \times Y_{l_1 m_1}(\theta_1, \phi_1)Y_{l_2, M - m_1}(\theta_2, \phi_2)$$

(7.2)

The moments $C_{LM}$ are then related to the tensor moments $a_{LM}(K'j', Kj)$ of the photon density matrix through

$$C_{LM}(l_1, l_2) = \sum_{K'j', Kj} G_{1}(K'j', Kj, l_1, l_2)a_{LM}(K'j', Kj).$$

(7.3)

Assumption (7.3) relies upon all the conditions of Section VI, except that $(\theta_1, \phi_1, \theta_2, \phi_2)$ replaces $(\theta, \phi)$ in condition III. The dynamical $G$ coefficients may depend upon the scalars (energy or time of emission) of the two electrons considered separately, but not upon the angle between the momenta of the two electrons.

The coefficient $C_{LM}(l_1, l_2)$ has parity $(-)^{l_1+1}$. Therefore, the tensor moments of unnatural parity $(-)^{L+1}$ can influence the two-particle angular distribution, and polarization can provide information which would otherwise be unavailable. In particular, it is apparent from (7.3) and Table II that $G_1(E_1, E_1, l_1, l_2)$ can be measured only with circular polarization, $G_3(E_1, E_2, l_1, l_2)$ only with plane polarization, and $G_2(E_1, M_1, l_1, l_2)$ and $G_2(E_1, E_2, l_1, l_2)$ only with plane or circular polarization. Whether these $G$ coefficients provide qualitatively new dynamical information depends, of course, upon the dynamical model.

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References


I. INTRODUCTION

The collision of an electron with an isolated atom or molecule can have a number of outcomes. Among them are the transfer of translational energy, electron exchange, excitation or deexcitation of internal states of the target, ionization, negative ion formation, molecular fragmentation, or a combination of several of these. For any case, the quantity which charac-
terizes the scattering process is known as the cross section. Phenomenologically, the cross section for the occurrence of a certain type of event during a collision is equal to the number of these events per unit time per target particle divided by the current density (particles per unit time per unit area) of incident electrons relative to the target.\textsuperscript{1} As a consequence of this definition, the cross section has the units of area per target particle.

For the particular process in which an electron collides with a stationary target and then scatters into a given direction (defined by spherical polar angles $\theta$, $\varphi$), the cross section per unit solid angle is called the "differential scattering cross section" (hereafter abbreviated as DCS) and has the units of area per unit solid angle per target particle. The corresponding "total cross section" is the integral of the DCS over all scattering directions $\theta$, $\varphi$. If we define a spherical polar coordinate system whose $z$ axis lies along the incident beam direction, then the scattering angle $\theta$ is the colatitude of this coordinate system and $\varphi$ is the azimuth (or longitude) measured with respect to an arbitrary reference plane containing the $z$ axis. If the target particles are randomly oriented with respect to the incident beam direction, then the DCS will not depend on $\varphi$.

Electron-impact spectrometry is concerned with the excitation of atoms and molecules and therefore with the measurement of the energy lost by the electron during the scattering process. In essence, the experimental method most often used involves the production of a monochromatic beam of electrons (incident beam), the passage of this beam through a gaseous sample of the target particles, and the measurement of the scattered electron intensity as a function of the incident electron energy, scattering angle, and energy loss (the kinetic energy lost by the incident electron through an inelastic collision). In elastic or inelastic scattering of electrons, a small part $\delta E$ of an electron's kinetic energy $E$ in the laboratory system is transformed into laboratory kinetic energy of the target. Namely, for elastic scattering,

$$\frac{\delta E}{E} \approx \frac{4m}{M} \frac{\sin^2 \theta}{2}$$

and for inelastic scattering

$$\frac{\delta E}{E} \approx \frac{2m}{M} \left[ 1 - \frac{W}{2E} - \left(1 - \frac{W}{E}\right)^{1/2} \cos \theta \right].$$

$M$ and $m$ are the mass of the target and electron, respectively; $\theta$ is the scattering angle, and $W$ is the energy lost by the incident electron into the internal states of the target. These equations can be derived from the
conservation of total energy and momentum during the collision.\(^{53}\) (For electronic excitation in the energy ranges discussed here, \(\delta E \sim 10^{-3} \text{ eV}\) and for vibrational excitation, \(\delta E \sim 10^{-2} \text{ eV}\)).

This paper deals with the limited area of low-energy electron-impact spectrometry in the 5 to 100 eV incident electron energy range. These energies are comparable to the binding energies of valence electrons in molecules and represent a most important region as far as chemistry is concerned. We have not attempted a complete review of even this limited area, but will consider several illustrative examples which are of special interest to the authors. The phenomena of resonances and some other aspects of low-energy electron scattering will not be discussed. We will consider scattering theory only insofar as it is directly related to the evaluation of experimental data except for a more detailed summary of some new calculations\(^{119}\) for the excitation of nuclear motion (Section V). Detailed descriptions of the omitted subjects are available in the literature.\(^2\text{-}^{10}\) A short historical background is given in Section II and the description of our electron-impact spectrometer and experimental procedures in Section III. Electronic excitation of He, H, H\(_2\), N, CO, C\(_2\)H\(_2\), and C\(_2\)H\(_4\) will be discussed in Section IV, while Section V deals with the vibrational excitation of the ground electronic state of H\(_2\) and N\(_2\).

It is of some interest to first summarize the important differences between optical and electron-impact spectroscopy.

1) The probabilities of observing different excitations by means of optical spectroscopy are governed by fairly stringent selection rules. In electron-impact spectrometry at high energies (over 100 eV), the selection rules\(^{25}\) closely resemble the optical ones and the cross sections are related to optical absorption coefficients. Many of the normal optical selection rules,\(^{11}\) however, can be broken by the judicious choice of incident electron energy and scattering angle. In particular, low-energy electrons (within a few tens of electron volts of the excitation threshold) can be quite effective in causing transitions between states of different spin multiplicity through the mechanism of electron-exchange excitation. This exchange process involves the interchange of the incident electron and one of the bound ones. These transitions are highly forbidden under photon impact in the absence of appreciable spin–orbit coupling. In addition, the probability of producing transitions which are optically symmetry forbidden can often be dramatically increased by the use of low-energy electrons.

To illustrate these marked differences, Table I presents a comparison of relative optical transition probabilities with the ones obtained by electron impact for three transitions in helium. The relative probability of exciting the \(2^1P\) level (optically-allowed transition) is taken as unity. The last two
TABLE I

A Comparison of Some Relative Electron-Impact Excitation Probabilities in Helium with Typical Optical Transition Probabilities. $P_{\text{opt}}$ is the Relative Optical Excitation Probability; $P_{\text{elec}}$ is the Relative Electron-Impact Excitation Probability for an Incident Energy of 35 eV; and $P_{\text{elec}}(\theta)$ is the Relative Probability for Electrons to Scatter at an Angle $\theta$ after Causing the Excitation for an Incident Energy of 35 eV.

| Transition | Type according to optical selection rules | $P_{\text{opt}}$ | $P_{\text{elec}}$ | $P_{\text{elec}}(0)$
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$1^1S \rightarrow 2^1P$</td>
<td>Electric dipole allowed</td>
<td>$1^a$</td>
<td>$1^a$</td>
<td>$1^a$</td>
</tr>
<tr>
<td>$1^1S \rightarrow 2^1S$</td>
<td>Electric dipole forbidden, electric quadrupole allowed</td>
<td>$10^{-5}$-$10^{-8}$</td>
<td>0.18$^d$</td>
<td>0.40</td>
</tr>
<tr>
<td>$1^1S \rightarrow 2^3P$</td>
<td>Spin-forbidden, electric dipole allowed</td>
<td>$\sim 10^{-10}$</td>
<td>0.12$^e$</td>
<td>0.023</td>
</tr>
</tbody>
</table>

$^a$ The relative probability of this transition is taken as unity.
$^b$ Ref. 11a.
$^e$ Ref. 69.
$^f$ Ref. 71.
but comparable in the vacuum uv), the ability to work with solid and liquid samples, and a well-developed practical theory with which to interpret experimental results.

II. HISTORICAL DEVELOPMENT

In 1914 Franck and Hertz\textsuperscript{12} initiated the field of electron-impact spectrometry with their classic experiments on the measurement of energy losses of electron swarms in atomic gases. However, it was not until 1927 that Dymond\textsuperscript{13} carried out the first measurements of the angular distribution of inelastically scattered electrons. At about the same time, Oppenheimer\textsuperscript{14} pointed out the possibility of an electron-exchange mechanism whereby optically spin-forbidden transitions could be produced. During the next few years, until the middle 1930's, the study of electron-impact phenomena reached a peak only to be followed by two decades of relative inactivity. A comprehensive review of this early work has been presented by Massey and Burhop.\textsuperscript{4}

Since the late 1950's there has been a renewed and increasing interest in this field, due possibly to the development of more sophisticated experimental techniques and a heightened awareness of the importance of electron-molecule (atom) interactions in radiation chemistry, upper-atmosphere phenomena, and plasma physics. A recent review of electron impact phenomena is given by Massey and Burhop.\textsuperscript{5} Up-to-date bibliographies and reference surveys are available from two information centers.\textsuperscript{15,16}

At present there are essentially two methods used to study molecular excited states through electron-impact excitation and the detection of the scattered electrons. One method, introduced by Schulz\textsuperscript{17} and usually denoted the "trapped-electron" method, involves the use of an incident electron beam of variable kinetic energy $E$ and the detection of only those electrons which have lost nearly all of their kinetic energy through single collisions with the target particles. If $W$ is a particular molecular excitation threshold, then a scattered signal is obtained for $E \approx W$. This signal, which contains contributions from electrons scattered at all angles, is proportional to the total excitation cross section in the vicinity of the excitation threshold. Since total cross sections for optically-forbidden transitions are usually larger near threshold than those for allowed ones,\textsuperscript{17} the "threshold excitation spectra" obtained by this method are often dominated by spin- and symmetry-forbidden transitions.

This method has been applied to several systems by Schulz\textsuperscript{18} and Bowman and Miller.\textsuperscript{19} Recently, relatively high resolution data have been ob-
tained by Brongersma and Oosterhoff,\textsuperscript{20} and Dowell and Sharp.\textsuperscript{21} However, the possibility of negative ion formation and the uncertainties in energy scale calibration and threshold behavior complicate the identification of the excited state.

An interesting variation of the threshold excitation method utilizes the fact that certain electron attachment or dissociative attachment reactions have sharply peaked cross sections at zero incident electron energy. Each electron that has lost almost all of its energy to excitation of a molecule produces a negative ion which can be detected by means of mass spectrometry\textsuperscript{22} or ion cyclotron resonance techniques.\textsuperscript{23}

The other electron scattering method involves the use of an incident electron beam of fixed (or variable) energy and the detection of electrons which have been scattered by single collisions with the target in a particular $\theta$, $\phi$ direction (or range of angles) after undergoing a particular energy loss ($W$). Although it has been recognized for some time that the angular dependence of the scattered electron intensity for a particular energy loss is sensitive to the nature of the transition giving rise to it,\textsuperscript{4,24} very little data have yet been obtained about these distributions. Most of the experiments have been performed at fixed angles (or a fixed range of angles), usually near 0 or 90$^\circ$.

Lassettre and co-workers\textsuperscript{25} were among the pioneers in the field of electron-impact spectrometry. The bulk of their work has been on relatively small molecules with incident electron energies above 200 eV and scattering angles below about 20$^\circ$. The results of their early work generally agreed with optical absorption measurements and indicated the validity of the Born approximation at low scattering angles and high incident energies. Later, they extended their studies to lower impact energies and observed many optically-allowed and several symmetry-forbidden (quadrupole allowed) transitions.\textsuperscript{26,31} At lower incident energies (30 to 60 eV) Skerbele, Dillon, and Lassettre\textsuperscript{29,30} have resolved several singlet $\rightarrow$ triplet transitions in both N$_2$ and CO. However, they pointed out that in a survey of 16 additional polyatomic molecules at incident energies as low as 35 eV, they failed to observe any singlet $\rightarrow$ triplet transitions.\textsuperscript{29,30} The results of high angle experiments\textsuperscript{32-34,56} indicate that the restriction of their observations to small scattering angles was probably responsible for this failure. More recently, Lassettre and co-workers published high-resolution electronic\textsuperscript{35} and pure vibrational\textsuperscript{56} excitation spectra of many molecules at impact energies between 33 and 100 eV and scattering angles up to 16$^\circ$.

Several years ago, Simpson\textsuperscript{37} constructed a high resolution, $\theta = 0^\circ$, electron-impact spectrometer. This instrument and a later version\textsuperscript{38} (with variable angle) provided the basis for the design of our spectrometer. The
work of Simpson and co-workers with the $0^\circ$ instrument has been confined to impact energies below 100 eV. Although their early investigations of He, H$_2$, and C$_2$H$_4$ did not reveal any singlet → triplet transitions at impact energies as low as 30 eV, improvements in the apparatus led to the detection of several such transitions in He, N$_2$, and H$_2$.

Recently their variable angle instrument was used to measure the scattered electron distribution ($\theta < 20^\circ$) for three excitations in He at impact energies of 100 to 400 eV. A large part of their work is presently directed toward the study of resonance phenomena and instrument design.

Kuppermann and Raff obtained energy-loss spectra for He, Ar, H$_2$, and C$_2$H$_4$ with impact energies on the order of 50 eV and an instrument geometry which collected electrons scattered in the range $22^\circ < \theta < 112^\circ$ (with $90^\circ$ favored). Under these conditions, singlet → triplet transitions were prominent features in the reported spectra. They were the first to detect triplet states by energy analysis of the scattered electrons. Recently Wei and Kuppermann have improved this machine and extended the list of molecules studied with it.

Doering and Williams have investigated the $90^\circ$ scattering of low-energy electrons by He, N$_2$, C$_2$H$_4$, and C$_6$H$_6$ and observed several spin-forbidden transitions.

Recently Ehrhardt and co-workers have put into operation an elegant electron-impact spectrometer in which the target is a molecular beam. This instrument has been used primarily for the study of resonances although the angular distribution (7 to 110$^\circ$) of electrons causing the $1^1S \rightarrow 2^3S$ transition in helium and the vibrational excitation of H$_2$ have been measured in nonresonant regions. In the field of electron impact ionization, their experiments on simultaneous detection of both electrons and their energy and angular correlations represent a unique effort.

Finally, the $\theta = 0^\circ$ energy-loss spectra of H$_2$, N$_2$, and C$_2$H$_4$ have been obtained at very high incident energies ($\sim 33$ keV) with very good resolution ($\sim 0.03$ eV) by Geiger and co-workers. Under these conditions (high energy, low angle), the Born approximation seems quite reliable and, as expected, these spectra are nearly identical with uv absorption spectra.

### III. EXPERIMENTAL

A short description of the electron-impact spectrometer used by us will serve as an example to illustrate the requisite experimental apparatus and procedures. More details are available elsewhere. Figure 1 shows a
schematic diagram of the apparatus which is basically the same type as the one discussed by Simpson\textsuperscript{37} and Kuyatt and Simpson\textsuperscript{38}. It consists of an electron gun, a scattering chamber, two hemispherical electrostatic analyzers (for generating a monochromatic electron beam and analyzing the energy of the scattered electrons), and a detector. The resolution of each of the two electrostatic analyzers is variable from 0.030 to 0.300 eV by appropriately adjusting the sphere potentials. The scattering chamber is a welded-bellows cylinder which allows a variation in scattering angle from $-30$ to $+90^\circ$. The convolutions of the bellows have an "S" shape and form an electron trap that reduces the effect of wall scattering which could seriously interfere with measurements at high angles. The scattering chamber sample pressure is normally in the $10^{-5}$ to $10^{-2}$ Torr region. The detector is a 20-stage electron multiplier coupled to a count rate meter or to a 1024-channel scalar system (Nuclear Data 181). An energy-selected electron beam with the required impact energy is introduced into the scattering chamber. Electrons that have lost a specific amount of energy and have undergone scattering by a specific angle are passed by the analyzer and

\hspace{1cm}

Fig. 1. Schematic diagram of the electron-impact spectrometer.
are detected. (The solid angle of collection is about $10^{-3}$ sr.) An analog signal $V_2$ (see Figure 1) generated by the scalar and synchronized with the memory advance is utilized to determine the energy loss of the electrons that will pass through the analyzer to the detector. A plot of the scattered signal intensity as a function of the sweep voltage (at a fixed scattering angle and electron-impact energy) represents an energy-loss spectrum. $V_2$ can also be used for sweeping the electron-impact energy (at a fixed scattering angle and energy loss) for the purpose of studying the energy dependence of a particular differential cross section. The sweeps can be repeated automatically until an acceptable signal-to-noise ratio is achieved.

This apparatus was designed for relative cross section measurements and is particularly suited for studying the variation of DCS with scattering angle and impact energy.

A schematic diagram of the scattering geometry is shown in Figure 2.

![Schematic diagram of the scattering geometry](image)

Fig. 2. Schematic diagram of the incident and scattered beam configuration at a scattering angle of $\theta \sim 45^\circ$. $V(\theta)$ is the volume in which single scattering events must occur if they are to be detected.

The scattered electron signal $I_p$ that is measured in the laboratory can be related to the DCS by the following equation:

$$I_p(E_2, \theta) \simeq \frac{I_0 L(\theta)}{kT} \Delta \Omega \rho \exp(-P/P_0) \epsilon(E_2) \frac{S(E, E_2, \theta)}{S(E, E_2, \theta)}$$  \hspace{1cm} (3)
with

\[ \Delta \Omega = \int_\Omega d\Omega \text{ (the acceptance solid angle)}, \]

\[ S(E, E_2, \theta) = \frac{1}{(\pi \Lambda)^{1/2}} \int_W \sigma(E, W, \theta) \exp \left[ -\frac{(E_2 - W)^2}{\Lambda^2} \right] dW, \]

and

\[ P_0 = kT[\bar{Q}(E)L_1 + \bar{Q}(E - E_2)L_2]. \]

Here \( I_0 \) is the total beam intensity entering the scattering chamber, \( L(\theta) \) is the "effective scattering path length" (see below), \( k \) is the Boltzmann constant, \( T \) is the absolute temperature of the target gas, \( P \) is its pressure, \( \sigma(E_2) \) is the overall efficiency of the apparatus for detecting electrons which after a collision have energy \( E - W \), \( E \) is the electron-impact energy; \( E_2 = |e|V_2 \), \( \Lambda \) is related to the analyzer resolution, \( \bar{Q}(E) \) is the average total scattering cross section, and \( \sigma(E, W, \theta) \) is the DCS. Phenomenologically, \( P_0 \) is the pressure (for a given apparatus, incident energy, and scattering angle) for which the mean free path of an electron in the scattering chamber is equal to the length of that chamber.

There are several requirements one has to satisfy in order to be able to relate the signals measured at different angles, impact energies, and energy losses to the appropriate differential cross sections. Kuyatt has reviewed several quantitative aspects of the measurement of electron scattering from a static gas target. Three especially pertinent considerations are discussed below.

A. Pressure Dependence

It has been pointed out that double scattering events may cause serious errors in the measurement of DCS. This problem seems most severe for inelastic processes measured at large scattering angles and high incident energies. However, the demonstration that the pressure dependence indicated by Eq. (3) holds at every angle, for all incident energies, and for every process investigated is sufficient to insure that only single scattering events are contributing to the measured signal. Although such a complete study is indeed sufficient, it may not be necessary. It seems more "economical" to determine the particular experimental conditions for which double scattering would have the highest probability and then demonstrate that Eq. (3) holds in this case.

The principal contribution to double scattering usually comes from large-angle elastic scattering in or near the scattering volume \( V(\theta) \) pre-
ceded, or followed, by small-angle inelastic scattering along the view cone. In particular, the current \( I_2 \) due to electrons which have scattered twice compared to that \( I_1 \) due to electrons which have scattered once varies approximately as:

\[
\frac{I_2(\theta)}{I_1(\theta)} \approx \rho l_{\text{eff}} \frac{\sigma(E, 0, \theta')\sigma(E, W, \theta - \theta')}{\sigma(E, W, \theta)}
\]

(4)

where \( \rho \) is the density of the target molecules, \( \sigma(E, W, \theta) \) is the differential cross section for the particular inelastic process being considered, \( \sigma(E, 0, \theta) \) is that for the elastic one, and \( l_{\text{eff}} \) is an "average" scattering path length on the order of 5.7 cm (see Figure 2). \( \langle \sigma(E, 0, \theta')\sigma(E, W, \theta - \theta') \rangle_{\theta'} \) is the product of DCS averaged over all possible combinations of scattering angles for the two events which would be detected as if from a single scattering event occurring within \( V(\theta) \) at an angle \( \theta \).

At incident energies high enough for the Born approximation to be valid \( \sigma(E, W, \theta) \) is much more sharply peaked forward than is \( \sigma(E, 0, \theta) \). The principal contribution to the average in (4) will come from terms in which \( \theta - \theta' \approx 0 \). Then

\[
\frac{I_2(\theta)}{I_1(\theta)} \approx \rho l_{\text{eff}} \frac{\sigma(E, 0, \theta)\sigma(E, W, 0)}{\sigma(E, W, \theta)}
\]

(5)

and double scattering becomes increasingly more important at higher scattering angles. The situation is not so clear for impact energies below about 50 eV. Inelastic processes, though certainly less intense, do not seem to decrease much more rapidly with angle than the elastic one. For example, the ratio of elastic to inelastic (\( \tilde{X} ^1\Sigma_g^+ \rightarrow \tilde{C} ^1\Pi_u \)) scattering in acetylene was found to be constant from 40 to 80° at an impact energy of 35 eV.\(^56\) In addition, spin-exchange inelastic processes are often nearly isotropic, and hence the ratio of elastic to inelastic scattering is actually largest at small angles.

For cases in which the elastic/inelastic ratio is nearly constant with angle, the value of the cross section product in (4) will be the same at both high and low \( \theta' \). If it is assumed that the principal contribution to the product is for \( \theta' \approx 0 \),

\[
I_2(\theta)/I_1(\theta) \sim \rho l_{\text{eff}}\sigma(E, 0, 0).
\]

(6)

Equation (6) implies, as expected, that double scattering will be least important in those instances for which the forward elastic DCS is lowest, regardless of the magnitude of the inelastic DCS. It also indicates that the effect is independent of angle.
Finally, there is the case of spin-exchange excitations in which \( \sigma(E, W, \theta) \) can be assumed to be independent of angle but \( \sigma(E, 0, \theta) \) is still forward peaked. The result (6) is also obtained under these conditions.

In conclusion, it seems that the relative effect of double scattering will not be highly angular dependent for low (<50 eV) incident energies. Thus, checking relation (3) as a function of pressure at one high and one low angle for the most sharply forward peaked cross section should be sufficient. Parenthetically, Doering\(^{33}\) did not observe double scattering effects at 90° scattering angles and 0.05 Torr sample pressures for low incident energies (of the order of 10–30 eV) while Chamberlain and co-workers\(^{54}\) found such effects to be quite prominent at higher energies.

**B. Effective Path Length Correction**

It is apparent from Figure 2 that the scattering volume is a function of the scattering angle, and further that the solid angle of acceptance \( \Delta \Omega \) is not constant over the length of the collision volume (it is a maximum at the volume center and vanishes at the ends). Therefore intensity measurements carried out at different scattering angles cannot be directly compared to each other. The matter is further complicated by the fact that the electron density of the incoming beam is not uniform.

The effective path length correction can be made by multiplying the signal at each angle by \( \sin \theta \), provided that \( \theta \) is much larger than the beam divergence angle. Otherwise a more accurate correction procedure has to be applied. Trajmar and co-workers\(^{57}\) considered the incoming electron beam to be a cone with a Gaussian electron density distribution having its maximum along the cone axis. Two apertures at the exit of the scattering chamber define the view cone (Figure 2). Scattered electrons can reach the detector from the volume defined by the intersection of the two cones. The volume elements were weighed for electron density, and the solid angle subtended at the exit apertures and integrated within the limits defined by the intersecting cone surfaces. The measured intensities at each angle were then divided by the value of this integral to obtain a differential cross section on an arbitrary scale.

**C. Energy Independent Electron Optics**

Spectral features of the spectrum corresponding to different energy losses (and therefore to different molecular excitations) and spectra obtained at different impact energies can be related to each other only if the efficiency of the spectrometer is a known function of energy. Due to the extreme difficulty in actually measuring such a dependence, it is a practical necessity that the efficiency be independent of energy-loss (for a fixed
impact energy) or impact energy (for a fixed energy loss). By the proper
design of electron optics, such a situation can obtain over a fairly wide
energy range.

The cross sections in most experiments are obtained in arbitrary units.
Only very few absolute measurements are available and they are almost
exclusively total cross sections. There are several routes one can follow to
obtain absolute DCS. The straightforward way of accurately measuring all
the quantities required to normalize the cross section (beam current,
scattered current, pressure, scattering geometry, and instrument efficiency)
is very difficult. Another approach is to calculate or measure a particular
absolute DCS for some gas and then utilize this to calibrate cross sections
in other samples by mixing the two. This method requires knowledge of the
partial pressures of the constituents under flow conditions. If absolute
total cross sections are available (e.g., from excitation functions), a third
way to calibrate the DCS measured in arbitrary units is to integrate it over
0 and $\varphi$ and normalize the integral to the known total cross section. To do
this one needs DCS up to $180^\circ$ or a reliable extrapolation beyond the angular
range actually covered.\textsuperscript{44} Several attempts are under way to measure
absolute DCS directly.\textsuperscript{58,59} In our laboratory, a simple scattering appara-
tus is being assembled which will allow the measurement of the total
scattered signal at 40 and $80^\circ$ (without energy resolution) as well as the
pressure, temperature, scattering geometry, and efficiency. The incoming
electron beam will be energy selected. The information obtained by these
measurements combined with spectra obtained by the high-resolution
spectrometer will make it possible to normalize all cross sections to an
absolute scale.

IV. ELECTRONIC EXCITATION

The excitation of atomic and molecular electronic states by electron
impact and the concomitant measurement of the energy loss and direction
of the scattered electron can provide information about optically-forbidden
states that may not be available from any other method. In particular, a
measurement of the energy loss determines the energy of the excited state
and, in principle, the corresponding differential excitation cross section
contains the information needed to characterize the electronic state of the
target. For impact energies within a few electron volts of an excitation
threshold, the DCS are often dominated by resonance scattering.\textsuperscript{9,10}
Potential scattering by both direct and electron exchange mechanisms
becomes increasingly more important at higher energies and predominates
in the region (5–50 eV above threshold) to be discussed below. At still
higher impact energies (\(\gtrsim 100\) eV), exchange excitation becomes negligible.
The effective use of the DCS measurements in this intermediate energy range is hampered by the lack of adequate theoretical calculations. There are as yet no precise ab initio calculations for even the simplest system of an electron + H atom, and the first-order, high-energy Born and Born-Oppenheimer approximations and their many modifications do not yield reliable results when applied at these intermediate energies.

Nevertheless, the primary difference between the angular distribution of electrons scattered after causing an optically spin-allowed transition and that due to electrons which cause a spin-forbidden one can be explained by applying the method of partial waves. This method involves the expansion of the total wave function in radial functions times spherical harmonics. If the possibility of exchange excitation is included, the desired radial functions are solutions of an infinite set of coupled integrodifferential equations.

A more fruitful qualitative approach (though certainly less rigorous) is to treat the electron plus target scattering as if it were due to an effective central field potential. The differences between the direct excitation mechanism, leading to optically allowed transitions, and the exchange one, leading to spin-forbidden transitions, are then included through the use of effective potentials of different ranges. To see that these interactions are indeed quite different, consider the following example. In a three-electron system, the "potential" leading to direct excitation is in some sense proportional to the electronic matrix element

\[ V_D(r_1) \propto \int \phi_n^*(r_2, r_3) \frac{1}{r_{12}} \phi_0(r_2, r_3) \, dr_2 \, dr_3 \quad (7) \]

while that for exchange is

\[ V_{EX}(r_1) \propto \int \phi_n^*(r_1, r_2) \frac{1}{r_{12}} \phi_0(r_2, r_3) \, dr_2 \, dr_3. \quad (8) \]

\( r_3, r_2, \) and \( r_1 \) are the respective coordinates of the two initially bound electrons and the incoming one. \( \phi_n \) and \( \phi_0 \) are the final and initial bound state spatial wavefunctions, respectively, of the target, \( r_{12} = |r_1 - r_2| \). \( 1/r_{12} \) can be expanded as

\[ \frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_2^l}{r_1^{l+1}} P_l(\cos \theta_{12}) \quad \text{for} \quad r_1 > r_2. \quad (9) \]

The \( P_l(\cos \theta_{12}) \) are Legendre polynomials and \( \cos \theta_{12} = r_1 \cdot r_2/r_1 r_2 \). Substitution of (9) into (7) and (8) yields the asymptotic behaviors

\[ V_D(r_1) = \frac{\varphi_1}{(r_1 r_2 r_3)^{1/2}} \int \frac{\phi_n^*(r_2, r_3) \phi_0(r_2, r_3)}{r_2} dr_2 dr_3 + \left[ \frac{1}{r_1^3} \right] \quad (10) \]
and

\[ V_{EX}(r_1) = \frac{1}{r_1} \int \phi_n^*(r_1, r_2) \phi_0(r_2, r_3) \, dr_2 \, dr_3 \]

\[ + \frac{\hat{r}_1}{r_1} \cdot \int \phi_n^*(r_1, r_2) \phi_0(r_2, r_3) \, dr_2 \, dr_3 + 0 \left[ \frac{1}{r_{10}^3} \right] \]  (11)

respectively, where \( \hat{r}_1 \) is a unit vector in the \( r_1 \) direction. However,

\( \phi_n^*(r_1, r_2) \phi_0(r_2, r_3) \) \[ r_{10}^m \exp (-\alpha_n r_{10}) \chi^*(r_2; \theta_1, \phi_1) \]  (12)

since \( r_1 \) is the coordinate of a bound electron in the excited state. Substitution of (12) into (11) yields

\[ V_{EX}(r_1) = \frac{1}{r_1} \int \chi^*(r_2; \theta_1, \phi_1) \phi_0(r_2, r_3) \, dr_2 \, dr_3 \]

\[ + 0[r_{10}^{m-2} \exp (-\alpha_n r_{10})]. \]  (13)

As a result \( V_{EX}(r_1) \) is of much shorter range than \( V_D(r_1) \) since the former decays exponentially while the latter decreases only as \( 1/r_{10}^2 \). Thus if we apply the partial wave method rigorously to the problem of elastic scattering from a central potential, the angular dependence of the direct and exchange differential cross sections can be qualitatively explained in terms of the different effective ranges of the direct and exchange "potentials."

The well-known result for the differential cross section in the partial wave expansion representation is \( \sigma(k, \theta) = \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l + 1)[\exp (2i\eta_l) - 1]P_l(\cos \theta) \right|^2. \)  (14)

\( k \) is the wave number of the incoming electron and \( \eta_l \) is the phase shift for the \( l \)th partial wave. If \( \eta_l \) is small, then it can be shown \( ^3b \) that

\[ \eta_l \approx -\frac{\pi}{2} \int_0^{\infty} U(r) [J_{l+1/2}(kr)]^2 r \, dr \]  (15)

where \( U(r) \) is the electron–molecule interaction potential and \( J_{l+1/2} \) is a Bessel function.

Suppose that \( r^2 U(r) \) has an effective range \( r_{\text{max}} \) and that within that range it never exceeds some finite value, i.e.,

\[ r^2 |U(r)| \leq a \quad 0 < r < r_{\text{max}} \]

\[ = 0 \quad r_{\text{max}} < r \]  (16)
If the impact energy is low enough so that \( kr_{\text{max}}/2 \ll 1 \), then the small argument form of \( J_{l+1/2} \) can be used in (15), the result being

\[
|\eta_l| \lesssim \frac{\pi}{2} \frac{a}{[\Gamma(l + \frac{1}{2})]^2} \int_0^{r_{\text{max}}} \left( \frac{kr}{2} \right)^{2l+1} \frac{dr}{r} \\
= \frac{2\pi a}{(2l + 1)^3} \left( \frac{kr_{\text{max}}}{2} \right)^{2l+1} \frac{1}{[\Gamma(l + \frac{1}{2})]^2}
\]

(17)

If \( \eta_l \) is small then (14) implies that

\[
\sigma(k, \theta) \approx \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l + 1)\eta_l P_l(\cos \theta) \right|^2.
\]

(18)

Each term in the expansion is called a "partial wave" and is often designated as an \( s, p, d, \) etc., wave depending on whether \( l = 0, 1, 2, \) etc.

Since the range of the interaction leading to excitation via a direct mechanism is much larger than that leading to excitation via exchange, many more \( \eta_l \)'s contribute to the DCS (18) in the former case, due to the \( r_{\text{max}} \) term in (17). From the nature of Legendre polynomials, the more of them which are included in (18), the more sharply peaked toward \( \theta = 0^\circ \) can be the differential cross section. Thus, we expect the angular distribution of electrons scattered after causing direct excitations to be relatively more forward peaked than that of electrons causing excitations via an exchange mechanism. Indeed, this has been found to be the case as shown below. Notice also that if \( k \) is lowered (lower impact energy), fewer \( \eta_l \)'s are required and both direct and exchange cross sections should become more isotropic. This also is observed experimentally.

**A. Helium**

The electron-impact excitation of helium has been the subject of a great many experimental and theoretical investigations.\(^{53,54}\) However, relatively few of these dealt specifically with the angular dependencies of inelastic DCS. Measurements at fixed scattering angles near 0°\(^{25}\),\(^{39,41}\) and 90°\(^{32,33}\) over a wide range of incident electron energies disclosed significant differences in the relative DCS for optically-allowed and -forbidden transitions. It was generally found that the ratios of DCS for forbidden transitions to those for allowed ones were greater for lower impact energies at a fixed scattering angle and for larger scattering angles at a fixed incident energy. Although the basis for this behavior is qualitatively well understood, no theoretical calculations have yet proved completely reliable in predicting the shape of the various inelastic DCS below about 100 eV (nor above this...