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Impact Excitation and Polarization of the Emitted Light*

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A new formulation is presented for the angular distribution and the polarization of light excited by atomic and electronic collisions and modulated in time by the action of internal and external fields. The formulation disentangles geometrical and dynamical effects and stresses the extraction of data on the alignment and orientation of radiating atoms from observations of the emitted light. The treatment is set in the context of recent experimental and theoretical literature and points to new avenues of research.

CONTENTS

I. INTRODUCTION

Excitation of an atom or molecule by collision in a gas, or by passage through a foil, leaves it generally in an anisotropic state. Light emitted in the subsequent decay manifests this anisotropy through its angular distribution and polarization. Measurements of the angular distribution and/or polarization of emitted light have been used since the '20s (S26, SA27) to determine the anisotropy of the source atom or molecule. The recent emphasis on this type of analysis (PS58, K69, MJ71), and the introduction of techniques for observing variations of the anisotropy during the light emission (HN65, A70, BH71, BS71, LDAF71) prompt us to review the theoretical connection between the radiated pattern and the relevant source parameters.

These parameters consist normally of an *orientation* vector proportional to the average angular momentum of the source atom, $\langle \mathbf{J} \rangle$, and of an *alignment* tensor whose components are proportional to the mean values of quadratic expressions in J_x, J_y, J_z, such as $\langle J_x^2 - J_y^2 \rangle$.

The theory will be articulated from an operational point of view to show, in the first place, just what characteristics of the radiating atoms are determined by observing the intensity and the polarization of the light emitted in various directions. In a second step the dynamical aspects of the emission process will be disentangled from the geometrical aspects. That is, we will show how the emission averaged over all directions depends on dynamical factors such as the line strength, while the anisotropy and polarization depend only on the alignment and orientation of the excited atoms. Then it will be shown how the number of independent nonzero alignment and orientation parameters is often restricted by the geometry of the exciting collision. Finally, we shall develop the theory of the time dependence of alignment and orientation in the interval between excitation and emission. It will emerge that the action of external fields during this interval may perturb the alignment and orientation of excited atoms to the extent of interlinking them with other parameters such as octupole or hexadecapole moments induced by the collision. Internal fields, on the other hand, yield reversible exchanges of orientation and alignment among orbits and electronic or nuclear spins. We shall thus endeavor to present a unified, geometrical picture of the phenomena, illustrated by experimental results and pointing to the limits of current advances and to opportunities for developing new theories and experimental designs.

In our problem, as in many others involving the angular distribution of reaction products, one faces considerable difficulty in directing attention to the main geometrical observable features of the phenomenon without resorting to unfamiliar formalisms. Most current treatments still proceed by summing or averaging explicitly over all unobserved magnetic quantum numbers; this method is elementary but laborious and furthermore fails to interpret the simplicity of the results. Compact formulations of the theory have existed since the early 1950's but they rely on somewhat abstract formulations using density matrices and extensive applications of Racah algebra (see, e.g., Chap. 19 of FR59, Sec. 3 of FS68). In this article we strive for a transparent formulation without explicit use of density matrices; to this end we shall use a minimum of Wigner–Racah algebra, introducing it by qualitative discussion where it becomes essential.

The connection between the anisotropy of the radiation source and the collision process from which it arises will be illustrated by outlining the theory of alignment by electron collision. Particular mention will be made of the striking loss of alignment which often occurs over a narrow energy band above threshold.

In the interest of brevity we are excluding from our subject several of its interesting aspects. Among these are the important influence of successive photon emissions by the same atom and the effects of magnetic resonance upon light emission. We also deal only with light emitted in electric dipole processes even though extension to other processes would be straightforward. This paper refers to "atoms" as the sources of light but is meant to apply, in essence, also to radiation by molecules and, in fact, by nuclei as well.

The first part of this article deals with light emitted in transitions between two sharply defined energy levels, that is, with light observed by high resolving power spectroscopy. Sharp definition of the energy levels requires, of course, that the time of emission be determined with correspondingly low resolution. The second part will consider the phenomena that occur, e.g., under the conditions of beam foil spectroscopy (B67) or when photons are detected in delayed coincidence with a colliding particle (M69, A70, IR71, McJ71, MJ71). Sharper definition of the time interval between a collision and the following light emission implies here a lower spectral resolution in determining the initial energy of the radiating atom. The observed light originates then typically from a nonstationary state and is modulated in time as represented by the coherent superposition of excited stationary states with different, unresolved energy eigenvalues. Our formulation will yield directly the modulation of the several alignment and orientation parameters.

Historically, the development of this subject has proceeded along two converging lines. On the one hand, the emission of light from nonstationary states has been extensively studied in connection with the Hanle effect (H23, Br33), optical pumping (H72), and level crossing experiments. Since the states are usually excited by optical radiation, the early theoretical developments (Br33, F61) treated the entire process of absorption and emission from the point of view of the quantum theory of radiation without reference to orientation or alignment of the atoms. On the other hand, measurements of static properties of radiation fields, such as their polarization and angular distribution have been used mainly to detect or verify simple source properties of collision excited atoms (S26, SA27, PS58).

Later experiments were aimed at demonstrating modulated decays following collision excitation. A direct observation of the modulation following excitation by a pulsed electron beam was made by Hadeishi and Nierenberg (HN65), but equivalent results had been obtained previously by Pebay-Peyroula and by Aleksandrov through modulation of the electron beam (PP63, A64) and by Series and co-workers through optical excitation (CS64, DKW64). Determination of source parameters was not emphasized in these experiments. Correspondingly, the theory of Franken (F61) and Kelly (K66) dealt mainly with the modulation aspects of impulsively excited line radiation.

The theory of light modulation was concerned initially, in this and other work (e.g., DS61, S67), with atoms in magnetic fields. With the advent of beam foil spectroscopy and coincidence techniques (IR71, McJ71) interest focused on emission from atoms in field-free regions and on the determination of source parameters (M69, A70, BH71, IR71, LDAF71, McJ71, MJ71). The theory related to such measurements essentially combines the treatment of modulated decays with the theory of angular correlations, and closely resembles the theory of perturbed angular correlations of nuclear physics (KMS64, FS68). Owing to the known dipole nature of most atomic transitions and to the simple vector coupling nature of fine and hyperfine interactions, the extraction of source parameters from data becomes an exercise in angular momentum recoupling, and can be carried out in a rather complete fashion. In addition, atoms respond to external magnetic fields in a way that provides additional information on the excited state populations.

A time dependence of the anisotropy and polarization of the emitted light occurs also when the source atoms interact appreciably with one another or with other atoms during the emission process. Typically the polarization of light emitted by a sufficiently dense medium following a pulsed excitation relaxes exponentially, whether or not it is also modulated by the mechanics of single atoms. The relaxation effects have been reviewed in (H72) and are not included in the

present article which deals only with emission by isolated atoms, i.e., by gases in the low-pressure limit. We note, however, that the treatment of relaxation centers, like ours, on the orientation and alignment of the source atoms—or on the equivalent dipole and quadrupole moments—because such tensorial quantities relax independently of one another in isotropic media. In particular, Barrat (B59) showed that the linear polarization of light emitted by an optically pumped dense gas decays faster than the total light intensity; the intensity depends, of course, on scalar properties of the source atoms while the polarization depends on their tensor alignment. The difference of relaxation rates of different tensorial parameters has been emphasized in more recent studies (DP65, O65, HS67) which represent the excited state of the source atoms by a density matrix expanded into irreducible tensor components (F57).

Our review concentrates on recent developments and emphasizes their potential for measuring the source parameters of collision excited atoms. Accordingly, we do not review the quantum theory of radiation from nonstationary states, but use its results. We stress instead the extraction of source parameters from data and their interpretation in a more direct manner than has been done previously.

II. LIGHT EMISSION IN THE DECAY OF A STATIONARY STATE

The intensity I measured by an ideal detector sensitive to light with the polarization vector $\hat{\epsilon}$ is proportional to $\sum_{m_f}\langle|(f\,|\,\hat{\epsilon}^*\cdot\mathbf{r}\,|\,i)|^2\rangle$, where $\mathbf{r}$ is the transition dipole operator of the atom, $\sum_{m_f}$ indicates summation over all values of the final state magnetic quantum number m_f, and $\langle\ \rangle$ indicates averaging over the initial m_i. The average is weighted by excitation amplitudes whose values are regarded here as unknown parameters, to be determined by measuring the light intensity I. Circular and elliptical polarizations are represented by complex vectors $\hat{\epsilon}$. We express I more precisely in the form

$$I=C\sum_{m_f}\langle(i'\,|\,\hat{\epsilon}\cdot\mathbf{r}'\,|\,f)(f\,|\,\hat{\epsilon}^*\cdot\mathbf{r}\,|\,i)\rangle, \qquad (1)$$

where one of the $\mathbf{r}$ and one of the i have been primed to distinguish the integration variables and quantum numbers of the two matrix elements. The factor

$$C=e^2\omega_{fi}{}^4/2\pi c^3R^2 \qquad (2)$$

incorporates the light frequency ω_{fi}, the detector's distance from the source atom R, and the other factors required to express I as a power flux.

Equation (1) warrants some discussion. Its main element is the average value of a physical quantity, that is, the mean or quantum mechanical expectation value of that quantity. The average pertains to the excited state generated by the collision. The notation allows this state to be represented by the coherent superposition of states with different magnetic quantum numbers, m_i, m_i'. Circumstances will be pointed out later in which this superposition becomes essential, but actually we need not concern ourselves here with it or, more generally, with the calculation of the average starting from collision theory. On the contrary, this paper concentrates on the averages themselves. That is, we deal with their determination from observational data, with the restrictions imposed on their values by experimental symmetries, and with theoretical relations between the averages of different physical variables.

As an incidental remark, we also note that the exponential decay of light intensity following the collision has been omitted from Eq. (1) for simplicity. This decay should be integrated over if the time resolution of the experiment were much longer than the mean life of the excitation. Similarly, Eq. (1) pertains to emission by a single excited atom and should be multiplied by an appropriate factor, including, e.g., a collision cross section, whenever it is to represent the light received from a macroscopic source.

The expression (1) is to be transformed so as to separate its dependence on the direction and polarization response of the detector from the anisotropy of the excited state expressed by the averaging $\langle(i'\,|\cdots|\,i)\rangle$. The transformation consists of three steps of increasing complexity: (a) taking explicit advantage of the isotropy that results from the summation over the unobserved final states, (b) disentangling the dependence of (1) on the direction of $(\hat{\epsilon},\ \hat{\epsilon}^*)$ from its dependence on $(\mathbf{r},\ \mathbf{r}')$ by recoupling these vectors, and (c) applying the Wigner–Eckart theorem to replace the dependence on $(\mathbf{r},\ \mathbf{r}')$ by the more familiar expressions of alignment and orientation as mean values of angular momentum operators.

(a) The sum over projections onto the several degenerate states of the final energy level, indicated by $\sum_{m_f}|f)\,(f|$, constitutes a single projection operator $P_f(\mathbf{r}',\ \mathbf{r})$ which is a *scalar*, i.e., is invariant under joint rotation of $\mathbf{r}'$ and $\mathbf{r}$. With this notation, Eq. (1) takes the form

$$I=C\langle(i'\,|\,\hat{\epsilon}\cdot\mathbf{r}'P_f(\mathbf{r}',\mathbf{r})\hat{\epsilon}^*\cdot\mathbf{r}\,|\,i)\rangle. \qquad (3)$$

(b) The product of scalar products $\hat{\epsilon}\cdot\mathbf{r}'\hat{\epsilon}^*\cdot\mathbf{r}$ can be recoupled into the form $\sum_k Q^{(k)}(\hat{\epsilon},\ \hat{\epsilon}^*)\cdot R^{(k)}(\mathbf{r}',\ \mathbf{r})$, such that each factor $Q^{(k)}$ can be pulled out of the matrix element (3). Here k represents the degree of an irreducible tensor, that is, $k=0$ indicates a scalar, $k=1$ a vector, and $k=2$ a quadrupole moment. The recoupling can be performed in our problem by elementary vector algebra, without resorting to more general procedures, since the polarization vector $\hat{\epsilon}$ is restricted to the plane perpendicular to the direction of observation. We take this direction as the $\hat{\zeta}$ axis of a "detector frame" of coordinates $(\xi,\ \eta,\ \zeta)$. We also take the $\hat{\xi}$ axis of this frame along the major axis of

the general elliptical polarization selected by the detector and represented by $\hat{\epsilon}$. In this frame we can then set $\hat{\epsilon}\equiv(\cos\beta, i\sin\beta, 0)$, whereby $\beta=0$ represents selection of linear polarization and $\beta=\frac{1}{4}\pi$ selection of right circular polarization. [When the polarization analyzer consists of a Nicol prism, or an analogous linear polarization filter, and of a $\frac{1}{4}$-wavelength plate, β is the angle between optical axes of Nicol and plate, see, e.g., (F49).] These definitions yield

$$\hat{\epsilon}\cdot\mathbf{r}'\hat{\epsilon}^*\cdot\mathbf{r}=\xi'\xi\cos^2\beta+\eta'\eta\sin^2\beta-i(\xi'\eta-\eta'\xi)\sin\beta\cos\beta. \tag{4}$$

The last term of Eq. (4), which peaks at $\beta=\pm\frac{1}{4}\pi$ and therefore represents the dependence of I on circular polarization, is proportional to the ζ component of the vector product $\mathbf{r}'\times\mathbf{r}$. The other terms can be rearranged so as to separate a contribution that does not depend on the polarization parameter β as well as contributions that depend separately on scalar and quadrupole moment combination of $\mathbf{r}'$ and $\mathbf{r}$. This rearrangement transforms Eq. (4) into

$$\begin{aligned}\hat{\epsilon}\cdot\mathbf{r}'\hat{\epsilon}^*\cdot\mathbf{r}&=\tfrac{1}{2}[(\xi'\xi+\eta'\eta)+(\xi'\xi-\eta'\eta)\cos 2\beta\\&\qquad-i(\xi'\eta-\eta'\xi)\sin 2\beta]\\&=\tfrac{1}{3}\mathbf{r}'\cdot\mathbf{r}-\tfrac{1}{6}(3\zeta'\zeta-\mathbf{r}'\cdot\mathbf{r})+\tfrac{1}{2}(\xi'\xi-\eta'\eta)\cos 2\beta\\&\qquad+\tfrac{1}{2}i^{-1}\mathbf{r}'\times\mathbf{r}\cdot\hat{\zeta}\sin 2\beta.\end{aligned} \tag{5}$$

Substituting this expression into (3) we obtain

$$\begin{aligned}I=C\tfrac{1}{3}\{&\langle(i'\,|\,\mathbf{r}'\cdot\mathbf{r}\,P_f(\mathbf{r}',\mathbf{r})\,|\,i)\rangle\\&-\tfrac{1}{2}\langle(i'\,|(3\zeta'\zeta-\mathbf{r}'\cdot\mathbf{r})P_f(\mathbf{r}',\mathbf{r})|i)\rangle\\&+\tfrac{3}{2}\langle(i'\,|(\xi'\xi-\eta'\eta)P_f(\mathbf{r}',\mathbf{r})|\,i)\rangle\cos 2\beta\\&+\tfrac{3}{2}\langle(i'\,|\,i^{-1}(\mathbf{r}'\times\mathbf{r})\cdot\hat{\zeta}\,P_f(\mathbf{r}',\mathbf{r})|\,i)\rangle\sin 2\beta\}.\end{aligned} \tag{6}$$

The first term in the braces of Eq. (6) depends on the matrix elements of a scalar operator and therefore has the same value for all degenerate states $|\,i)$; in fact it coincides with the Condon–Shortley "line strength" parameter to within a factor $e^2(2j_i+1)$. This term represents the average emission over all directions and polarizations and will be called S. The second term depends on the direction $\hat{\zeta}$ of the detector and represents the anisotropy of emission, still averaged over the polarization. The third and fourth terms represent the anisotropy with linear and with circular polarization, respectively.

Each term of Eq. (6) is proportional to the mean value of an operator of the irreducible tensor type which may be indicated by a two-index symbol $S^{[k]}{}_q$. Thus we shall indicate by $S^{[0]}{}_0$ the scalar operator $\mathbf{r}'\cdot\mathbf{r}\,P_f$ with the mean value $\langle S^{[0]}{}_0\rangle=S$. Similarly, $i^{-1}\mathbf{r}'\times\mathbf{r}\cdot\hat{\zeta}\,P_f$ is the ζ component $S^{[1]}{}_0$ of a vector operator, whose index $k=1$ indicates "vector" while $q=0$ indicates "invariance under rotations about the ζ axis." Further, $(3\zeta'\zeta-\mathbf{r}'\cdot\mathbf{r})P_f=S^{[2]}{}_0$ is the axially symmetric component of a quadrupole moment tensor and $(\xi'\xi-\eta'\eta)P_f=S^{[2]}{}_{2+}$ is another component of the same tensor that transforms like $\cos 2\varphi$ under rotations about ζ.

Real tensor components $S^{[k]}{}_{q\pm}=N_{kq\pm}[S^{[k]}{}_q\pm S^{[k]}{}_{-q}]$, with $q>0$, are used in this article in preference to the complex components $S^{[k]}{}_q$ commonly used in analytical work. Here N is a normalization factor which we adjust to simplify the final expressions even though this entails nonunitary transformation matrices for coordinate rotations. The definitions of $S^{[2]}{}_0$ and $S^{[2]}{}_{2+}$ given above imply $N_{20}/N_{22+}=6^{1/2}$. In the following we shall express the matrix elements and the mean values of $S^{[1]}{}_0$, $S^{[2]}{}_0$, and $S^{[2]}{}_{2+}$ in terms of the matrices and mean values of corresponding tensor components that are functions of the angular momentum operator $\mathbf{J}$.

(c) The mean values of the squared-dipole operators in expression (6) depend on the one hand on the alignment and orientation of the excited state generated by the collision and on the other hand on the dynamics of the dipole transition and, through it, on characteristics of the final state. These two dependences will be sorted out, using the fact that the mean values of any two tensorial operators $S^{[k]}{}_q$ and $T^{[k]}{}_q$ with the same indices k and q depend equally on the alignment and orientation of the excited atom. Specifically the Wigner–Eckart theorem states that the ratio of matrix elements $(i'\,|\,S^{[k]}{}_q\,|\,i)$ and $(i'\,|\,T^{[k]}{}_q\,|\,i)$ is independent of the magnetic quantum numbers m_i' and m_i; indeed this ratio equals the ratio of "reduced matrix elements" $(i\,||\,S^{[k]}\,||\,i)$ and $(i\,||\,T^{[k]}\,||\,i)$, each of which is wholly independent of m_i', m_i, and of q. the (unknown) alignment and orientation of the state i determine what averaging should be taken over m_i and m_i'; since this averaging is the same for the matrices of any two $S^{[k]}{}_q$ and $T^{[k]}{}_q$ we can write

$$\begin{aligned}\langle(i'\,|\,S^{[k]}{}_q\,|\,i)\rangle&=\langle(i'\,|\,T^{[k]}{}_q\,|\,i)\rangle\\&\quad\times(i\,||\,S^{[k]}\,||\,i)/(i\,||\,T^{[k]}\,||\,i).\end{aligned} \tag{7}$$

The structure of Eq. (7) is designed to sort out the anisotropy of the excited atom from the dynamics of light emission. On its left-hand side the operators $S^{[k]}{}_q$ will be the functions of $\mathbf{r}$, $\mathbf{r}'$ and P_f whose averages must be entered in Eq. (6); these averages depend both on the state of the excited atom and on the emission process. On the right-hand side we shall enter operators $T^{[k]}{}_q$ constructed as products of the angular momentum components J_ξ, J_η, J_ζ, because each of these components is a constant of motion of an isolated atom, such that their averages depend only on the state of the excited atom and not on the dynamics of light emission. The averages $\langle(i'\,|\,T^{[k]}{}_q\,|\,i)\rangle$ in Eq. (7) will then depend on alignment and orientation only, while the ratios of reduced matrix elements will depend on the dynamics of

dipole transitions irrespective of alignment or orientation. Equation (7) is particularly convenient because it allows us considerable freedom in defining the operators $S^{[k]}{}_q$ and $T^{[k]}{}_q$ insofar as normalization factors cancel out in this equation; normalization factors matter only in the application of coordinate transformations.

Notice now that the dynamics of light emission expresses itself through the dipole transition matrix elements $(f \mid \mathbf{r} \mid i)$, and that the matrices of *all tensors* $S^{[k]}{}_q$ in our problem are expressed in terms of *the same* $(f \mid \mathbf{r} \mid i)$. The tensors $S^{[k]}{}_q$ with different k and q differ only in the coupling of the vectors $\mathbf{r}'$ and $\mathbf{r}$ to form a scalar, a vector, or a tensor. Hence the dependence of reduced matrix elements on k involves only the coupling of vector operators, that is, geometrical considerations, and can be worked out by Racah algebra in terms of $6j$ coefficients.

The relevant tensorial considerations can be sketched as follows. The matrix element $(f \mid \mathbf{r} \mid i)$ of the operator $\mathbf{r}$ (which is a vector; i.e., an irreducible tensor with $k=1$) is constructed with wave functions of angular momenta j_f and j_i; we indicate this tensorial structure by the 3-digit symbol $(j_f j_i)1$ which may be read "j_f and j_i coupled to $k=1$." The construction of the matrix of a tensor $S^{[k]}$ of degree k, as the product of $\mathbf{r}'$ and $\mathbf{r}$ with the matrices $(i' \mid \mathbf{r}' \mid f)$ and $(f \mid \mathbf{r} \mid i)$, is then indicated by the composite symbol $[(j_i j_f)1(j_f j_i)1]^{(k)}$. On the other hand, we want to obtain the matrix of $S^{[k]}$ between states $(i' \mid$ and $\mid i)$ after coupling the final states into the scalar P_f (with $k=0$); this second construct is indicated by the composite symbol $[(j_i j_i)k(j_f j_f)0]^{(k)}$. The transformation from the first to the second of these alternative tensorial constructs is indicated in Racah algebra by a "recoupling coefficient" which is an element of an orthogonal transformation matrix and is indicated by

$$((j_i j_i)k(j_f j_f)0 \mid (j_i j_f)1(j_f j_i)1)^{(k)}.$$

The reduced matrix element $(i \,||\, S^{[k]} \,||\, i)$ depends on k exclusively through this recoupling coefficient, whose value is usually expressed in terms of the standard $6j$-coefficient

$$\begin{Bmatrix} j_i & j_i & k \\ 1 & 1 & j_f \end{Bmatrix}.$$

[The relevant expression is given by Eq. (15.15) of (FR59) or Eq. (7.1.1) of (E57).] The same considerations apply to the reduced matrix elements $(i \,||\, T^{[k]} \,||\, i)$, except that the tensors $T^{[k]}$ are constructed with the vector operators $\mathbf{J}$ whose matrices $(i'' \mid \mathbf{J} \mid i)$ are diagonal in the quantum number j_i. Therefore j_i replaces j_f in the recoupling coefficient applicable to $T^{[k]}$. Thus one obtains the dependence on k of the ratio of matrices of $S^{[k]}$ and $T^{[k]}$ in the form

$$\frac{(i \,||\, S^{[k]} \,||\, i)}{(i \,||\, T^{[k]} \,||\, i)} = (-1)^{j_i - j_f} \left(\begin{Bmatrix} j_i & j_i & k \\ 1 & 1 & j_f \end{Bmatrix} \Big/ \begin{Bmatrix} j_i & j_i & k \\ 1 & 1 & j_i \end{Bmatrix} \right) \times \frac{(i \,||\, S^{[0]} \,||\, i)}{(i \,||\, T^{[0]} \,||\, i)},$$

$$= h^{(k)}(j_i, j_f)\ (i \,||\, S^{[0]} \,||\, i)/(i \,||\, T^{[0]} \,||\, i). \qquad (8)$$

The dependence of this ratio on the quantum number j_f of the final state reflects the loss of angular and polarization dependence which results from summing over m_f. The values of the $6j$ coefficients are tabulated in (RBMW59). The phase normalization factor $(-1)^{j_i - j_f}$ is required for (8) to hold identically for $k=0$.

In the particular case of $k=0$, that is, for scalar operators, inspection of Eq. (6) identifies the scalar $S^{[0]}{}_0$ as the operator $\mathbf{r}' \cdot \mathbf{r}\, P_f$, whose nonzero matrix elements have been called S and are independent of m_i. The corresponding scalar $T^{[0]}{}_0$ constructed with $\mathbf{J}$ is $\mathbf{J}^2$, whose nonzero matrix elements equal $j_i(j_i+1)$ for all states $\mid i)$. Hence we can write

$$(i \,||\, S^{[0]} \,||\, i)/(i \,||\, T^{[0]} \,||\, i) = S/j_i(j_i+1) \qquad (9)$$

and substitute this ratio in (8).

In the final application to Eq. (6) we replace each component of the vectors $\mathbf{r}'$ or $\mathbf{r}$ by the corresponding component of $\mathbf{J}$ and P_f by 1, compensating for this substitution by the factor $h^{(k)}S/j_i(j_i+1)$. Thus we obtain

$$I = \tfrac{1}{3}CS\{1 - \tfrac{1}{2}h^{(2)}(j_i, j_f)[\langle (i' \mid 3J_\xi^2 - \mathbf{J}^2 \mid i) \rangle / j_i(j_i+1)] + \tfrac{3}{2}h^{(2)}(j_i, j_f)[\langle (i' \mid J_\xi^2 - J_\eta^2 \mid i) \rangle / j_i(j_i+1)] \cos 2\beta + \tfrac{3}{2}h^{(1)}(j_i, j_f)[\langle (i' \mid J_\xi \mid i) \rangle / j_i(j_i+1)] \sin 2\beta\}, \qquad (10)$$

where the formula $i^{-1}\mathbf{J} \times \mathbf{J} = \mathbf{J}$ has been used. The second term in the braces shows that the anisotropy of emission is proportional to the alignment of the emitter along the direction of emission. The third and fourth terms show the linear and circular polarization to be proportional to the alignment within the plane of polarization (ξ, η) and to the component of the orientation $\langle \mathbf{J} \rangle$ in the direction of emission, respectively.

Experimental analysis of the *variation of light intensity* as a function of the detector's direction $\hat{\zeta}$ determines the dependence of the alignment parameter $\langle (i' \mid 3J_\zeta^2 - \mathbf{J}^2 \mid i) \rangle$ on $\hat{\zeta}$ and thus reconstructs the direction and magnitude of the axes of *the alignment tensor*. The same result is achieved, often with higher sensitivity, by determining $\langle (i' \mid J_\xi^2 - J_\eta^2 \mid i) \rangle$ through measurements of the intensity variation that accompanies the rotation of a linear polarization analyzer,

that is, the rotation of the $\hat{\xi}$ axis, for two fixed directions $\hat{\zeta}$. *Measurement of the circular polarization* observed as a function of the direction $\hat{\zeta}$ determines instead the various components of *the orientation vector* $\langle(i' \mid \mathbf{J} \mid i)\rangle$.

To simplify the notation we introduce in the detector frame two alignment parameters

$$A_0^{\text{det}} = \langle(i' \mid 3J_\zeta^2 - \mathbf{J}^2 \mid i)\rangle / j_i(j_i+1), \tag{11}$$

$$A_{2+}^{\text{det}} = \langle(i' \mid J_\xi^2 - J_\eta^2 \mid i)\rangle / j_i(j_i+1), \tag{12}$$

and one orientation parameter

$$O_0^{\text{det}} = \langle(i' \mid J_\zeta \mid i)\rangle / j_i(j_i+1), \tag{13}$$

whereby Eq. (10) takes the form

$$I = \tfrac{1}{3}CS\{1 - \tfrac{1}{2}h^{(2)}(j_i, j_f)A_0^{\text{det}} + \tfrac{3}{2}h^{(2)}(j_i, j_f)A_{2+}^{\text{det}} \cos 2\beta + \tfrac{3}{2}h^{(1)}(j_i, j_f)O_0^{\text{det}} \sin 2\beta\}. \tag{14}$$

The most familiar type of polarization experiment deals with light excited by collisions that produce only alignment along a single axis $\hat{z}$, as described in the following paragraphs. Light is observed at 90°, that is, in a direction $\hat{\xi}$ perpendicular to $\hat{z}$, with a linear polarization filter, that is, setting $\beta = 0$. One sets the $\hat{\xi}$ axis alternately parallel and perpendicular to $\hat{z}$ thus obtaining two intensity measurements $I_{\parallel}$ and $I_{\perp}$ and defines the degree of polarization as $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. In the notation of Eq. (14), $I_{\parallel}$ differs from $I_{\perp}$ by sign reversal of A_{2+}^{det}. This gives

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3h^{(2)}(j_i, j_f)A_{2+}^{\text{det}}}{2 - h^{(2)}(j_i, j_f)A_0^{\text{det}}}, \tag{15}$$

with reference to $\hat{\xi}$ parallel to $\hat{z}$.

II.1. Alignment and Orientation by Collision

The radiator's anisotropy is represented in Eq. (14) by components of the alignment tensor and of the orientation vector in the detector frame (ξ, η, ζ). The collision process determines, of course, the components of this tensor and vector in a "collision frame" (x, y, z), whose $\hat{z}$ axis usually coincides with the direction of an incident particle beam. Components of the alignment tensor in this frame will be denoted by A^{col}.

In the simplest cases (e.g., an unpolarized particle beam incident on gas molecules without detection of scattered or recoil particles, or an ion beam emerging perpendicularly from a foil surface) the experimental arrangement identifies only this $\hat{z}$ axis and has cylindrical symmetry about it. Under these circumstances, the alignment tensor has a single nonzero component, namely A_0^{col}. Only in this familiar, but simple, case—or under equivalent circumstances—does symmetry require the excited state to be representable as the incoherent superposition of pure states with different magnetic quantum numbers m_i. Here we have

$$A_0^{\text{col}} = \sum_{m_i}[3m_i^2 - j_i(j_i+1)]\sigma(m_i) / j_i(j_i+1)\sum_i \sigma(m_i), \tag{16}$$

where $\sigma(m_i)$ indicates the partial cross section for excitation of the state $\mid j_i m_i)$.

From the value of A_0^{col} we obtain the parameters A_0^{det} and A_{2+}^{det} in the detector frame by a coordinate transformation. [One must allow here for our nonstandard normalization of tensor components. The appropriate transformation formulas can be obtained by transforming separately each Cartesian component of $\mathbf{J}$ in the expression of $\mathbf{A}$.] The result is

$$A_0^{\text{det}} = A_0^{\text{col}}\tfrac{1}{2}(3\cos^2\theta - 1),$$

$$A_{2+}^{\text{det}} = A_0^{\text{col}}\tfrac{1}{2}\sin^2\theta \cos 2\psi, \tag{17}$$

where $\cos\theta = \hat{\zeta}\cdot\hat{z}$ and ψ is the angle between the detector's axis $\hat{\xi}$ and the plane $(\hat{\zeta}\hat{z})$. In this same case the *orientation* vector $\langle(i' \mid \mathbf{J} \mid i)\rangle$ *vanishes* altogether, because it is an axial vector (pseudovector) and no such quantity can be identified in a frame characterized by a single incidence vector $\hat{z}$, unless the incident particles have nonzero helicity.

Equation (17) contains two well-known results. The source anisotropy has no effect upon the light intensity emitted at the "magic angle" $\theta =$ arc cos $(\frac{1}{3})^{1/2} = 54°44'$, where A_0^{det} vanishes. That is, intensity measurements in this direction are independent of alignment. On the other hand, the polarization vanishes in the forward or backward directions, $\theta = 0°$ or 180°, under the condition of symmetry about the collision axis, irrespective of the source alignment.

The collision frame loses its axial symmetry when the scattering direction (or a recoil direction) $\hat{z}'$ is observed in coincidence with the light emission. In beam foil excitation, the state of an atom emerging from the foil depends presumably on its interaction with the surface layers of the foil and hence on the orientation of this surface; therefore one can spoil the axial symmetry by tilting the normal to the foil, $\hat{z}'$, away from the beam axis $\hat{z}$.

When an axis $\hat{z}' \neq \hat{z}$ is thus singled out we may lay the $\hat{x}$ axis in the plane $(\hat{z}\hat{z}')$ and the collision identifies the axial vector $\hat{z}\times\hat{z}'$ parallel to $\hat{y}$. The *orientation* parameter $O_{1-}^{\text{col}} \propto \langle(i' \mid J_y \mid i)\rangle$ is now generally *nonzero* and there occur two additional nonzero alignment components, namely, $A_{2+}^{\text{col}} \propto \langle(i' \mid J_x^2 - J_y^2 \mid i)\rangle$ and $A_{1+}^{\text{col}} = \langle(i' \mid J_xJ_z + J_zJ_x \mid i)\rangle / j_i(j_i+1)$. (It is just the occurrence of such nonzero components which implies *coherent superposition* of states with different m_i values.) The residual symmetry still causes all other components of orientation and alignment to vanish. A frame trans-

formation yields now

$$O_0^{\rm det}=O_{1-}^{\rm col}\sin\theta\sin\phi,$$

$$A_0^{\rm det}=A_0^{\rm col}\tfrac{1}{2}(3\cos^2\theta-1)+A_{1+}^{\rm col}\tfrac{3}{2}\sin 2\theta\cos\phi+A_{2+}^{\rm col}\tfrac{3}{2}\sin^2\theta\cos 2\phi,$$

$$A_{2+}^{\rm det}=A_0^{\rm col}\tfrac{1}{2}\sin^2\theta\cos 2\psi+A_{1+}^{\rm col}\{\sin\theta\cos\phi\sin 2\psi+\sin\theta\cos\theta\sin\phi\cos 2\psi\}+A_{2+}^{\rm col}\{\tfrac{1}{2}(1+\cos^2\theta)\cos 2\phi\cos 2\psi-\cos\theta\sin 2\phi\sin 2\psi\},\quad(18)$$

where ϕ is the angle between the planes $(\hat{z}\hat{x})$ [i.e., $(\hat{z}\hat{z}')$] and $(\hat{z}\hat{\zeta})$. That is, θ and ϕ are the polar coordinates of the light detector while ψ is the third Euler angle, required to identify the orientation of a linear polarization analyzer. Other components of $\mathbf{O}^{\rm det}$ and $\mathbf{A}^{\rm det}$ are not given here, being irrelevant to light observations.

The several components of the orientation vector and alignment tensor are independent parameters in the sense that the value of any one of them may be changed by a change of the excitation process while the others remain fixed. There are, however, upper limits to the sum of their squares. Such an upper limit is reached for example for the pure state identified in a given frame by $m_i=j_i$. In this event we have $(i\,|\,J_z\,|\,i)=j_i$ and $(i\,|\,3J_z^2-\mathbf{J}^2\,|\,i)=j_i(2j_i-1)$ but all other components of $\mathbf{O}^{\rm col}$ and of $\mathbf{A}^{\rm col}$ vanish. One can also see directly that full circular polarization would imply total absence of any linear polarization, and vice versa.

For purposes of illustration we consider some simple cases which have been studied experimentally and treated successfully by earlier procedures, reformulating their treatment in the language of this article. In one example, the scattered particle is detected after collision in coincidence with the emitted photon, but just in the direction of incidence, i.e., at 0° deflection. This arrangement was suggested by Imhoff and Read (IR71) to test detailed theoretical predictions of (PS58) and was then successfully applied (KAR72). The arrangement implies not only that the $\hat{z}'$ axis coincides with $\hat{z}$, thus restoring axial symmetry, but also that the collision imparts to the atom no angular momentum component parallel to the $\hat{z}$ axis (except for possible spin exchange). If the target atom was initially in a ^1S state, without any angular momentum, the collision will then leave it in a state with $m_i=0$ and, therefore, with $\langle 3J_z^2-\mathbf{J}^2\rangle=-j_i(j_i+1)$ and $A_0^{\rm col}=-1$. Light emission by decay to any final state with $j_f=0$, which occurs by a dipole process when $j_i=1$, has then full linear polarization according to (PS58). In the present formulation the same result is retrieved by setting $A_0^{\rm col}=-1$ in Eq. (17), $j_i=1$ and $j_f=0$ in (8) which yields $h^{(2)}(1,0)=-2$, and $\beta=0$ for detection of linear polarization. The intensity formula (14) gives then

$$I=CS\sin^2\theta[\tfrac{1}{2}(1+\cos 2\psi)],\quad(19)$$

which is the result expected for a linear polarization detector placed along $\hat{\zeta}$, i.e., at an angle θ with respect to a radiating dipole parallel to $\hat{z}$, and with its $\hat{\xi}$ axis at an angle ψ with respect to the (ζz) plane. The degree of polarization P given by Eq. (15) reduces now to $\cos 2\psi$, and more specifically to 1 when $\hat{\xi}$ lies in the (ζz) plane, i.e., when $\psi=0$, as assumed by the definition of P.

Another application of angular momentum and other symmetry considerations is afforded by measurements of Lyman-α excitation by charge transfer collision of protons with helium. The experiment by McKnight and Jaecks (JCMc70, McJ71) was designed to measure a coincidence rate between photons and scattered H atoms, which would be proportional to the excitation cross section and independent of unknown parameters such as the polarization of the emitted light. The design utilized the invariance of the collision process under reflection in the scattering plane, $(zz')\equiv(xz)$. Excitation of the p_y state, odd under this reflection, is then forbidden provided the He^+ ion is left in its even-parity ground state. Since the excluded p_y state has $J_y=0$, the p state which is actually excited must have $J_y^2=1$. This circumstance was exploited by placing the photon counter, i.e., the ζ axis of the detector frame, along the y axis of the collision frame. Accordingly we substitute in Eq. (11) $\langle J_\zeta^2\rangle=J_y^2=1$ and $\mathbf{J}^2=j_i(j_i+1)=2$ and thus obtain $A_0^{\rm det}=\frac{1}{2}$. Recalling that $h^{(2)}=-2$ for a $p\rightarrow s$ optical transition and averaging Eq. (14) over β, as appropriate to a counter insensitive to polarization, we have finally

$$I=CS\tfrac{1}{6},\quad(20)$$

which is indeed independent of unknown parameters.

II.2. Excitation by Electron Impact

Basic experiments on light excited by electron impact (S26, SA27) and their theoretical framework (O27) date from the mid-1920's. Theory provides clear predictions both for high collision energies and for energies very close to threshold. Interpolation between the results valid in the two limits seems plausible but the resulting prediction was soon found erroneous. We outline this development to illustrate both the power and the limitations of simple geometrical and dynamical considerations.

At high collision energies the Born approximation, which treats a collision as an impulsive transfer of momentum $\mathbf{q}$ by the incident electron, prevails; this transfer provides for target excitation. The vector $\mathbf{q}$, which can be determined for each collision by observing the direction and energy of the scattered electron, is

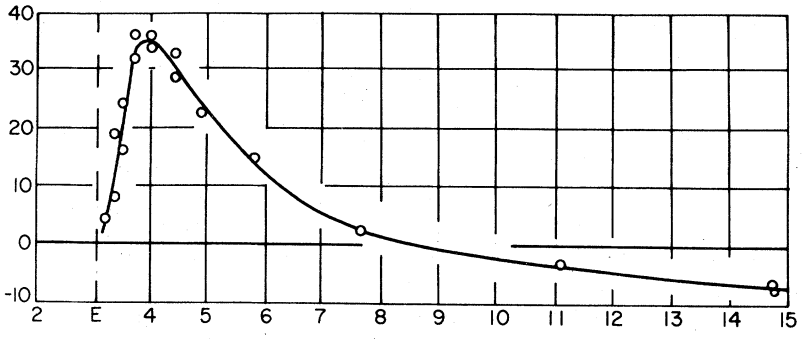

FIG. 1. Percent linear polarization of mercury light observed at 90° from the direction of incidence (SA27). Note the sign reversal of the polarization at ~80 eV and its disappearance near threshold. The energy scale [in $(\text{eV})^{1/2}$] is nonlinear and the energy resolution not very high.

the only collision parameter on which alignment and orientation can depend. Since $\mathbf{q}$ is a polar vector, this implies that *no orientation* can occur in this approximation. Further, symmetry about the direction of $\mathbf{q}$ implies that the only nonzero component of the alignment tensor, in a frame with axis $\mathbf{q}$, is $A_0^{\hat{q}}=\langle(i'\mid 3(\mathbf{J}\cdot\hat{q})^2-\mathbf{J}^2\mid i)\rangle/j_i(j_i+1)$. Finally, the transfer of momentum $\mathbf{q}$ cannot impart to the target any nonzero value of $\mathbf{J}\cdot\hat{q}$, from which follows $A_0^{\hat{q}}=-1$. Transformation to the collision frame, with $\hat{z}$ in the direction of impact and $\hat{x}$ in the plane of scattering, then yields

$$A_0^{\text{col}}=-\tfrac{1}{2}[3(\hat{q}\cdot\hat{z})^2-1],$$
$$A_{1+}^{\text{col}}=-\tfrac{1}{2}\hat{q}\cdot\hat{z}[1-(\hat{q}\cdot\hat{z})^2]^{1/2},$$
$$A_{2+}^{\text{col}}=-\tfrac{1}{2}[1-(\hat{q}\cdot\hat{z})^2]. \qquad (21)$$

Normally, the scattering direction remains undetected and an average must be taken over the direction $\hat{q}$. Recalling that A_{1+}^{col} and A_{2+}^{col} are proportional to $\langle J_xJ_z+J_zJ_x\rangle$ and $\langle J_x^2-J_y^2\rangle$, respectively, and that the orientation of the $\hat{x}$ and $\hat{y}$ axes rotates about $\hat{z}$ in the course of averaging over $\hat{q}$, we see that A_{1+}^{col} and A_{2+}^{col} average out. We are thus left, as expected, with a single nonzero parameter, namely,

$$A_0^{\text{col}}=-\tfrac{1}{2}[3\langle(\hat{q}\cdot\hat{z})^2\rangle-1]. \qquad (22)$$

A final step of the theory utilizes energy-momentum considerations in the collision (I71) to predict that $\hat{q}$ is predominantly transverse to $\hat{z}$ at very high impact energies and parallel to $\hat{z}$ at lower energies. The resulting *sign reversal* of A_0^{col} occurs as the energy decreases through a range of the order of ten times the threshold energy (Be33). In the high-energy limit we have $\langle(\hat{q}\cdot\hat{z})^2\rangle\to 0$ and $A_0^{\text{col}}\to\frac{1}{2}$.

In the opposite, low-energy limit, i.e., just above threshold, the electron must be scattered inelastically into an s state; otherwise it would have to escape by tunneling through a centrifugal potential barrier. Hence the departing electron does not weigh on the angular momentum balance, apart from spin exchange which is often disregarded. Any nonzero alignment of the excited atom reflects then only the contribution of the incident electron, whose orbital momentum component vanishes in the direction of incidence. Setting thus $\langle J_z^2\rangle=0$, i.e., *disregarding spin exchange*, we have

$$(A_0^{\text{col}})_{\text{thresh}}=-1. \qquad (23)$$

Remarkably, this value coincides with the low-energy limit of Eq. (22), since $\hat{q}$ must be parallel to $\hat{z}$ at threshold. This coincidence may lead to the surmise that A_0^{col} should interpolate smoothly, and that the Born approximation result might hold uninterruptedly—if only approximately—down to threshold. Early measurements of the dependence of light polarization upon the velocity of incident electrons (SA27) disproved this surmise. As shown in Fig. 1, the polarization seems to disappear when the incident energy drops to within a few electron volts of threshold.

This remarkable drop of polarization near threshold, in apparent disagreement with a clearcut theoretical prediction, was studied in increasing detail between 1955 and 1970 through a sequence of experiments, mostly on helium (LM57, McF64, HK67, McF67, SFG67). Actually, none of these experiments could measure the degree of light polarization at energies sufficiently close to threshold to allow unequivocal application of the argument leading to Eq. (23). Note that since the scattered electron leaves the atom in an excited state with a radius of $\sim n^2$ atomic units (n is the principal quantum number of the state less its quantum defect and n^2 its reciprocal binding energy in units of 13.6 eV), the centrifugal barrier which hinders its escape with orbital quantum number $l>0$ lies at radial distances larger than n^2 and peaks at

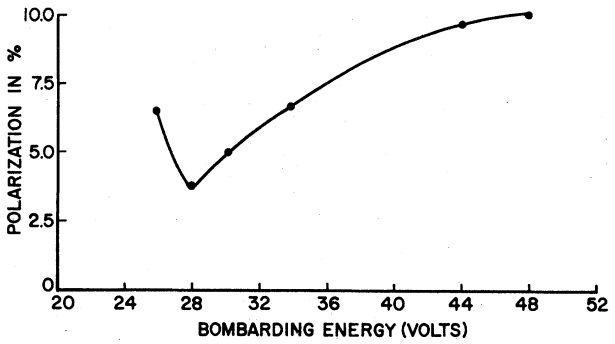

FIG. 2. Same as Fig. 1 for the 3889-Å line of helium (LM57). The scale is linear and greatly expanded with respect to Fig. 1. Note the low minimum and the incipient rise toward the threshold which lies at 23 eV.

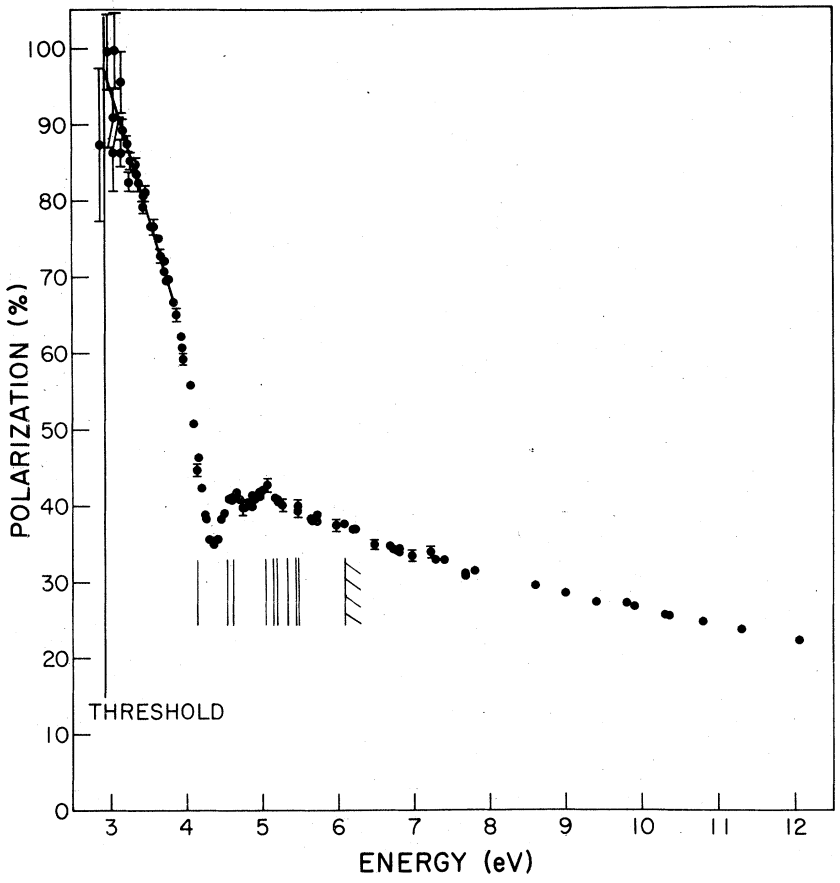

FIG. 3. Polarization of the calcium 4227-Å resonance line ($^1P_1° \rightarrow {}^1S_0$) as a function of the energy of exciting electrons (EG73). Note the rapid drop from the maximum at threshold and the unsmoothness in the range of expected, but unresolved, resonances.

energies smaller than $l(l+1)/n^4$ a.u. Equation (23) may then apply only within a fraction of 1 eV above threshold. The experimental evidence provided, e.g., by the left-hand portion of the curve in Fig. 2, is thus not inconsistent with Eq. (23). Similar evidence is found in the recent data of (OHK72) on mercury. In other instances, particularly in the excitation of the resonance lines of the alkalis and alkaline earths (HKK65, EG72, EG73), the observed polarization tends rather clearly to the appropriate threshold value, as shown in Fig. 3.

Assuming then that Eq. (23) does hold at threshold, the experimental data indicate that $A_0^{\rm col}$ drops in many cases to a very low value shortly above threshold, returning then to its Born approximation value only at higher energies. This drop has not been explained in any detail but is probably related to the occurrence of conspicuous resonances in inelastic electron–atom cross sections near threshold. At resonance the colliding electron and the one being excited in the atom remain strongly correlated for a time interval sufficient to allow extensive exchange of angular momentum between them, with a resulting decrease of $A_0^{\rm col}$. The necessary time interval is of the order of the reciprocal optical frequency for transitions between excited states, i.e., $\lesssim 10^{-14}$ sec. Various, albeit fragmentary, evidence on hand points to the conclusion that such extensive correlations occur normally in the process of excitation by electron impact and persist in the spectrum over a range $\gtrsim 10$ eV above threshold.

Indeed careful extensive studies of optical excitation by highly monochromatic electrons might prove very effective in establishing and refining our knowledge of these correlations. The occurrence of resonances near threshold, superimposed on a smooth dependence of polarization on impact energy, has been demonstrated clearly in a very recent experiment on the excitation of the resonance line of Ba^+ (CTD73). As seen from these results, in Fig. 4, the resonances fail in this case to reduce the average polarization to a near zero value. Figure 4 also demonstrates a smooth variation of polarization as a function of collision energy (on a logarithmic scale) from $\sim$7 to 500 eV, with sign reversal at an energy $\sim$10 times threshold in agreement with the crude rule indicated above. The Ba^+ data are quite analogous in this respect to those of Ca (EG73) which extrapolate at high energy to the 100% negative polarization limit predicted by Eq. (15) with $h^{(2)}=-2$ and with the limiting value $A_0^{\rm col} \rightarrow \frac{1}{2}$. By contrast, the Ba^+ and Ca data differ in

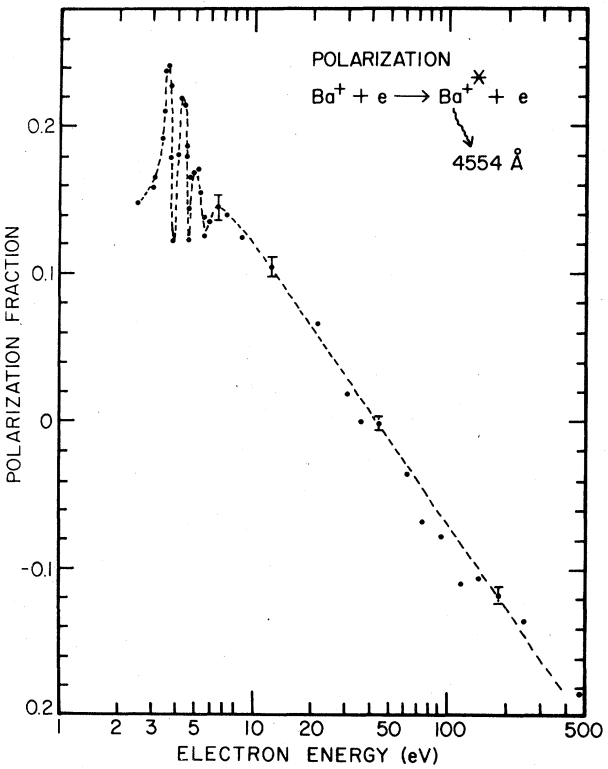

FIG. 4. Polarization of the 4554-Å Ba^+ resonance line ($^2P_{3/2}{}^\circ \rightarrow {}^2S_{1/2}$) as a function of the energy of exciting electrons (CTD73). Note the clearly resolved resonances and the smooth variation and sign reversal of the polarization on the logarithmic scale.

that the polarization shown in Fig. 3 drops rapidly from threshold to a region where barely resolved resonances appear to exist.

Note added in proof: Private communications have been received regarding current experiments that extend and complement the material of this section. Each of these experiments pertains to the polarization of helium lines excited by electron collisions.

Heddle and collaborators (to be published in *J. Phys. B*) have increased the resolution of incidence energy to the point of detecting changes of polarization resulting from 0.01 eV step-ups in energy. The polarization of the lines studied in this work drops sharply from threshold over a few energy steps and then exhibits a number of resonances within a few eV.

Resonances have also been detected in the helium light polarization at much higher bombarding energy by A. Defrance (University of Rennes, France). These resonances occur near 58 eV and correspond to the formation of triply excited He^- levels, whose presence had been detected in several other processes since 1965.

Coincidence detection of photon and scattered electron has been achieved by Kleinpoppen and collaborators [*Phys. Rev. Lett.* (to be published)]. The collision energy was ~80 eV, that is, sufficiently low to yield departures from the predictions of Born approximation theory. As explained above, Born approximation yields an alignment tensor with axial symmetry about the momentum transfer $\mathbf{q}$ and with a single nonzero component $A_0{}^{\hat{q}} = -1$. Departures from this prediction may be described in terms of changes of direction and magnitude of the principal axes of the alignment tensor (MJ71). (A principal-axes coordinate frame is characterized by $A_{2-}{}^{\text{princ}} = A_{1+}{}^{\text{princ}} = A_{1-}{}^{\text{princ}} = 0$.) The coincidence experiment found a principal axis to depart from $\mathbf{q}$ by about 8° in the plane of electron scattering. The value of $A_0{}^{\text{princ}}$ also departs from -1. These initial observations are confined to photon emission in the scattering plane.

III. EMISSION BY ATOMS IN NONSTATIONARY STATES

Light emission by excited atoms has been studied widely in recent years under conditions of high time resolution, which determine the time interval between excitation and emission to within 10^{-10} or even 10^{-11} sec (H67). When the atoms travel in a beam of known velocity, this time interval is determined by the distance between the point of collision and the field of view of the light detector. Alternatively one may time the collision by detecting a scattered particle and the emitted light by photon counting in delayed coincidence.

Sharp definition of the time of excitation requires the collision to be of short duration and hence capable of populating coherently a range of energy levels. Similarly, a sharp definition of the time of emission within an interval $\Delta\tau$ prevents the spectral analysis of the light from resolving levels spaced much closer than $\hbar/\Delta\tau$. The observed light originates then from a nonstationary state represented by the coherent superposition of stationary states with different, unresolved, energy eigenvalues. We discuss in this second part how the intensity, anisotropy, and polarization of the emitted light are modulated in accord with the coherent superposition of radiation with different, unresolved frequencies.

As in Sec. II we will express the anisotropy and polarization of light in terms of the alignment and orientation of the excited states. The time modulation of these parameters provides information on both the energy and eigenfunctions of the unresolved levels as well as on their superposition generated initially by the collision. The energy splittings of the unresolved levels are due in general to hyperfine interactions, spin–orbit coupling, or the action of external fields. The time modulation of atomic orientation and alignment may be interpreted as due to oscillations or precession of electron orbitals under influence of the interactions.

A typical collision excites the orbital motion of electrons leaving the electronic and nuclear spins unaffected. (Collisions with electron exchange or rearrangement are exceptional in this respect, since they may introduce an initial spin polarization.) We

deal here, then, with the alignment and/or orientation of the orbital motion which is responsible for the subsequent light emission by electric dipole transitions. By contrast, spin–orbit interactions and external fields have the effect of disturbing the initial alignment and orientation. The observations of light with high spectral resolution, considered in Sec. I, display the mean orbital orientation and alignment in individual hyperfine or fine structure levels. The observations with high time resolution to be considered in this part display instead the time dependence of the orbital anisotropy.

It should be noted that spin–orbit interactions and external fields affect only the anisotropy of the orbital motion, but do not affect the rate of light emission. Therefore the variations of alignment and orientation to be considered here merely modulate the anisotropy of the exponential decay. This decay is normally characterized by a single constant Γ, pertaining to the unresolved multiplet. Exceptional in this respect are the experiments where levels with different orbital classification also remain unresolved, because these levels radiate at intrinsically different rates. The decay constant Γ then becomes a matrix. The hydrogenic systems provide an outstanding example of this effect because their orbitals with equal n and different l quantum numbers are nearly degenerate. Normally, however, the interactions that change the orbital classification are so strong as to yield easily resolved term splittings. The resulting modulations of light emission are then too fast for resolution by current techniques.

The theory of the modulation phenomena is still fragmentary. We present here a general formulation and develop it analytically for a few simple examples. We shall also indicate where complications arise in other problems and how they may be treated. The analytical approach to be followed here utilizes the shortcuts to Racah algebra introduced in Sec. II but its physical substance and its main results are common to the theory of perturbed angular correlations of nuclear radiations, as presented, e.g., in Sec. 9 of (FS68).

III.1. General Approach

The anisotropy and polarization of electric dipole radiation are related by Eq. (6) to the mean values of irreducible components $S^{[k]}{}_q$ of the tensor

$$\mathbf{r}' P_f(\mathbf{r}', \mathbf{r})\, \mathbf{r} = \mathbf{r}' \sum_f |f)\,(f|\, \mathbf{r}, \qquad (24)$$

where f represents the quantum numbers of the final state of the radiating atom. We have seen in Sec. II how the Wigner–Eckart theorem relates the mean values of $S^{[k]}{}_q$ to those of the irreducible tensor components $T^{[k]}{}_q$ constructed as products of angular momentum operators. The mean values $\langle T^{[k]}{}_q \rangle$ constitute alignment and orientation parameters of the excited atom. The following treatment of nonstationary states deals explicitly with the time dependence of the mean values of $S^{[k]}{}_q$ but the relationship to the mean values of $T^{[k]}{}_q$ remains unchanged. This relationship insures that the modulation of the emitted light depends only on $\langle T^{[k]}{}_q \rangle$, and hence on the state of the excited atoms, and not on the emission process itself.

To study the time dependence of the anisotropy and polarization of the emitted light, we evaluate the mean values of $S^{[k]}{}_q$ at the time t of emission. Recall, in this connection, that the averaging process indicated in Eq. (6) by $\langle (i' \cdots i) \rangle$ pertains to the state of excitation generated by the collision process at the initial time $t=0$. Under these circumstances it appears convenient to introduce the time dependence using the Heisenberg representation. This is done by replacing each of the parameters of Eq. (6) according to the prescription

$$\langle (i'|\, S^{[k]}{}_q \,|i) \rangle \rightarrow \langle (i'|\exp(iHt/\hbar) S^{[k]}{}_q \times \exp(-iHt/\hbar)|\, i) \rangle, \qquad (25)$$

where H is the Hamiltonian operator of the atom. [Note that one arrives at the same prescription in the Schrödinger representation by regarding the states $(i'|$ and $|\, i)$ as time-dependent, the dependence being represented by $\exp(\pm iHt/\hbar)$, respectively.] From this point of view, the original formula (6) pertains to the case where $(i'|$ and $|\, i)$ are stationary states with same energy eigenvalue E_i. In that event the operator H may be replaced by E_i; the two factors $\exp(\pm iE_i t/\hbar)$ cancel then in Eq. (25) and $\langle S^{[k]}{}_q \rangle$ becomes time independent. Our task consists of evaluating the time dependence introduced in Eq. (25) when $(i'|$ and $|\, i)$ are not stationary. More specifically, we shall express the right-hand side of Eq. (25) in terms of its value for $t=0$ which has been discussed in Sec. II.

The modulations which we consider result from interactions that are not only weak but also of little relevance to the initial excitation by collision. This is why we relate the initial excitation to states $|\, i)$ that would be stationary only in the absence of weak interactions. In fact, these states differ from the eigenstates $|\, n)$ of the complete Hamiltonian with energy levels E_n. The evaluation of the time-dependent parameters in Eq. (25) requires us then to take into account not only the level splittings but also the connection between the stationary states $|\, n)$ and the nonstationary states $|\, i)$.

We consider particularly atomic excitations in which the states of both sets, $|\, i)$ and $|\, n)$, are fully identified by specific—although different—sets of angular momentum quantum numbers. Stationary states of hyperfine structure are thus identified as $|\, FM_F)$, where $\mathbf{F}$ is the constant resultant of two coupled momenta, namely, $\mathbf{I}$ of the nucleus and $\mathbf{J}$ of the electrons. On the other hand, $\mathbf{I}$ and $\mathbf{J}$ are uncoupled in the $|\, i)$ states which may thus be labeled by the

magnetic quantum numbers of the separate nuclear and electronic states, $|M_I M_J)$. Similarly, the stationary states of an atom in an external field are classified by their magnetic quantum number in a frame with its $\bar{z}$ axis parallel to the field, whereas the $|i)$ states are naturally identified in the collision frame introduced in Sec. II. In this class of problems the connection between the sets of stationary and nonstationary states is fully determined by angular momentum theory or by other general considerations independent of dynamical details. We single out this class because it is amenable to analytical treatment, thus providing a framework for the introduction of more complex phenomena.

The interactions which modulate the light emission fall into two broad types, namely, interactions among internal orbits and spins and interactions of the atom with external fields. As noted above, the light emission depends on the orientation and alignment of electron orbits. Its modulation by internal couplings reflects then reversible exchanges of angular momentum between orbits and spins, and the accompanying exchange of alignment and orientation. Usually the exciting collision leaves the spins unpolarized. In this event the spins can only draw from the initial alignment and orientation of the orbits, thus reducing it albeit reversibly without contributing any input. Moreover, the scalar character of the initial spin distribution and of the interaction Hamiltonian leaves unchanged the tensorial character of each $S^{[k]}_q$ operator of the orbits. Therefore, in this case the interaction merely modulates the magnitude of each separate parameter $\langle S^{[k]}_q \rangle$.

In contrast, the presence of an external field introduces a new reference frame and thus tends to interlink the modulations of the different parameters $\langle S^{[k]}_q \rangle$. We shall deal first with the simple case of a weak field Zeeman effect, where the modulation may be represented as a precession of the collision frame about the field direction $\hat{\bar{z}}$.

We have emphasized that the modulation of light emission reflects the nonstationary character of the excited state. However, the evaluation of the parameters $\langle S^{[k]}_q \rangle$ must also take into account that observations with low spectral resolution generally detect simultaneously light emitted in transitions to different final states. These different emissions are superposed incoherently, barring separate observations of the final state. Their existence is included in the theory by specifying that the summation in the definition of the operator P_f in Eq. (24) extends to include all unresolved final states.

By way of illustration consider transitions leading to unresolved hyperfine levels $|IJ_f F_f M_{Ff})$. The sum over final states runs here over both F_f and M_{Ff}, at fixed J_f. This set of states spans the same Hilbert space as the set of uncoupled states $|IM_I J_f M_{Jf})$. Therefore the operator P_f factors into two scalars, one operating on electrons and the other on the nuclear spin,

$$P_f = \sum_{F_f M_{Ff}} |F_f M_{Ff})(F_f M_{Ff}| = [\sum_{M_I} |IM_I)(IM_I|][\sum_{M_{Jf}} |J_f M_{Jf})(J_f M_{Jf}|]. \tag{26}$$

The last factor of Eq. (26) represents a projection on the electronic final states with $J=J_f$ and the preceding one is simply the unit operator in the space of nuclear states with the fixed spin I. The operator P_f defined by Eq. (26) should be entered in Eq. (24) together with the electron dipole operators $\mathbf{r}$ and $\mathbf{r}'$. Each of the resulting tensorial operators $S^{[k]}_q$ factors then into an irreducible tensor component operating only on the electron variables multiplied by the unit operator of nuclear spin.

In this example we would then construct the operator $T^{[k]}_q$ from components of $\mathbf{J}$ rather than from components of $\mathbf{F}=\mathbf{I}+\mathbf{J}$. Similarly, when fine structure is also unresolved one should further factor the scalar P_f of electronic variables into its orbital and spin parts. Each tensor component $S^{[k]}_q$ would then factor into a tensorial part operating on orbital variables only, multiplied by the unit operator of electron spin. The operators $T^{[k]}_q$ would be constructed from the components of $\mathbf{L}$ rather than of $\mathbf{J}=\mathbf{L}+\mathbf{S}$.

III.2. Weak Field Effect on Emission from a Single Level

As an initial example, we consider here an excited state which would be stationary, as in Sec. II, with angular momentum quantum number j, except for the action of a magnetic field $\mathbf{B}$. The strength of $\mathbf{B}$ is sufficiently small for us to neglect any field-induced coupling to other excited states; that is, the mean value of the magnetic interaction is far smaller than the separation of zero-field levels. The excited state has then a definite gyromagnetic ratio γ_i and the Hamiltonian has the eigenvalues

$$E_i - \hbar\gamma_i B\bar{m}_i, \tag{27}$$

where $\bar{m}_i$ is the magnetic quantum number in a frame with $\bar{z}$ axis parallel to $\mathbf{B}$. The set of eigenstates $|n)$ of the Hamiltonian is identified here as $|j_i\bar{m}_i)$, with j_i fixed.

In this case one may consider the tensor components $S^{[k]}_q$ in the frame with axis $\bar{z}$. The matrix elements of the time-dependent operator are then easily evaluated as follows:

$$\begin{aligned}(j_i\bar{m}_i' &| \exp(iHt/\hbar) S^{[k]}_{\bar{q}} \exp(-iHt/\hbar) | j_i\bar{m}_i) \\ &= \exp[i(E_i/\hbar - \gamma_i B\bar{m}_i')t](j_i\bar{m}_i' | S^{[k]}_{\bar{q}} | j_i\bar{m}_i) \\ &\quad \times \exp[-i(E_i/\hbar - \gamma_i B\bar{m}_i)t] \\ &= \exp[-i\gamma_i B(\bar{m}_i' - \bar{m}_i)t](j_i\bar{m}_i' | S^{[k]}_{\bar{q}} | j_i m_i).\end{aligned} \tag{28}$$

Since a selection rule on the matrices of tensorial

operators requires the matrix element to vanish unless $\bar{m}_i'-\bar{m}_i=\bar{q}$, the time-dependent factors of Eq. (28) depend only on $\bar{q}$, rather than on the separate $\bar{m}_i'$ and $\bar{m}_i$, and can be factored out of the mean value, yielding

$$\langle(i' \mid \exp(iHt/\hbar)S^{[k]}_{\bar{q}}\exp(-iHt/\hbar) \mid i)\rangle = \exp(-i\bar{q}\gamma_i Bt)\langle(i' \mid S^{[k]}_{\bar{q}} \mid i)\rangle. \quad (29)$$

This equation represents the familiar result that the field cannot alter the mean value of any irreducible tensor component in the $\bar{z}$ frame but merely causes its complex phase to change in the course of time. The phase change is the same as that which results from a rotation of $(\bar{x}, \bar{y})$ axes about $\bar{z}$ at the rate of $-\gamma_i B$ rad/sec.

Once this result is established, it becomes unnecessary to consider the tensorial components $S^{[k]}_{\bar{q}}$ in the $\bar{z}$ frame explicitly. It is sufficient to consider the parameters $\langle S^{[k]}_q\rangle$ calculated at $t=0$ in the collision frame, as in Sec. II, and then to state that each of these parameters remains constant in a rotating frame which coincides with the collision frame at $t=0$ and precesses about the field direction at the uniform rate of $-\gamma_i B$ rad/sec. The effect of this precession can be combined with the eventual transformation to the detector frame represented by Eq. (18).

A direct demonstration of this Larmor precession was provided by Hadeishi and Nierenberg's (HN65) observation of the 3261-Å line of Cd excited by a pulsed electron beam in a magnetic field **B** of 0.88 G. The electron pulse, lasting $\sim$2 nsec, excites the atoms and starts the timing of the photon counting. The time-resolved counts in Fig. 5 clearly show that the light intensity reaching a counter placed at 90° from $\hat{B}$ precesses at twice the Larmor frequency; this is the result to be expected since the intensity depends linearly on A_0^{det} according to Eq. (14) and A_0^{det} depends in turn on $A_{\bar{q}}^{\hat{B}}$ with $\bar{q}=\pm 2$ in the geometry

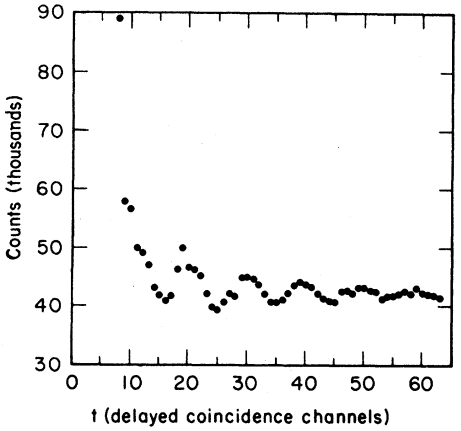

FIG. 5. Larmor precession in the decay of the 3261-Å transition in Cd excited by pulsed electrons, as observed by Hadeishi and Nierenberg (HN65).

of this experiment. Similar modulations were obtained by Dodd, Kaul, and Warrington (DKW64) using pulsed optical excitation. Equivalent results have also been obtained by periodic modulation of the primary source of excitation, a procedure that is experimentally easier although less direct than excitation by a single pulse (BB61, K61, PP63, A64, CS64).

The result (29) has been derived by Nedelec (N65) for atoms excited by electron impact, using a density matrix representation of the state of the excited atom equivalent to the treatment of the present paper. In fact, density matrix treatments serve to obtain equivalent results in various forms for any particle of interest (see, e.g., F57) and have also permitted the generalization of the Larmor precession Eq. (29) to describe the effects of nonuniform external fields of arbitrary multipolarity (F64).

III.3. Modulation Due to Unresolved Hyperfine Structure

The next example concerns the time dependence of the alignment or orientation parameters

$$\langle(i' \mid \exp(iHt/\hbar)S^{[k]}_q\exp(-iHt/\hbar) \mid i)\rangle \quad (30)$$

which results from the coherent superposition of the states of a hyperfine multiplet. In this case, both the operators $S^{[k]}_q$ and the sets of states $(i' \mid$ and $\mid i)$ to be entered in Eq. (30) are defined with reference to uncoupled states $\mid IM_IJM_J)$ whereas the Hamiltonian H is diagonal in the basis of coupled states $\mid IJFM_F)$. The evaluation of Eq. (30) will then proceed through a sequence of transformations involving two reciprocal changes of coupling. Starting from the matrix of $S^{[k]}_q$ in the uncoupled representation we shall transform it to the coupled representation $\mid IJFM_F)$. Next we shall multiply this matrix by the matrices of $\exp(\pm iHt/\hbar)$ which are now diagonal. The product will be transformed back to the uncoupled representation and will then finally be averaged according to $\langle(i' \mid \cdots \mid i)\rangle$.

Our task is made easier by the invariance of the interaction Hamiltonian under joint rotation of electronic and nuclear coordinates. Owing to this invariance, the product of each operator $S^{[k]}_q$ by $\exp(\pm iHt/\hbar)$ is a new tensorial operator $\tilde{S}^{[k]}_q$ with the same indices k and q. Moreover the calculation of the matrix transformations and products can be carried out independently of the magnetic quantum numbers which pertain to a specific coordinate system; therefore it is sufficient to calculate in terms of reduced matrix elements.

Recalling that the operator $S^{[k]}_q$ actually consists of an electronic factor identical to that considered in Sec. II multiplied by a unit operator of the nuclear spin, we write its single nonzero reduced matrix element in the uncoupled basis

$$(I \,||\, 1^{[0]} \,||\, I)(J \,||\, S^{[k]} \,||\, J). \quad (31)$$

The transformation to the basis of coupled states projects the single element (31) onto a whole reduced matrix with many nonzero elements, nondiagonal as well as diagonal in F. The transformation involves a recoupling of wave functions and tensorial operators analogous to that which led us to Eq. (8). The initial product of matrix elements in Eq. (31) has a structure represented by the coupling symbol $[(II)0(JJ)k]^{(k)}$; the desired matrix of $S^{[k]}$ in the new basis has a structure represented by $[(IJ)F'(IJ)F]^{(k)}$. The orthogonal matrix that transforms tensor operator matrices from the old to the new basis consists of recoupling coefficients expressed in terms of standard $6j$ coefficients by

$$\begin{aligned}&((IJ)F'(IJ)F \mid (II)0(JJ)k)^{(k)}\\&\quad=(-1)^{I+J+F'+k}[(2F+1)(2F'+1)/(2I+1)]^{1/2}\\&\qquad\times\begin{Bmatrix}F' & F & k\\ J & J & I\end{Bmatrix}.\end{aligned}\tag{32}$$

The result of the transformation is given by Eq. (15.7′) of (FR59) or (7.1.8) of (E57), taking into account that $(I \| 1^{(0)} \| I)$ has the standard value $(2I+1)^{1/2}$,

$$\begin{aligned}(IJF' \| S^{[k]} \| IJF)&=(-1)^{I+J+F'+k}[(2F'+1)(2F+1)]^{1/2}\\&\times\begin{Bmatrix}F' & F & k\\ J & J & I\end{Bmatrix}(J \| S^{[k]} \| J).\end{aligned}\tag{33}$$

This reduced matrix element may now be multiplied by the eigenvalues of $\exp(\pm iHt/\hbar)$, i.e., by $\exp(iE_{F'}t/\hbar)$ and $\exp(-iE_Ft/\hbar)$. Introducing the oscillation frequencies

$$\omega_{F'F}=(E_{F'}-E_F)/\hbar,\tag{34}$$

we have

$$\begin{aligned}&(IJF' \| \exp(iHt/\hbar)S^{[k]}\exp(-iHt/\hbar)\| IJF)\\&\qquad=\exp(i\omega_{F'F}t)(IJF' \| S^{[k]} \| IJF).\end{aligned}\tag{35}$$

When the hyperfine interaction has the simple magnetic form $A\mathbf{I}\cdot\mathbf{J}$ (see, e.g., p. 69 of A71), the frequencies (34) take the explicit form

$$\omega_{F'F}=(A/2\hbar)[F'(F'+1)-F(F+1)].\tag{36}$$

For the purpose of evaluating the mean value in Eq. (30) we must now transform Eq. (35) back to the coupled basis. Since we are dealing with collisions that leave the nucleus unpolarized, the operator of interest is actually the *average over nuclear spin states* of the operator $\exp(iHt/\hbar)S^{[k]}{}_q\exp(-iHt/\hbar)$. This average, denoted by $\mathrm{Trace}_{\mathrm{nucl}}\{\exp(iHt/\hbar)S^{[k]}{}_q\times\exp(-iHt/\hbar)\}/(2I+1)$, is still an operator of the electronic system. Its reduced matrix element $(J \| \cdots \| J)$ is obtained from Eq. (35) using the transformation matrix reciprocal to Eq. (32), which has the same elements as (32) owing to orthogonality. Thus we multiply each element $(F'F)$ in the matrix Eq. (35) once more by Eq. (32) and sum over F' and F. We also divide by the normalization factor $(I \| 1^{[0]} \| I)=(2I+1)^{1/2}$ and obtain

$$\begin{aligned}&(J \| (2I+1)^{-1}\\&\quad\times\mathrm{Trace}_{\mathrm{nucl}}\{\exp(iHt/\hbar)S^{[k]}\exp(-iHt/\hbar)\} \| J)\\&\quad=\textstyle\sum_{F'F}((II)0(JJ)k \mid (IJ)F'(IJ)F)^{(k)}e^{i\omega_{F'F}t}\\&\quad\times((IJ)F'(IJ)F \mid (II)0(JJ)k)^{(k)}(J \| S^{[k]} \| J)\\&=\left[\sum_{F'F}\frac{(2F'+1)(2F+1)}{(2I+1)}\begin{Bmatrix}F' & F & k\\ J & J & I\end{Bmatrix}^2\cos\omega_{F'F}t\right]\\&\qquad\times(J \| S^{[k]} \| J).\end{aligned}\tag{37}$$

This reduced matrix element simply replaces the matrix element $(J \| S^{[k]} \| J)$, used in Sec. II, for the purpose of evaluating Eq. (30).

Equation (37) contains the main result of our calculation and deserves considerable illustration, interpretation, and amplification. One of its essential features lies in the fact that its right-hand side consists simply of the time independent matrix element $(J \| S^{[k]} \| J)$ multiplied by the modulation factor in the bracket. This factor equals unity at $t=0$ owing to a sum rule of $6j$-coefficients rooted in the orthogonality of the transformation matrix Eq. (32). At all other times this factor remains no larger than unity and constitutes the Fourier expansion of the matrix of $S_q^{[k]}$. Modern measurements of the modulation of emitted light have provided the input for Fourier analysis by computer, which determines the frequencies $\omega_{F'F}$ and the Fourier coefficients as shown in Fig. 8 below (BSPAWG73). The modulation factor resumes its initial value 1 periodically when Eq. (36) holds, or anyhow when all frequencies $\omega_{F'F}$ have a common divisor. [The imaginary term of $\exp(i\omega_{F'F}t)$ drops out of the sum in Eq. (37) because it is odd under permutation of F' and F, for which $\omega_{F'F}=-\omega_{FF'}$.] As we had anticipated, the time dependence of Eq. (37) represents a multiply periodic depolarization of the radiating atoms, i.e., a loss of orientation for $k=1$ and a loss of alignment for $k=2$. Equation (37) was derived by Alder (A52) in the equivalent form pertaining to nuclear orientation and alignment, that is, with I and J interchanged, as detailed in (FS68).

Because the time modulation factors out of the reduced matrix elements in Eq. (37), it also factors out of the final averaging process in Eq. (30). This averaging bears only on the electronic magnetic quantum numbers $(M_{J'}, M_J)$ of the states $(i' \mid$ and $\mid i)$ since the averaging over the nuclear M_I is already

included in Eq. (37), and is to be carried out exactly as though the states $(i'|$ and $|i)$ were stationary. That is, one should perform the averaging by the method of Sec. II, ignoring the existence of hyperfine interactions. The tensorial operators $T^{[k]}_q$, whose mean values constitute the actual orientation and alignment parameters, are constructed in this case with components of the electronic angular momentum $\mathbf{J}$, rather than of the total $\mathbf{F}$, as noted in Sec. III.1.

Recalling that $\mathbf{F}=\mathbf{J}+\mathbf{I}$ is a constant of the motion, while $\langle\mathbf{J}\rangle$ oscillates according to Eq. (37), we see that the periodic loss of electron orientation represented by the oscillation of $\langle\mathbf{J}\rangle$ must reappear as a nuclear orientation $\langle\mathbf{I}\rangle$ oscillating 180° out of phase with $\langle\mathbf{J}\rangle$. In essence the initial orientation is conserved and could be recovered completely by measuring the nuclear spin polarization as well as the electronic orientation.

A similar conservation rule holds for the alignment which is represented by mean values of second rank tensors. Because these tensors are quadratic in $\mathbf{J}$, the alignment branches into three terms, which represent, respectively, the purely electronic alignment, a purely nuclear alignment, and a correlation of nuclear and electronic properties. The complete alignment would be recovered by detecting the circular polarization of the light in coincidence with the nuclear spin polarization, so as to reconstruct both separate alignments and a correlation of orientations.

The transfer of orientation or alignment from the electrons to the nucleus may be illustrated by adapting the derivation of Eq. (37) to evaluating, instead of (30), the mean value of a nuclear multipole component $\langle\exp(iHt/\hbar)M^{[k]}_q\exp(-iHt/\hbar)\rangle$. The reduced matrix element (31) is then replaced by $(I\|M^{[k]}\|I)(J\|1^{[0]}\|J)$. With regard to the transformation coefficient (32), we note that it actually represents only one row of an orthogonal matrix because one of its indices has the fixed value zero, corresponding to the scalar character of the unit nuclear spin operator in (31). The general element of this orthogonal matrix is represented by $((IJ)F'(IJ)F\,|\,(II)k_n(JJ)k_e)^{(k)}$, where k_n and k_e indicate the degree (i.e., the multipolarity) of nuclear and electronic tensorial operators. To transform $(I\|M^{[k]}\|I)(J\|1^{[0]}\|J)$, we set $k_n=k$ and $k_e=0$, thus replacing (32) by

$$((IJ)F'(IJ)F\,|\,(II)k(JJ)0)^{(k)}$$
$$=(-1)^{J+I+F+k}[(2F+1)(2F'+1)/(2J+1)]^{1/2}\begin{Bmatrix}F' & F & k\\ I & I & J\end{Bmatrix}. \quad (38)$$

The rest of the calculation proceeds exactly as in the derivation of Eq. (37) and yields

$$(J\|(2I+1)^{-1}$$
$$\times\mathrm{Trace}_{\mathrm{nucl}}\{\exp(iHt/\hbar)M^{[k]}\exp(-iHt/\hbar)\}\|J)$$
$$=\sum_{F'F}((II)0(JJ)k\,|\,(IJ)F'(IJ)F)^{(k)}$$
$$\times\exp(i\omega_{F'F}t)\,((IJ)F'(IJ)F\,|\,(II)k(JJ)0)^{(k)},$$
$$\times(I\|M^{(k)}\|I)(2J+1)^{1/2}(2I+1)^{-1/2}$$
$$=\left[\sum_{F'F}(-1)^{F'-F}\frac{(2F'+1)(2F+1)}{2I+1}\times\begin{Bmatrix}F' & F & k\\ I & I & J\end{Bmatrix}\begin{Bmatrix}F' & F & k\\ J & J & I\end{Bmatrix}\cos\omega_{F'F}t\right]$$
$$\times(I\|M^{[k]}\|I). \quad (39)$$

This expression, the product of the *nuclear* reduced matrix element and of a modulation factor that vanishes at $t=0$ for $k\neq0$, replaces the *electronic* reduced matrix element in the calculation of Sec. II. It thus represents the result we were seeking, namely, the induction of nuclear spin polarization by the hyperfine interaction following a collision which aligns or orients the electrons rather than the nucleus itself.

This approach could be extended to calculate the correlations between the alignments or orientations of electronic and nuclear states, represented by the mean values of operator products $\exp(iHt/\hbar)M^{[k_n]}_{q_n}S^{[k_e]}_{q_e}\times\exp(-iHt/\hbar)$. It could also be extended to include the effects of collisions that polarize the nucleus as well as the electronic state.

The joint effect of electronic and nuclear polarizations has been demonstrated recently by exciting unresolved hyperfine components of the $7P_{3/2}$ state of cesium by a pulse of polarized resonant laser light (HPS73). The light source was sufficiently monochromatic to excite only atoms in one of their ground state hyperfine components; hence the initial alignment was shared between the excited electron and the nucleus. The nuclear portion of the alignment caused then a precession of the electron alignment $\mathbf{A}$ expressed through out-of-phase modulations of its various components.

Note, finally, that the values of the intensity observed with various detectors and of the polarization parameter P may increase or decrease as the alignment varies, depending on the sign of the relevant terms in Eqs. (14) or (15) and in transformation formulas such as Eq. (17). Therefore the modulation of these values may be in or out of phase with that of the alignment $\mathbf{A}$, even when only the magnitude of $\mathbf{A}$ is modulated and starts from a maximum value at $t=0$.

III.4. Unresolved Fine Structure

The fine structure splittings are small in the light atoms and may remain unresolved, while the complementary modulation of light emission due to beats among the multiplet components is sufficiently slow to be resolved. The treatment of this phenomenon follows from that of hyperfine modulation by straightforward generalization, if the hyperfine structure remains much smaller than the fine structure, that is, if the energy eigenstates have good quantum numbers $|I(SL)JFM_F)$. The operators $S_q^{[k]}$ are now constructed in the representation with basis states $|IM_ISM_SLM_L)$, in which the nuclear and the electronic spins are decoupled from the orbital momentum. The transformation of the reduced matrix elements from this representation consists of two separate factors, one for coupling **S** and **L** and one for coupling **I** and **J**. The result, analogous to Eq. (37), is

$$(L \,||\, (2I+1)^{-1}(2S+1)^{-1} \times \mathrm{Trace}_{\mathrm{nucl,spin}}\{\exp(iHt/\hbar)S^{[k]}\exp(-iHt/\hbar)\} \,||\, L)$$
$$= \sum_{F'FJ'J} \frac{(2F'+1)(2F+1)(2J'+1)(2J+1)}{(2I+1)(2S+1)} \times \begin{Bmatrix} F' & F & k \\ J' & J & I \end{Bmatrix}^2 \begin{Bmatrix} J' & J & k \\ L & L & S \end{Bmatrix}^2 \cos\omega_{F'J',FJ}t \times (L \,||\, S^{[k]} \,||\, L). \quad (40)$$

As noted before, the tensorial operators $T^{[k]}_q$ should now be constructed with components of **L**, instead of **J** or **F**.

Previous treatments of the modulation of light excited by collisions have incorporated the oscillatory factor of Eq. (40), but have not separated it from the averages that define the atomic alignment and orientation. The treatment by Franken (F61) and the later more detailed discussion by Kelly (K66) emphasize that collision excitation is impulsive and that various closely spaced levels of atoms, possibly split by external fields, can be excited coherently. It follows that the subsequent radiation is modulated; however these papers do not perform the angular momentum algebra necessary to obtain Eq. (40).

This algebra had been performed by Percival and Seaton (PS58), in their earlier theory of the polarization of line radiation excited by electron impact, but only for geometries with cylindrical symmetry. The results thus obtained pertain only to the alignment parameter A_0^{col}. The theory of (PS58) uses a time-independent formulation wherein the light is considered as resulting from transitions between continuum states of the electron–atom system and its intensity is effectively integrated over the whole time interval after the collision. The results relate then to our Eq. (40) multiplied by $\exp(-\Gamma t)$ and integrated over time, an operation that replaces the $\cos\omega t$ factor by $\Gamma/(\Gamma^2+\omega^2)$. The resulting coefficient of the initial alignment and orientation tensors simply represents a constant depolarization due to the presence of internal fields. An illustration of this result is found in experiments by Kleinpoppen and collaborators (HKK65, HKl67, KN67) and in related calculations (FS67).

A calculation by Macek and Jaecks (MJ71) treats light detected in coincidence with scattered particles and gives expressions for the coincidence rate in terms of four parameters, equivalent to the total cross section and to the three time-dependent alignment parameters A_0^{col}, A_{1+}^{col}, and A_{2+}^{col}. Circular polarization and orientation were not considered. The modulation term of Eq. (40) was obtained in that calculation but it was not explicitly factored from the initial alignment; the results were given in terms of nonreduced components of the density matrix. Berry, Subtil, and Carré (BSC72) formulated the theory of time-resolved alignment measurements employing irreducible components of the density matrix, a procedure substantially equivalent to that of the present paper. They considered cylindrical symmetry only and consequently discussed only A_0^{col}. Their results do factor the modulation term from the initial alignment as in Eq. (37).

Jacobs (J72) has recently developed the theory of atomic photoionization measurements including measurements of light emitted by the residual ion. This theory is formulated quite generally in terms of irreducible components of the density matrix of the excited ion, incorporating both the modulation term and the angular momentum algebra necessary to separate the modulation factor from the initial alignment. In these respects the results of Jacobs and of Berry *et al.* are similar to those presented here. We emphasize, however, the interpretation of the alignment and orientation in terms of expectation values of angular momentum operators, thereby tracing the modulation to a reversible exchange of angular momentum between internal degrees of freedom.

This interpretation applies even to measurements with no time definition, where the unobserved modulation results in a depolarization of the light. In the example of n^3P–2^3S emission by helium, the loss of circular polarization due to fine structure implies that the metastable ^3S atoms are partially spin polarized to precisely the degree necessary to compensate for the loss of initial light polarization. This spin polarization could be calculated by means of Eq. (39).

Several recent experiments illustrate various aspects of Eqs. (37) and (40). The advent of time-of-flight analysis following beam-foil excitation provides the time resolution necessary to observe zero-field modulations. Macek (M69, M70) suggested that the modulations could be observed. Their direct observation was first accomplished by Andrä (A70). The decay of the

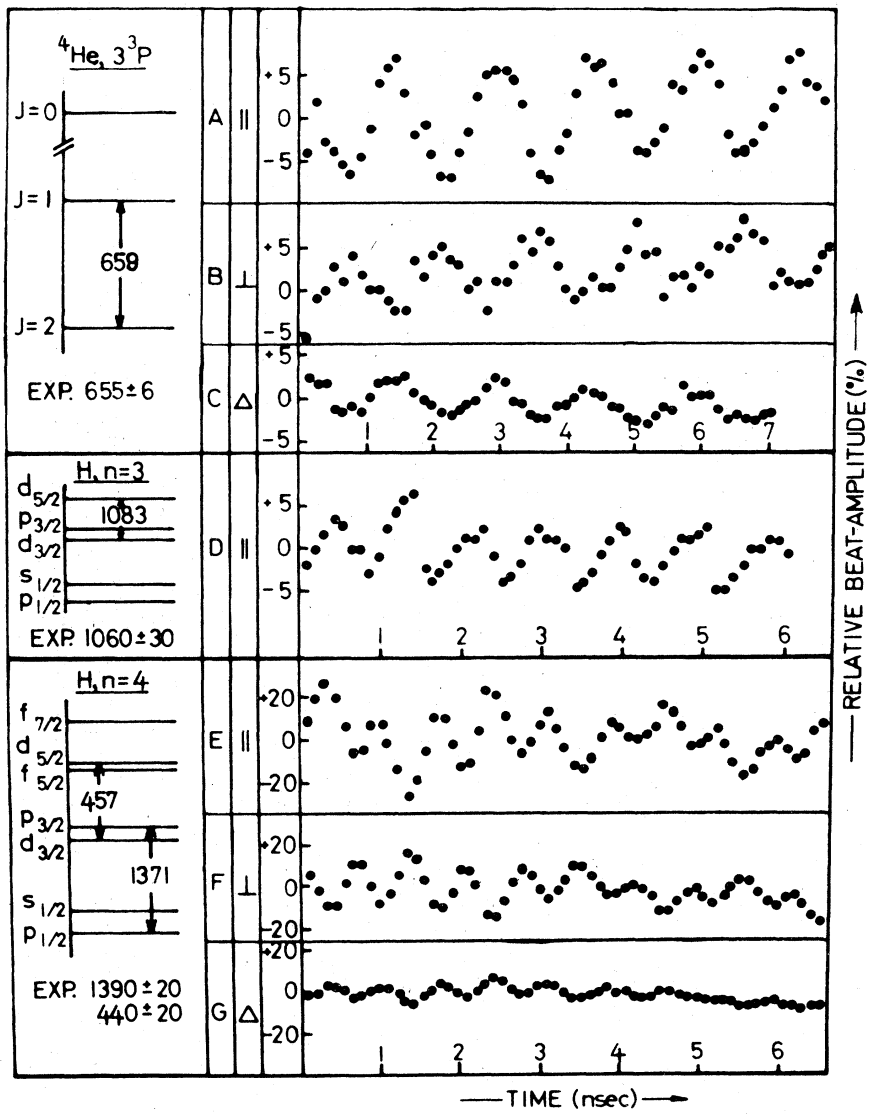

FIG. 6. Zero-field modulations in the decay of foil-excited 3 ^3P states of helium (upper three curves) and hydrogen (lower four curves) observed by Andrä (A70).

3889-Å helium line excited by collisions of He^+ ions with a thin carbon foil, shown in Fig. 6, exhibits definite modulations at the fine structure frequency. Since it is the alignment term with $k=2$ in Eq. (40) which oscillates, these results also show that the foil-excited atoms are partially aligned.

All of the modulation factors in Eqs. (37) and (40) start out at unity at $t=0$, and subsequently decrease, recovering their initial value periodically. The zero value of the initial phase of oscillation reflects the assumed random orientation of the electronic and nuclear spins. Since the modulation represents the reversible transfer of alignment from orbital to spin coordinates, and since the spins are initially random, the transfer of alignment takes place initially from the orbital to the spin coordinates; this is why Eqs. (37) and (40) predict an initial decrease of orbital alignment. On the other hand, if the spins were partially aligned in the collision, exchange of alignment could result in an initial increase of orbital alignment; more generally, the initial phase of the modulation would be nonzero. Burns and Hancock (BH73) demonstrated, by precise measurements of the initial phase of oscillations in the 3889-Å helium light, that the polarization and the alignment start at their maximal value at $t=0$ and subsequently decrease, recovering their initial value periodically. Their data are shown in Fig. 7.

These measurements, and earlier ones (BH71), also show that it is the alignment rather than the total intensity which oscillates. Setting $\theta=90°$ and $\psi=54°44'$ in Eq. (17) and $\beta=0°$ in Eq. (14) gives an intensity independent of A_0^{col}. The corresponding decay curve then does not oscillate. Measurements

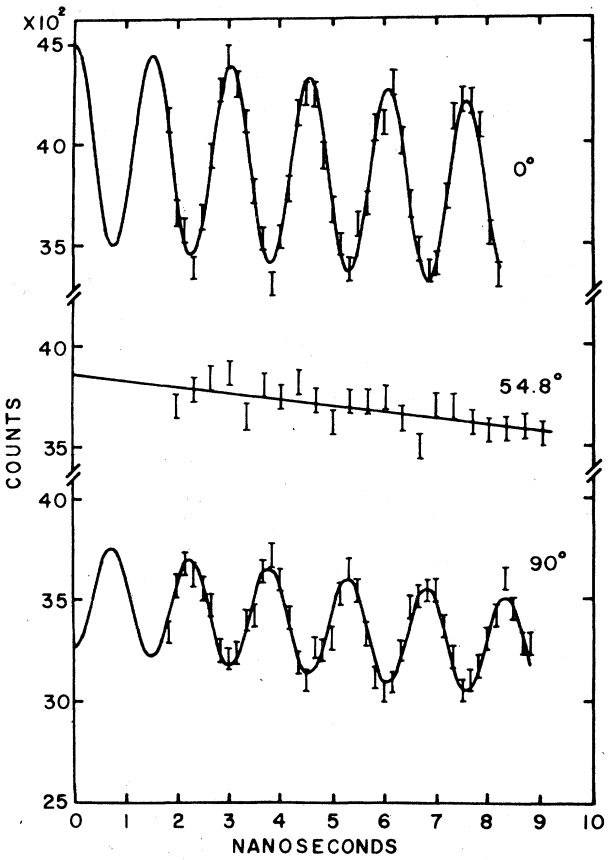

FIG. 7. Zero-field modulations in the decay of foil-excited $3\,^3P$ states of helium, illustrating the zero phase of the oscillations and the absence of oscillations when the polarization analyzer is oriented at 54°44′. From Burns and Hancock (BH73).

with the polarizer set at 54°44′ to the beam axis indeed show no modulation within experimental error. These experiments, as well as those of (HPS73) display both in- and out-of-phase modulation of light with different polarization, thus illustrating the remarks at the end of Sec. III.3.

As mentioned at the end of Sec. III.2 and at the end of Sec. III.3, substantially equivalent modulations of the polarization of emitted light are observed when the excitation is produced not only by collision but also by pulsed or resonantly modulated incident light. The time distribution of the emitted light can be sharpened—thus facilitating the observation and study of its modulations—by means of the photon echo technique (A69). Such observations have in fact been made and interpreted along the lines of the present article (LCA69, LCA71, L73).

III.5. A Problem Requiring Dynamical Calculation

The assumptions leading to Eq. (40) are seldom realistic because, when the modulation due to spin–orbit coupling is sufficiently slow to be analyzed, this coupling is only marginally stronger than the hyperfine interaction—if the latter is present at all. When both of these interactions are present and of comparable strength, the electronic quantum number J is no longer a "good" quantum number for the energy eigenstates. These eigenstates should then be classified as $|(ISL)\alpha FM_F)$, where α is an index that replaces J for the purpose of distinguishing different levels with the same total F but does not correspond to the eigenvalue of any constant of the motion which may replace $\mathbf{J}^2$.

To determine these eigenstates and calculate the corresponding eigenvalues $E_{\alpha F}$ one may start by constructing the matrix of the Hamiltonian H, including all interactions between orbit, electronic, and nuclear spins in the base of uncoupled states. In a simple case H may have the form $a\mathbf{L}\cdot\mathbf{S}+b\mathbf{L}\cdot\mathbf{I}+c\mathbf{S}\cdot\mathbf{I}$. One can then solve the algebraic Schrödinger equation

$$\sum_{M_I'M_S'M_L'}(IM_I, SM_S, LM_L \mid H \mid IM_I', SM_S', LM_L')\times(IM_I', SM_S', LM_L' \mid (ISL)\alpha FM_F) = (IM_I, SM_S, LM_L \mid (ISL)\alpha FM_F)E_{\alpha F}. \quad (41)$$

The rotational invariance of H insures, of course, that F and M_F are good quantum numbers and that the eigenvalues are degenerate in M_F. For our purposes, the essential difference between this problem and the preceding one lies in the fact that the eigensolutions of Eq. (41), namely, the coefficients $(IM_I, SM_S, LM_L \mid (ISL)\alpha FM_F)$, are not constructed with standard Wigner coefficients but depend upon the relative strength of different interactions, e.g., on the ratios of the parameters a, b, and c.

These eigensolutions will then replace Wigner coefficients in the construction of the modulation factor which is to replace the expression in the brackets of Eq. (40). What we must calculate is the appropriate transformation coefficient, analogous to the coefficient in Eq. (32). To this end we take as a model the expression of the coefficient in Eq. (32) itself in terms of Wigner coefficients, namely,

$$((IJ)F'(IJ)F \mid (II)0(JJ)k)^{(k)} = \sum_{M_IM_J'M_JM_F'M_F}(F'Fkq \mid F'-M_F', FM_F)\times(IJFM_F \mid IM_I, JM_J)(IJF'-M_F' \mid I-M_I, J-M_J')\times(J-M_J', JM_J \mid JJkq)(-1)^{I-M_I}(2I+1)^{-1/2}. \quad (42)$$

[Note that the index q appears explicitly in Eq. (42), but the whole expression is independent of q and invariant under coordinate rotations.] This model expression will be utilized by decoupling the electron spin from the orbit—a step included by implication in the construction of Eq. (40)—and particularly by replacing the Wigner coefficients $(IJFM_F \mid IM_I, JM_J)$ by the eigensolutions of Eq. (41). The desired trans-

formation coefficient is thus defined by

$$((ISL)\alpha'F'(ISL)\alpha F\,|\,(II)0(SS)0(LL)k)^{(k)}$$
$$=[(2I+1)(2S+1)]^{-1/2}$$
$$\times\sum_{M_IM_SM_{L'}M_LM_{F'}M_F}(-1)^{I-M_I+S-M_S}$$
$$\times(F'Fkq\,|\,F'-M_{F'},FM_F)$$
$$\times((ISL)\alpha FM_F\,|\,IM_I,SM_S,LM_L)$$
$$\times((ISL)\alpha'F'-M_{F'}\,|\,I-M_I,S-M_S,L-M_{L'})$$
$$\times(L-M_{L'},LM_L\,|\,LLkq),\quad(43)$$

and is to be calculated for each specific problem. The modulation factor which should replace that of Eq. (40) is then

$$\sum_{\alpha'F',\alpha F}[((II)0(SS)0(LL)k\,|$$
$$\times(ISL)\alpha'F'(ISL)\alpha F^{(k)})]^2$$
$$\times\cos(\omega_{\alpha'F',\alpha F}t).\quad(44)$$

Studies of the hyperfine interaction in excited ions represent a recent notable application of time resolved alignment measurements. Two experiments (BSPAWG73, TAW73) demonstrate that hyperfine coupling constants of useful accuracy can be extracted from measurements of the zero-field modulations subsequent to beam-foil excitation. In both instances, Eq. (44), which incorporates a dynamical calculation of the Fourier amplitudes rather than the simpler but approximate Eq. (40), applies. The measurements of the 5485-Å transition in ^{6}LiII by Berry *et al.* (BSPAWG73) illustrate the technique. Their measured decay curve with the superposed modulations is shown on the upper graph in Fig. 8, while its Fourier transform is shown on the lower graph. Five frequencies stand out clearly. Numerical calculation of the coefficients and frequencies with the hyperfine coupling constant as a fitting parameter gave $A=0.091\pm0.001$ cm^{-1}.

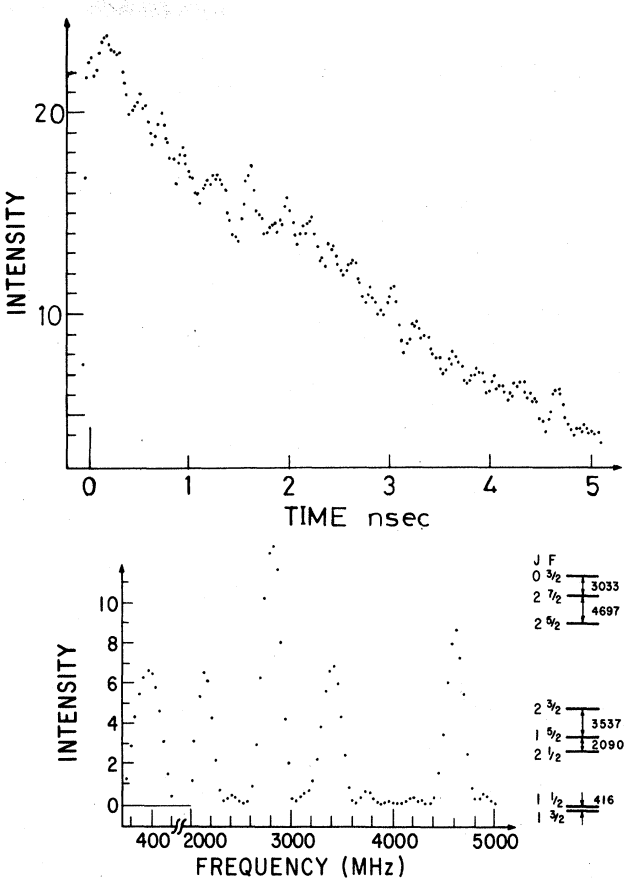

FIG. 8. Intensity decay curve and its Fourier transform for the 3684-Å transition in ^{7}LiII measured by Berry *et al.* (BSPAWG73).

III.6. Combined Effect of Internal Coupling and External Field

We have seen how the action of a weak field causes a simple precession of the alignment and orientation of atoms in an otherwise stationary state. We have also seen how hyperfine or fine structure interactions cause a simple modulation of each separate alignment or orientation parameter. It will now be shown how the combination of the two actions has a much more drastic effect.

As in Eq. (28), we consider the time dependence of the matrix elements of a tensor component $S^{[k]}_{\bar{q}}$, where the index $\bar{q}$ pertains to coordinates with axis $\bar{z}$ parallel to a magnetic field **B**. Here, however, we deal with atoms whose unresolved fine structure levels correspond to coupled eigenstates $|IJF\bar{M}_F)$, with $\bar{M}_F$ pertaining to the axis $\bar{z}$. Each matrix element of $S^{[k]}_{\bar{q}}$ between two states of this set may be expressed, according to the Wigner–Eckart theorem, as the product of a reduced matrix element and of a standard $3j$ coefficient, thus permitting us to use the reduced matrix elements given by Eq. (33). Thus we have

$$(IJF'\bar{M}_{F'}\,|\,\exp(iHt/\hbar)S^{[k]}_{\bar{q}}\exp(-iHt/\hbar)\,|\,IJF\bar{M}_F)$$
$$=\exp[i(E_{F'}-\gamma_{F'}B\bar{M}_{F'}\hbar)t/\hbar](IJF'\,||\,S^{[k]}\,||\,IJF)$$
$$\times\begin{pmatrix}F' & k & F\\ -\bar{M}_{F'} & q & \bar{M}_F\end{pmatrix}(-1)^{F'-\bar{M}_{F'}}$$
$$\times\exp[-i(E_F-\gamma_FB\bar{M}_F\hbar)t/\hbar].\quad(45)$$

The time dependence in this formula differs decisively from that of Eq. (28), because Eq. (28) involves a single gyromagnetic ratio γ, while Eq. (45) contains two ratios, $\gamma_{F'}$ and γ_F, which coincide only for $F'=F$. Owing to $\gamma_{F'}\neq\gamma_F$ the oscillation frequency of Eq. (45) depends not only on the difference of quantum numbers $\bar{M}_{F'}-\bar{M}_F=\bar{q}$, but also on the separate values of $\bar{M}_{F'}$ and $\bar{M}_F$. In other words the phase variation of Eq. (45) in the course of time cannot be interpreted as the effect of a coordinate rotation on a tensor component $S^{[k]}_{\bar{q}}$. A further and more important consequence is that the time-dependent matrix elements of Eq.

(45) no longer belong to the matrix of a single irreducible tensor component $S^{[k]}_q$. This result is not surprising because the Hamiltonian no longer has spherical invariance in the presence of the field **B**.

Formally one verifies this result through a calculation designed to invert the Wigner–Eckart theorem. If Eq. (45) represented the matrix element of a single irreducible tensor component, the reduced matrix element of this tensor would be obtained by multiplying Eq. (45) by the $3j$ coefficient

$$(-1)^{F'-\bar{M}_{F'}}\begin{pmatrix} F' & k' & F \\ -\bar{M}_{F'} & \bar{q} & \bar{M}_F \end{pmatrix}(2k'+1),$$

summing over $\bar{M}_{F'}$ and $\bar{M}_F$ and applying a closure property of the $3j$ coefficients. The essential step of this procedure consists of calculating the double summation

$$\sum_{M_{F'}M_F}\begin{pmatrix} F' & k & F \\ -\bar{M}_{F'} & \bar{q} & \bar{M}_F \end{pmatrix} \times \exp\left[i(E_{F'}-\gamma_{F'}B\bar{M}_{F'}\hbar-E_F+\gamma_F B\bar{M}_F\hbar)t/\hbar\right] \times\begin{pmatrix} F' & k' & F \\ -\bar{M}_{F'} & \bar{q} & \bar{M}_F \end{pmatrix}(2k'+1). \quad (46)$$

If we had $\gamma_{F'}=\gamma_F$, the time-dependent factor would reduce to $\exp\left[i(E_{F'}-E_F-\gamma\bar{q}B\hbar)t/\hbar\right]$ and factor out, after which the summation would reduce to $\delta_{k'k}$, thus yielding the desired reduced matrix element with $k'=k$. In fact, we have $\gamma_{F'}\neq\gamma_F$, the exponential does not factor, and Eq. (46) has a nonzero value, in general, for several values of k' other than k.

Physically, this means that the time-dependent operator $\exp(iHt/\hbar)S^{[k]}_{\bar{q}}\exp(-iHt/\hbar)$ splits into a number of tensor components $S^{[k']}_{\bar{q}}$ with the same value of $\bar{q}$ but with different k'. As we know, light emission depends directly only on the alignment and orientation parameters $\langle S^{[k]}_q\rangle$ with $k=2$ or 1; we find here that the value of these parameters observed at $t\neq 0$ may depend on the value at $t=0$ of different parameters $S^{[k']}_q$ with $k'>2$. This remark extends the range of data on excitation by collision which can be obtained, in principle, from studies of light emission in the presence of external fields. The opportunity for this extension has been mentioned previously (W72) but remains to be exploited experimentally and theoretically.

More specifically, an excited atom with angular momentum j_i can display $2^{k'}$-pole moments with all values of $k'\leq 2j_i$. For $j_i=1$ this means just a dipole and a quadrupole moment, represented by the orientation **O** and alignment **A** which are determined by analysis of the emitted light. For $j_i>1$, the atom may have additional nonzero moments (octupole, hexadecapole, etc.) which are not normally observed through optical emission. However, the presence of an external field causes the time-modulation of each multipole moment to depend on the multipoles of different orders. The determination of **O** and **A** at time t may thus provide evidence on the $2^{k'}$-pole moments with $k'>2$ generated by collision at $t=0$.

An illustration of this principle has been treated theoretically and verified experimentally by Lombardi (L69), though under different circumstances. Atoms were excited and aligned—but *not* oriented—by electron impact and subjected to an inhomogeneous electric field acting, in effect, crosswise upon their quadrupole moment. The emitted light was found to be circularly polarized, thus showing a nonzero orientation **O** to have arisen from the coupling of an initial alignment **A** with a quadrupolar field.

III.7. Effect of a Strong Field

An external field, magnetic or electric, is said to be "strong" when its interaction with an atom is comparable to the energy separation of zero-field levels with different angular momenta. In this event, the energy levels in the presence of the field are no longer classified by a total angular momentum quantum number. (Angular momentum quantum numbers may become relevant again at very strong fields, sufficient to overcome internal couplings completely.) It then becomes necessary to solve a Schrödinger equation to establish the connection between the actual stationary states and the basis of uncoupled states which serve to construct the operators $S^{[k]}_q$ and to determine their averages. The problem of calculating the alignment and orientation resembles in this respect that which arises when fine and hyperfine structure interactions have comparable strength and which is treated by solving the Schrödinger equation (41). In addition, however, the external field spoils the invariance of the Hamiltonian. Hence the alignment and orientation parameters which relate to the light emission at time t may depend on the initial values of parameters $\langle S^{[k]}_q\rangle$ with $k>2$. This more complicated problem does not appear to have been studied.

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