[11]L. E. Snyder and J. M. Hollis, to be published.
[12]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955), p. 19.
[13]POLYATOM (Version 2), Quantum Chemistry Program Exchange (Department of Chemistry, Indiana University) (unpublished).

Alignment and Orientation Effects in Beam-Foil Experiments*

Yehuda B. Band†
James Franck Institute, University of Chicago, Chicago, Illinois 60637
(Received 19 November 1974; revised manuscript received 25 June 1975)

I present a theory of the orientation and alignment of atoms observed upon emergence from tilted foils. The interaction with the foil surface is taken into account in the production process of particular states. Once they are produced, the evolution of these states, under the influence of the residual field near the surface, is calculated in the fashion introduced by Eck. The most general effect of this evolution is presented.

Light emitted from fast atoms emerging from foils tilted with respect to the beam axis has a nonvanishing component of circular polarization.[1,2] This indicates a net angular momentum of the excited electronic state along the axis of the circular polarization. I present the theory predicting and describing the orientation and alignment of excited atoms or molecules that are produced in collisions with foil targets.

Let the normal to the plane of the foil ($\hat{u}$) make an angle α with the beam axis ($\hat{z}$), as in Fig. 1 of Ref. 1, and let the light be viewed along the $\hat{x}$ axis. The circular polarization is proportional to the atomic orientation parameter defined by[3,4]

$$O_0^{\det} = \langle (i'|\, J_x |\, i)\rangle / j_i(j_i+1)$$

where the states $|\, i\rangle$ refer to the excited states produced and j_i is the angular momentum quantum number of the states. If we quantize the angular momentum of the excited state about the viewing axis $\hat{x}$,

$$O_0^{\det} = \sum_i m_i \sigma(m_i) / j_i(j_i+1) \sum_k \sigma(m_k)\ ,$$

where $\sigma(m_i)$ is the cross section for producing a state with azimuthal quantum number m_i. Unequal populations of states with quantum number m and $-m$, a requirement if $O_0^{\det}$ is to be nonvanishing, can arise only if an axial vector can be constructed in the direction of the $\hat{x}$ axis. Such a vector is given by $\vec{k}\times\hat{u}$ where $\vec{k}$ is the momentum of the fast particle. The circular polarization dependence and thus the atomic orientation effects must therefore originate with the interaction of the incident particles with the surface as a whole. This is true of the alignment parameter A_{1+}[4]. This interaction must be included in the description of the *production* process of the excited states. The energy associated with the interaction of the beam with the foil surface is quite large and thus its inclusion in the production process is imperative. The effect of the foil-surface interaction upon departing atoms in their final excited states, if the interaction is divorced from the *creation* process,[5] is not sufficient to explain the observed phenomena.[6] That is, the precession of the multipole moments of excited states due to this interaction potential does not describe the observations.

Consider the excitation of the atoms or molecules in the beam from some initial electronic state $|\, \beta\rangle$ to a particular state of the manifold $|\, i\rangle$ of interest.[7] Assume the excited states of interest can be characterized as excitations of only one electron. The "active" electron of state $|\, \beta\rangle$ may interact with electrons in the foil to cause excitation. However, there are interactions with the surface as a whole, as well as the interactions within the interior of the foil between electrons bound in the projectile and foil electrons. Inside the solid electrons experience an average potential determined by the work function φ plus the Fermi energy ϵ_F. Positively charged particles encounter the negative of this potential. These potentials which abruptly end at the vicinity of the surface are also capable of producing excitation of $|\, \beta\rangle$. The essential difference between the atom-surface interaction and the interactions between atom and bulk electrons must be stressed.

The cumulative foil-surface interaction with the atomic core plus active electron must be described by a separate term in the transition ma-

trix for the excitation. This collective many-body effect is treated through the effective surface potential, which may be obtained by considering the bulk properties of the media. The transition matrix element, T_m, for excitation from $|\beta\rangle$ to the $|i\rangle$ manifold (the $|nlm\rangle$ states with m defined with respect to the $\hat{x}$ axis) is given by the sum of the bulk interaction potential term and the surface interaction potential. In what follows the detailed structure of the potential between the jth foil electron and the core of the atom, $V_c(\vec{R}-\vec{r}_j)$, the jth foil electron and the active electron, $-V_e(\vec{R}+\vec{r}_c-\vec{r}_j)$, and the surface interactions $V_0\theta_c(\vec{R}\cdot\hat{u})$ and $-V_0\theta_e((\vec{R}+\vec{r}_c)\cdot\hat{u})$ on the core and active electron will not be specified. Their actual form is not necessary for the analysis to proceed; I have done calculations with specific microscopic models, but these are not important to the general theory that follows here. It should be noted that a surface charge on the foil could be included in the surface interaction terms θ.

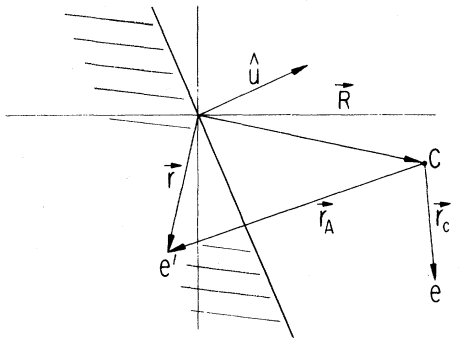

FIG. 1. Definition of position vectors. $\vec{R}$ is the displacement from origin of coordinate system to center of mass of atomic core (C), $\vec{r}_c$ is the displacement of bound electron (e) from core, $\vec{r}_A$ is the displacement of jth foil electron (e') from core, $\vec{r}$ is the displacement of the jth foil electron from origin, $\hat{u}$ is the normal to foil.

T_m is given by

$$T_m=(2\pi)^{-3}\int d^3R\int d^3r_c\exp\{-i\vec{k}'\cdot[\vec{R}+\vec{r}_c/(M_c+1)]\}\psi_{nlm}{}^*(\vec{r}_c)$$
$$\times\langle M'|\textstyle\sum_j[V_c(\vec{R}-\vec{r}_j)-V_e(\vec{R}+\vec{r}_c-\vec{r}_j)]+V_0[\theta_c(\vec{R}\cdot\hat{u})-\theta_e((\vec{R}+\vec{r}_c)\cdot\hat{u})]|M\rangle$$
$$\times\exp\{i\vec{k}\cdot[\vec{R}+\vec{r}_c/(M_c+1)]\}\psi_\beta(\vec{r}_c). \qquad (1)$$

The position vectors employed are defined in Fig. 1. M_c is the mass of the core of the atom (the proton in the case of hydrogen atoms), $\vec{k}$ and $\vec{k}'$ are the initial and final momenta of the atom (in atomic units), $\vec{R}+\vec{r}_c/(M_c+1)$ is the center of mass of the atom. The plane wave factors incorporate the initial and final translation of the atom. The state vectors $|M\rangle$ and $|M'\rangle$ are the electronic states of the foil before and after excitation; ψ_β is the initial eigenstate of the particle in the foil (which might differ considerably from the free atom state because of the influence of the foil electrons). The first two interaction terms are the sums of the two-particle potentials between the bound electron in the atom and the foil electrons, and between the core of the atom and the foil electrons, respectively. The remaining interaction terms describe the effective surface potential which contains the discontinuity at the foil surface. V_0 is given by $(\varphi+\epsilon_F)$. The form of the arguments of the θ functions, rather than their detailed analytic structure (which would be of the general shape of a rounded-step function plus surface-charge contribution) is what matters. The last two terms of the interaction potential are explicitly independent of the foil electronic wave functions so that performing the integrations over $\vec{r}_j$ yields $\delta_{MM'}$ for these terms (thus indicating a collective excitation).

Performing the integration over $\vec{R}$ in Eq. (1) and simplifying, we obtain

$$T_m=(2\pi)^{-3}\int d^3r_c\exp\{i\vec{q}\cdot[\vec{r}_c/(M_c+1)]\}\psi_{nlm}{}^*(\vec{r}_c)\{[V_c(\vec{q})-V_e(\vec{q})\exp(-i\vec{q}\cdot\vec{r}_c)]\langle M'|\textstyle\sum_j\exp(i\vec{q}\cdot\vec{r}_j)|M\rangle$$
$$+V_0(2\pi)^2\delta^2(\vec{q}_\parallel)[F_c(q_\perp)-F_e(q_\perp)\exp(-iq_\perp\vec{r}_c\cdot\hat{u})]\delta_{MM'}\}\psi_\beta(\vec{r}_c), \qquad (2)$$

where $V(\vec{q})=\int d^3\rho\exp(i\vec{q}\cdot\vec{\rho})V(\vec{\rho})$, $F(q_\perp)=\int d\rho_\perp\exp(iq_\perp\rho_\perp)\theta(\rho_\perp)$, and where we have defined the momentum transfer $\vec{q}=\vec{k}-\vec{k}'$, $\vec{q}_\perp=\vec{q}\cdot\hat{u}\hat{u}$, and $\vec{q}_\parallel=\vec{q}-\vec{q}_\perp$. For simplicity take β to be a spherically symmetric state. Similar conclusions are obtained when using an arbitrary state with equal populations in substates of all azimuthal quantum numbers, to assure a spherically symmetric density matrix for the

states β. The m and α dependence of the transition matrix element reduces to

$$T_m = \frac{1}{(2\pi)^3}\left\{ f_{nl,\beta}\left(\frac{q^2}{(M_c+1)^2}\right)\left[V_c(\vec{q})F_{M',M}(\vec{q})Y_{lm}^*(\hat{q}) + V_0(2\pi)^2\delta^2(\vec{q}_\parallel)F_c(q_\perp)\delta_{MM'}Y_{lm}^*(\hat{u})\right] \right.$$
$$\left. -(-1)^l f_{nl,\beta}\left(\frac{M_c^2 q^2}{(M_c+1)^2}\right)\left[V_e(\vec{q})F_{M',M}(\vec{q})Y_{lm}^*(\hat{q}) + V_0(2\pi)^2\delta^2(\vec{q}_\parallel)F_e(q_\perp)\delta_{MM'}Y_{lm}^*(\hat{u})\right]\right\}, \quad (3)$$

where $F_{M'M}(\vec{q})$ is the foil form factor $\langle M'|\sum_j \exp(i\vec{q}\cdot\vec{r}_j)|M\rangle$ and $f_{nl,\beta}(\rho^2)$ is the radial part of the Fourier transform $\int d^3r_c \exp(i\vec{p}\cdot\vec{r}_c)\psi_{nlm}^*(r_c)\psi_\beta(\vec{r}_c)$. Although Eq. (3) is derived from Eq. (1), which is an approximation because the *exact* scattering wave function $\psi^{(+)}$ was not used, the symmetry properties and the α dependence of the present results are not drastically modified. However, I have not included terms with the surface interaction acting upon a non-spherically-symmetric component of the density matrix which may be present before encounter of the surface. Consideration of such terms will follow elsewhere.

Take the azimuthal angle in the y-z plane in a counter-clockwise direction from the y axis as viewed in Fig. 1 of Ref. 1. The dependence on m and α of T_m is given by

$$T_m = A(nl,\beta,M,M')Y_{lm}^*(\hat{q}) + B(nl\beta)\delta_{M,M'}\delta^2(\vec{q}_\parallel)P_{lm}(0)e^{-im(\alpha+\pi/2)}, \quad (4)$$

where the coefficients A and B are easily identified from Eq. (3). However, before expectation values of any operator are taken we must account for the precession of the $|i\rangle$ manifold states due to the effective potential. Once the states in the manifold of interest are produced, that part of the effective potential which does not completely vanish past the edge of the surface is still capable of modifying the density matrix as the atoms move away from the surface. The surface interaction is thereby included in the production mechanism and the precession of $|i\rangle$. Neglecting either yields predictions that differ with experimental results.[6] The precession coefficients which account for the angular frequency variations due to the effective potential are

$$B_{\mu m} = (\mu|\exp i\textstyle\int_0^\infty H\,dt|\,m) = \left(\mu\left|\exp\frac{i\int_0^\infty - V_0\theta_e(u)\,du}{v\cos\alpha}\right|m\right),$$

where u is along the direction normal to the foil and v is the particle speed. The expectation value of any operator O in the $|i\rangle$ manifold is given by

$$\langle O\rangle = \sum_{mm'\mu\mu'} O_{\mu'\mu}B_{\mu m}B_{\mu' m'}{}^*\langle T_m T_{m'}{}^*\rangle_{\vec{q}},$$

where the brackets indicate average over initial states and the sum over final states (integral over allowed $\vec{q}$ space). The $B_{\mu m}$ are most easily evaluated by interposing a complete set of states σ in the $|i\rangle$ manifold, quantized along the $\hat{u}$ axis,

$$B_{\mu m} = \sum_{\sigma\sigma'}(\mu|\,\sigma)\exp\left(\frac{i\omega_{|\sigma|}}{v\cos\alpha}\right)\delta_{\sigma\sigma'}(\sigma'|\,m) = \sum_\sigma D_{\mu\sigma}^{\,l}(\alpha'\beta'\gamma')\exp\left(\frac{i\omega_{|\sigma|}}{v\cos\alpha}\right)D_{m\sigma}^{\,l}{}^*(\alpha'\beta'\gamma'),$$

where the D's are rotation functions, $(\alpha'\beta'\gamma')$ are Euler angles for a rotation of $\hat{x}$ to $\hat{u}$, and $\omega_{|\sigma|}$ are integrated angular frequency phase factors which clearly depend only on the absolute value of σ. Using this expression for $B_{\mu m}$ and Eq. (4) we compute $\langle L_x\rangle$, $\langle L_y{}^2 - L_z{}^2\rangle$, $\langle L_yL_z + L_zL_y\rangle$, $\langle L_x{}^2\rangle$ to evaluate the Stokes parameters which can be formed from these expectation values. The analysis[8] for an $l=1$ manifold yields the results[9]

$$S/I = -E\sin2\alpha\sin(\omega/v\cos\alpha), \quad M/I = -E + F^2\cos2\alpha + 2E\sin^2\!2\alpha\sin^2(\omega/2v\cos\alpha),$$
$$C/I = F^2\sin2\alpha - E\sin4\alpha\sin^2(\omega/2v\cos\alpha), \quad (5)$$

where E and F^2 are functions of A and B of Eq. (4) and therefore energy dependent, e.g.,

$$F^2 = \frac{\langle|B|^2\rangle_{\vec{q}}}{\langle|A|^2P_{11}{}^2(\cos\theta_q) + |B|^2\rangle_{\vec{q}}}, \quad E = \frac{\langle|A|^2P_{11}{}^2(\cos\theta_q)\cos2\varphi_q\rangle_{\vec{q}}}{\langle|A|^2P_{11}{}^2(\cos\theta_q) + |B|^2\rangle_{\vec{q}}},$$

$\langle|B|^2\rangle_{\vec{q}}$ is proportional to $(v\cos\alpha)^{-2}$, and ω is the difference between the phase factors for the degenerate states $\sigma=1,-1$ and $\sigma=0$. The most general result is obtained by performing the calculation with

a *complex* value of ω, thus accounting for the relative change of amplitude of the $\sigma = 1, -1$ and $\sigma = 0$ states as well as the phase change between them and thereby generalizing the result of Eck.

For amorphous materials, the bumpy character of the surface may be taken into account by folding these results with the probability distribution describing the random deviations from the macroscopic tilt angle of the surface. For materials with small deviations this consideration is unimportant, and it has been neglected by all previous authors in this spirit. The detailed analysis of these constants can be carried through using specific models for V_c, V_e, θ_c, and θ_e. Setting $\omega = 0$ would correspond to ignoring the precession of the $|i\rangle$ manifold. Taking $F^2 = 0$ corresponds to neglecting the foil surface interaction upon the production process of $|i\rangle$. If $\omega/v \cos\alpha$ is small, as may be the case for $\alpha \ll \pi/2$ (except if there is a net residual surface charge), $\sin(\omega/v \cos\alpha)$ can be replaced by its argument. The analysis for manifolds with larger l values can be carried out similarly.

Charge capture processes might also contribute to the orientation. As a proton passes through the foil it may pick up a foil electron into an $|nlm\rangle$ state. The transition matrix element for the charge capture process is given by[10]

$$T_m = \frac{1}{(2\pi)^3} \int d^3R\, e^{-i\vec{k}'\cdot\vec{R}} \left\langle M'', \exp\left(\frac{i\vec{k}'\cdot\vec{r}_A}{M_c+1}\right)\Psi_{nlm}(\vec{r}_A)\right| \sum_i V_c(|\vec{R}-\vec{r}_j|) + V_0\,\theta_c(\vec{R}\cdot\hat{u}) \left| M\right\rangle e^{i\vec{k}\cdot\vec{R}} \tag{6}$$

where $\vec{r}_A$ is defined in Fig. 1. $\langle M'', \exp[(i\vec{k}'\cdot\vec{r}_A)/(M_c+1)]\Psi_{nlm}(\vec{r}_A)|$ is the antisymmetrized product state of the electron about the core with the remaining electron wave function of the solid. For the free electron jellium model of $|M\rangle$ it can be shown that the surface term does not contribute and the only effect of including charge capture is an additional contribution to A in Eq. (4).

The parameters of the theory can be chosen to fit within experimental error the existing data for the α dependence of the Stokes parameters for the light emitted from excited atoms in beam-foil collisions. There is a wealth of information concerning the dependence on the foil properties, the excited-state manifold, projectile energy, etc., yet to be extracted experimentally and theoretically. These considerations as well as quantum beat phenomena in the Stokes parameters are now being studied.

The author would like to thank Professor H. G. Berry, Professor R. S. Berry, Professor T. G. Eck, and Professor U. Fano for stimulating discussions, and Professor T. G. Eck for helping to perform the algebra which led to Eq. (5).

---

*Work supported by National Science Foundation Grants No. GH-33636, No. MPS75-01549, and No. MRL(NSF).

†Present address: Argonne National Laboratory, Argonne, Ill. 60439.

[1]H. B. Berry, L. J. Curtis, D. G. Ellis, and R. M. Schechtman, Phys. Rev. Lett. 32, 751 (1974).

[2]D. A. Church, W. Kolbe, M. C. Michel, and T. Hadeishi, Phys. Rev. Lett. 33, 565 (1974); C. H. Liu, S. Bashkin, and D. A. Church, Phys. Rev. Lett. 33, 993 (1974); D. A. Church, M. C. Michel, and W. Kolbe, Phys. Rev. Lett. 34, 1140 (1975).

[3]D. G. Ellis, J. Opt. Soc. Am. 63, 1232 (1973).

[4]U. Fano and J. H. Macek, Rev. Mod. Phys. 45, 553 (1973).

[5]T. G. Eck, Phys. Rev. Lett. 33, 1055 (1974).

[6]H. G. Berry, L. J. Curtis, and R. M. Schechtman, Phys. Rev. Lett. 34, 509 (1975).

[7]We shall at points refer to the manifold $|i\rangle$ as $|nlm\rangle$ states, but it should be emphasized that the present formalism is valid for arbitrary atoms or molecules.

[8]The correct analysis begins with the expression for the intensity of light with polarization vector $\hat{\epsilon}$ as

$$I = C\sum_{fii'} (i'|\hat{\epsilon}\cdot\vec{r}'|f)(f|\hat{\epsilon}^*\cdot\vec{r}|i)\langle T_i T_{i'}{}^*\rangle_{\vec{q}}$$

may be put into the form

$$I = C\sum_{ii'} (i'|\hat{\epsilon}\cdot\vec{r}'\,P_f(\vec{r}',\vec{r})\,\hat{\epsilon}^*\cdot\vec{r}|i)\langle T_i T_{i'}{}^*\rangle_q ,$$

where P_f is a scalar which depends upon l_f. The expressions for the Stokes parameters obtained from this expression contain the dependence upon l_f through the coefficients $h^{(k)}(l_i, l_f)$ [defined in Eq. (8) of Ref. 4].

[9]The data published in Refs. 1 and 6 correspond to negative values of α as drawn in Fig. 1 of Ref. 1. R. M. Schectman, private communication.

[10]The nonorthogonality terms indicated in Y. B. Band, Phys. Rev. A 8, 243 (1973), are assumed unimportant.