Interferences in photodissociation in the classical limit

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(Received 16 July 1987)

The interference between different values of the total angular momentum of photofragmentation, and its behavior in the high-J limit, are discussed using the semiclassical angular momentum theory of G. Ponzano and T. Regge [in *Spectroscopic and Group Theoretical Methods in Physics,* edited by F. Bloch *et al.* (North-Holland, Amsterdam, 1968)]. Taking the angular momentum of an unobserved part as a quantization axis reveals an interesting aspect of the interference in the high-J limit. The result indicates that a high-J limit does not necessarily correspond to a "classical" limit. The relation between the representation of angular momentum transfer and of total angular momentum is also obtained in the high-J limit in the same way. This relation completes the quantum derivation of classical results for the polarization of fluorescence excited by photodissociation.

I. INTRODUCTION

Interference is often regarded as a quantum phenomenon. This interference derives from the quantum-mechanical superposition principle for probability amplitudes. Incoherence between alternative processes is usually assumed in the classical limit. For example, anisotropies[1] (alignment, orientation) of interest to us here for fluorescence in photofragmentation are usually[2] obtained by simple averaging over alternative values J of the total angular momentum in the high-J limit, which is usually regarded as a classical limit. Anisotropies from transitions parallel or perpendicular to a molecular axis are also simply averaged to obtain their net effect.[2]

However, different values of the total angular momentum interfere with each other in quantum-mechanical formulas for anisotropies. This interference derives from the incompatibility of the total angular momentum basis set with the anisotropy of a photofragment, let us say, A. In other words, the commutation relations between the total $\mathbf{J}^2$ and the anisotropy operators $3(\mathbf{J}_A)_z^2 - \mathbf{J}_A^2, (\mathbf{J}_A)_z, \ldots,$ for the photofragment A do not vanish. This interference is of purely geometrical nature since no dynamical interaction couples them. It seems to produce no spectacular effect in contrast to interference between bound and continuum states, which produces the profound resonance effect. Its presence seems only to add more terms to calculations, making it more difficult to extract useful dynamical information. Consideration of the classical limit is then important. Further simplification of photodissociation in the classical limit is provided by the independence of its dynamics on the magnitudes of angular momenta whose values become very large.

As the result of Ref. 3 implies, it is not trivial to introduce incoherence in the classical limit of quantum formulas. Actually, there are several fundamental questions unanswered so far. Do interference terms between different values of the total angular momentum disappear in the high-J limit? If they do, in what way? If they do not, in what situations? A further important question arises from the work of Fano and Dill,[4] who separated an anisotropy by an incoherent sum over alternative angular momentum transfers regardless of the angular momentum value. The representation of angular momentum transfer and of the total angular momentum seem thus to be related somehow in the high-J limit beyond their recoupling transformation. How are they related? A theoretical tool to use in answering these questions has been developed by Ponzano and Regge[5] and utilized recently by Lee.[6] In their semiclassical theory of the $6j$ coefficient, the highest $3nj$ coefficient appearing in this paper, they showed that the square of the volume of a tetrahedron (which is the geometrical realization of the $6j$ coefficient) corresponds to a "kinetic energy" in the usual semiclassical theory. It may be used as a criterion for whether some value of the angular momentum belongs to the classically allowed or forbidden ranges based on its positive or negative value. From this kind of consideration the quantum-mechanical derivation of the classical result[7] for the degree of fluorescence polarization in photofragmentation processes is completed, which has been the motivation of this study. We hope that our results may elucidate the transition from quantum to classical processes and clarify the role of quantum effects in the dynamics of photodissociation.

In Sec. II we describe the semiclassical theory of Ponzano and Regge which will serve as a basic method for the later sections. Section III discusses the interference between different values of the total angular momentum and its unimportance in the classical limit for anisotropies of an observed photofragment and for the angular distribution of the relative motion of fragments. Classically allowed angular momentum transfers and the quantum derivation of the classical results for fluorescence polarization are considered in Secs. IV and V, respectively.

II. CLASSICALLY ALLOWED AND FORBIDDEN VALUES OF ANGULAR MOMENTUM IN THE CLASSICAL LIMIT

Ponzano and Regge[5] have developed a very detailed semiclassical theory of the $6j$ coefficient in terms of the geometrical parameters of a tetrahedron. Its edges correspond to six angular momenta in the $6j$ coefficient with lengths equal to the semiclassical values, e.g., $l \rightarrow l+\frac{1}{2}$. Their theory has not found much application so far. However, its application to an electron-atom collision has been recently discussed in Refs. 6 and 8. With its help, a structure analogous to the classical model (the so-called rolling-ball model[9]) in the quantum formula is identified and the significance of the propensity rule is stressed in intermediate- and high-energy electron-atom collisions.[8] This paper provides another application.

According to Ref. 5, a $6j$ coefficient can be expressed as a product of amplitude and phase functions,

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} \approx \frac{1}{\sqrt{12\pi V}} \cos\left[\sum_{h>k=1}^{4} j_{hk}\theta_{hk} + \frac{1}{4}\right] \quad \text{when } V^2>0 , \tag{1}$$

where V is the volume of the tetrahedron and θ_{hk} is the angle between the outer normals of the tetrahedron faces which intersect along j_{hk}; j_{hk} represents the semiclassical replacement of $(a,b,\ldots)$ with $(a+\frac{1}{2},b+\frac{1}{2},\ldots)$. Notice that its amplitude is expressed here in terms of the volume of the tetrahedron instead of the physical momentum appearing in the usual semiclassical theory. By analogy, it may be said that a particular value of the angular momentum belongs to a classically forbidden range when it produces a negative value for the square of the volume (which can be calculated by the Cayley determinant[5] only by knowing the lengths of the edges as in Henon's formula for the area of a triangle).

In the following discussion, we encounter the case where a, b, d, and e become very large while c and f remain small. Here c and f represent opposite edges of the tetrahedron. Reference 10 introduced for this case the transformation

$$\begin{aligned} \sigma&=(a+b+d+e)/2, \quad \tau=(a+b-d-e)/2 , \\ \eta&=(a-b+d-e)/2, \quad \zeta=(a-b-d+e)/2 . \end{aligned} \tag{2}$$

Permutations and Regge transformations[11] of indices of the $6j$ coefficient which leave its value unaltered change only the sign of values of (σ,τ,ζ,η), without changing their absolute values. This sign ambiguity in the definition (2) is removed in later sections by choosing the total angular momentum quantum number J and J' as a and b. Here only σ can run to infinity while τ, η, and ζ are restricted by the values of c and f. Calculation in this case shows that the square of the volume becomes negative when $\sigma \rightarrow \infty$ unless $\eta=0$ (see Appendix). Thus the values of a, b, d, and e (or σ, τ, η, and ζ) belong to a classically allowed range in the high-J limit $\sigma \rightarrow \infty$ only when $\eta=0$.

Whether a value is classically forbidden or allowed can also be judged from the calculation of angle between two opposite angular momentum vectors in the tetrahedron as in Ref. 6,

$$\mathbf{c}\cdot\mathbf{f}=(\sigma+1)\eta+\tau\zeta . \tag{3}$$

Now, if η is an integer $\neq 0$, the right-hand side of (3) goes to infinity with σ, while $\mathbf{c}\cdot\mathbf{f} \leq |\mathbf{c}|\,|\mathbf{f}|$ if the angle between $\mathbf{c}$ and $\mathbf{f}$ is real. Thus a given value of the angular momentum belongs to the classically forbidden range when the value of σ makes the angle complex. (Note that the angle between two angular momentum vectors which form a triangle with one other angular momentum vector cannot be complex.) When $\eta=0$, only certain real values of angles between $\mathbf{c}$ and $\mathbf{f}$ are allowed in the high-J limit $\sigma \rightarrow \infty$ and are determined by the values of τ and ζ. The square of the volume of the tetrahedron approaches $[(c+\frac{1}{2})^2-\zeta^2][(f+\frac{1}{2})^2-\tau^2]\sigma^2$ as $\sigma \rightarrow \infty$. Then, from Eq. (1), the closer the magnitude of $|\tau|$ (or $|\zeta|$) is to f (or c), the larger the value of the $6j$ coefficient [using the more accurate Airy function formula[6] instead of (1) in the classical limit $\sigma \rightarrow \infty$ when $\eta=0$ will not change the result].

III. INTERFERENCE BETWEEN DIFFERENT VALUES OF THE TOTAL ANGULAR MOMENTUM

Total angular momentum, including that of the photon, is conserved in photodissociation. We thus need to consider only processes whose initial and final total angular momenta are equal. However, if we consider the photofragment angular distribution characterized by a parameter β or the anisotropies of the photofragment fluorescence, interference terms appear between different values of the total angular momentum. The presence of these interference terms does not conflict with the conservation of total angular momentum. This interference is possible because anisotropy measurements select eigenstates of operators which do not commute with $\mathbf{J}^2$, and because all $\mathbf{J}^2$ eigenstates are degenerate in energy. Normally, we expect that such interference terms should be of no importance in the classical limit since they are intrinsically quantum mechanical. This idea will be tested in this section.

Let us consider the photodissociation of an AB molecule (not necessarily diatomic) into fragments A and B,

$$h\nu(j_{\mathrm{ph}})+AB(J_{AB}) \rightarrow [A(J_A)+B](\mathbf{p}) , \tag{4}$$

where j_{ph}, J_{AB}, and J_A denote the angular momentum quantum numbers of the photon, AB, and A, respectively: $\mathbf{p}$ denotes the momentum of the relative motion of A and B. B is assumed to have $J_B=0$ for the time being. The expectation value of the response of a detector D_A of a specific state of A may be expressed in the total angular momentum representation [see Eqs. (18.24) and (19.3) of Ref. 12],

$$\begin{aligned} \langle D_A \rangle = \sum_{K,Q}\sum_{J,J',l} (-1)^{J-J'+Q}((J_A l)J\,|\,D_A\,|\,(J_A l)J')_Q^{(K)}((j_{\mathrm{ph}}J_{AB})J'\,|\,\rho_{AB}\rho_{\mathrm{ph}}\,|\,(j_{\mathrm{ph}}J_{AB})J)_{-Q}^{(K)} \\ \times (J_A l\,|\,S(J)\,|\,j_{\mathrm{ph}}J_{AB})(J_A l\,|\,S(J')\,|\,j_{\mathrm{ph}}J_{AB})^* , \end{aligned} \tag{5}$$

where K stands for the 2^K-pole moment of a pair of rotational states (J,J') of the whole system; ρ_{AB} and $\rho_{\rm ph}$ represent the initial density matrices of AB and photon states, respectively. The matrix element

$$((J_A l)J \mid D_A \mid (J_A l)J')$$

may be expanded in terms of the separate multipole moments of the photofragment A and the relative motion of the photofragments (A,B) [Eq. (18.17) of Ref. 12],

$$((J_A l)J \mid D_A \mid (J_A l)J')_Q^{(K)}=[(2l+1)(2K+1)(2J+1)(2J'+1)]^{1/2}\sum_{K_A}(J_A \mid D_A \mid J_A)_Q^{(K_A)}\begin{Bmatrix} J_A & l & J \\ J_A & l & J' \\ K_A & 0 & K \end{Bmatrix}\delta_{K_A,K}$$

$$=(-1)^{J_A+l+J'+K}[(2J+1)(2J'+1)]^{1/2}(J_A \mid D_A \mid J_A)_Q^{(K)}\begin{Bmatrix} J_A & J & l \\ J' & J_A & K \end{Bmatrix} . \tag{6}$$

The above equation shows that the interference between different values of the total angular momentum is caused by the presence of the anisotropy (i.e., of the nonzero 2^K-pole moment) of the whole system and by its influence on the observables of interests. (Only $K=0$ plays an active role in the total photofragmentation cross section, which does not include any interference between different J and J'.) A single sum over l occurs in (5) when the angular distribution of photofragments is not observed thus allowing only $K_l=0$ (and $l'=l$) for the multipole moments of $|lm)(l'm'|$.

Let us now consider the high-J limit where J_A and J become large. The behavior of the $6j$ coefficient in this limit has been considered in Sec. II. Only the values of J and J' which satisfy the relation $\eta=0$, i.e., $J_A+J'=J+J_A$, were shown to yield the positive values of the squared volume of the tetrahedron corresponding to the $6j$ coefficient in (6), thus belonging to the classically allowed range. Thus in the high-J limit only $J=J'$ provides nonvanishing terms, showing the unimportance of interference between different values $(J\neq J')$ of the angular momentum. A more intuitive explanation might be that in the high-J limit, the order of multipole moment K is much smaller than J and J', and that the system looks isotropic; in fact, this remark is not relevant to the vanishing of interference terms in the high-J limit.

If B has a nonzero value $(J_B\neq 0)$ of the angular momentum but still is not observed in experiments, we would have the same results as above except that (1) l in the density matrix D_A and in the scattering matrices in (5) and (6) are replaced by $(J_B l)J_{\rm UO}$ where $\mathbf{J}_{\rm UO}$ is defined as $\mathbf{J}_{\rm UO}=\mathbf{J}_B+\mathbf{l}$ and represents an unobserved angular momentum, (2) there is one more summation over the values of $\mathbf{J}_{\rm UO}$ in (5), and (3) the l appearing in the $6j$ and $9j$ coefficients in (6) is replaced by $J_{\rm UO}$. This change does not affect the result that only an incoherent sum over J survives in the high-J limit, but produces some depolarization.

The angular distribution of a relative motion of photofragments (A,B) for the system (4) is described, in the absence of fluorescence analysis, by the expectation value $\langle D_{\rm p}\rangle$ of the detector operator $D_{\rm p}=|\mathbf{p})(\mathbf{p}|$ of momentum eigenstates

$$\langle D_{\rm p}\rangle=\sum_{K,Q}\sum_{J,J',l,l'}([(J_AJ_B)J_{\rm UO}l]J \mid D_{\rm p} \mid [(J_AJ_B)J_{\rm UO}l']J')_Q^{(K)}((j_{\rm ph}J_{AB})J' \mid \rho_{AB}\rho_{\rm ph} \mid (j_{\rm ph}J_{AB})J)_{-Q}^{(K)}(-1)^{J-J'+Q}$$
$$\times((J_AJ_B)J_{\rm UO}l \mid S(J) \mid j_{\rm ph}J_{AB})((J_AJ_B)J_{\rm UO}l' \mid S(J') \mid j_{\rm ph}J_{AB})^* . \tag{7}$$

The density matrix of $D_{\rm p}$ in (7) may be expanded in the same way as in (6)

$$([(J_AJ_B)J_{\rm UO}l]J \mid D_{\rm p} \mid [(J_AJ_B)J_{\rm UO}l']J')_Q^{(K)}=(-1)^{J_{\rm UO}+l+J'+K}[(2J+1)(2J'+1)]^{1/2}(l \mid D_{\rm p} \mid l')_Q^{(K)}\begin{Bmatrix} l & J & J_{\rm UO} \\ J' & l' & K \end{Bmatrix} . \tag{8}$$

For the $6j$ coefficient in (8), only those values of l, l', J, and J' which satisfy $l-l'=J-J'$ are classically allowed. Only these give nonzero contributions to the sums in (7) as $(l,l',J,J')\to\infty$. (In the photodissociation into two heavier fragments, large values of the relative angular momentum quantum numbers frequently dominate.) The sums $\sum_l \sum_{l'} \sum_J \sum_{J'}$ may be transformed into $\sum_{\sigma_l}\sum_{\sigma_J}\sum_\tau$, where

$$\sigma_l=l+l', \quad \sigma_J=J+J', \quad \tau=l-l'=J-J' . \tag{9}$$

Now there are still interference terms having $\tau\neq 0$.

We note here that different l appear and interfere to yield the observed multipole moments of the relative motion of (A,B), in contrast to the previous case of fragment orientation and alignment where only a single value is usually allowed for the angular momentum of the fragment A. We also note that for the electric dipole photofragmentation procęsses the nonzero $|J-J'|$ equals K. The proof of this is as follows: The angular distribution of photofragmentation allows only the even values 0 and 2 of $\hbar$ for its 2^K-pole moments. The parity restriction $l+l'+K=$even in

$$(l \mid D_p \mid l')_Q^{(K)}=(4\pi)^{-1/2} i^{l-l'} (l \| C^{(K)} \| l')$$

allows only even values of $|l-l'|$, whereby τ can be 0 or 2. If τ equals 2, the triangular relation $K \geq |l-l'| = |\tau|$ tells us that it equals the multipole moment K.

Thus when there are two kinds of degenerate quantities like l and J, the values of the total angular momentum belonging to the P and R branches interfere in the high-J limit. The Q branch fails to interfere with other branches in the dipole transition. Interestingly, the P and R branches have identical alignment, orientation, line strength, and so on in the high-J limit.[1]

If the high-J limit corresponds to a classical limit, the survival of the interference terms in this limit seems to contradict the common-sense notion that interference is a purely quantum phenomenon. For the angular distribution of the relative motion of photofragments, the unit $\hbar$ of j_{ph} limits ΔJ to at most $2\hbar(|\Delta J| \leq K_{ph} \leq 2j_{ph})$. Thus $\Delta J \Delta\theta$ is an order of $\hbar$, showing that a classical situation is not obtained here in the high-J limit. On the other hand, the unit $\hbar$ of j_{ph} cannot seem to confine the values of the total angular momentum to the quantum regime for the observation of the anisotropies of the fragment A. We first note that the direct observation of anisotropies of the fragment A may not be possible due to the negative energy of the state of A. Its anisotropies may be observed from angular distribution of the fluorescence intensity instead. For the light which is regarded as a wave in the classical limit, the relation $\Delta J \Delta\theta \sim \hbar$ may no longer be used as a criterion for whether a given process belongs to the quantum or classical regime. We failed to give the full account of this phenomenon at this stage.

A. Commutator and incoherence

As said before, the interference between different values of total angular momentum for the anisotropy of a photofragment A is derived from the incompatibility between the operators $\mathbf{J}^2$ and $\mathbf{J}_A$, which has manifested itself into the nonzero value of the commutator $[\mathbf{J}^2,\mathbf{J}_A]$. However, we note that the unimportance of interferences does not mean that the commutator vanishes. Nevertheless, they are closely related.

For the anisotropy measurement of the fragment A, the total angular momentum is defined as $\mathbf{J}=\mathbf{J}_A+\mathbf{J}_{UO}$. In this case,

$$[\mathbf{J}^2,\mathbf{J}_A]=2i\hbar\mathbf{J}_A \times \mathbf{J}_{UO} \ . \tag{10}$$

If $\mathbf{J}_A$ and $\mathbf{J}_{UO}$ are parallel to each other, the commutator becomes zero. This condition is met when $J=J_A \pm J_{UO}$, which yields $J_A-J=J_A-J'=\pm J_{UO}$ or $J_A-J=J'-J_A=\pm J_{UO}$ (the latter is not the physical solution). Therefore the vanishing of the commutator yields a much stricter condition than $\eta=0$, i.e., $J_A-J=J_A-J'$. If the commutator is zero, only a single value of the total angular momentum will appear in the formula for the anisotropies of the fragment A. Especially, the zero of the commutator (10) restricts its value to either J_A+J_{UO} or J_A-J_{UO} for a given value of J_A and J_{UO}. On the other hand, $\eta=0$, the incoherence condition for the anisotropies in the fragment A yields an incoherent sum over *all* values of angular momentum, indicating the failure to observe some information.[13] Absence of the analysis of both $\mathbf{J}_{UO}$ and the relative motion between photofragments brings about such a loss of information for the anisotropies of a fragment A. The high-J limit itself bears no direct relation to the loss of information because of its irrelevance to the measurement. However, a decrease in the amount of loss of information may result with increase of J as some angular momentum couplings become classically forbidden. In the most extreme case of a complete loss of information, all the different values of the angular momentum would be equally populated [in the language of density matrix, $\rho_{JM,J'M'}=\delta_{J,J'}\delta_{M,M'}(2J+1)^{-1}$].

B. $\hat{\mathbf{J}}_{UO}$ as a quantization axis

A simple situation occurs when $\hat{\mathbf{J}}_{UO}$ is taken as a quantization axis. It provides not only the correlation between $(\mathbf{J},\mathbf{J}_A,\mathbf{K},\mathbf{K}_A)$ and $\mathbf{J}_{UO}$ but also sheds light on the unimportance of interference terms in the high-J limit.

The angle between $\mathbf{J}_A$ and $\mathbf{J}_{UO}$ can be obtained from the triangle that they form with $\mathbf{J}$ in the vector model. In the classical limit,

$$\hat{\mathbf{J}}_A \cdot \hat{\mathbf{J}}_{UO} \rightarrow \frac{J-J_A}{J_{UO}} \quad \text{when } J \rightarrow \infty \ , \tag{11}$$

whereby the projection quantum number M_A *known as a Landé g factor*[14] *of* $\mathbf{J}_A$ on $\mathbf{J}_{UO}$ is given by $M_A=J_A[(J-J_A)/J_{UO}]$. Even though the unobserved $\mathbf{J}_{UO}$ orients randomly in space, its angle with $\mathbf{J}_A$ is not random and has the definite value for a given total angular momentum quantum number. Likewise, we have the projection quantum number M of $\mathbf{J}$ on $\mathbf{J}_{UO}$ given by $M=J[(J-J_A)/J_{UO}]$. This yields the projection quantum numbers $Q_A=J_A(J'-J)$ and $Q=J^2-J'^2+J_A(J'-J)$ of the multipole moment operators $\mathbf{K}_A$ and $\mathbf{K}$ from the relation $Q=M-M'$. On the other hand, we have $K=K_A$ and $Q=Q_A$ owing to the failure to observe the photofragment B and the relative motion of A and B, as explicitly shown in (6), whereby $J_A(J'-J)=J^2-J'^2+J_A(J'-J)$ or $J=J'$. Thus both Q_A and Q vanish in the high-J limit. In the vector notation, $\mathbf{K}_A \cdot \mathbf{J}_{UO}=\mathbf{K}\cdot\mathbf{J}_{UO}=0$. This alternatively implies a minimal correlation[15] between observed $(\mathbf{K}_A,\mathbf{K})$ and unobserved $\mathbf{J}_{UO}$.

This alternative derivation of $J=J'$ reveals another aspect of incoherence between different values of the total angular momentum, i.e., that there exists a "*dynamic*" *symmetry axis* on which the *projection values* Q of multipole moment operators are *zero* (the word "dynamic" is used here since the projection axis $\mathbf{J}_{UO}$ processes about a space fixed quantization axis). This aspect will repeat in another situation in the Sec. VI.

In the angular distribution measurement of the relative motion of fragments (A,B), in the absence of fluorescence analysis, the projection value of the multipole moment operator $\mathbf{K}$ on $\mathbf{J}_{\rm UO}$ is no longer zero in the high-J limit and given from (3) by

$$\mathbf{K}\cdot\mathbf{J}_{\rm UO}=\zeta\tau\ , \tag{12}$$

where $\zeta=(J+J'-l-l')/2\le J_{\rm UO}$ and τ is defined in (9). Thus the survival of interference terms in the high-J limit brings about the nonzero projection value of multipole moment $\mathbf{K}$ on $\hat{\mathbf{J}}_{\rm UO}$ or the spatial correlation between observed $\mathbf{K}$ and unobserved $\mathbf{J}_{\rm UO}$ larger than minimal.

Thus the condition $\mathbf{K}\cdot\mathbf{J}_{\rm UO}=0$ is a *necessary and sufficient* condition for the *vanishing of coherent terms* among different J. $K=0$ brings about a zero of $\mathbf{K}\cdot\mathbf{J}_{\rm UO}$ and is a *sufficient but not a necessary* condition for an *incoherent sum.*

Projection of multipole moment operator on $\mathbf{J}$ considered in the above calls for caution. For example, $\mathbf{J}_A$ cannot be taken as a quantization axis for $\mathbf{K}$ since the presence of its counterpart in adjoint space with which it forms $\mathbf{K}_A$ prevents us from having a unique projection value of $\mathbf{K}$. For $\mathbf{J}_{\rm UO}$, this problem has not taken place due to the zero value of its multipole moment $\mathbf{K}_{\rm UO}$. The fact that $\mathbf{K}$ is a vector in Liouville space[16,17] while $\mathbf{J}$ is a vector in the Euclidean space of the vector model brought about this strange situation. However, the problem may arise even in case of the presence of the unique projection axis such as whether the projection can be made within Euclidean geometry. As we saw in Sec. II, sometimes such a projection can only be made by allowing the complex angle between $\mathbf{K}$ and the axis in Euclidean space which we never encounter in the case of projection of the angular momentum vector in Euclidean space onto an axis in its own space.

IV. ANGULAR MOMENTUM TRANSFERS IN THE HIGH-J LIMIT

A. Density-matrix formalism in the angular momentum transfer representation

Now we may want a type of representation that expands the interpretation of noninterference from the classical limit to the case of small angular momentum quantum numbers. The angular momentum transfer representation was introduced by Fano and Dill[4] exactly in this way. It separates observed and unobserved variables. Equality of the angular momentum quantum numbers j_t and j_t' results from the vanishing of all multipole moments of unobserved variables. We shall illustrate this statement using the density-matrix formalism in the angular momentum transfer representation developed in Ref. 18.

Anisotropies of the photofragment A for the system (4) can be calculated with the density matrix $\rho_A\rho_B\rho_{\rm p}$ of the final state

$$\langle D_A\rangle=\mathrm{tr}(D_A\rho_A\rho_B\rho_{\rm p})\ . \tag{13}$$

Using the scattering matrix for the photofragmentation, the final density matrix can be obtained from the initial density matrix $\rho_{AB}\rho_{\rm ph}$,

$$\langle D_A\rangle=\mathrm{tr}(D_A S\rho_{AB}\rho_{\rm ph}S^{-1})\ . \tag{14}$$

From a straightforward manipulation of angular momentum algebra, (14) can be written in terms of matrices of the observed or prepared parts, $D_A\rho_{\rm ph}$, and of the unobserved part ρ_{AB} of operators

$$\begin{aligned}\langle D_A\rangle=\sum_{j_t,l}&((J_Aj_{\rm ph})j_t\,|\,D_A\rho_{\rm ph}\,|\,(J_Aj_{\rm ph})j_t)^{(0)}\\&\times((J_{AB}l)j_t\,|\,\rho_{AB}\,|\,(J_{AB}l)j_t)^{(0)}\\&\times|(J_Al\,|\,S(j_t)\,|\,J_{AB}j_{\rm ph})|^2\ .\end{aligned} \tag{15}$$

The $K=0$ index represents the isotropy resulting from averaging over the variables of the unprepared part ρ_{AB} unable to transfer any multipole moment to the prepared or observed part $D_A\rho_{\rm ph}$. The only contribution to $D_A\rho_{\rm ph}$ consists of the *incoherent* sum over the angular momentum transfer quantum numbers in (15).

The incoherent sum over angular momentum transfer quantum numbers simplifies the discussion about photofragmentation dynamics greatly since we can talk about it as an average over separate angular momentum transfer "processes." The geometrical aspects of photodissociation for a given momentum transfer process are completely contained in the density matrix $[(J_aj_{\rm ph})j_t\,|\,D_A\rho_{\rm ph}\,|\,(J_Aj_{\rm ph})j_t']^{(0)}$ regardless of detailed dynamical information contained in $|(J_Al\,|\,S(j_t)\,|\,J_{AB}j_{\rm ph})|^2$ (lack of anisotropy in ρ_{AB} simplifies the discussion). For example, the problem of whether photofragmentation takes place parallel or perpendicular to the direction of the electric vector of the linearly polarized incident light can be answered from the sign of the density matrix.[1] We can discuss $\langle D_{\rm p}\rangle$ in a similar fashion, but since there is not much new physics, we will not present it here.

B. Angular momentum transfers in the high-J limit

From the previous discussion, we learned that observables are given by an incoherent sum in the angular momentum transfer representation. Now we have two representations, both of which provide an incoherent sum in the high-J limit for the anisotropies of a fragment A. Note, however, that they are related by a recoupling transformation

$$((j_{\rm ph}J_A)j_t(J_{AB}l)j_t\,|\,(j_{\rm ph}J_{AB})J(lJ_A)J)^{(0)}=[(2J+1)(2j_t+1)]^{1/2}(-1)^{l+J_{AB}+j_t}\begin{Bmatrix} l & J_A & J\\ j_{\rm ph} & J_{AB} & j_t\end{Bmatrix}\ . \tag{16}$$

For a given value of the total angular momentum, three values of angular momentum transfer, $J_A\pm1$ and J_A, are allowed with the probability amplitudes given by (16). If all the three values of angular momentum transfer appear with significant magnitude in the high-J limit, there will be interference terms reflecting the coherence of different values of the angular momentum transfer contradicting the discussion in Sec. IV A. Actually only one of them will contribute significantly, belonging to a classically allowed range.

In the classical limit of large J, J_A, J_{AB}, and j_t, the $6j$ coefficient in (16) is classically allowed only for the values of angular momenta satisfying the relation $J_A+J_{AB}=J+j_t$. Thus for a given branch of the total angular momentum, only a single value of j_t belongs to the classically allowed range and vice versa,

$$J=\begin{cases} J_{AB}-1, & P\text{ branch} \\ J_{AB}, & Q\text{ branch} \\ J_{AB}+1, & R\text{ branch} \end{cases} \Longleftrightarrow j_t=\begin{cases} J_A+1 \\ J_A \\ J_A-1\ . \end{cases} \tag{17}$$

A one-to-one correspondence relation similar to (17) will also hold for the angular distribution measurement of the relative motion between photofragments (A,B), even though interference terms between different values of the total angular momentum survive in this case in the high-J limit. This implies that the two representations are completely correlated in the high-J limit. Geometrically, the scalar product $\mathbf{J}\cdot\mathbf{j}_t$ approaches $\pm Jj_t$ in the high-J limit so that $\mathbf{J}$ and $\mathbf{j}_t$ are parallel or antiparallel to each other. Or, $\mathbf{J}$ and $\mathbf{j}_t$ have identical projections but for the sign.

How fast two other branches become unimportant can be seen by considering the scalar product of $\boldsymbol{l}\cdot\mathbf{j}_{\text{ph}}$ and the transformation (2) with $\{a,b,d,e\}$ replaced by (J_{AB},J_A,J,j_t),

$$\begin{aligned} \sigma&=(J+J_A+j_t+J_{AB})/2\ , \\ \tau&=(J-J_A+j_t-J_{AB})/2\ , \\ \eta&=(J+J_A-j_t-J_{AB})/2\ , \\ \zeta&=(J-J_A-j_t+J_{AB})/2\ . \end{aligned} \tag{18}$$

From (3), the scalar product $\boldsymbol{l}\cdot\mathbf{j}_{\text{ph}}$ is given by

$$\boldsymbol{l}\cdot\mathbf{j}_{\text{ph}}=(\sigma+1)\eta+\tau\zeta\ . \tag{19}$$

The case of unit value of $\mathbf{j}_{\text{ph}}$ was considered extensively in Ref. 6, which shows that $\eta\neq0$ is classically forbidden for almost all values of σ. Thus the incoherent sum over the total angular momentum quantum numbers is obtained rapidly for a dipole transition.

V. DEGREE OF POLARIZATION

Now let us consider the quantum derivation of the classical polarization P of fluorescence,[7]

$$P=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}}\ . \tag{20}$$

In the classical theory of light interacting with matter, the polarization P of light emitted after photodissociation by linearly polarized incident light is obtained from the angle α between the dipole moments of absorption and fluorescence

$$P=\frac{3\cos^2\alpha-1}{\cos^2\alpha+3}\ . \tag{21}$$

According to the group-theoretical argument,[19] these transition dipole moments are perpendicular to $\hat{\mathbf{J}}$ for the P and R branches and parallel to it for the Q branch. If both absorption and fluorescence take place by the P or R branches, the angle α will be given by $\pi/4$ since the transition dipole moments for both processes will rotate in the plane perpendicular to $\hat{\mathbf{J}}$ without correlation (in the high-J limit, the rotation time of the molecule will be much faster than the absorption and emission time of light). Then the value of polarization is given by $\frac{1}{7}$. If one of the processes belongs to a P or R branch and the other to a Q branch, the angle α becomes $\pi/2$. Then the polarization is given by $-\frac{1}{3}$. Similarly, the remaining case with both absorption and emission following the Q branch leads to $\alpha=0$ and hence $P=\frac{1}{2}$ (if interference terms survived in the high-J limit, we should have calculated the degree of polarization for those).

From the quantum-mechanical formulas, it is straightforward to get the alignment value for a given angular momentum transfer process for the photodissociation by linearly polarized light. In particular, their values in the classical limit are given by $\frac{2}{5}$ for the parity favored $j_t=J_A\pm1$ and $-\frac{4}{5}$ for the parity unfavored $j_t=J_A$.[1] The alignment A_0 and the degree of polarization P are related by

$$P=\frac{3h^{(2)}(J_A,J_{Af})A_0}{4+h^{(2)}(J_A,J_{Af})A_0}\ , \tag{22}$$

where $H^{(2)}(J_A,J_{Af})$ is a function that depends only on the values of J_A and J_{Af} and appears a coefficient of the alignment in the fluorescence intensity formula;[1] Af denotes the state of the fragment A after the fluorescence. Putting into (22) the values of $h^{(2)}(J_A,J_{Af})$ (see Table I of Ref. 1), which are $-\frac{1}{2}$ for the P and R branches and 1 for a Q branch in the high-J limit, and making use of (17) which replaces the values of j_t by those of J, we get the degree of polarization $\frac{1}{7}$ for ($P_\uparrow$ or $R_\uparrow$,$P_\downarrow$ or $R_\downarrow$) and $-\frac{1}{3}$ for ($Q_\uparrow$, $P_\downarrow$ or $R_\downarrow$) or ($P_\uparrow$ or $R_\uparrow$,$Q_\downarrow$) and $\frac{1}{2}$ for ($Q_\uparrow$,$Q_\downarrow$). This is exactly the same result as the classically derived degree of polarization (e.g., the table of MacPherson, Simons, and Zare[7]).

VI. RESULT AND DISCUSSION

We have found that interference between different values of angular momentum does not always disappear in the high-J limit. Additional interpretation appears to be called for. However, details for how interference terms behave as the angular momentum quantum numbers become large have been answered by applying the Ponzano-Regge semiclassical theory of angular momentum. Several interesting aspects of the behavior of the interference terms were found in the high-J limit.

Besides the interferences discussed so far, there are other interesting interferences such as the one between transitions parallel and perpendicular to a molecular axis for a diatomic molecule (or a plane for a nonlinear triatomic one). The interference for the diatomic molecule case is already discussed in Ref. 3. In order to have only incoherent sums, Ref. 3 considered the anisotropies of the fluorescence from a rotational-state-unresolved fragment. Let us explain this a little in detail here since Ref. 3 did not explain clearly how the interference terms disappear in the high-J limit.

The relation[20] of the scattering matrix for the photoionization of a diatomic molecule (in the angular momentum transfer representation) in the space-fixed frame appearing in Eq. (15) to that in the body frame can be obtained by following the procedure similar to Eqs. (19)–(22) of Ref. 4:

$$\begin{aligned}|(\lambda_A J_A l\,|\,S(j_t)\,|\,\lambda_{AB}J_{AB}j_{\rm ph})|^2=&(2J_A+1)(2J_{AB}+1)\\&\times\sum_{\lambda,\lambda_{\rm ph}}\sum_{\lambda',\lambda'_{\rm ph}}(-1)^{\lambda_{\rm ph}+\lambda}(-1)^{\lambda'+\lambda'_{\rm ph}}\begin{bmatrix} l & J_{AB} & j_t\\ -\lambda & \lambda_{AB} & \lambda-\lambda_{AB}\end{bmatrix}\\&\times\begin{bmatrix} J_A & j_{\rm ph} & j_t\\ -\lambda_A & \lambda_{\rm ph} & \lambda_A-\lambda_{\rm ph}\end{bmatrix}\begin{bmatrix} l & J_{AB} & j_t\\ -\lambda' & \lambda_{AB} & \lambda'-\lambda_{AB}\end{bmatrix}\\&\times\begin{bmatrix} J_A & j_{\rm ph} & j_t\\ -\lambda_A & \lambda'_{\rm ph} & \lambda_A-\lambda'_{\rm ph}\end{bmatrix}(\lambda_A l\lambda\,|\,S\,|\,\lambda_{AB}j_{\rm ph}\lambda_{\rm ph})\\&\times(\lambda_A l\lambda'\,|\,S^\dagger\,|\,\lambda_{AB}j_{\rm ph}\lambda'_{\rm ph})\,,\end{aligned}\qquad(23)$$

where λ's denote the projection quantum numbers of the corresponding angular momentum onto the molecular axis. Among them λ_A and λ_{AB} can also be the projection quantum numbers of the electronic orbital momenta of A and AB molecules[4] which are explicitly included to the indices of S matrix in Eq. (15) for clarity. In Eq. (15), anisotropies of a photofragment A are obtained from the universal alignment or orientation functions,[1] i.e., the part of density matrices weighted by the scattering matrices of (23). In the high-$\{J_A,J_{AB},j_t\}$ limit (For a given l), these universal anisotropies become independent of J_A. Thus J_A-dependent terms comes only from (23).[21] In a J_A-unresolved experiment, the sum over J_A,

$$\sum_{J_A}(2j_A+1)\begin{bmatrix} J_A & j_{\rm ph} & j_t\\ -\lambda_A & \lambda_{\rm ph} & \lambda_A-\lambda_{\rm ph}\end{bmatrix}\times\begin{bmatrix} J_A & j_{\rm ph} & j_t\\ -\lambda_A & \lambda'_{\rm ph} & \lambda_A-\lambda'_{\rm ph}\end{bmatrix},\qquad(24)$$

yields $\delta_{\lambda_{\rm ph},\lambda'_{\rm ph}}$. From their invariance under space rotation, scattering matrices in the body frame in (23) yield $\lambda_A+\lambda=\lambda_A+\lambda_{\rm ph}$ and $\lambda_A+\lambda'=\lambda_A+\lambda'_{\rm ph}$, whereby λ equals λ'. thus interference terms between transitions parallel and perpendicular to the molecular axis disappear in the high-J limit in the J_A-unresolved fluorescence measurement of A. From this result, *projections* of multipole moments of both (l,l) and $(j_{\rm ph},j_{\rm ph})$ on the *molecular axis* become *zero* in the high-J limit. Zero projection values of multipole moments were also encountered in the Sec. V. In this case, $\mathbf{J}_A$ plays a similar role to that of $\mathbf{J}_{\rm UO}$.

Further studies on interference between different channels will be of interest since this interference is derived from *dynamical coupling*. The simplest case of only two-channel coupling was considered by Dill.[22] As the high-J limit does not necessarily bring about the results anticipated classically, some additional theory appears to be called for.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation under Grant No. PHY-8740404. I would like to thank Dr. Greene for suggesting the research topic, many helpful discussions, and continuous encouragement. I am indebted to Professor Fano for carefully reading and editing the manuscript, and for numerous helpful suggestions. Discussions with Dr. Lai-Him Chan are also acknowledged.

APPENDIX

The volume of the tetrahedron corresponding to the $6j$ coefficient in Eq. (1) is calculated from the Cayley determinant[5] by

$$f(c^2)=288V^2=\det\begin{vmatrix} 0 & \bar f^2 & \bar d^2 & \bar e^2 & 1\\ \bar f^2 & 0 & \bar b^2 & \bar a^2 & 1\\ \bar d^2 & \bar b^2 & 0 & \bar c^2 & 1\\ \bar e^2 & \bar a^2 & \bar c^2 & 0 & 1\\ 1 & 1 & 1 & 1 & 0\end{vmatrix}\,,\qquad(\text{A1})$$

where $\{\bar a,\bar b,\ldots\}$ represents the semiclassical replacement of $\{a,b,\ldots\}$ with $\{a+\frac12,b+\frac12,\ldots\}$. The above equation shows that $f(c^2)$ is a quadratic equation in c^2,

$$f(c^2)=A(c^2)^2+B(c^2)+C\,.\qquad(\text{A2})$$

The coefficients of (A2) can be easily calculated from the differentiation of (A1) with respect to c^2 evaluated at $c^2=0$ and given by

$$2A = \left[\frac{\partial^2 f}{(\partial c^2)^2} \right]_{c^2=0} = -4\bar{f}^2 ,$$

$$B = \left[\frac{\partial f}{\partial c^2} \right]_{c^2=0} = -2[\bar{f}^4 - \bar{f}^2(\bar{a}^2+\bar{b}^2+\bar{d}^2+\bar{e}^2) + (\bar{a}^2-\bar{e}^2)(\bar{b}^2-\bar{d}^2)] ,$$

$$C = f(c^2=0) = -2[\bar{f}^2(\bar{b}^2-\bar{a}^2)(\bar{d}^2-\bar{e}^2) + (\bar{a}^2-\bar{b}^2+\bar{d}^2-\bar{e}^2)(\bar{a}^2\bar{d}^2-\bar{b}^2\bar{e}^2)] . \quad \text{(A3)}$$

By substituting (A3) into (A2), we get the simple form of (A1)

$$-144V^2 = \bar{c}^2\bar{f}^2[\bar{c}^2+\bar{f}^2-(\bar{a}^2+\bar{b}^2+\bar{d}^2+\bar{e}^2)] + \bar{c}^2(\bar{a}^2-\bar{e}^2)(\bar{b}^2-\bar{d}^2) + \bar{f}^2(\bar{b}^2-\bar{a}^2)(\bar{d}^2-\bar{e}^2) + (\bar{a}^2-\bar{b}^2+\bar{d}^2-\bar{e}^2)(\bar{a}^2\bar{d}^2-\bar{b}^2\bar{e}^2) . \quad \text{(A4)}$$

In terms of new quantum numbers,

$$-144V^2 = \bar{c}^2\bar{f}^2[\bar{c}^2+\bar{f}^2-(\bar{\sigma}^2+\tau^2+\zeta^2+\eta^2)] + \bar{c}^2(\bar{\sigma}^2-\zeta^2)(\tau^2-\eta^2) + \bar{f}^2(\zeta^2-\eta^2)(\bar{\sigma}^2-\tau^2) + (\bar{\sigma}^2\eta^2-\tau^2\zeta^2)(\bar{\sigma}^2-\tau^2-\zeta^2+\eta^2) , \quad \text{(A5)}$$

where $\bar{\sigma}$ is the usual semiclassical replacement of σ with $\sigma + 1$. In the high-J limit $\sigma \to \infty$, we get

$$144V^2 \to \begin{cases} -\sigma^4 & \text{when } \eta \neq 0 \\ (\bar{f}^2-\tau^2)(\bar{c}^2-\zeta^2) & \text{when } \eta = 0 , \end{cases} \quad \text{(A6)}$$

which directly shows that the square of the volume of the tetrahedron becomes negative when $\eta \neq 0$ in the high-J limit $\sigma \to \infty$. This strange case can be solved mathematically with the same geometrical formulas for a tetrahedron in Euclidean space by simply allowing complex values for the angles.

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[14]According to the so-called projection theorem for vector operators **V**, which is the specific case of the Wigner-Eckart theorem for tensors of rank one, there holds

$$(JM' \mid \mathbf{V} \mid JM) = [\mathbf{J}\cdot\mathbf{V}/J(J+1)](JM' \mid \mathbf{J} \mid JM) = g_J(V)(JM' \mid \mathbf{J} \mid JM) ,$$

where $g_J(V)$ is called the Landé g factor. Here the matrix element of **V** in the $|JM)$ representation is calculated first in the representation where **J** is taken as a quantization axis and then in the $|JM)$ where a space-fixed axis is taken as the quantization axis. The Landé g factor than represents the projection value (quantum number) of **V** on **J**.

[15]The degree of correlation between two vectors in the vector model can be deduced from the compatible ranges of the projection of one vector for a given projection of another.

[16]See, for example, Sec. VI of Ref. 13. The order K itself appears as a magnitude of the multipole moment operator $T_Q^{(K)}$ when the coupling of the latter with **J** and **J′** or the projection of it on $\mathbf{J}_{\mathrm{UO}}$ are considered. The vector version of $T_Q^{(K)}$ in the vector model is denoted by **K** here. However, its magnitude in Liouville space is an order of $[J(J+1)]^{K/2}$, which can be shown explicitly, e.g., by the orthogonality relation of the multipole operator $Y_{KQ}(\mathbf{J})$ considered by Schwinger (Ref. 17):

$$\mathrm{tr}^{(J)} Y_{K_1Q_1}(\mathbf{J})^\dagger Y_{K_2Q_2}(\mathbf{J}) = \frac{2J+1}{4\pi}\{J(J+1)\}^{K_1}\delta_{K_1K_2}\delta_{Q_1Q_2} ,$$

where the trace operation corresponds to the scalar product in Hilbert space. Note that a more likely relation for the magnitude of $Y_{KQ}(\mathbf{J})$,

$$\sum_q Y_{KQ}(\mathbf{J})Y_{KQ}(\mathbf{J})^\dagger = \frac{2K+1}{4\pi}\{\mathbf{J}^2\}^K ,$$

with

$$\{\mathbf{J}^2\}^K = \prod_{n=0}^{K-1}\left[J^2 - \frac{n}{2}\left[\frac{n}{2}+1\right]\right] ,$$

is an operator identity not a scalar equation.

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