Theory of alignment and orientation in beam-foil experiments

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The preferential population of magnetic quantum levels of atomic states produced in beam-foil collisions is explained using a density-matrix formulation. The density matrix for the beam in the interior of the foil is evolved in time to obtain the density matrix after emergence from the foil. The dependence upon tilt angle of the foil relative to the beam is calculated. The Stokes parameters of the light emitted by decay of the atomic state are given in terms of the density matrix. Formulas which are valid for arbitrary angular momentum of the atomic state are derived. Comparison with experiment shows good agreement with data.

I. INTRODUCTION

The purpose of this paper is to describe alignment and orientation effects in atomic beam-foil collisions within the density-matrix formalism.[1] After passage of a beam of atoms through a thin foil, there is a distribution of the atoms in excited states with a given angular momentum quantum number l, magnetic quantum numbers m and an additional quantum number label $\{n\}$ describing the excited states. If there is a preferential probability for the population of given magnetic quantum states of this l manifold, a net alignment or orientation of this manifold exists. If this l state decays radiatively to lower energy states, the radiation is polarized as a result of this preferential population of the magnetic sublevels. By studying the polarization we obtain information concerning the preferential population of these states. Experimentally, the quantities that are measured are the intensity I of the light in a given viewing solid angle, and the quantities S/I, C/I, and M/I, where S, C, and M are the Stokes parameters of the emitted light.[2] These experimentally measured parameters are related to the expectation value of angular momentum operators over the l state manifold of the excited state.

In experiments the angle of incidence relative to the foil normal, α, is changed by rotating the foil (see Fig. 1). S/I, C/I, M/I, and I then become functions of α. The variation of these parameters with tilt angle indicates that surface effects are important, for it is only through the presence of the surface that the tilt angle is defined. The interior of an amorphous foil remains unaffected on the average by rotating the foil. Varying the incident velocity of the beam particles yields a velocity dependence of these quantities. There can also be a dependence on the properties of the foil. Furthermore, it is clear that these parameters are dependent upon the excited-state manifold as well as the states to which this manifold decays by radiative processes. A complete theory must explain all of these dependences. Our aim will be to describe only those features understandable from symmetry considerations and the general nature of beam-foil interactions.

We employ the density-matrix formulation of quantum mechanics because it is particularly suited for describing these beam-foil collisions. The description in terms of ordinary quantum mechanics necessitates calculating transition amplitudes for all the processes resulting in the formation of states in the l-state manifold of interest. These transition matrix elements must be calculated for every initial state of the foil, every final state of the foil, and every momentum transfer vector to the incident beam particles, and then the averaging over initial states and summing over final states must be done. For this kind of problem, the benefit of using the Liouville representation of quantum mechanics, in which the density matrix rather than the wave function plays the central role, has been amply stressed in the literature. Within this approach, the separation of the dynamical and geometrical (e.g., symmetry-related) aspects of the problem of alignment and orientation is most easily accomplished. With the ordinary quantum-mechanics approach, such a separation is very difficult for this type of process, because the symmetry exists only after averaging and summing over the initial and final states.

In Sec. II we construct and evolve the density matrix for the beam of particles as it travels through the foil, reaches the region near the rear surface of the foil, and emerges from the foil. The density matrix and the evolution operators will be described in terms of their decompositions into irreducible representations of the rotation group. The assumptions and methods of previous treatments are compared with ours. In Sec. III, the expressions for the Stokes parameters in terms of the expectation values of angular momentum operators are constructed for dipole radi-

ation, details being presented in Appendix A. Explicit formulas for any excited l-state manifold are derived. In Sec. IV the evaluation of the relevant expectation values is carried out with the angular momentum algebra presented in Appendix B. Section V contains a comparison with experimental data.

In this treatment we assume the most general form for the density matrix of an $\{n\}$-state manifold at the second surface of the foil that is invariant with respect to rotations about the beam axis and with respect to reflections in any plane containing the beam axis. This initial density matrix is independent of α. Furthermore, we assume that the evolution of the density matrix from the surface to far away from the surface can be characterized by an interaction potential with the foil through which the atom must pass, and this potential is invariant with respect to the translations parallel to the foil surface. The evolution operator is a function of α. We carry through the analysis of the evolution operator to second order in the interaction and form the evolved density matrix.

Previous treatments[1,3-5] differ from the treatment presented here in both the assumptions for the initial density matrix ρ_0 and the determination of the evolution operator. Their description of the initial state is incomplete [see Eq. (1′)], and the evaluation of the evolution operator was carried through assuming that the atom experiences a time-independent field. Also, the analysis in these references was restricted to the case of radiation from a p-state manifold to an s-state manifold. Reference 5 employs a semiphenomenological approach whose validity seems questionable. The analysis of this reference implies that the density matrix for the electronic degrees of freedom depends in an unrealistic way upon where the atom intersected the foil and validity of the approach depends upon the unimportance of multiple collisions within the foil.

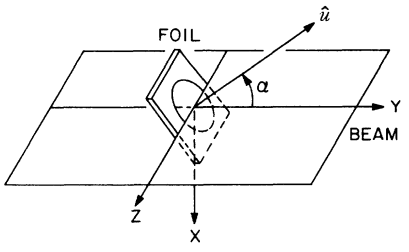

FIG. 1. Beam-foil geometry and coordinate axes. The foil normal u is tilted at an angle α to the beam axis y. Light may be viewed along the z axis.

II. DENSITY MATRIX

The density matrix for the system is composed of the tensor product of density matrices for the heavy-particle motion, the density matrix describing the "active" electron about the heavy particle that finally manifests itself as an excited electron which changes state and thereby emits light, and the density matrix for the remainder of the foil variables. The energy of the entering particle is large compared with its energy loss during the passage through the macroscopically thin foil. Furthermore, we may view the heavy-particle motion as classical.

We shall construct the form of the density matrix (for the "active" electron) within the foil just before the particle enters the region close to the rear surface of the foil. The encounter with the front surface has long been forgotten because of the multiple interactions within the foil, which modifies the density matrix to its value in the interior of the foil. The density matrix can be written as a sum of terms each of which transforms as an irreducible tensor under rotations. Within the interior of the foil the density matrix is axially symmetric about the incident particle direction. In addition to this symmetry, there is symmetry under reflections in any plane containing the axial symmetry axis. These conditions are enough to determine that the density matrix within a given l_i-state manifold is of the form

$$\rho(l_i, l_i) = T_0^{[0]y} + T_0^{[2]y} + T_0^{[4]y} + \cdots = \sum_{k=0}^{l_i} T_{q=0}^{[2k]y}, \tag{1}$$

where $[2k]$ is the rank of the irreducible tensors and q is the component of q along the incident particle direction (the y axis of Fig. 1). Only $q=0$ terms appear in ρ, because the state is axially symmetric around the y axis. The odd-k terms cannot be present because of the symmetry under reflections in any plane containing the y axis. This is the form taken for the initial density matrix in Refs. 1, 3, and 5. More generally, it is possible to have correlations in the density matrix between different angular momentum manifolds. That is, we can have terms in the density matrix of the form

$$\rho_q^{[k]y}(l, l') = a_{(l,l')}^{[k]} \sum_{m,m'} (-1)^{l-m} \begin{pmatrix} l & l' & k \\ -m & m' & q \end{pmatrix} \times |lm)(l'm'|,$$

with different values of l and l'. Because of the axial symmetry we must still have $q=0$, and the

symmetry under reflection in a plane limits the k values such that $l+l'+k$ equals an *even* integer. Thus for $l=1$, $l'=0$, k can take on odd-integer values. Thus including these correlation terms we have

$$\rho=\sum_{l,l'}\sum_{k=0}^{l+l'}{}'T_0^{[k]\nu}(l,l')\,, \tag{1'}$$

where the prime on the sum indicates that $[k]$ is restricted by the above condition. The Hermiticity of ρ determines that $T_0^{[k]}(l,l')=T_0^{[k]\dagger}(l',l)$. Some of these off-diagonal terms in l,l' are contained in the initial density matrix of Ref. 4, but the complete description as presented here was not attempted.

It should be noted that the details of the wave functions of the electrons in the cloud about the particle when it is within the foil are very complicated. Certainly the eigenstates of the electrons about the particle are nothing like the electronic eigenstates about the atom in free space. However, these details do not affect our ability to determine which irreducible tensor components may be present in ρ, this being determined solely from geometrical considerations.

Inside the foil we can think of the density matrix as having reached the quasiequilibrium state of Eq. (1'), $d\rho/dt\approx 0$. Upon reaching the surface the density matrix is therefore given by Eq. (1'). It must now be evolved through the region near the rear surface. Electrons in the region of the surface experience a potential which is quite large,[6] of the order of the Fermi energy plus work function of the foil. This potential modifies the density matrix as the particle passes through the surface region. The detailed character of this surface potential is not particularly relevant for the discussion that follows. All that we really need know about this potential is that to a good approximation it is a function only of the distance of the electron from the surface. Let us define the coordinate vector from the laboratory frame to the center of the mass of the particle by $\vec{\mathrm{R}}$, and the coordinate vector to the electron from the c.m. of the particle by $\vec{\mathrm{r}}$. The surface potential is then given by $V((\vec{\mathrm{R}}+\vec{\mathrm{r}})\cdot\hat{u})$, where $\hat{u}$ is the unit vector normal to the foil surface. All that we need know about the surface potential is that it is a function of the indicated variable (the distance of the electron from the surface of the foil) and that it approaches a constant value inside the foil and a constant value (taken to be zero) at a very small distance beyond the surface (less than 20 Å).[6] This is true except for a (relatively very weak) longer-range residual induced image dipole interaction. We calculate the evolution of the density matrix from the time that the particle reaches the surface until it passes through the surface region. Let us define the origin of time by when the particle reaches the surface. The density matrix at a time t when the particle is outside of the surface interaction region is given by

$$\rho_t=U(t,0)\rho_0U^\dagger(t,0)\,, \tag{2}$$

where ρ_0 is given by Eq. (1') and

$$U(t,0)=T\exp\left(-i\int_0^t V_I(t')\,dt'\right), \tag{3}$$

where the subscript I denotes the interaction representation. We can write $V(t)$ more explicitly as

$$V(t)=V_0'[\theta(\vec{\mathrm{R}}(t)\cdot\hat{u})-\theta((\vec{\mathrm{R}}(t)+\vec{\mathrm{r}})\cdot\hat{u})]\,, \tag{4}$$

with V_0' of the order of the Fermi energy plus the work function and where the first term in Eq. (4) is a c-number term which does not affect the electron distribution and is included for convenience (it is not a function of $\vec{\mathrm{r}}$). The function $\theta(d)$ approaches zero for $d>20$ Å. The details of its structure are unimportant. Since the heavy-particle motion is perturbed only slightly, we can evaluate the integral in Eq. (3) by substituting $\vec{\mathrm{R}}(t)=\vec{v}t$ and obtain the following α dependence of U:

$$U\propto 1-i\frac{V_0}{v\cos\alpha}\vec{\mathrm{r}}\cdot\hat{u}-\frac{A}{2}\left(\frac{V_0}{v\cos\alpha}\right)^2(\vec{\mathrm{r}}\cdot\hat{u})^2 + O((V_0\vec{\mathrm{r}}\cdot\hat{u}/v\cos\alpha)^3)\,, \tag{5}$$

where v is the velocity of the particle. For $\theta(d)$ taken as $1-\Theta(d)$, with $\Theta(d)$ denoting the step function, and for experimental velocities such that the penetration time through the surface potential is small compared with the inverse of frequency differences within the $\{n\}$ manifold, so that $V_I(t')$ in Eq. (3) can be replaced by $V(t)$, the coefficients $A=1$ and $V_0=V_0'$. In general V_0 and A will depend upon the eigenvalues of the Hamiltonian for the free atom. Coefficients of the higher-order terms can also be evaluated, given an explicit function θ. The quantity $\vec{\mathrm{r}}\cdot\hat{u}$ transforms under rotation as $T_0^{[1]u}$, where u indicates the axis of symmetry. Under inversions $\vec{\mathrm{r}}\cdot\hat{u}$ is transformed to $-\vec{\mathrm{r}}\cdot\hat{u}$; $\vec{\mathrm{r}}$ is an odd-parity operator. As we shall see, this will have implications with regard to the possible vanishing of certain terms in the traces of observable operators multiplied by the density matrix. For small values of $(V_0/(\hbar)v)\langle r\rangle$, where $\langle r\rangle$ is some average expectation value, higher-order terms become less important.

The evolution of the density matrix to t includes the effects of the residual electrostatic interaction V^R which the electron feels owing to the image dipole field.[1,3,4] This field is also directed along the foil normal. It too is capable of inducing phase

changes in and transitions into and out of the l-state manifold of interest. As with θ, because of the symmetry of the interaction, the amplitude and phase changes of the magnetic sublevels along the $\hat{u}$ axis owing to this field are equal for states with the same value of $|m_u|$. The form of $U(t,0)$, when taken in a basis representation $|\{n_i\}l_i m_j\rangle$, with m_j quantized along the z axis, is given by

$$\langle l_1 m_1 | U(t,0) | l_2 m_2 \rangle = \sum_\sigma D^{[l_1]}_{m_1\sigma}(\alpha',\beta',\gamma') \times \exp[i\omega_{|\sigma|}(l_1,l_2)] D^{*[l_2]}_{m_2\sigma}(\alpha',\beta',\gamma'), \quad (6)$$

where α', β', and γ' are Euler angles for a rotation of z to $\hat{u}$; $\omega_{|\sigma|}(l_1,l_2)$ are the complex numbers giving the amplitude and phase factors for states with given σ magnetic quantum number along the u axis,

$$\exp[i\omega_{|\sigma|}(l_1,l_2] = \langle l_1\sigma | T \exp\left(-i\int_0^t V_I(t')\,dt'\right) | l_2\sigma\rangle . \quad (7)$$

There is an α dependence in $\omega_{|\sigma|}(l_1,l_2)$. If the surface potential were constant, so that in the rest frame of the atom the potential were time independent, the dependence of $\omega_{|\sigma|}(l_1,l_2)$ would be $1/\cos\alpha$. However, this α dependence is not simply $1/\cos\alpha$, as was previously assumed in Refs. 1, 3, and 4. The α dependence of $\omega_{|\sigma|}(l_1,l_2)$ is in general more complicated. Thus the calculation of the α dependence of the evolution operator in our treatment is different from previous treatments.

If we take t large enough, it is clear that $U(\infty,t)$ tends to the unit operator, since $\omega^{(\infty,t)}_{|\sigma|}(l_1,l_2)$ tends to $\delta_{l_1,l_2}\epsilon^{l_1}_{|\sigma|}$, with $\epsilon^{l_1}_{|\sigma|}$ infinitesimally small, and the effects of the residual field are then included in $U(t,0)$. In what follows, we shall choose t large enough for this to be the case. The first order Stark effects owing to the residual field are then included in the term proportional to $V_0/v\cos\alpha$, a second-order effect in the $(V_0/v\cos\alpha)^2$ term, etc. For α very near $\frac{1}{2}\pi$ we will have to keep the higher-order terms.

We have now completed the evolution of the density matrix to the region beyond the foil where radiative decay processes occur. Doing the algebra is all that remains. We must express the experimentally measurable quantities in terms of traces of observable operators times the density matrix. From the symmetry properties of the density matrix we will obtain the α dependence of the observables. We would also like to obtain the dependence on impact velocity, foil properties, and properties of the atomic states. However, many of these properties are hidden in the T's of Eq. (1′), which themselves are velocity and foil dependent. Some of the velocity and foil dependence does appear explicitly through V_0/v in Eq. (5); this dependence may be extracted, so that the remaining intrinsic variation of the parameters may be obtained from experiments.

III. STOKES PARAMETERS

The intensity of light of a given polarization $\hat{\epsilon}$ emitted from the atomic states $\{(i)\}$ that decay by dipole selection rules is given by[7,8]

$$I = \left(C\hat{\epsilon}\cdot\sum_f (f|\vec{r}\rho^{\{i\}}\vec{r}|f)\cdot\hat{\epsilon}^*\right)\Big/\mathrm{Tr}_{\{i\}}\rho = \left(C\hat{\epsilon}\cdot\mathrm{Tr}_{\{i\}}\cdot\vec{r}\rho\vec{r}\sum_f |f)(f|\cdot\hat{\epsilon}^*\right)\Big/\mathrm{Tr}_{\{i\}}\rho , \quad (8)$$

where C is a constant which is inversely proportional to the square of the distance from the emitting atoms and proportional to the frequency of the light, ω, to the third power, $\rho^{\{i\}}$ is the density matrix of the emitting atoms in the excited-state manifold of interest, $\{i\}$, and $|f)$ denotes the final states to which the excited atomic states decay upon emission of radiation of frequency ω. We shall derive the expressions for the intensity (I) of the light radiated along the z direction of Fig. 1, the difference between the intensity of right-hand and left-hand circular polarization (S), the difference between the intensity of light polarized along the y and x axes (M), and the difference between light polarized along 45° and 135° relative to the x axis (C).[9] In order to do so we must take the traces indicated in Eq. (8). Appendix A outlines the derivation of the equations for the Stokes parameters in terms of traces over the density matrix of angular momentum operators. The results are

$$I = \frac{CS}{3\,\mathrm{Tr}_{\{i\}}\rho}\left(2\,\mathrm{Tr}_{\{i\}}\rho - \frac{h^{(2)}(l_i,l_f)}{l_i(l_i+1)}\,\mathrm{Tr}_{\{i\}}(3L_z^2 - L^2)\rho\right), \quad (9)$$

$$M = -\frac{CS}{\mathrm{Tr}_{\{i\}}\rho}\frac{h^{(2)}(l_i,l_f)}{l_i(l_i+1)}\,\mathrm{Tr}_{\{i\}}(L_x^2 - L_y^2)\rho , \quad (10)$$

$$C = +\frac{CS}{\mathrm{Tr}_{\{i\}}\rho}\frac{h^{(2)}(l_i,l_f)}{l_i(l_i+1)}\,\mathrm{Tr}_{\{i\}}(L_xL_y + L_yL_x)\rho , \quad (11)$$

$$S = +\frac{CS}{\mathrm{Tr}_{\{i\}}\rho}\frac{h^{(1)}(l_i,l_f)}{l_i(l_i+1)}\,\mathrm{Tr}_{\{i\}}L_z\rho . \quad (12)$$

If the light observed is not resolved into separate components composed of emission from individual angular momentum states, $\{i\}$ must include all angular momentum states whose emission is not

resolved. The factors $h(l_i, l_f)/l_i(l_i+1)$ must then appear within $\mathrm{Tr}_{\{i\}}$.

IV. EVALUATION OF THE TRACES

We first consider the trace using ρ_0 as the density matrix, and then calculate the trace with the expansion for ρ_t [Eq. (5)] as the density matrix.

The evaluation of $\mathrm{Tr}_{\{i\}} L_q^{[k]} \rho_0$ involves only that part of ρ_0 diagonal in $\{n_i\} l_i$: $\rho_0(l_i, l_i)$. This diagonal matrix element is proportional to linear combinations of irreducible tensors composed of angular momentum operators

$$\rho_0(l_i, l_i) = b_0 L_0^{[0]} + b_2 L_0^{[2]} + \cdots + b_{2l_i} L_0^{[2l_i]y} . \quad (13)$$

Thus for $l_i = 1$, for example,

$$\rho_0(l_i, l_i) = b_0 L_0^{[0]} + b_2 L_0^{[2]y} = b_0 1 + \sqrt{\tfrac{2}{3}}\, b_2 (3L_y^2 - L^2) . \quad (14)$$

Performing the traces shows that S and C are zero and I and M are nonzero, as is to be expected from their definition and the simplest symmetry considerations.

Quite generally the traces in Eqs. (9)–(12) using ρ_t as the density matrix are of the form

$$\mathrm{Tr}_{\{i\}} L_q^{[k]} \left(\sum_{n=0}^{\infty} r_0^{[n]u} \right) \left(\sum_m{}' T_0^{[m]y} \right) \left(\sum_{j=0}^{\infty} r_0^{[n]u^\dagger} \right) .$$

Let us now evaluate

$$\mathrm{Tr}_{\{i\}} L_q^{[k]} U(t,0) \rho_0 U^\dagger(t,0)$$

after expanding

$$[U(t,0)\rho_0 U^\dagger(t,0)] = \rho_t$$

to obtain

$$\rho_t = \rho_0 + -i \frac{V_0}{v\cos\alpha} [\vec{r}\cdot\hat{u}, \rho_0] + \left(\frac{V_0}{v\cos\alpha} \right)^2 \{ (\vec{r}\cdot\hat{u})\rho_0(\vec{r}\cdot\hat{u}) - A[\tfrac{1}{2}(\vec{r}\cdot\hat{u})^2\rho_0 + \rho_0 \tfrac{1}{2}(\vec{r}\cdot\hat{u})^2] \} . \quad (15)$$

We must now take the part diagonal in $\{n_i\}, l_i$ in the evaluation of the trace. In so doing components of ρ_0 which are off-diagonal in these quantum numbers can contribute to the last two terms. For instance, it is clear that only off-diagonal terms in ρ_0 contribute to diagonal matrix elements in $[\vec{r}\cdot\hat{u}, \rho_0]$ because $\vec{r}\cdot\hat{u}$ is odd under a parity transformation and only even-parity operators can contribute to the diagonal (in l_i) matrix elements of this operator. To evaluate $\rho_t(l_i, l_i)$ we can make use of the following formulas:

$$[r^{[k_1]} \times T^{[k_2]}]^{[k]} = \sum_{\beta'' l''} (-1)^k \begin{Bmatrix} l_i & l_i & k \\ k_2 & k_1 & l'' \end{Bmatrix} (\{n_i\} l_i \| r^{[k_1]} \| \beta'' l'') \frac{(\beta'' l'' \| T^{[k_2]} \| \{n_i\} l_i)}{(\{n_i\} l_i \| L^{[k]} \| \{n_i\} l_i)} L^{[k]} , \quad (16)$$

which holds for matrix elements diagonal in $\{n_i\}, l_i$, and

$$[r^{[k_1]} \times T^{[k_2]}]^{[k]} = \sum (-1)^{l+l'+k} \begin{Bmatrix} l & l' & k \\ k_2 & k_1 & l'' \end{Bmatrix} (nl \| r^{[k_1]} \| \beta' l'') (\beta'' l'' \| T^{[k_2]} \| n' l') [\,|nl\rangle \times \tilde{U}^{l'} \{n' l'|\,]^{[k]} , \quad (17)$$

for off-diagonal matrix elements, where we use the notation of Ref. 10, and where U is the rotating matrix by π about the y axis. Equation (17) is employed for the evaluation of the last set of terms in Eq. (15). Using Eq. (16) with the substitution of $r^{[1]}$ and the irreducible tensor components of ρ_0 for $r^{[k_1]}$ and $T^{[k_2]}$, respectively, the statement that only the off-diagonal components of ρ_0 contribute to traces to the second term of (15) is easily understood from the reduced matrix elements (parity selection rule). The vanishing of the 6-j symbols for certain combinations of angular momentum, and restrictions imposed by the vector coupling coefficients which enter, serve to reduce the number of terms even further. To emphasize this point let us remark that as a result of these considerations, the second term of Eq. (15) contributes only to traces of $L_0^{[1]}$ with contributions to $L_0^{[0]}$, $L_0^{[2]}$, and $L_{\pm 2}^{[2]}$ vanishing. Furthermore, just by looking at the last terms in Eq. (15) we note that only terms proportional to $[\hat{u}\times\hat{u}]^{[0]}$ and $[\hat{u}\times\hat{u}]^{[2]}$ survive.

We will proceed to extract the α dependence of the quantities in Eqs. (9)–(12) by calculating the traces $\mathrm{Tr}\, L_q^{[k]} \rho_t$, but first let us derive some formulas that are needed in the calculation. From the properties of irreducible tensors we know that

$$T_0^{[k']y} = \sum_{q'} D_{0q'}^{[k']}(R) T_{q'}^{[k']z} ,$$

where R is a rotation which takes $\hat{y}$ to $\hat{z}$, and thus

$$D^{[k']}_{0q'}(R) = [4\pi/(2k'+1)]^{1/2}\, Y^{[k']*}_{q'}(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi).$$

The decomposition of $\vec{r}\cdot\hat{u}$ into terms which transform as irreducible tensors is effected by the formula

$$\vec{r}\cdot\hat{u} = \frac{4\pi}{3}\sum_{\mu}(-1)^{\mu}\, Y^{[1]}_{-\mu}(\hat{u}) r Y^{[1]}_{\mu}(\hat{r}).$$

For the coordinate system of Fig. 1 we have[11]

$$Y^{[1]}_{-\mu}(\hat{u}) = (1/\sqrt{2\pi})\theta_{1\mu}(\cos\tfrac{1}{2}\pi) e^{-i\mu(\alpha+\pi/2)}.$$

Using these properties we can calculate the terms that appear in the expression for $\mathrm{Tr}\, L^{[k]}_q \rho_t$,

$$\mathrm{Tr}\, L^{[k]}_q \rho_t = [1]^{[k]}_q + (V_0/v\cos\alpha)\tfrac{4}{3}\pi[2]^{[k]}_q + (V_0/v\cos\alpha)^2(\tfrac{4}{3}\pi)^2[3]^{[k]}_q. \quad (18)$$

The analysis of the α dependence of the terms [1], [2], and [3] is presented in Appendix B.

Keeping terms to order $(V_0/v)^2$ we find

$$\mathrm{Tr}_{\{i\}} L^{[0]}_0 \rho = A + (V_0/v\cos\alpha)^2(B + C\cos 2\alpha), \quad (19)$$

$$\mathrm{Tr}_{\{i\}} L^{[2]}_0 \rho = D + (V_0/v\cos\alpha)^2(E + F\cos 2\alpha), \quad (20)$$

$$\mathrm{Tr}(L^2_x - L^2_y)\rho = G + (V_0/v\cos\alpha)^2(H + I\cos 2\alpha), \quad (21)$$

$$\mathrm{Tr}(L_x L_y + L_y L_x)\rho = (V_0/v\cos\alpha)^2(I\sin 2\alpha), \quad (22)$$

$$\mathrm{Tr} L^{[1]}_{0\rho} = [(V_0/v)J + (V_0/v)^2 K]\tan\alpha. \quad (23)$$

The coefficients A, B, etc. are velocity, foil, and state dependent. They depend upon $\langle l \| T^{[k]} \| l'\rangle$ [and $\langle l \| r Y^{[1]} \| l'\rangle$ and A of Eq. (15), which are calculable]. Odd-k components enter only in the first term of Eq. (23), and in Appendix B we have shown that only the $k=1$ odd component of ρ_t contributes. These equations may be substituted into Eqs. (9)–(12) to calculate the physically measurable quantities

$$\frac{S}{I} = \frac{c\tan\alpha}{1 + a/\cos^2\alpha + b\cos 2\alpha/\cos^2\alpha}, \quad (24)$$

$$\frac{C}{I} = \frac{2d\tan\alpha}{1 + a/\cos^2\alpha + b\cos 2\alpha/\cos^2\alpha}, \quad (25)$$

$$\frac{M}{I} = \frac{-[e + (f + d\cos 2\alpha)/\cos^2\alpha]}{1 + a/\cos^2\alpha + b\cos 2\alpha/\cos^2\alpha}. \quad (26)$$

The dependence on l_f is easily extracted and is contained entirely in the $h^{(m)}(l_i, l_f)$ that enter the coefficients. Higher-order terms in V_0/v will add to the complexity of these equations. Terms linear in V_0/v are what might be called first-order Stark terms, the $(V_0/v)^2$ terms are the second-order Stark terms, etc. As $\alpha \to \frac{1}{2}\pi$ higher-order terms will be important. Note that the α dependence is the same regardless of l_i and l_f; only the coefficients vary. To this order in V_0/v, S/I and C/I are proportional. However, S/I contains contributions from first- and second-order terms.

For a foil that has a rough surface on the microscopic scale we would have to average the expressions for I, S, M, and C over the probability function $P(\alpha|\alpha_0)$ for the probability of α, given that α_0 is the macroscopic tilt angle, and then form S/I, C/I, and M/I.

Charge capture processes taking place as the particle passes the surface will not add any additional terms but will add only contributions to the coefficients in Eqs. (24)–(26). In the charge exchange process the density matrix, immediately after the charge capture, is assumed to be of the form $T^{[0]u}_0 + T^{[1]u}_0 + \cdots$, and then the density matrix is evolved by an evolution operator similar to that of Eq. (5).

It is clear that reflection of an incident atom off a surface to produce a net alignment and orientation of excited atomic states can be described by a similar formalism.

V. COMPARISON WITH EXPERIMENT

Figure 2 plots the experimentally determined percentage polarizations S/I, M/I, and C/I as a function of tilt angle α for the $3p'\,{}^1F \to 3s'\,{}^1D$ transition in Ne III with 1-MeV incident beam energy. Figure 3 is for the $3p\,{}^1P \to 2s\,{}^1S$ transition in He I with 245-keV incident beam energy. Both sets of data were taken with an amorphous carbon foil. The solid curves show the excellent fit of the present theory to the data. The least-squares determination of the parameters yield $a = 0.95$, $b = 0.68$, $c = 0.20$, $d = -0.01$, $e = -0.13$, and $f = -0.03$ for Ne III and $a = 1.15$, $b = 0.28$, $c = 0.53$, $d = -0.10$, $e = -0.14$, and $f = -0.07$ for He I. The effect of averaging over $P(\alpha|\alpha_0)$, which was not performed, would have little effect, because the curves are slowly varying as a function of α [unless the mean

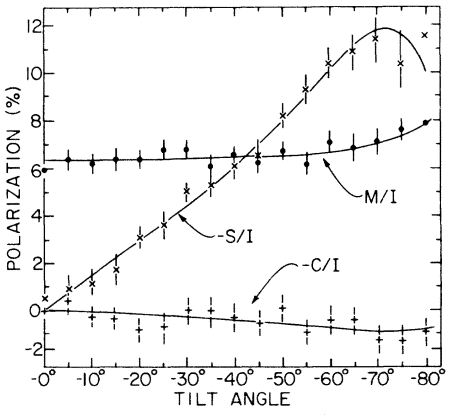

FIG. 2. Percentage polarizations S/I, C/I, M/I as a function of tilt angle for the Ne III 2866-Å $3p'\,{}^1F \to 3s'\,{}^1D$ transition with incident 1-MeV-energy beam. Curves are the least squares fits to the data. Unpublished data courtesy of H. G. Berry and R. M. Schectman.

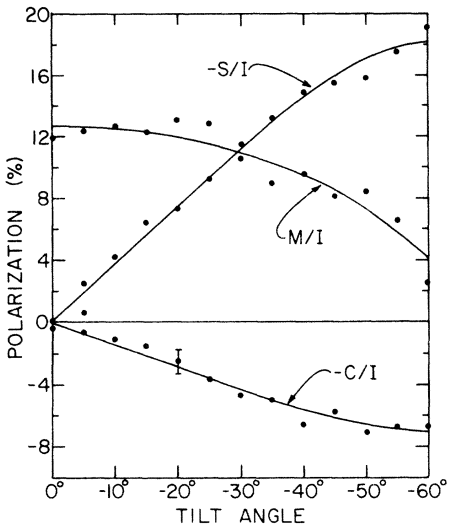

FIG. 3. Percentage polarizations S/I, C/I, M/I as a function of tilt angle for the He I 5015-Å $3p\,^1P \rightarrow 2s\,^1S$ transition with incident 245-keV-energy beam. Curves are the least-squares fits to the data. Representative error bar on data shown. Experimental data from H. G. Berry *et al.*, Phys. Rev. Lett. 34, 509 (1975).

squared deviation of $P(\alpha\,|\,\alpha_0)$ were large]. Close to 90° the higher-order terms in the theory would have to be included.

The parameters can be expressed in terms of reduced matrix elements of the initial density matrix $\langle l \| T^{[k]} \| l' \rangle$, together with quantities $\langle l \| r Y^{[1]} \| l' \rangle$ and $h^{(j)}(l, l')$, which can be calculated given the manifold of interest, and V_0/v and A of Eq. (15), which can be obtained given a particular effective surface potential. From an analysis of the above six parameters we can thereby learn about the velocity, foil, and state dependence of $\langle l \| T^{[k]} \| l' \rangle$. However, there may be more reduced density elements than the number of parameters. As an example, consider the decay of a $3p$ manifold. There are three (real) $k=0$, two (complex) $k=1$, three (two real and one complex) $k=2$, and one (complex) $k=3$ independent reduced density elements which may be nonzero (recall that $l+l'+k$ must be even). We have already shown that the $k=3$ components do not enter into the Stokes parameters when the surface interaction is taken to second order, leaving eight elements, a total of eleven numbers. Therefore in principle we can obtain a maximum of six relations among the eight reduced matrix elements. In practice, often we will not be able to determine completely all of the relations possible in principle. For example, the analysis of the matrix of second derivatives of χ^2 with respect to the six parameters for the Ne data indicates that one of the eigenvalues of the matrix is very small. We therefore must conclude that the linear combination of parameters which forms the eigenvector of this small eigenvalue is not well determined by the least-squares analysis, leaving only five relations among the eight $\langle l \| T^{[k]} \| l' \rangle$.

It is expected that a systematic study of such data for many transitions as a function of incident energy and various target foils will lead to a better understanding of the energy, foil, and state dependences of the coefficients, and therefore of the interaction process.

ACKNOWLEDGMENTS

It is my pleasure to thank Murray Peshkin for many enlightening discussions and comments. I would also like to thank Richard M. Schectman for the comparison with the experimental data.

APPENDIX A: DERIVATION OF STOKES PARAMETERS

The trace in Eq. (8) depends upon the alignment and orientation of the states generated by the beam-foil collision and the dynamics of the dipole transition (and therefore upon the characteristics of f). To simplify the evaluation we can use Racah algebra and the Wigner-Eckart theorem to reduce the trace over f to sums of terms involving traces of tensorial angular momentum operators times ratios of reduced matrix elements.[8,10] It is easy to reduce (8) to a sum of terms containing traces of the density matrix times operators $S_q^{[k]}$ which transform as irreducible representations under rotations,

$$S_q^{[k]} = \left[\left[\vec{r} \times \sum_f |f)(f|\right] \times \vec{r}\right]_q^{[k]} . \tag{A1}$$

Note that $\sum_f |f)(f|$ is a scalar under rotations. By the Wigner-Eckart theorem the matrix elements $(i\,|S_q^{[k]}\,|i)$ and matrix elements of the irreducible tensors $L_q^{[k]}$ composed of $\vec{L}$ and $(i'\,|L_q^{[k]}\,|i)$, are proportional, with the proportionality constant equal to the ratio of the reduced matrix elements $(i \| S^{[k]} \| i)/(i \| L^{[k]} \| i)$. The dependence of this ratio on k, l_i, and l_f can be determined by Racah algebra. The result of this analysis[8] is

$$(i\,|S_q^{[k]}\,|i') = (i\,|\,L_q^{[k]}\,|i')h^{(k)}(l_i, l_f)S/l_i(l_i+1), \tag{A2}$$

where

$$S = \frac{(i \| S^{[0]} \| i)}{(i \| L^{[0]} \| i)} l_i(l_i+1) = (i \| S^{[0]} \| i)\frac{l_i(l_i+1)}{(2l_i+1)^{1/2}},$$

and

$$h^{(k)}(l_i, l_f) = (-1)^{l_i - l_f} \begin{Bmatrix} l_i & l_i & k \\ 1 & 1 & l_f \end{Bmatrix} \Big/ \begin{Bmatrix} l_i & l_i & k \\ 1 & 1 & l_i \end{Bmatrix}. \tag{A3}$$

For $(l_i, l_f) = (1, 0)$, we obtain $h^{(2)}(l_i, l_f) = -2$, $h^{(1)}(l_i, l_f) = 2$; for $(l_i, l_f) = (1, 2)$, $h^{(2)}(l_i, l_f) = -\frac{1}{5}$, $h^{(1)}(l_i, l_f) = -1$; for $(l_i, l_f) = (2, 1)$, $h^{(2)}(l_i, l_f) = -1$, $h^{(1)}(l_i, l_f) = \frac{1}{3}$.

It is now a simple matter to take Eq. (A2), multiply it by density-matrix elements $(i'|\rho|i)$, and form the $[\ ]^k_q$ component of the tensor composed of $\hat{\epsilon}\hat{\epsilon}^*$, coupling to make a scalar. We can then proceed to substitute the expressions for $\hat{\epsilon}$ for the polarizations we choose and calculate the intensity as a function of polarization. The results for the Stokes parameters are given in Eqs. (9)–(12).[9]

In terms of the components of angular momentum operators the irreducible angular momentum operators are given by

$$L_0^{[0]} = 1, \tag{A4}$$

$$L_0^{[1]} = L_z, \tag{A5}$$

$$L_0^{[2]} = \sqrt{\tfrac{2}{3}}\,(3L_z^2 - L^2), \tag{A6}$$

$$L_2^{[2]} + L_{-2}^{[2]} = 2(L_x^2 - L_y^2). \tag{A7}$$

$$L_2^{[2]} - L_{-2}^{[2]} = 2i(L_x L_y + L_y L_x). \tag{A8}$$

APPENDIX B: ANALYSIS OF TERMS IN $\mathrm{Tr}L_q^{[k]}\rho_t$

It is a simple matter to form the terms in the expansion of $\mathrm{Tr}L_q^{[k]}\rho_t$ in powers of $V_0/\hbar v\cos\alpha$,

$$[1]_q^{[k]} = \sum_{m_i m_i' q' k' \text{ (even)}} (l_i m_i | L_q^{[k]} | l_i m_i')D_{0q'}^{[k']}(l_i m_i' | T_{q'}^{[k']} | l_i m_i), \tag{B1}$$

$$[2]_q^{[k]} = (-i) \sum_{\substack{m_i m_i' q' k' \text{ (odd)} \\ \mu l m}} (-1)^\mu Y_{-\mu}^{[1]}(\hat{u})(l_i m_i | L_q^{[k]} | l_i m_i')D_{0q'}^{[k']}$$

$$\times [(l_i m_i' | rY_\mu^{[1]}(\hat{r}) | lm)(lm | T_{q'}^{[k']} | l_i m_i) - (l_i m_i' | T_{q'}^{[k']} | lm)(lm | rY_\mu^{[1]} | l_i m_i)], \tag{B2}$$

$$[3]_q^{[k]} = \sum_{\substack{m_i m_i' q' k' \text{ (even)} \\ \mu\mu' l m l' m'}} (-1)^{\mu+\mu'} Y_{-\mu}^{[1]}(\hat{u}) Y_{-\mu'}^{[1]}(l_i m_i | L_q^{[k]} | l_i m_i')D_{0q'}^{[k']}$$

$$\times [(l_i m_i' | rY_\mu^{[1]} | l'm')(l'm' | T_{q'}^{[k']} | lm)(lm | rY_\mu^{[1]} | l_i m_i)$$

$$- \tfrac{1}{2}A\,(l_i m_i' | rY_\mu^{[1]} | l'm')(l'm' | rY_{\mu'}^{[1]} | l'm' | rY_{\mu'}^{[1]} | lm)(lm | T_{q'}^{[k']} | l_i m_i)$$

$$- \tfrac{1}{2}A(l_i m_i' | T_{q'}^{[k']} | l'm')(l'm' | rY_\mu^{[1]} | lm)(lm | rY^{[1]} | l_i m_i)]. \tag{B3}$$

The first term is easily reduced to

$$[1]_q^{[k]} = \langle l_i \| L^{[k]} \| l_i \rangle \sum_{0 \le k' \text{ (even)} \le 2l_i} \langle l_i \| T^{[k']} \| l_i \rangle \sum_{q'} D_{0q'}^{[k']} \sum_{m_i m_i'} (-1)^{-m_i - m_i'} \begin{pmatrix} l_i & k & l_i \\ m_i & q & m_i' \end{pmatrix} \begin{pmatrix} l_i & k' & l_i \\ -m_i & q' & m_i \end{pmatrix}$$

$$= \begin{cases} n_{kq} \langle l_i \| L^{[k]} \| l_i \rangle \langle l_i \| T^{[k]} \| l_i \rangle = N_{[2]kq}(l_i), & k = \text{even}, \\ 0, & k = \text{odd}, \end{cases} \tag{B4}$$

where $n_{00} = 1$, $n_{20} = \frac{1}{2}$, and $n_{2\pm 2} = -\frac{1}{2}\sqrt{\frac{3}{2}}$. As was expected, there is a finite contribution to M and I but vanishing contribution to C and S (since this terms gives the ρ_0 contribution). The second term reduces to

$$[2]_q^{[k]} = (-i)\langle l_i \| L^{[k]} \| l_i \rangle \sum_\mu (-1)^\mu Y_{-\mu}^{[1]}(\hat{u})$$

$$\times \sum_{l, 1 \le k' \text{ (odd)} \le l + l_i} \langle l_i \| rY^{[1]} \| l \rangle \langle l \| T^{[k']} \| l_i \rangle [1 - (-1)^{1+k'+k}] \begin{Bmatrix} l_i & l_i & k \\ k' & 1 & l \end{Bmatrix} \sum_{q'} \begin{pmatrix} k' & 1 & k \\ q' & \mu & q \end{pmatrix} D_{0q'}^{[k']}. \tag{B5}$$

For even k it can be shown that since k' is summed over odd values only, [2] vanishes; odd-k terms do not vanish and the α dependence is easily extracted as $[2]_{q=0}^{k=1} = (\sin\alpha)N_{[2]10}(l_i)$. From elementary symmetry arguments we know that S, which is proportional to $\mathrm{Tr}L_0^{[1]}\rho$, must vanish when the tilt angle goes to zero, and from the fact that [2] is proportional to terms linear in $Y^{[1]}(\hat{u})$ we conclude that

the $\sin\alpha$ dependence is the only possibility, thus corroborating our result. Furthermore, the 3-j symbol properties determine that only the $k'=1$ term contributes to $[2]^{[1]}$. The $\sin\alpha$ dependence of $[2]_0^{[1]}$ holds for any value of l_i. No contribution to I, C, or M results from [2]. The third term can be dealt with in the same manner. After some angular momentum algebra we obtain

$$[3]_q^{[k]} = \langle l_i \| L^k \| l_i \rangle \sum_{\mu\mu'} (-1)^{\mu+\mu'} Y_{-\mu}^{[1]}(\hat{u}) Y_{-\mu'}^{[1]}(\hat{u}) \sum_{\substack{l,l',K,Q \\ 0\le k' \text{ (even)} \le l+l'}} \sum_{q'} D_{0q'}^{[k']} \Big[\langle l_i \| r Y^{[1]} \| l \rangle \langle l \| T^{[k']} \| l' \rangle \langle l' \| r Y^{[1]} \| l_i \rangle$$

$$\times \begin{Bmatrix} l & l_i & K \\ 1 & K' & l' \end{Bmatrix} \begin{Bmatrix} l_i & l_i & k \\ K & 1 & l \end{Bmatrix} \begin{pmatrix} k & 1 & K \\ q & \mu & -Q \end{pmatrix} \begin{pmatrix} k' & K & 1 \\ q' & Q & \mu' \end{pmatrix}$$

$$+ (-\tfrac{1}{2}A) \langle l_i \| r Y^{[1]} \| l \rangle \langle l \| r Y^{[1]} \| l' \rangle \langle l' \| T^{[k']} \| l_i \rangle \begin{Bmatrix} l_i & l' & K \\ 1 & 1 & l \end{Bmatrix} \begin{Bmatrix} l_i & l_i & k \\ k' & K & l' \end{Bmatrix} [1 + (-1)^{k+k'+K}] \begin{pmatrix} k & K & k' \\ q & Q & q' \end{pmatrix} \begin{pmatrix} K & 1 & 1 \\ -Q & \mu & \mu' \end{pmatrix} \Big]. \tag{B6}$$

The $Y^{[1]}(\hat{u})$ can now be coupled together, and we observe that $Y_Q^{[K]}(\hat{u})$ with only $K=0, 2$ appear. The second term in this equation is quite simple to reduce, because the sum over μ and μ' can be easily performed, leaving

$$(-1)^K \frac{3}{\sqrt{4\pi}} \frac{1}{\sqrt{2K+1}} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} Y_Q^{[K]}(\hat{u})$$

(which vanishes for odd K). The term in square brackets therefore indicates that $k+k'$ must be even. We are left with

$$\sum_{K=0,2;Q} Y_Q^{[K]}(u) \sum_{k' \text{ (even)}} \sum_{q'} D_{0q'}^{[k']} \begin{pmatrix} k & K & k' \\ q & Q & q' \end{pmatrix} \times [1 + (-1)^{k+k'}] N_{[3],k,k',K} \tag{B7}$$

which vanishes for k odd (and therefore does not contribute to circular polarization). Proceeding in a similar fashion with the first term of [3] we eventually obtain a result similar to Eq. (B7), without the term in square brackets and with the coefficient proportional to a 9-j symbol. Finally, we find

$$[3]_0^0 = N_{[3]00} + M_{[3]00} \cos 2\alpha\,, \tag{B8}$$

$$[3]_0^1 = N_{[3]10} \sin 2\alpha\,, \tag{B9}$$

$$[3]_0^2 = N_{[3]20} + M_{[3]20} \cos 2\alpha\,, \tag{B10}$$

$$[3]_{\pm 2}^2 = N_{[3]2\pm 2} + M_{[3]2\pm 2} e^{\pm 2i\alpha}. \tag{B11}$$

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[11] Part of the reason for choosing the coordinate system of Fig. 1 is so that we can have the simple exponential α dependence given here.