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Theory of level splitting: Spectrum of the octahedrally invariant fourth-rank tensor operator*†

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The theory of level splitting of certain vibration - rotation states (including the ground state) in spherical-top molecules is developed within the framework of the standard Racah-Wigner tensor algebra, thus demonstrating the direct applicability of these general techniques without making the usual modifications associated with the anomalous commutation relations of the body-fixed angular momentum components. The eigenvalue spectrum of the octahedrally invariant fourth-rank tensor operator is examined in detail, and the unexpected periodic symmetry and asymptotic degeneracy features of the spectrum are described.

I. INTRODUCTION

Recent experimental and theoretical developments have resulted in a renaissance of effort in research on high-resolution spectroscopy of spherical-top molecules. These systems have characteristic tetrahedral (T_d) or octahedral (O_h) symmetry. The prototypical molecules are CH_4 and SF_6, respectively.[1]

Much of the motivation for present studies of high-resolution infrared spectra of CH_4 is the existence of enormous amounts of this gas in the atmospheres of the outer planets.[2] Theoretical and experimental work on CH_4 extended to high values of the rotational angular momentum quantum number J, form the basis for analyses of planetary data to obtain atmospheric parameters.

Developments in ultrahigh-resolution laser techniques have produced infrared spectra of tremendous complexity. It has been possible to measure T_d and O_h fine-structure splittings in methane[3] and sulfur hexaflouride[4,5] for which quantum-number assignments have been made to very high J values. Considerable research is underway which will require more refined theoretical developments.

A theoretical prediction[6] of pure rotational transitions in the conventionally nonpolar vibronic ground state of T_d molecules motivated several experimental verifications[7] and theoretical extensions.[8] An intriguing consequence of this line of research is the potential detection of interstellar methane by radio-frequency transitions.[6]

The purpose of this paper is twofold: First, we present the theory of the Hamiltonian which dominates the fine-structure splitting in certain regions of the vibration-rotation spectrum of spherical-top molecules having tetrahedral or octahedral symmetry. This basic problem falls within the framework of the Racah-Wigner angular momentum calculus. In order to exhibit the fact that this molecular theory is abstractly the same as a variety of other physical theories (crystal-field, complex-ion theory), and in order to reach a wider audience, we have chosen to develop the theory in the abstract formulation of angular momentum theory, rather than in terms of the particular notations of specialized areas.[9] Second, we present a basic eigenvalue problem to be solved. This is developed abstractly as well as in particular realizations. The remarkable result here is that the energy splittings (coming from the eigenvalue problem) exhibit unexpected degeneracies for large angular momenta, and it is an intriguing problem to attempt to understand from a fundamental point of view this curious asymptotic behavior.

We have organized our work in the following way. In Sec. II, we develop, in the way of review, the general structure of the molecular problem in terms of the general language of the theory of level splitting.[10] While some of this material is of a review nature, it is not so familiar to molecular spectroscopists. Furthermore, it is desirable to have the relevant mathematical results brought together in a form directly useful to the molecular problem. In Sec. III, the general theory is particularized to a case of practical importance in the interpretation of ultrahigh-resolution spectra of CH_4 and SF_6. Here the invariance properties of the particular problem are set forth in detail. Various general features of the eigenvalues (giving the level splitting) are presented in Sec. IV together with specific features based on explicit numerical calculation. The method of numerical calculation is also discussed briefly in Sec. IV. In Sec. V, some of the ideas we have explored in attempts to interpret the numerical results are discussed briefly. None of these attempts has been successful in providing a detailed explanation of the calculated spectrum. (Time-reversal symmetry is examined in Appendix A.)

II. GENERAL MATHEMATICAL FRAMEWORK OF THE PHYSICAL PROBLEM

Although most of the general theory to be described in this section is well known,[11-15] it is convenient to review it briefly for the purpose of establishing notations and collecting together the material most relevant to the theory of the vibration-rotation levels of spherical-top molecules.

We consider a physical system which is described approximately by a Hamiltonian operator H_0 (having an abundance of bound states) which has as its invariance group either a group of 3×3 real, proper,[16] orthogonal matrices or a group of 2×2 unitary unimodular matrices[17] [SU(2)].

To describe this invariance property more precisely, let (J_1, J_2, J_3) denote the angular momentum operators obeying the standard commutation relations $[J_j, J_k] = i\epsilon_{jkl}J_l$ and corresponding to the generators of SO(3) [SU(2)]. Then the invariance property of H_0 is expressed infinitesimally by the commutation relations

$$[H_0, J_k] = 0, \quad k = 1, 2, 3 \ . \tag{1}$$

It is assumed here that H_0 and J_k are Hermitian operators on the state vector space of the Hamiltonian H_0. Following standardized procedures and notations,[18] we let $|\alpha jm\rangle$ denote the simultaneous eigenstates of the commuting Hermitian observables H_0, $J^2 = J_1^2 + J_2^2 + J_3^2, J_3$. Then the basis states $|\alpha jm\rangle$ satisfy the following familiar system of equations:

$$\begin{aligned}
&H_0|\alpha jm\rangle = E(\alpha, j)|\alpha jm\rangle \ , \\
&J^2|\alpha jm\rangle = j(j+1)|\alpha jm\rangle \ , \\
&J_3|\alpha jm\rangle = m|\alpha jm\rangle \ , \\
&J_\pm|\alpha jm\rangle = (J_1 \pm iJ_2)|\alpha jm\rangle \\
&\qquad = [(j \mp m)(j \pm m + 1)]^{1/2}|\alpha jm \pm 1\rangle \ , \\
&\langle \alpha' j' m'|\alpha jm\rangle = \delta_{\alpha'\alpha}\delta_{j'j}\delta_{m'm} \ ,
\end{aligned} \tag{2}$$

where j (and j') are either nonnegative integers [invariance group SO(3)] or nonnegative integers and half integers [invariance group SU(2)], and where for each allowed value of j the allowed m values are $m = j, j-1, \ldots, -j$.

It is useful to note explicitly the unitary transformations generated by the operators (J_1, J_2, J_3). For this purpose, we first describe convenient parametrizations of the groups SO(3) and SU(2).

The parametrization of the group SO(3) [SU(2)] in terms of the *angle of rotation* θ *about the direction* $\hat{n} = (n_1, n_2, n_3)$ (the positive sense of θ and the direction $\hat{n}$ always to be related by the right-hand rule) is particularly useful in molecular and crystal problems possessing a point symmetry group. In this parametrization, each angle θ in the interval $0 \leq \theta < \pi$ and each unit vector $\hat{n}$ ($\hat{n}\cdot\hat{n} = n_1^2 + n_2^2 + n_3^2 = 1$) defines a *unique* proper orthogonal matrix

$$R(\theta, \hat{n}) = e^{-i\theta\hat{n}\cdot\vec{M}} = I + N\sin\theta + N^2(1 - \cos\theta) \ , \tag{3}$$

where $\hat{n}\cdot\vec{M} = n_1M_1 + n_2M_2 + n_3M_3$, $(M_j)_{kl} = -i\epsilon_{jkl}$, and $N = -i\hat{n}\cdot\vec{M}$. The angle $\theta = \pi$ and each of the unit vectors $\pm\hat{n}$ determine the same proper orthogonal matrix, $R(\pi, \hat{n}) = R(\pi, -\hat{n}) = e^{-i\pi\hat{n}\cdot\vec{M}}$, which is also *symmetric*. (These are the exceptional orthogonal matrices.[19]) Conversely, each proper orthogonal matrix R may be expressed in the form (3) for parameters $\theta, \hat{n}$ satisfying $0 \leq \theta \leq \pi, \hat{n}\cdot\hat{n} = 1$, where $\theta, \hat{n}$ are unique unless $\theta = \pi$ in which case $\hat{n}$ is determined only up to sign (and this happens only when R is symmetric and not the identity). This parametrization is often put in correspondence with the points of a *solid sphere* of radius π, where diametrically opposite points on the surface of the sphere are identified.

In similar fashion, each angle θ in the interval $0 \leq \theta \leq 2\pi$ and each unit vector $\hat{n}$ uniquely determine a unitary unimodular matrix

$$\begin{aligned}
U(\theta, \hat{n}) &= e^{-i\theta\hat{n}\cdot\vec{\sigma}/2} \\
&= \begin{pmatrix} \cos(\frac{1}{2}\theta) - in_3\sin(\frac{1}{2}\theta) & (-in_1 - n_2)\sin(\frac{1}{2}\theta) \\ (-in_1 + n_2)\sin(\frac{1}{2}\theta) & \cos(\frac{1}{2}\theta) + in_3\sin(\frac{1}{2}\theta) \end{pmatrix},
\end{aligned} \tag{4}$$

where $(\sigma_1, \sigma_2, \sigma_3)$ are the Pauli matrices.

The numbers (Cayley-Klein parameters) $(\alpha_0, \alpha_1, \alpha_2, \alpha_3)$ defined by $\alpha_0 = \cos(\frac{1}{2}\theta)$, $\alpha_i = n_i\sin(\frac{1}{2}\theta)$ satisfy $\alpha_0^2 + \alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$ and cover the points on the surface of a sphere in four-dimensional Euclidean space as we let $\theta, \hat{n}$ range over all values $0 \leq \theta \leq 2\pi$ and $\hat{n}\cdot\hat{n} = 1$. Conversely, each unitary unimodular matrix U may be written in the form (4) for unique parameters $\theta, \hat{n}$ which define a point on the sphere in four space. (There is a one-to-one correspondence between points on surface of the sphere in four space and the 2×2 unitary unimodular matrices.)

The relation (homomorphism) between the 3×3 proper orthogonal matrix $R(\theta, \hat{n})$ and the 2×2 unitary unimodular matrix $U(\theta, \hat{n})$ is expressed by

$$R_{ij}(\theta, \hat{n}) = \tfrac{1}{2}\,\mathrm{tr}[\sigma_i U(\theta, \hat{n})\sigma_j U^\dagger(\theta, \hat{n})] \ , \tag{5}$$

where the dagger indicates Hermitian conjugation. Noting that

$$U(2\pi - \theta, \hat{n}) = -U(\theta, \hat{n}), \quad 0 \leq \theta \leq \pi \ ,$$

one sees that both $U(\theta, \hat{n})$ and $U(2\pi - \theta, \hat{n})$ define the same 3×3 proper orthogonal matrix $R(\theta, \hat{n})$ [the 2-to-1 homomorphism of SU(2) onto SO(3)].

Consider now the unitary operator $T(\theta, \hat{n})$ de-

fined by

$$T(\theta,\hat{n}) = e^{-i\theta\hat{n}\cdot\vec{J}} , \tag{6a}$$

where

$$\hat{n}\cdot\vec{J} = n_1J_1 + n_2J_2 + n_3J_3 . \tag{6b}$$

The action of $T(\theta,\hat{n})$ on the state vector $|\alpha jm\rangle$ is expressed by

$$T(\theta,\hat{n})|\alpha jm\rangle = \sum_{m'} D^j_{m'm}(\theta,\hat{n})|\alpha jm'\rangle , \tag{7}$$

where the $D^j(\theta,\hat{n})$ matrix is the standard Wigner D matrix expressed in the notation of Rose,[13] but explicitly in the $\theta,\hat{n}$ parametrization. The explicit $D^j_{m'm}(\theta,\hat{n})$ functions may be described most succinctly by introducing more general functions.

Let Z denote an *arbitrary* 2×2 matrix of complex numbers:

$$Z = \begin{pmatrix} z_{11} & z_{12} \\ z_{21} & z_{22} \end{pmatrix} , \tag{8}$$

and introduce the functions as follows, defined on the elements z_{ij} of Z:

$$\mathfrak{D}^j_{m'm}(Z) = [(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2} \times \sum_{[\alpha]} \frac{(z_{11})^{\alpha_{11}}(z_{12})^{\alpha_{12}}(z_{21})^{\alpha_{21}}(z_{22})^{\alpha_{22}}}{(\alpha_{11})!(\alpha_{12})!(\alpha_{21})!(\alpha_{22})!} , \tag{9a}$$

where the α_{ij} are nonnegative integers which are to be summed over in such a way that the entries in the square array

$$\begin{matrix} \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix} & \begin{matrix} j+m' \\ j-m' \end{matrix} \\ \begin{matrix} j+m & j-m \end{matrix} & \end{matrix} \tag{9b}$$

have the row and column sums indicated by the integers $j\pm m', j\pm m$ standing outside the $[\alpha]$ array. This highly redundant way of writing the summation (there is only one free summation index) has the advantage of being easily remembered and making transparent the symmetries of the $\mathfrak{D}^j_{m'm}(Z)$ functions[20] and generalizes directly to SU(n).[21] Furthermore, the correspondence $Z \to \mathfrak{D}^j(Z)$, where $\mathfrak{D}^j(Z)$ is the $(2j+1)\times(2j+1)$ matrix having row index m' ($m' = j, j-1, \ldots, -j$ from the left to right across the columns) and the column index m ($m = j, j-1, \ldots, -j$ from top to bottom down the rows), has the general property of preserving multiplication, that is, $Z \to \mathfrak{D}^j(Z)$ and $Z' \to \mathfrak{D}^j(Z')$ implies $Z'Z \to \mathfrak{D}^j(Z'Z)$.

The matrix $D^j(\theta,\hat{n})$ with elements $D^j_{m'm}(\theta,\hat{n})$ is now obtained from the $\mathfrak{D}^j(Z)$ by

$$D^j(\theta,\hat{n}) = \mathfrak{D}^j[U(\theta,\hat{n})] , \tag{10}$$

where $U(\theta,\hat{n})$ is the 2×2 unitary unimodular matrix given by Eq. (4).

The unitary matrices $D^j(\theta,\hat{n})(0\le\theta\le\pi)$ for $j = 0, 1, 2, \ldots$, comprise all the inequivalent irreducible representations of the rotation group SO(3), the correspondence between group elements and unitary representations being given by

$$R(\theta,\hat{n}) \to D^j(\theta,\hat{n}), \quad 0\le\theta\le\pi .$$

The unitary matrices $D^j(\theta,\hat{n})$ $(0\le\theta\le2\pi)$ for $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, comprise all the inequivalent irreducible representations of the unitary group SU(2), the correspondence between group elements and unitary representations being given by

$$U(\theta,\hat{n}) \to D^j(\theta,\hat{n}), \quad 0\le\theta\le2\pi .$$

These results are, of course, all well known from the early work of Wigner.[12]

We conclude the discussion of the properties of H_0 by noting that the infinitesimal invariance property (1) may now be expressed as the group invariance relation

$$T(\theta,\hat{n})H_0T^{-1}(\theta,\hat{n}) = H_0 \tag{11}$$

for all $\theta,\hat{n}$ which define the elements of SO(3) [SU(2)].

We next introduce a Hermitian interaction term H_1 which is a sum of irreducible tensor operators with respect to SO(3) [SU(2)], but an invariant with respect to a subgroup G of SO(3) [SU(2)]. Thus, H_1 has the general form[22]

$$H_1 = \sum_{k,\mu} a_{k\mu}T_{k\mu} , \tag{12}$$

where $T_{k\mu}$ is the μth component of an irreducible tensor T_k of rank k [$k = 0, 1, 2, \ldots$, for SO(3); $k = 0, \frac{1}{2}, 1, \ldots$, for SU(2); $\mu = k, k-1, \ldots, -k$]. Thus, the components $T_{k\mu}$ ($\mu = k, k-1, \ldots, -k$) obey the transformation law

$$T(\theta,\hat{n})T_{k\mu}T^{-1}(\theta,\hat{n}) = \sum_{\mu'} D^k_{\mu'\mu}(\theta,\hat{n})T_{k\mu'} . \tag{13}$$

The invariance of H_1 with respect to G requires

$$T(\theta',\hat{n}')\left(\sum_\mu a_{k\mu}T_{k\mu}\right)T^{-1}(\theta',\hat{n}') = \left(\sum_\mu a_{k\mu}T_{k\mu}\right) \tag{14}$$

for all parameter values θ',n' which define the elements $G(\theta',\hat{n}')$ of $G\subset$SO(3) [SU(2)]. Combining Eqs. (13) and (14), one obtains the result which follows:

Lemma 1: *The necessary and sufficient condition that* $\sum_\mu a_{k\mu}T_{k\mu}$ *be an invariant with respect to* G *is*

$$D^k(\theta',\hat{n}')A = A, \quad \text{all } G(\theta',\hat{n}') , \tag{15}$$

where

$$A = \mathrm{col}(a_{kk}, a_{kk-1}, \ldots, a_{k-k}) \ .$$

A second very useful result is also easily proved:

Lemma 2: *The operator* $\sum_\mu a_{k\mu} T_{k\mu}$ *is an invariant with respect to* G *if and only if the state vector* $\sum_\mu a_{k\mu} |k\mu\rangle$ *is an invariant with respect to* G.

With these basic preliminaries concluded, let us now suppose we have given a Hermitian interaction H_1 for the physical system. [Since $k=0$ gives a constant energy shift, we henceforth restrict the sum on k in H_1 to $k=1,2,3,\ldots,k_{\max}$ (or equivalently we may define $a_{00}=0$).] We now ask for the energy corrections to H_0 in first-order perturbation theory. These corrections are found by diagonalizing the $(2j+1)\times(2j+1)$ Hermitian matrix with elements

$$\langle \alpha j m' | H_1 | \alpha j m \rangle = \sum_k \langle \alpha j \| T_k \| \alpha j \rangle \, a_{k,m'-m} C^{jkj}_{m,m'-m,m'} \ , \quad (16)$$

where $C^{jkj}_{m\mu m'}$ denotes a Wigner coefficient, and the form of the right-hand side of this result has been obtained by applying the Wigner-Eckart Theorem.[23] We will also assume that the reduced matrix elements $\langle \alpha j \| T_k \| \alpha j \rangle$ are real.

It is a common trick in perturbation theory to replace a physical operator defined on the whole of state space by another operator which has the same matrix elements on a subspace of state space (but need not agree outside the subspace).

In the case of Eq. (16), these procedures are well known. We define[13,24] $\mathcal{T}_{kk}$ by

$$\mathcal{T}_{kk} = (-1)^k [(2k)!/k!\,k!]^{1/2} (J_+)^k \ , \quad (17a)$$

and $\mathcal{T}_{k\mu} (\mu = k-1, \ldots, -k)$ by

$$\mathcal{T}_{k\mu} = [(k+\mu)!/(2k)!\,(k-\mu)!]^{1/2} [J_-, \mathcal{T}_{kk}]_{(k-\mu)} \ , \quad (17b)$$

where $[A,B]_{(0)} = B, [A,B]_{(1)} = [A,B]$, $[A,B]_{(2)} = [A,[A,B]]$, etc. Then

$$C^{jkj}_{m,\mu,m+\mu} = \frac{\langle jm+\mu | \mathcal{T}_{k\mu} | jm \rangle}{[(2j-k+1)_k (2j+2)_k]^{1/2}} \ , \quad (18)$$

where

$$(\alpha)_k = \alpha(\alpha+1)\cdots(\alpha+k-1) \quad [(\alpha)_0 = 1]$$

denotes a rising factorial. Thus, the Hermitian operator

$$T = \sum_k \frac{\langle \alpha j \| T_k \| \alpha j \rangle}{[(2j-k+1)_k (2j+2)_k]^{1/2}} \sum_\mu a_{k\mu} \mathcal{T}_{k\mu} \quad (19)$$

has the matrix elements which agree with those of H_1 on the $(2j+1)$-dimensional space $\mathcal{H}_j$ with basis

$$\{ |\alpha j m\rangle : m = j, j-1, \ldots, -j \} \ , \quad (20)$$

and has zero matrix elements (unlike the physical interaction H_1) between the spaces $\mathcal{H}_j$ and $\mathcal{H}_{j'} (j' \neq j)$.

Having arrived at the operator (19), we now see that

$$[J^2, T] = 0 \ , \quad (21)$$

so that the entire problem of first-order perturbation theory has been reduced to the simultaneous diagonalization of J^2 and T. *We are now free to use any basis of the space* $\mathcal{H}_j$ *and need not be tied to the* $|jm\rangle$ *basis.* This is one of the principal reasons for mapping the perfectly good eigenvalue problem (16) to an equivalent operator formulation.

It should be noted that, in the physical problem, the irreducible tensor $T_{k\mu}$ appearing in Eq. (12) may itself be a sum of irreducible tensors $T^{(s)}_{k\mu}$ of rank k,

$$T_{k\mu} = \sum_s A_s T^{(s)}_{k\mu}, \quad A_s \text{ real} \ , \quad (22)$$

where s is an index serving to indicate that the tensors $T^{(1)}_{k\mu}, T^{(2)}_{k\mu}, \ldots$, have different physical origins, e.g., $T^{(1)}_{k\mu}$ may be built only from internal coordinates, $T^{(2)}_{k\mu}$ may be built from a mixture of internal coordinates and total angular momenta, etc. Observe, however, that the effect of making the substitution (22) in Eq. (12) is simply to make the replacement

$$\langle \alpha j \| T_k \| \alpha j \rangle \to \sum_s A_s \langle \alpha j \| T^{(s)}_k \| \alpha j \rangle \equiv \lambda_k (\alpha j) \quad (23)$$

in Eq. (19). The point to be made here is that no matter how complicated are the internal motions leading to the interaction $T_{k\mu}$, the general form of Eq. (19) is unaltered:

$$T = \sum_k \frac{\lambda_k (\alpha j)}{[(2j-k+1)_k (2j+2)_k]^{1/2}} \sum_\mu a_{k\mu} \mathcal{T}_{k\mu} \ . \quad (24)$$

It may also happen that there exist several independent Hermitian invariants of rank k with respect to G,

$$\mathcal{T}^{(n)}_k \equiv \sum_\mu a^{(n)}_{k\mu} \mathcal{T}_{k\mu}, \quad n = 1, 2, \ldots, n_k \ , \quad (25)$$

where n_k is the number of linearly independent solutions to Eq. (15) (without loss of generality, we may take the column vectors $A^{(1)}, A^{(2)}, \ldots, A^{(n_k)}$ to be orthonormal). Thus, the most general form of T is

$$T = \sum_k \sum_{n=1}^{n_k} \frac{\lambda^{(n)}_k (\alpha j)}{[(2j-k+1)_k (2j+2)_k]^{1/2}} \mathcal{T}^{(n)}_k \ , \quad (26)$$

containing a number of real constants $\lambda^{(n)}_k (\alpha j)$ equal to $n_k N$, where N is the number of values over which k ranges.

Let us also note that since

$$\mathcal{T}^{\dagger}_{k\mu} = (-1)^{\mu}\mathcal{T}_{k,-\mu} \ , \tag{27}$$

the condition that $\mathcal{T}^{(n)}_{k}$ be Hermitian is

$$a^{(n)*}_{k,-\mu} = (-1)^{\mu}a^{(n)}_{k,\mu} \ . \tag{28}$$

Let us now particularize Eq. (24). In many practical cases, the rank k of a tensor operator corresponds to the order of the perturbation theory. In this case, off-diagonal elements (in j) of the lowest-rank tensor, say k_0, occurring in H_1 [Eq. (12)] may be more important than the diagonal elements of the next higher rank (k_0+1) tensor. In the spirit of first-order perturbation theory, one would then retain only the lowest-rank term in the preceding theory. Thus, Eq. (26) is replaced by

$$T = \sum_{n=1}^{n_{k_0}} \frac{\lambda^{(n)}_{k_0}(\alpha j)\mathcal{T}^{(n)}_{k_0}}{[(2j-k_0+1)_{k_0}(2j+2)_{k_0}]^{1/2}} \ , \tag{29}$$

containing n_{k_0} real constants which from a phenomenological point of view may be considered to be parameters which may be varied [as is also the case in Eq. (26)].

One can say practically nothing about the details (other than general statements about the group-subgroup reduction) of the simultaneous diagonalization of J^2 and T [even for the simpler case given by Eq. (29)]. We therefore turn now to the still simpler case where $n_{k_0}=1$, so that only a single term occurs in T. Aside from parameters which may occur in H_o, this theory has but one additional parameter (j dependent, however) no matter how complicated the physical system.

III. SIMPLIFIED MODEL

A. Structure of the molecular problem

Before proceeding to detailed discussions of our simplified model, let us first indicate in a fairly general way how the molecular problem fits into the abstract structure outlined in Sec. II.

In a molecular vibration-rotation problem for spherical-top molecules, the angular momentum (J_1,J_2,J_3) is composed of two parts,

$$J_i = K_i + L_i \ , \tag{30}$$

where $P_i = -K_i$ is the component of the total angular momentum of the molecule along the ith axis of the Eckart frame[25,26] and L_i is the ith component (relative to the Eckart frame) of the orbital angular momentum carried by, for example, a triply degenerate (ν_3) normal mode of oscillation. The SO(3) group of the preceding section is then identified with the *diagonal subgroup*[25] of the direct product group $SO_{lab}(3)\times SO_{int}(3)$, where $SO_{lab}(3)$ is the group of orthogonal matrices generated by $\vec{K}$ and $SO_{int}(3)$ is the group of orthogonal matrices generated by the internal angular momentum $\vec{L}$. One is thus working in the coupled representation of angular momentum theory, i.e., the states $|\alpha jm\rangle$ of the abstract theory are actually the Wigner coefficient coupled states of frame wave functions and oscillator wave functions. The Hamiltonian H_0 already contains the Coriolis interaction term $\vec{K}\cdot\vec{L}$ (diagonal in the coupled representation). The SO(3) symmetry (diagonal subgroup) is broken by interaction terms (polynomials in the normal coordinates and the components of K_i) which are tensor operators under SO(3) and invariants under the O_h (or T_d) subgroup of the diagonal subgroup SO(3).

In the dominant approximation of Hecht,[27] one considers only tensor operator interactions of the lowest rank which can be (nontrivial) invariants under O_h or T_d. In either case, the interaction is the sum of fourth-rank tensors as follows:

$$H_1 = (\tfrac{14}{5})^{1/2}T_{4,0} + T_{4,4} + T_{4,-4} \ , \tag{31}$$

where the factor $(\frac{14}{5})^{1/2}$ is required for the $O_h(T_d)$ symmetry (see Sec. III B).

While the details of the problem may appear to be rather intricate, the mathematical problem to be solved (for first-order perturbation theory in the physical problem) is simply stated—diagonalize the operator

$$T_0 = (\tfrac{14}{5})^{1/2}\mathcal{T}_0 + (J_+^4 + J_-^4) \tag{32a}$$

on the space $\mathcal{H}_j$. In this result, we have

$$\begin{aligned}\mathcal{T}'_0 &= (\tfrac{14}{5})^{1/2}\mathcal{T}_0 = \tfrac{1}{120}[J_-, J_+^4]_{(4)} \\ &= \tfrac{6}{5}(J^2)^2 - 12J^2J_3^2 + 14J_3^4 - \tfrac{12}{5}J^2 + 10J_3^2 \ .\end{aligned} \tag{32b}$$

It is the structure of this problem which is discussed in the remainder of this paper.

B. Orbital angular-momentum model

For integer values of the angular momentum j, the *mathematical problem* of simultaneously diagonalizing J^2 and T_0 may be solved fully by choosing the operators J_k to be the orbital angular momentum operators for a single particle in ordinary three-space:

$$L_j = -i\left(x_k\frac{\partial}{\partial x_l} - x_l\frac{\partial}{\partial x_k}\right) \ , \tag{33}$$

where j,k,l are cyclic in $1,2,3$. Since this simplified model also provides a technique for writing out tensor operators which are invariants under a subgroup of SO(3) [SU(2)], we examine it in some detail.

Consider a single, structureless particle moving

in ordinary three space $(x)=(x_1,x_2,x_3)$ in a spherical potential (so that the orbital angular momentum is conserved) and having Hamiltonian H_0 (bound states). Let the particle be perturbed by a potential field which is a harmonic polynomial invariant $P(x)$ of the group O_h (or T_d), limiting ourselves to the first nontrivial invariant.

This type of problem has a rich history of development, beginning with the early classic work of Bethe.[28,29] The construction of harmonic polynomial invariants under the various subgroups of the rotation-inversion group has also generated much mathematical interest[30] and is still active.[31] Jahn[32] was one of the first to use these techniques in molecular problems.

Referring to the convenient tabulations of Meyer,[30] we find that the lowest (nontrivial) degree polynomial invariant for either O_h or T_d is $x_1^4+x_2^4+x_3^4$, and its harmonic projection is

$$-\tfrac{3}{5}(x_1^2+x_2^2+x_3^2)^2+(x_1^4+x_2^4+x_3^4) = [8\pi/(5)(7)(9)]^{1/2} \times[(\tfrac{14}{5})^{1/2}\mathcal{Y}_{4,0}(x)+\mathcal{Y}_{4,4}(x)+\mathcal{Y}_{4,-4}(x)] \ , \quad (34)$$

where $\mathcal{Y}_{lm}$ denotes a solid harmonic of degree l as tabulated, for example, by Edmonds.[14]

Corresponding to the harmonic invariant (34), we have (Lemma 2) the invariant angular momentum operator

$$T_0=(\tfrac{14}{5})^{1/2}\mathcal{T}_0+(L_+^4+L_-^4) \ , \quad (35a)$$

where the commutator

$$(\tfrac{14}{5})^{1/2}\mathcal{T}_0=\tfrac{1}{120}[L_-,L_+^4]_{(4)} \quad (35b)$$

has already been given by Eq. (32b) (substitute L_i for J_i and denote J^2 by L^2). It is also useful to write T_0 in terms of the components L_i.[33] Except for a lower degree invariant which can only be a constant plus a constant times L^2, the result must be in agreement with Eq. (34) under the mapping $L_i \to x_i$. Noting that

$$\mathcal{Y}_{4,4}(x)=(x_1+ix_2)^4/16[2\pi/(5)(7)(9)]^{1/2} \ ,$$

we see that

$$T_0=-\tfrac{24}{5}(L^2)^2+8(L_1^4+L_2^4+L_3^4)+\tfrac{8}{5}L^2 \ . \quad (36)$$

No additive constant occurs in Eq. (36) because $\langle 00|T_0|00\rangle=0$, and the coefficient $\frac{8}{5}$ multiplying L^2 can be obtained by noting that $\langle 10|T_0|10\rangle=0$.

Thus, the first-order perturbation problem for this model (orbital motion) problem is equivalent to the simultaneous diagonalization of L^2 and T_0, and the solution to this problem[34,35] yields the solution to the molecular problem.

Let us now restrict our attention to O_h, although similar procedures may be followed for T_d (or other point groups). For completeness, we next note the explicit transformations of Euclidean three space induced by the group O_h.

We begin with the observation that the two matrices

$$R=R(\tfrac{1}{2}\pi,\hat{e}_1)=\begin{pmatrix}1&0&0\\0&0&-1\\0&1&0\end{pmatrix} \ , \quad S=R\left(\pi,\frac{(\hat{e}_1+\hat{e}_2)}{\sqrt{2}}\right)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&-1\end{pmatrix} \quad (37a)$$

satisfy

$$R^4=S^2=(RS)^3=I \ , \quad (37b)$$

and hence generate[36] the group O (24 elements) of pure rotations which map the regular octahedron onto itself. Our model here locates the vertices of the octahedron at the eight points $(\pm1,\pm1,\pm1)$ corresponding to any combination of + and − signs. The unit vectors $\hat{e}_1,\hat{e}_2,\hat{e}_3$ have their tails at (0, 0, 0) and their heads at (1, 0, 0), (0, 1, 0), and (0, 0, 1), respectively. To obtain the group O_h, we adjoin the inversion

$$\bar{I}=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix} \quad (38)$$

to the group O. Then R, S, and $\bar{I}$ generate O_h. The actions of the 48 elements of O_h on an arbitrary vector (x_1,x_2,x_3) are to produce the 48 mappings

$$(x_1,x_2,x_3)\to(\pm x_i,\pm x_j,\pm x_k) \ , \quad (39)$$

where (i,j,k) is any permutation of (1, 2, 3), and the + and − signs may be in any combination [O_h is a direct product group isomorphic to $S_3\times D_4$].

It is clear [Eq. (33)] that under the transformations (39) we obtain the following mappings of the angular momentum components:

$$(L_1,L_2,L_3)\to(\alpha_1L_i,\alpha_2L_j,\alpha_3L_k) \ , \quad (40)$$

where $\alpha_i=\pm1$ $(i=1,2,3)$, but $\alpha_1\alpha_2\alpha_3=1$ if (i,j,k) is an even permutation of (1, 2, 3) and $\alpha_1\alpha_2\alpha_3=-1$ if (i,j,k) is an odd permutation of (1, 2, 3). These are just the transformations generated by R and S, i.e., by the elements of the group O, since under the inversion operation $\bar{I}$ we have

$$(L_1,L_2,L_3)\to(L_1,L_2,L_3) \quad (41)$$

($\vec{L}$ is a pseudovector).

Let us hasten to note, however, that both L^2 and T_0 are invariant under the time-reversal transformation

$$(L_1, L_2, L_3) \to (-L_1, -L_2, -L_3)\,. \tag{42}$$

The consequences of time-reversal invariance for the present problem are examined in Appendix A.

To conclude this discussion of the orbital theory, we note that the $|jm\rangle$ (we now drop α) become the solid harmonics $\mathcal{Y}_{lm}$. In this case, the transformation (7) is realized by the operator T_R

$$(T_R f)(x) = f(R^{-1}x)\,, \tag{43}$$

where $R = R(\theta, \hat{n})$ and $x' = R^{-1}x$, where $x = \mathrm{col}(x_1, x_2, x_3)$.

One of the advantages of working in a particular realization of the angular momentum operators is that one need no longer use the $|lm\rangle$ basis, that is, one may try to diagonalize T_0 directly on the space H_l of homogeneous harmonic polynomials of degree l.

C. Abstract model

We now extend the results to the general abstract case of integral and half integral j [SU(2)] so that the model includes all possible physical realizations. Thus, the problem to be considered is that of diagonalizing J^2 and

$$\begin{aligned} T_0 &= -\tfrac{24}{5}(J^2)^2 + \tfrac{8}{5}J^2 + 8(J_1^4 + J_2^4 + J_3^4) \\ &= \mathcal{T}_0' + J_+^4 + J_-^4 \end{aligned} \tag{44}$$

for the general case of integers and half integers.

Let $\mathcal{H}_j$ denote the $(2j+1)$-dimensional Hilbert space spanned by the set of vectors $\{|jm\rangle$: $m = j, j-1, \ldots, -j\}$. We next construct the transformations of this space corresponding to the transformations of the octahedral group O. The method of doing this is well known and discussions of the method may be found in Hamermesh.[29]

The 2×2 unitary unimodular matrices corresponding to the generators R and S of O are given by [cf. Eqs. (4) and (5)]

$$\begin{aligned} r &= e^{-i\pi\sigma_1/4} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}, \quad r' = e^{3\pi i\sigma_1/4} = -r, \\ s &= e^{-i\pi(\sigma_1+\sigma_2)/2(2)^{1/2}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -1-i \\ 1-i & 0 \end{pmatrix}, \\ s' &= e^{i\pi(\sigma_1+\sigma_2)/2(2)^{1/2}} = -s\,, \end{aligned} \tag{45}$$

where we note that the homomorphism from $\overline{O} \subset \mathrm{SU}(2)$ to $O \subset \mathrm{SO}(3)$ is expressed in terms of the generators by

$$(r, r') \to R, \quad (s, s') \to S\,. \tag{46}$$

The group $\overline{O}$ contains 48 elements and is the finite subgroup of SU(2) which maps to the 24 elements of the octahedral group $O \subset \mathrm{SO}(3)$ by the homomorphism (5). Since $r^4 = s^2 = -\sigma_0$ ($\sigma_0 = 2\times 2$ unit matrix) and $(rs)^3 = \sigma_0$, the generators of $\overline{O}$ are the elements r and s satisfying $r^8 = s^4 = (rs)^3 = \sigma_0$. $\overline{O}$ is often called the double group of O.

From the 2×2 matrix realization of $\overline{O}$, we can now write out the generators of the unitary operator realization of this group on the abstract space $\mathcal{H}_j$ [cf. Eqs. (6) and (7)]:

$$\begin{aligned} \mathcal{R} &= e^{-i\pi J_1/2}, \quad \mathcal{R}' = e^{i3\pi J_1/2} = \mathcal{R}e^{2\pi i J_1}, \\ \mathcal{S} &= e^{-i\pi(J_1+J_2)/(2)^{1/2}}, \\ \mathcal{S}' &= e^{i\pi(J_1+J_2)/(2)^{1/2}} = \mathcal{S}e^{2\pi i(J_1+J_2)/(2)^{1/2}}, \end{aligned} \tag{47}$$

where we note [cf. Eqs. (7)–(10)] that

$$e^{2\pi i\hat{n}\cdot\vec{J}} = (-1)^{2j}, \quad \hat{n} \text{ arbitrary}\,, \tag{48}$$

on the space $\mathcal{H}_j$. Hence, on the space $\mathcal{H}_j$, we have

$$\mathcal{R}' = (-1)^{2j}\mathcal{R}, \quad \mathcal{S}' = (-1)^{2j}\mathcal{S}\,. \tag{49}$$

[While $\mathcal{R}$ and $\mathcal{S}$ alone generate the unitary operator realization of $\overline{O}$ on the space $\mathcal{H}_j$, it is convenient to carry along $\mathcal{R}'$ and $\mathcal{S}'$ ($\mathcal{R}' = \mathcal{R}^5$ and $\mathcal{S}' = \mathcal{S}^3$).]

If the physical realization of the angular momentum operators admits only integral values of j, then $\mathcal{R}' = \mathcal{R}$ and $\mathcal{S}' = \mathcal{S}$. In this case, the theory is isomorphic to the theory of orbital angular momentum, using the group of proper orthogonal matrices.

The following relation plays the key role in verifying the transformation properties of the operator T_0:

$$\begin{aligned} &e^{-i\theta\hat{n}\cdot\vec{J}}\vec{J}e^{i\theta\hat{n}\cdot\vec{J}} \\ &\quad = \vec{J}\cos\theta + \hat{n}(\hat{n}\cdot\hat{J})(1-\cos\theta) - (\hat{n}\times\hat{J})\sin\theta\,, \end{aligned} \tag{50}$$

where we have written $\vec{J} = J_1\hat{e}_1 + J_2\hat{e}_2 + J_3\hat{e}_3$, and it is important in this relation that $[J_i, \hat{e}_j] = \vec{0}$ [vector notation is just convenient bookkeeping for the component relations implied by (50)]. Equation (50) is valid for any vector $\vec{V}$ which satisfies $[\hat{n}\cdot\vec{J}, \vec{V}] = -i(\hat{n}\times\vec{V})$, and the proof follows from the general multicommutator expansion

$$e^A B e^{-A} = \sum_k \frac{[A, B]_{(k)}}{k!}\,.$$

One may now verify explicitly the following results:

$$\mathcal{R}\vec{J}\mathcal{R}^{-1} = \mathcal{R}'\vec{J}\mathcal{R}'^{-1} = J_1\hat{e}_1 + J_3\hat{e}_2 - J_2\hat{e}_3\,, \tag{51a}$$

$$\mathcal{S}\vec{J}\mathcal{S}^{-1} = \mathcal{S}'\vec{J}\mathcal{S}'^{-1} = J_2\hat{e}_1 + J_1\hat{e}_2 - J_3\hat{e}_3\,, \tag{51b}$$

that is, the action of $\mathcal{R}$ or $\mathcal{R}'$ is to give the transformation of angular momentum components

$$\mathcal{R}: \ (J_1, J_2, J_3) \to (J_1, J_3, -J_2)\,, \tag{52a}$$

while the action of $\mathcal{S}$ or $\mathcal{S}'$ is

$$\mathcal{S}:\ (J_1, J_2, J_3) \to (J_2, J_1, -J_3)\,. \tag{52b}$$

[While the action of $\mathcal{R}$ and $\mathcal{R}'$ ($\mathcal{S}$ and $\mathcal{S}'$) is the same on angular momentum components, their action is, of course, different on state vectors when j is half-integral.]

We have yet to consider the inversion. Quite generally, the inversion operator $\mathcal{I}$ (the operator on any physical space $\mathcal{H}_j$ corresponding to $\bar{I}$) satisfies $\mathcal{I}^2$ equal to identity, and it commutes with the angular momenta $\vec{J}$ of any physical system

$$\mathcal{I}\vec{J} = \vec{J}\mathcal{I}\,. \tag{53}$$

These properties imply that it is always possible to choose the vectors of $\mathcal{H}_j$ such that

$$\mathcal{I}\Phi_j = \pm\Phi_j, \quad \text{each } \Phi_j \in \mathcal{H}_j\,, \tag{54}$$

and we assume this to be done. Hence, spatial inversions play no further role in the problem of diagonalizing T_0 on $\mathcal{H}_j$. Thus, it is the finite groups O (integral j) and $\bar{O}$ (half integral j) which enter into the discussion of the properties of T_0. Observe by looking at the transformations (51a) and (51b) and the form (44) that T_0 is trivially invariant with respect to $\bar{O}$.

The transformations associated with $\bar{O}$ do not include

$$(J_1, J_2, J_3) \to (-J_1, -J_2, -J_3) \tag{55}$$

which clearly leaves J^2 and T_0 invariant. This operation is Wigner's[37] time-reversal transformation. It is interesting to examine the consequences of time reversal for the present problem, and this is carried out in Appendix A. The result demonstrated is: *the eigenvectors of T_0 may be obtained as real linear combinations $\sum_m \alpha_m |jm\rangle$, α_m real.* However, we already know this property to be valid—it follows from the fact that the matrix with elements $\langle jm'|T_0|jm\rangle$ is a real symmetric matrix because *the Wigner coefficients are real.* Hence, the matrix may be diagonalized by a real orthogonal matrix. In this sense, we learn nothing new from the time-reversal symmetry of T_0, a result already anticipated by Wigner.[37] For this reason, one usually pays little attention to time-reversal symmetry in the molecular vibration-rotation problem (other than to verify its presence).

D. Spinor or boson model

Another convenient realization of angular-momentum theory (which admits both integral and half-integral values of j) is the spinor realization[38] which is abstractly equivalent (isomorphic) in structure to the boson realization introduced by Jordan[39] and developed further by Schwinger.[24] Each of these structures is, in turn, isomorphic to the following realization[20]: Consider the space $\mathcal{P}_j$ of polynomials which are homogeneous of degree $2j$ in two complex variables ξ and η. Thus, the polynomial $P(\xi, \eta)$ belongs to $\mathcal{P}_j$ if and only if

$$P(\lambda\xi, \lambda\eta) = \lambda^{2j} P(\xi, \eta)\,. \tag{56}$$

If P and Q are arbitrary polynomials,

$$P(\xi, \eta) = \sum_{m,n} a_{mn} \xi^m \eta^n, \quad a_{mn} \text{ complex},$$

$$Q(\xi, \eta) = \sum_{m,n} b_{mn} \xi^m \xi^n, \quad b_{mn} \text{ complex},$$

the scalar product (P, Q) is defined by

$$(P, Q) = \left[P^*\left(\frac{\partial}{\partial\xi}, \frac{\partial}{\partial\eta}\right) Q(\xi, \eta)\right]_{\xi=\eta=0}, \tag{57}$$

where $P^*(\xi, \eta)$ is the polynomial obtained from $P(\xi, \eta)$ by complex conjugating the coefficients a_{mn}.

An orthonormal basis of the space $\mathcal{P}_j$ is given by the familiar spinor functions

$$\Phi_{jm}(\xi, \eta) = \xi^{j+m}\eta^{j-m}/[(j+m)!(j-m)!]^{1/2}\,, \tag{58}$$

where $m = j, j-1, \ldots, -j$. The realizations of $J_\pm$ and J_3 on this space are

$$J_+ = \xi\frac{\partial}{\partial\eta}, \quad J_- = \eta\frac{\partial}{\partial\xi}\,, \tag{59a}$$

$$J_3 = \frac{1}{2}\left(\xi\frac{\partial}{\partial\xi} - \eta\frac{\partial}{\partial\eta}\right). \tag{59b}$$

Thus, with $|jm\rangle = \Phi_{jm}(\xi, \eta)$ and with the definitions (59), one duplicates the abstract properties (2). Finally, one observes that $J_1 = \frac{1}{2}(J_+ + J_-)$, $J_2 = (J_+ - J_-)/2i$, and J_3 are Hermitian operators on the space $\mathcal{P}_j$ in consequence of the property

$$\xi^\dagger = \frac{\partial}{\partial\xi}, \quad \eta^\dagger = \frac{\partial}{\partial\eta}\,. \tag{60}$$

Let us next recall the unitary transformation properties of the space $\mathcal{P}_j$. We define the operator (linear, unitary) T_U, each $U \in \mathrm{SU}(2)$, by

$$(T_U P)(\xi, \eta) = P(\xi', \eta')\,. \tag{61}$$

where

$$\begin{pmatrix}\xi'\\ \eta'\end{pmatrix} = \bar{U}\begin{pmatrix}\xi\\ \eta\end{pmatrix}. \tag{62}$$

Then for $U = U(\theta, \hat{n})$ [cf. Eq. (4)] the action of T_U on Φ_{jm} is precisely that given by Eq. (7), i.e., $T_{U(\theta,\hat{n})} = T(\theta, \hat{n})$. In particular, the generators r and s of $\bar{O} \subset \mathrm{SU}(2)$ effect the transformations (62) given by

$$r:\ (\xi, \eta) \to (1/\sqrt{2})(\xi - i\eta, -i\xi + \eta)\,, \tag{63a}$$

$$s:\ (\xi, \eta) \to (1/\sqrt{2})((-1-i)\eta, (1-i)\xi)\,, \tag{63b}$$

and under these transformations of variables

(J_1,J_2,J_3) transform, respectively, according to

$$\mathcal{R}:\ (J_1,J_2,J_3)\to(J_1,J_3,-J_2)\,, \tag{64a}$$

$$\mathcal{S}:\ (J_1,J_2,J_3)\to(J_2,J_1,-J_3)\,. \tag{64b}$$

Again, as in the case of the orbital theory, the advantage of using a particular realization is that it frees us from the $|jm\rangle$ basis—we may try to diagonalize T_0 directly on the space of homogeneous polynomials of degree $2j$ in ξ and η.

E. Summary

In this section, we have indicated how the molecular vibration-rotation problem fits into the general scheme of Sec. I in the dominant approximation. The first-order perturbation theory is then equivalent to simultaneously diagonalizing two operators: J^2 and T_η. We then gave the orbital angular-momentum realization of the problem, developing explicitly (in the O_h case) the transformations which leave T_0 invariant. Using the homomorphism between SU(2) and SO(3), we then extended the problem back to its general abstract setting, being able now to give explicitly the transformations which leave the abstract theory invariant. Finally, we particularized the abstract theory to the spinor realization, giving the transformations of the spinor space induced by the invariance group $\overline{O}$ of T_0. Each of the three frameworks presented in Secs. III B–III D, respectively, may be used to formulate the problem of simultaneous diagonalization of J^2 and T_0; each offers certain advantages.

IV. EIGENVALUE PROBLEM

A. General group-theoretic results

In this section, we outline the main results which are available from general group-theoretical methods.

We will use the notation $\mathcal{H}_j$ to denote any one of the spaces H_l, $\mathcal{H}_j$, or $\mathcal{P}_j$ of Secs. III B–III D, respectively. Then J^2 is automatically diagonal on $\mathcal{H}_j$ with eigenvalue $j(j+1)$ and requires no further discussion. All the results of this section refer then to the space $\mathcal{H}_j$ and its subspaces.

From the general viewpoint of representation theory (setting T_0 aside for the moment), the space $\mathcal{H}_j$ is the carrier space of the irreducible representation (irrep) $D^j(\theta,\hat{n})$ of SU(2); it is also the carrier space for a $(2j+1)\times(2j+1)$ *reducible representation* Γ^j of $\overline{O}$. This is the representation generated by the two unitary matrices [cf. Eqs. (37), (45), (9), and (10)]

$$\Gamma_1\equiv D^j(\tfrac{1}{2}\pi,\hat{e}_1),\quad \Gamma_2\equiv D^j(\pi,(\hat{e}_1+\hat{e}_2)/\sqrt{2})\,. \tag{65}$$

The irreducible constituents of $\overline{O}$ contained in Γ^j may then be found by the standard group character methods (and are given, for example, in Hamermesh[29]), and we state here the relevant results.

The group $\overline{O}$ has 48 elements partitioned into eight classes under the conjugation action. The eight irreps are denoted in spectroscopic notation by

$$A_1,A_2,E,F_1,F_2,E_1',E_2',G' \tag{66}$$

of dimensions 1, 1, 2, 3, 3, 2, 2, 4, respectively (A_1 is the identity representation).

The symbols A_1,A_2,E,F_1,F_2 also denote the irreps of O, and are the only irreps of $\overline{O}$ which occur in the reduction of Γ^j (j integral), the reason for this being that the transformations of the space $\mathcal{H}_j$ generated by $\mathcal{R}$ and $\mathcal{S}$ then become identical for $\overline{O}$ and O. Similarly, the reduction of Γ^j for j half integral entails only E_1', E_2', and G'.

The explicit reduction formulas may be given in the following way: Define the representation R (for regular) of $\overline{O}$ by (+ means direct sum)

$$R=A_1+A_2+2E+3F_1+3F_2 \quad \text{for } j \text{ integral}\,, \tag{67a}$$

$$R=2E_1'+2E_2'+4G' \quad \text{for } j \text{ half-integral}\,. \tag{67b}$$

Then the following formulas hold:

$$\Gamma^q+\Gamma^{11-q}=R\,, \tag{68a}$$

$$\Gamma^{12p+q}=pR+\Gamma^q\,, \tag{68b}$$

where q is an integer or half-integer in the interval $0\leq q\leq 11$ and $p=0,1,\ldots$. Equation (68a) serves for calculating all Γ^q, $0\leq q\leq 11$, knowing only those for $q\leq 5$ (the explicit results are listed in Ref. 29, pp. 339 and 367), and Eq. (68b) then gives the general reduction.

While one knows (from the representation theory of finite groups) that there exists a unitary similarity transformation A such that $A^\dagger\Gamma^jA$ is fully reduced, A is not unique (due to the freedom of making unitary transformation between those subspaces of $\mathcal{H}_j$ which carry the same irrep of $\overline{O}$).

The introduction of the operator T_0 serves to distinguish between those subspaces of $\mathcal{H}_j$ which carry the same irrep of $\overline{O}$. Thus, it follows from $T_0\mathcal{R}=\mathcal{R}T_0$ and $T_0\mathcal{S}=\mathcal{S}T_0$ that $\mathcal{R}\Phi$ and $\mathcal{S}\Phi$ are eigenvectors of T_0 having eigenvalue λ provided

$$T_0\Phi=\lambda\Phi\,. \tag{69}$$

Let us denote by S_λ the subspace $S_\lambda\subset\mathcal{H}_j$ of functions satisfying Eq. (69) for a given λ. Then S_λ is the carrier space of a representation of $\overline{O}$. The more important point, however, is that S_λ carries an *irreducible representation* of $\overline{O}$. This means that T_0 serves as a *complete labeling operator* for the group chain $\mathrm{SU}(2)\supset\overline{O}$ [or $\mathrm{SO}(3)\supset O$] in the sense defined by Dirac[40] and investigated extensively in the general work of Patera, Sharp,

and Winternitz and collaborators.[41] The proof that T_0 splits completely the "multiplicity problem" for $SU(2)\supset\bar{O}$ has been given by Moshinsky and Kramer[42] and may also be inferred from the work of Michelot and Moret-Bailly.[35] (It is not our purpose to review this problem here, since our numerical calculations fully verify these results.)

It is quite interesting to note, however, that the implication of time-reversal symmetry (cf. Appendix A) is that A may be chosen to be a real orthogonal matrix, that is, the Wigner coefficients for the group-subgroup reduction $SU(2)\downarrow\bar{O}$ may be chosen to be real.

B. Properties of the eigenvalues

In place of the operator T_0, we choose to investigate the operator

$$T=5(\tfrac{7}{12})^{1/2}T_0/[(2j-3)_9]^{1/2}, \tag{70}$$

which has for its matrix elements the $3j$ symbols (multiplied by appropriate numerical constants):

$$\langle jm\pm4|T|jm\rangle=(\tfrac{5}{24})^{1/2}(-1)^{j+m}\begin{pmatrix} j & 4 & j \\ m & \pm4 & -m\mp4\end{pmatrix}, \tag{71a}$$

$$\langle jm|T|jm\rangle=(\tfrac{7}{12})^{1/2}(-1)^{j+m}\begin{pmatrix} j & 4 & j \\ m & 0 & -m\end{pmatrix}. \tag{71b}$$

These matrix elements of T are then bounded for all j.

We have calculated numerically the eigenvalues of the operator T for all integral values of j in the interval $0\leq j\leq100$. [These eigenvalues are related[43] to the $F^{(4)}$ coefficients introduced by Moret-Bailly by a phase, $\lambda(T)=(-1)^jF^{(4)}$.] The set of eigenvalues of T exhibits a number of remarkable features, and the purpose of this section is to describe them.

We begin by noting some exact results. For $j=0$, $\frac{1}{2}$, 1, and $\frac{3}{2}$, the matrix of T_0 on the $|jm\rangle$ basis is the zero matrix so that T_0 has only zero eigenvalues for these cases. For $j=2$, $\frac{5}{2}$, 3, $\frac{7}{2}$, and 4, there is no multiplicity, and the characteristic equation of T_0 must factorize. In these cases the characteristic equations are as follows[44]:

$$\begin{aligned}
&j=2: && (\lambda-\tfrac{144}{5})^2(\lambda+\tfrac{96}{5})^3=0,\\
&j=\tfrac{5}{2}: && (\lambda-48)^4(\lambda+96)^2=0,\\
&j=3: && (\lambda-144)^3(\lambda+48)^3(\lambda+288)=0,\\
&j=\tfrac{7}{2}: && (\lambda-336)^2(\lambda-48)^4(\lambda+432)^2=0,\\
&j=4: && (\lambda-672)(\lambda-336)^3(\lambda-96)^2(\lambda+624)^3=0.
\end{aligned} \tag{72a}$$

For later reference, we also include the $j=\frac{11}{2}$ characteristic equation:

$$j=\tfrac{11}{2}: \ [\lambda+240-24(4516)^{1/2}]^4(\lambda-1056)^2\times[\lambda+240+24(4516)^{1/2}]^4(\lambda+2016)^2=0. \tag{72b}$$

By considering the trace of various powers of the operator T and using well-known properties of the $3j$ symbols, one can also derive relations between the eigenvalues of T. Let λ_s denote the eigenvalues of T, where the index s runs over the values $1,2,\ldots,10p+n_q$, in which n_q denotes the number (repetitions counted) of irreps occurring in Γ^q. If we let Γ_s denote the irrep label (symmetry type) assigned to level λ_s, then we have

$$\sum_s(\dim\Gamma_s)\lambda_s=0, \tag{73a}$$

$$\sum_s(\dim\Gamma_s)\lambda_s^2=\tfrac{1}{9}, \tag{73b}$$

$$\sum_s(\dim\Gamma_s)\lambda_s^3=14W(4j4j;j4)/3[(6)(11)(13)]^{1/2}, \tag{73c}$$

where $W(abcd;ef)$ denotes a Racah coefficient.[11,45] Equation (73a) has already been noted by Hecht[27] (the operator T_0 is traceless). Equation (73b) is particularly useful since this result shows that *the eigenvalues of T are bounded as $j\to\infty$.*

One can, in fact, derive asymptotic bounds on the eigenvalues.[46] The procedure is quite simple and is an application of Gerschgorin's theorem.[47] First, we set $m=\alpha j$, $-1\leq\alpha\leq1$, and use the following well-known estimates of the Wigner coefficients[48] for large j:

$$C^{j4j}_{m0m}\cong\tfrac{5}{16}[\tfrac{6}{5}-12\alpha^2+14\alpha^4], \tag{74a}$$

$$C^{j4j}_{m,\pm4,m\pm4}\cong\tfrac{1}{16}(70)^{1/2}(1-\alpha^2)^2. \tag{74b}$$

Combining these results with Eqs. (71), we obtain

$$\langle jm\pm4|(2j+1)^{1/2}T|jm\rangle\cong k(1-\alpha^2)^2, \tag{75a}$$

$$\langle jm|(2j+1)^{1/2}T|jm\rangle\cong k[\tfrac{6}{5}-12\alpha^2+14\alpha^4], \tag{75b}$$

where $k=\frac{5}{16}(\frac{7}{12})^{1/2}$. We next define the closed interval $I(\alpha)$ by

$$I(\alpha)=[a(\alpha),b(\alpha)], \tag{76a}$$

where

$$b(\alpha)=k(16\alpha^4-16\alpha^2+\tfrac{16}{5}), \tag{76b}$$

$$a(\alpha)=k(12\alpha^4-8\alpha^2-\tfrac{4}{5}). \tag{76c}$$

The union of the intervals $I(\alpha)$ for $\alpha\in[1,-1]$ is now calculated to be

$$\bigcup_\alpha I(\alpha)=[-\tfrac{32}{15}k,\tfrac{16}{5}k], \tag{77}$$

and Gerschgorin's theorem implies that for j sufficiently large we have

TABLE I. Eigenvalues of the operator T for $j=28$ and $j=29$. Symmetry type is denoted by the letter to the left of each eigenvalue.

$100\,\lambda_s\,(j=28)$	$100\,\lambda_s\,(j=29)$
A_1 8.487 462 046	F_1 8.392 214
F_1 8.487 456 801	F_2 8.392 211
E 8.487 454 178	E 5.500 724
F_2 5.458 988	F_1 5.500 673
F_1 5.458 814	A_1 5.500 571
E 2.932 765	F_1 3.071 227
F_2 2.931 506	F_2 3.069 673
A_2 2.928 978	A_2 1.082 843
F_2 0.880 008	F_2 1.069 511
F_1 0.859 569	E 1.062 693
A_1 −0.656 581	F_1 −0.487 973
F_1 −0.747 841	F_2 −0.562 430
E −0.800 266	E −1.618 549
F_2 −1.796 085	F_1 −1.710 588
F_1 −2.135 241	A_1 −2.008 739
E −2.643 086	F_1 −2.512 100
F_2 −2.773 106	F_2 −2.708 534
A_2 −3.707 218	A_2 −2.907 678
F_2 −3.826 045	F_2 −3.797 060
F_1 −3.916 492	E −3.873 022
A_1 −3.992 826	F_1 −3.948 714
F_1 −5.698 117	F_2 −5.632 286
E −5.707 309	E −5.639 471
F_2 −5.716 390	F_1 −5.646 405

$$-\tfrac{2}{3}(\tfrac{7}{12})^{1/2} \leq (2j+1)^{1/2}\lambda_s \leq (\tfrac{7}{12})^{1/2} \qquad (78)$$

for each eigenvalue λ_s. It is easy to see (use the $m=j$ equation) that the upper asymptotic limit $(\frac{7}{12})^{1/2}$ is the least upper bound and the numerical calculations also indicate that the lower asymptotic limit $-\frac{2}{3}(\frac{7}{12})^{1/2}$ is the greatest lower bound.

We next turn to the description of the properties of the eigenvalue spectrum of T which have been obtained by numerical methods.

We display in a vertical column the eigenvalues of T (for a given j with $j=12p+q$, $0\leq q\leq 11$) in decreasing order as read, say, from top to bottom, assigning to each eigenvalue its corresponding irrep label [cf. Table I]. Each such display then contains $10p+n_q$ eigenvalues together with the assigned irrep labels. We next describe with the aid of Fig. 1 the general properties of the sequence S_j (j integral) of irrep labels obtained by reading the display either from top to bottom $S_j(\downarrow)$ or from bottom to top, $S_j(\uparrow)$.

Figure 1 shows ten equally spaced points on the circumference of a circle (the solid circle), each point being assigned one of the ten irrep labels appearing in the regular representation R. The integers $0,1,2,3$ and $\bar{0},\bar{1},\bar{2},\bar{3},\bar{4},\bar{5}$ denote, respectively, the values of $j \pmod 4$ and $j \pmod 6$. The placement of irrep labels and integers in Fig. 1 has the following significance: Let $[q \pmod 4, q \pmod 6]$, $0\leq q\leq 11$, denote the set of points (subset of the ten displayed points) with initial point $q \pmod 4$ and final point $q \pmod 6$, including all points in between as obtained by reading clockwise for even q and counterclockwise for odd q. Then the irrep labels in Fig. 1 corresponding to the set of points $[q \pmod 4, q \pmod 6]$ are just those contained in Γ^q for each $q\in\{0,1,\ldots,11\}$. (Note also that we may obtain the Γ^q by interchanging the initial and final points in the above description and reading counterclockwise for even q and clockwise for odd q.) Indeed, using these results, one quickly reads off all Γ^q. For example, $\Gamma^5=F_1+F_2+E+F_1$ is obtained by reading off (counterclockwise) all irrep labels on and between the points 1 and $\bar{5}$. (The dashed lines in Fig. 1 serve to partition the irrep labels for purposes to be explained later.)

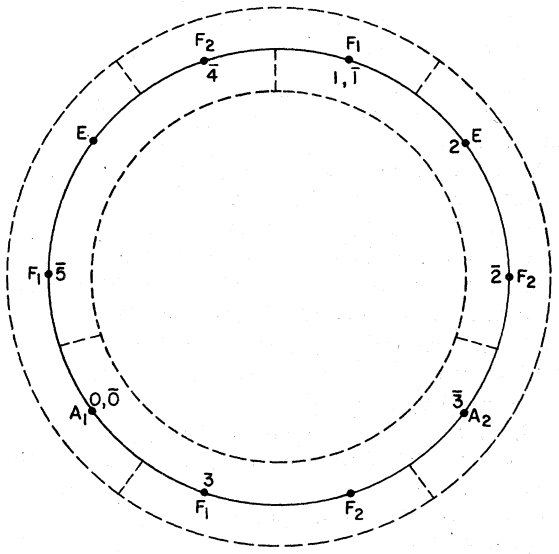

FIG. 1. Sequence S_j ($\downarrow$) ($j=12p+q$, $p=0,1,2,\ldots$; $q=0,1,\ldots,11$) of irrep labels assigned to the eigenvalues of T as read from the highest to the lowest value is obtained by entering the solid circle at the point $k=j \pmod 4$ and reading off the irrep labels clockwise for even j, counterclockwise for odd j, completing p full cycles and one partial cycle which terminates at the point $\bar{k}=j \pmod 6$. The dashed lines partition the irrep labels of the regular representation into sixfold (outside dashed circle and radial lines) levels and eightfold (inside dashed circle and radial lines) levels which describe the symmetries of the asymptotic clusters at the high and low ends of the spectrum, respectively.

We may now give complete descriptions of the sequences $S_j(\downarrow)$ and $S_j(\uparrow)$ for integral $j = 12p + q$, $0 \leq q \leq 11$:

The sequence $S_j(\downarrow)$ is obtained by entering Fig. 1 at the point $k = j \pmod 4 = q \pmod 4$ and reading off the irrep labels, in turn, by going clockwise for even j and counterclockwise for odd j, completing p full cycles and one partial cycle which terminates with the irrep label at the point $\bar{k} = j \pmod 6 = q \pmod 6$.

The sequence $S_j(\uparrow)$ is obtained by entering Fig. 1 at the point $\bar{k} = j \pmod 6 = q \pmod 6$ and reading off the irrep labels, in turn, by going counterclockwise for even j and clockwise for odd j, completing p full cycles and one partial cycle which terminates with the irrep label at the point $k = j \pmod 4 = q \pmod 4$.

Remark. While it is obvious that $S_j(\uparrow)$ [since it is just $S_j(\downarrow)$ read backwards] is described as above, it is useful for subsequent discussions to have this description written out fully.

If we define an R sequence (R for regular) to be any sequence of irrep labels containing one A_1, one A_2, two E's, three F_1's, and three F_2's, we may characterize each S_j sequence associated with the spectrum of T more colorfully by the statement: *Each S_j sequence has a definite R sequence as its period, repeats this period p times, and contains at the end a partial period made up of as much of the R sequence as needed to meet dimensionality requirements.* Figure 1 serves to delineate the details of the R sequence for each j value.

We find it quite remarkable that the irrep labels assigned to the eigenvalues of T should exhibit such a periodic structure. (We emphasize again the empirical nature of this result, it being verified, without exception, for all integral j from 0 to 100.) Table I shows two examples of the general structure described above.

We next turn to the description of several features of the spectrum of T which become more pronounced with increasing j. If one examines the entries in Table I ($j = 28$), one observes that certain eigenvalues are almost degenerate. At the top of the display, one sees that the levels are combined into sixfold nearly degenerate levels of symmetry types (reading downward), respectively,

$$A_1+F_1+E,\quad F_2+F_1,\quad E+F_2+A_2,\quad F_2+F_1, \tag{79a}$$

this grouping of levels by common approximate eigenvalue becoming rather bad for the next A_1+F_1+E. On the other hand, reading upward from the bottom of Table I ($j = 28$), one sees that the levels are combined into eightfold nearly degenerate levels of symmetry types, respectively,

$$F_2+E+F_1,\quad A_1+F_1+F_2+A_2,\quad F_2+E+F_1, \tag{79b}$$

this grouping of levels by common approximate eigenvalue being rather bad for the last F_2+E+F_1 in this sequence. Similar features, involving the same sixfold levels (79a) and the same eightfold levels (79b) are exhibited by the $j = 29$ column of Table I.

Qualitatively, the sequence of eigenvalues of T (integral j) may be partitioned into three sets described as follows: (i) the high eigenvalue end, where the eigenvalues associated with each R sequence in $S_j(\downarrow)$ exhibit the sixfold (approximate) degeneracies of levels of symmetry types A_1+E+F_1, F_1+F_2, A_2+E+F_2, and F_1+F_2; (ii) the low eigenvalue end, where the eigenvalues associated with each R sequence in $S_j(\uparrow)$ exhibit the eightfold (approximate) degeneracies of levels of symmetry types $E+F_1+F_2$, $A_1+A_2+F_1+F_2$, and $E+F_1+F_2$; and (iii) a transition region between the high and low eigenvalue end which contains four to seven levels having eigenvalues which follow no pattern other than being close.

The dashed lines in Fig. 1 serve to partition the irrep labels of the regular representation into the sixfold (outside dashed circle) levels and the eightfold (inside dashed circle) levels going, respectively, with the high and low eigenvalue ends of the spectrum. As an example, for $j = 28$, we enter Fig. 1 at the point 0 and read clockwise two full cycles, finishing with the partial cycle ending at $\bar{4}$, thus obtaining the sequence $S_{28}(\downarrow)$. The partition indicated by the outside dashed circle then instructs us to split up the regular representation according to A_1+F_1+E, F_2+F_1, $E+F_2+A_2$, and F_2+F_1. The levels at the high end of the spectrum then exhibit these sixfold degeneracies. Similarly, to obtain the sequences $S_{28}(\uparrow)$ we enter Fig. 1 at the point $\bar{4}$ and read counterclockwise two full cycles and one partial cycle ending at 0. The partition indicated by the inside dashed lines then instructs us to split up the regular representation according to F_2+E+F_1, $A_1+F_1+F_2+A_2$, F_2+E+F_1. The levels at the low end of the spectrum then exhibit these eightfold degeneracies.

Directing our attention again to Table I, we see additional qualitative features which are typical of each spectrum: (i) the clustering of eigenvalues into sixfold and eightfold degenerate levels is best at the ends of the sequence and becomes poorer for those levels nearer the middle; and (ii) the clustering into sixfold degenerate levels (high end) is more pronounced and continues further into the sequence than the clustering into eightfold degenerate levels (low end).

To give some indication of how the clustering phenomenon improves with high j, we have (Table

TABLE II. Eigenvalues (multiplied by 100) of the operator T for $j=100$. Symmetry type is denoted by the letter to the left of each eigenvalue.

A_1	5.125 690 090 113 115 680 256 257 41
F_1	5.125 690 090 113 115 680 256 246 55
E	5.125 690 090 113 115 680 256 241 11
F_2	4.613 143 588 753 669 695 986 086 41
F_1	4.613 143 588 753 669 695 984 526 12
E	4.123 813 565 974 013 576 249 958 69
F_2	4.123 813 565 974 013 576 195 545 78
A_2	4.123 813 565 974 013 576 086 719 95
F_2	3.657 180 034 191 149 605 188 983 55
F_1	3.657 180 034 191 149 600 281 883 37
A_1	3.212 732 649 388 184 644 879 787 44
F_1	3.212 732 649 388 184 484 121 005 93
E	3.212 732 649 388 184 403 741 615 18
F_2	2.789 971 626 892 359 674 156 371 85
F_1	2.789 971 626 892 355 597 481 874 43
E	2.388 408 909 335 097 267 599 682 75
F_2	2.388 408 909 335 055 641 500 819 30
A_2	2.388 408 909 334 972 389 303 092 32
F_2	2.007 569 673 405 330 918 805 171 95
F_1	2.007 569 673 403 924 645 927 347 27
A_1	1.646 994 299 230 227 427 363 868 59
F_1	1.646 994 299 210 200 870 576 139 99
E	1.646 994 299 200 187 592 180 041 52
F_2	1.306 240 983 446 697 745 268 577 70
F_1	1.306 240 983 202 868 013 774 524 95
E	0.984 889 268 710 685 073 571 903 90
F_2	0.984 889 267 428 308 849 092 921 45
A_2	0.984 889 264 863 556 326 927 654 06
F_2	0.682 544 915 774 415 105 086 555 01
F_1	0.682 544 892 285 740 302 042 659 88
A_1	0.398 846 926 458 295 844 008 468 22
F_1	0.398 846 738 104 829 771 571 132 97
E	0.398 846 643 927 897 998 386 189 49
F_2	0.133 477 415 121 653 930 832 118 01
F_1	0.133 476 087 600 358 713 277 347 41
E	−0.113 820 550 714 971 537 012 721 75
F_2	−0.113 824 670 725 801 047 764 678 17
A_2	−0.113 832 911 516 736 218 647 037 97
F_2	−0.343 211 700 124 708 016 123 815 95
F_1	−0.343 256 749 021 544 314 879 348 59
A_1	−0.554 586 765 960 791 560 014 224 37
F_1	−0.554 802 947 346 126 586 805 606 85
E	−0.554 911 306 144 353 572 766 778 27
F_2	−0.747 916 422 095 131 911 371 734 66
F_1	−0.748 829 443 283 038 391 070 882 10
E	−0.921 740 940 781 814 669 346 563 49
F_2	−0.923 367 440 228 536 798 770 416 95
A_2	−0.926 750 544 469 145 034 187 247 51
F_2	−1.073 780 721 465 328 536 413 833 16
F_1	−1.083 217 941 412 453 593 557 705 35
A_1	−1.190 130 139 104 612 221 122 307 78
F_1	−1.211 465 541 115 730 083 575 430 55
E	−1.223 807 792 495 174 406 634 504 30
F_2	−1.298 669 531 856 416 780 417 344 07
F_1	−1.357 463 645 331 767 352 225 532 58
E	−1.398 953 665 318 508 955 615 312 30
F_2	−1.413 942 186 561 829 616 697 199 63
A_2	−1.530 407 059 651 272 556 104 560 10
F_2	−1.542 737 626 348 819 454 833 532 19
F_1	−1.552 860 244 399 062 344 812 493 06
A_1	−1.561 835 047 007 528 733 480 626 01
F_1	−1.735 872 930 017 428 548 567 057 65
E	−1.738 329 462 409 720 394 247 929 18
F_2	−1.740 792 637 826 024 220 948 537 19
F_1	−1.958 800 917 925 736 438 246 769 67
E	−1.959 211 917 221 652 421 431 964 77
F_2	−1.959 617 474 398 551 574 555 539 92
A_2	−2.205 690 537 106 250 549 362 472 70
F_2	−2.205 740 107 216 926 575 826 673 52
F_1	−2.205 789 633 426 881 222 180 206 50
A_1	−2.205 839 115 846 819 559 087 037 52
F_1	−2.475 887 153 282 221 645 230 334 37
E	−2.475 891 508 594 447 061 256 675 41
F_2	−2.475 895 863 794 787 859 379 167 96
F_1	−2.768 492 514 561 974 034 171 497 12
E	−2.768 492 779 390 955 664 450 115 70
F_2	−2.768 493 044 217 690 926 871 150 73
A_2	−3.082 960 347 082 066 430 850 404 83
F_2	−3.082 960 357 090 862 681 561 542 41
F_1	−3.082 960 367 099 656 707 919 444 58
A_1	−3.082 960 377 108 448 509 925 335 12
F_1	−3.418 969 545 015 500 357 195 826 09
E	−3.418 969 545 193 238 111 742 763 24
F_2	−3.418 969 545 370 975 865 769 605 86

II) given to 26 significant figures the calculated eigenvalue spectrum of T for $j=100$ (within the highest multiplet A_1+F_1+E, the eigenvalues differ only in the 24th significant figure!) That the clustering is an asymptotic (in j) phenomenon is clearly indicated by the entries in Table II. It is remarkable that already at $j=10$ (Table III) the clustering begins to make its appearance.

We can make several more observations by introducing the "center of gravity" of a cluster [we have already noted in Eq. (73a) that the center of gravity of the full spectrum is at the origin]. If we let C denote the set of indices (subset of $1,2,\ldots,10p+n_q$) which enumerate the levels in a

TABLE III. Eigenvalues of the operator T for $j=10$. Symmetry type is denoted by the letter to the left of each eigenvalue.

	$100\,\lambda_s$ $(j=10)$
E	10.459 417
F_2	10.349 646
A_2	10.112 306
F_2	0.783 190
F_1	−0.358 120
A_1	−3.512 696
F_1	−6.454 381
E	−7.436 370
F_2	−8.535 570

cluster, then the center of gravity λ_C of the cluster is defined by

$$\lambda_C = \sum_{c\in C} \frac{(\dim\Gamma_c)\lambda_c}{N_C}, \tag{80}$$

where N_C is the number of levels λ_c in the cluster C.

In terms of this nomenclature, we may make two semiquantitative observations: (i) the transition region between the high end (where the clustering into sixfold degenerate levels occurs) and the low end (where the clustering into eightfold degenerate levels occurs) is comprised of four to seven levels located to either side of the point which lies below 0 at a distance equal to three-eighths the distance from 0 to the low end; and (ii) within a cluster C, we have

$$|\lambda_C - \lambda_{c'}|\dim\Gamma_{c'} = |\lambda_C - \lambda_c|\dim\Gamma_c \tag{81}$$

for each pair of levels λ_c and $\lambda_{c'}$ not equal to λ_C. Each case of Eq. (81) is displayed graphically in Fig. 2.

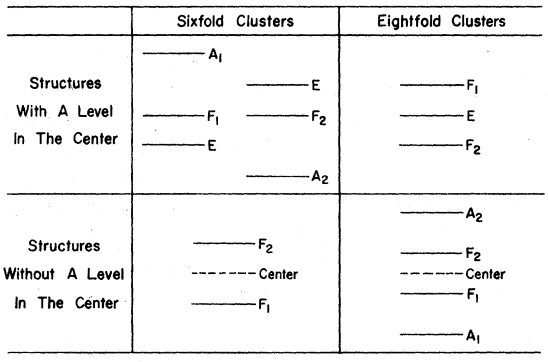

FIG. 2. Relative splittings of eigenvalues within the various types of clusters are inversely proportional to the degeneracy of the level.

For actual spectra, it is useful to know the positions λ_C of the clusters since the hyperfine structure within a cluster may not be resolved or may appear as a blended line at λ_C. To illustrate this behavior, we have plotted in Fig. 3 the values $100\lambda_C$ for $j=100$ as a function of the cluster index C. We have assigned $C=1,2,\ldots,21$ to the sixfold degenerate clusters (see Table II) $C=0$ to all four of the levels in the transition region, and $C=-1,-2,\ldots,-8$ to the eightfold degenerate clusters. The resulting points fall on the smooth curve shown.

Dorney and Watson[33] have noted certain features of the spectrum described above. They first of all observed the clustering (79) into levels of approximate common eigenvalue in their calculations of the spectrum of $-\frac{5}{4}T_0$ for $j=2,\ldots,20$. Second, they gave a classical argument as to the origin of this approximate degeneracy, an argument that suggests that the molecule prefers to spin about one of the threefold (group $\mathcal{C}_3$) or fourfold (group $\mathcal{C}_4$) axes of the octahedron. They further noted that the diagonal elements of T for $j=m,m-1,\ldots,$ give a rough approximation to the centers of gravity of the clusters at the sixfold end of the spectrum. This observation is substantiated for large j and m (where $\alpha\cong 1$) by Eqs. (74) and (75). For a similar approximation to the centers of gravity of the clusters at the eightfold end of the spectrum, they noted that one

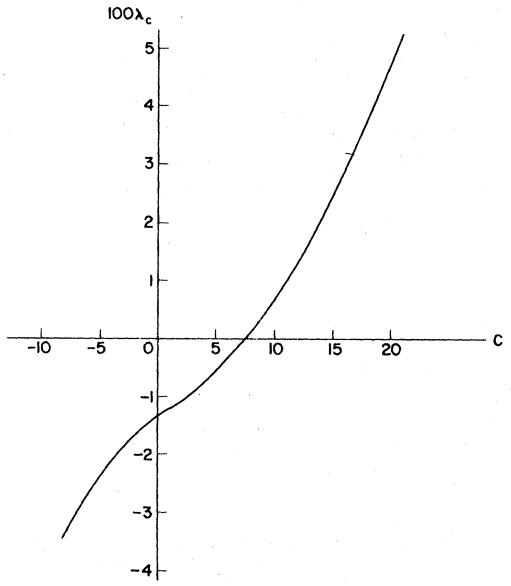

FIG. 3. Plot of the center of gravities of the clusters vs the cluster index defines a smooth relation as illustrated here for $j=100$.

should consider the diagonal elements of the operator T' which is the transformation of T to one of the threefold axes. These results already give considerable insight into the explanation of the calculated spectrum.

This completes our discussion of the properties of the eigenvalue spectrum of T for integral j, and we now turn to the case of half integral j.

A remarkable observation due to Harter and Patterson[49] allows us to make a prediction as to the general nature of the spectrum of T for j half-integral. (This prediction is a *conjecture* because it is based on the assumption that the structure of the half-integral case will parallel that for the integer case.) Harter and Patterson observed that the three eight-dimensional representations of O given by $A_1+A_2+F_1+F_2$, $E+F_1+F_2$, $E+F_1+F_2$ are just the representations obtained by inducing[50] from the $\mathcal{C}_3$ subgroup of O, the representation $A_1+A_2+F_1+F_2$ being induced from the identity representation of $\mathcal{C}_3$, and the representation $E+F_1+F_2$ being induced once from each of the (one dimensional) complex-conjugate representations of $\mathcal{C}_3$. Similarly, the four six-dimensional representations A_1+E+F_1, A_2+E+F_2, F_1+F_2, F_1+F_2 are just the representations of O induced, respectively, from the four one-dimensional representations of the $\mathcal{C}_4$ subgroup of O. The observation of Harter and Patterson should certainly play a key role in the theoretical explanation of the eigenvalue spectrum of T, but at this point we will regard it only as an intriguing fact.

Let us apply this idea to the double groups $\bar{\mathcal{C}}_3 \subset \bar{O}$ and $\bar{\mathcal{C}}_4 \subset \bar{O}$. $\bar{\mathcal{C}}_3$ has six one-dimensional representations, and the corresponding eight-dimensional-induced representations of $\bar{O}$ are $A_1+A_2+F_1+F_2$, $E+F_1+F_2$ (twice), $2G'$, and $E_1'+E_2'+G'$ (twice); $\bar{\mathcal{C}}_4$ has eight one-dimensional representations, and the corresponding six-dimensional-induced representations of $\bar{O}$ are A_1+E+F_1, A_2+E+F_2, F_1+F_2 (twice), $E_1'+G'$ (twice), and $E_2'+G'$ (twice).

The implication of these results is clear: The four six-dimensional representations

$$E_1'+G',\quad E_1'+G',\quad E_2'+G',\quad E_2'+G' \tag{82a}$$

are playing the same role in the half-integer problem as are the four six-dimensional representations (79a) in the integer problem. Similarly, the three eight-dimensional representations

$$2G',\quad E_1'+E_2'+G',\quad E_1'+E_2'+G' \tag{82b}$$

are playing the same role in the half-integer problem as are the three eight-dimensional representations (79b) in the integer problem. Observe that the irreps of $\bar{O}$ appearing in either Eq. (82a) or (82b) sum to $R = 2E_1' + 2E_2' + 4G'$, which is the appropriate cycle for reducing Γ^j for j half-integral [cf. Eq. (67b)].

We now consider for half-integral j the problem of constructing a circle analogous to Fig. 1. The idea is: (i) to find an assignment of the irrep labels $E_1', E_1', E_2', E_2', G', G', G', G'$, to eight points equally spaced on the periphery of a circle such that four radial (dashed) lines outside the circle partition the letters into pairs going with the induced representations $E_1'+G'$, $E_1'+G'$, $E_2'+G'$, $E_2'+G'$, while at the same time three radial (dashed) lines inside the circle partition the letters into those occurring in the induced representations $2G'$, $E_1'+E_2'+G'$, $E_1'+E_2'+G'$; and (ii) to find an unambiguous assignment of the half-integers $k=j(\mathrm{mod}4)$ and $\bar{k}=j(\mathrm{mod}6)$ to the eight points such that when we enter the circle at the point k and exit at the first point $\bar{k}$, reading clockwise[51] for $j=(4n+1)/2 (n=0,1,\ldots,)$ and counterclockwise for $j=(4n+3)/2$ $(n=0,1,\ldots,)$, we read off the irreps occuring in the known[52] Γ_q, $q=\frac{1}{2},\frac{3}{2},\ldots,\frac{23}{2}$.

There are only four diagrams (obtained by considering all possibilities) which meet the two stipulations above. One of the possible diagrams is shown in Fig. 4. The other three are obtained by exchanging E_2' and G' in the upper-left-hand quadrant and/or by exchanging E_2' and G' in the lower-left-hand quadrant. If we further assume that one diagram works for obtaining all sequences $S_j(\mathfrak{h})$, then the calculated eigenvalues for $j=\frac{7}{2}$ and $j=\frac{11}{2}$ [cf. Eqs. (72)] require that we pick Fig. 4.

The conjecture is: to obtain the sequence $S_j(\mathfrak{h})$ $(j=12p+q, p=0,1,\ldots, q=\frac{1}{2},\frac{3}{2},\ldots)$, we enter the circle at the point $k=j(\mathrm{mod}4)$, read off the letters clockwise for p full cycles for $j=\frac{1}{2}(4n+1)$ [counterclockwise for $j=\frac{1}{2}(4n+3)$], and continue for a partial cycle to the point $\bar{k}=j(\mathrm{mod}6)$. Furthermore, we expect the clustering at the high-eigenvalue end as given by the sixfold degenerate levels read off the outside partition and we expect the clustering at the low-eigenvalue end as given by the eightfold degenerate levels read off the inside partition.

To test this conjecture, we calculated the spectrum of T for all half integral j in the interval $\frac{5}{2} \leqslant j \leqslant \frac{59}{2}$, although we did not make the assignment of symmetry type to the levels.[53] The resulting sequences of fourfold and twofold degenerate eigenvalues in $S_j(\mathfrak{h})$ for $\frac{5}{2} \leqslant j \leqslant \frac{59}{2}$ agree with the results read off Fig. 4. Furthermore, the clustering phenomenon occurs just as predicted (see Table IV) with relative spacings in accord with Eq. (81).

C. Method of calculation of eigenvalues

For integral j the calculation of the eigenvalue spectrum of T was done in the space H_l of solid

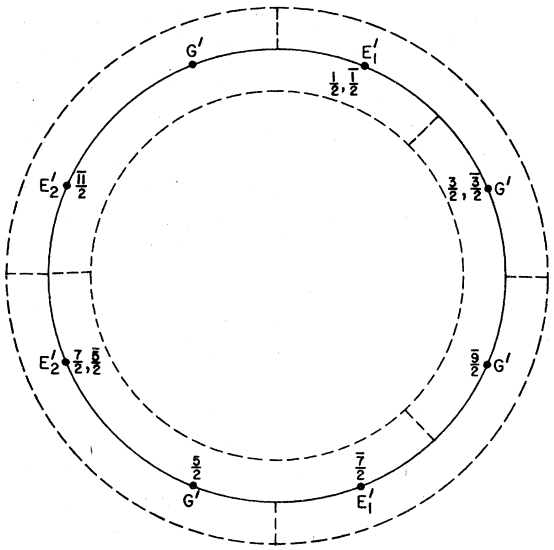

FIG. 4. Sequence S_j ($\downarrow$) ($j = 12p + q, p = 0, 1, \ldots$; $q = \frac{1}{2}, \frac{3}{2}, \ldots, \frac{23}{2}$) of irrep labels assigned to the eigenvalues of T as read from the highest to the lowest value is obtained by entering the solid circle at the point $k = j$ (mod4) and reading off the irrep labels clockwise for $j = \frac{1}{2}(4n+1)$, $n = 0, 1, 2, \ldots$, counterclockwise for $j = \frac{1}{2}(4n+3)$, $n = 0, 1, 2, \ldots$, completing p full cycles and one partial cycle which terminates at the point $\bar{k} = j$(mod6). The dashed lines partition the irrep labels of the R representation into sixfold (outside dashed circle and radial lines) levels and eightfold (inside dashed circle and radial lines) levels which describe the symmetries of the asymptotic clusters at the high and low ends of the spectrum, respectively.

harmonics. We first split the space H_l into invariant subspaces (with respect to O) which carry only one (with repetitions) of the irreps A_1, A_2, E, F_1, or F_2, this being accomplished by standard projection techniques:

$$H_l = H_l(A_1) \oplus H_l(A_2) \oplus H_l(E) \oplus H_l(F_1) \oplus H_l(F_2), \tag{83a}$$

where, for $l = 12p + q$, we have

$$\dim H_l(\Gamma_i) = (\dim \Gamma_i)(p + k_{\Gamma_i}), \tag{83b}$$

in which k_{Γ_i} is the number of occurrences of irrep Γ_i in Γ^q, $0 \leq q \leq 11$. It is this step of the analysis which allows the irrep labels Γ_i to be assigned to the various levels.

It is also useful to observe from the recursion relations based on the matrix elements (71) that the space H_l also may be split into a direct sum of four invariant subspaces with respect to T:

$$H_l = H_l(0) \oplus H_l(1) \oplus H_l(2) \oplus H_l(3), \tag{84a}$$

where $H_l(k)$ is the subspace of H_l spanned by the solid harmonics in the set:

$$\{\mathcal{Y}_{lm} : m = k(\mathrm{mod}4)\}. \tag{84b}$$

Thus, each eigenvector Φ of T must simultaneously belong to one of the spaces $H_l(\Gamma_i)$ and one of the spaces $H_l(k)$.

The detailed method used for splitting the spaces $H_l(\Gamma_i)$ into $p + k_{\Gamma_i}$ perpendicular spaces each carrying irrep Γ_i has been described elsewhere.[54]

All calculations have been carried out with double precision (relative accuracy 5×10^{-29}) on the CDC 7600 computer at Los Alamos. It is noted that at the high end of the $j = 100$ eigenvalue spectrum (cf. Table II), Eq. (81) is satisfied to 26 significant figures.

V. CONCLUDING REMARKS

There are two general features of the eigenvalue spectrum of T which remain to be explained: (i) the general cycle structure with period R; (ii) the asymptotic (in j) clustering phenomenon together with the internal spacings of levels within a cluster.

We have made no substantial progress in explaining either of these features. (One would like to understand the structure of the problem without having to construct the details of the complete solution.) Our approaches to the problem have included the following: (i) If one splits the problem into the four pieces corresponding to Eq. (84a), the problem is reduced to the study of four Jacobi matrices in which the elements are $3j$ symbols. One may study the three-term recursion relations directly in hopes of explaining the cycle structure, and one may use asymptotic forms of the $3j$ symbols in hopes of explaining the asymptotic features. (ii) One might attempt to construct directly (by using symmetry techniques) p bases,

TABLE IV. Eigenvalues of the operator T for $j = \frac{59}{2}$. Numbers in parentheses denote the multiplicity. Symmetry type was not determined.

$100\,\lambda_s$ ($j = \frac{59}{2}$)	$100\,\lambda_s$ ($j = \frac{59}{2}$)
(4) 8.345 566 7	(4) −1.552 780 8
(2) 8.345 564 4	(2) −1.740 156 5
(4) 5.518 761 7	(2) −2.365 819 9
(2) 5.518 678 9	(4) −2.610 359 1
(2) 3.135 817 2	(2) −2.878 837 1
(4) 3.134 524 2	(4) −3.815 355 7
(2) 1.171 438 0	(4) −3.935 089 1
(4) 1.159 854 2	(2) −5.598 630 9
(4) −0.394 908 3	(4) −5.606 346 7
(2) −0.461 954 4	(2) −5.613 833 8

each carrying the reducible representation R, such that the interaction T between these R-representation spaces is small for large j. One could then attempt to study each R-representation space using the ideas of induced representations of Harter and Patterson.[49] (iii) One may implement analytically an approximate group-theoretical reduction of the problem using the methods of Michelot and Moret-Bailly,[35] looking carefully for those structural characteristics of the method responsible for the observed features of the eigenvalue spectrum.

Added note.—After this paper was accepted for publication, we received two manuscripts[55] by Harter and Patterson in which they combined their ideas on induced representations with the suggestions of Dorney and Watson.[33] They have now developed a perturbation treatment of T (and its transform to a threefold axis) that yields good agreement with the calculated spectrum for clusters near either of the two ends of the spectrum. Their analyses also show that our circle in Fig. 4 gives an incorrect result for $j=\frac{1}{2}(4n+3)$. The correct result is obtained by interchanging E_1' and E_2' in the result obtained by our rules. It thus requires *two circles* to make the irrep label assignments to the levels for j half-integral.

We are indebted to Dr. Harter and Dr. Patterson for their recent manuscripts, for pointing out the significance of Dorney and Watson's work, and for correcting our "half-integral circle."

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APPENDIX A: CONSEQUENCES OF TIME REVERSAL

Wigner[37] has proved that the time-reversal operator Θ may be written as a product

$$\Theta = UK, \tag{A1}$$

where U is a linear unitary operator and K is an antilinear, antiunitary operator. It is instructive to see the simple form which this result assumes within the framework of the present problem.

Let us first give an explicit construction of Θ on the space $\mathcal{H}_j$. A general vector Φ of $\mathcal{H}_j$ has the form

$$\Phi = \sum_m \alpha_m |jm\rangle, \tag{A2}$$

where the α_m are, in general, complex numbers. The scalar product (Φ,Φ') of two vectors is given by

$$(\Phi,\Phi') = \sum_m \alpha_m^* \alpha_m', \tag{A3}$$

where "*" signifies complex conjugation. We next define two operators K and U by giving their actions on an arbitrary vector of $\mathcal{H}_j$:

$$K\Phi = \sum_m \alpha_m^* |jm\rangle, \tag{A4}$$

$$U\Phi = \sum_m \alpha_m (-1)^{j+m} |j,-m\rangle. \tag{A5}$$

Using these definitions, it is now an elementary exercise to prove the following results: $K(\Phi+\Phi') = K\Phi + K\Phi'$, $K(\lambda\Phi) = \lambda^*(K\Phi)$, $(K\Phi, K\Phi') = (\Phi,\Phi')^*$, that is, K is antilinear and antiunitary on $\mathcal{H}_j$; also, $U(\Phi+\Phi') = U\Phi + U\Phi'$, $U(\lambda\Phi) = \lambda(U\Phi)$, $(U\Phi, U\Phi') = (\Phi,\Phi')$, that is, U is linear and unitary; furthermore $K^2 = 1$, $K^{-1} = K$, $U^2 = (-1)^{2j}$, $U^{-1} = U^\dagger$, and $UK = KU$.

Using next the action of $J_\pm$ given by Eqs. (2), an elementary derivation establishes $UJ_+\Phi = -J_-U\Phi$, that is, $UJ_+U^\dagger = -J_-$. In similar fashion, one derives the following results:

$$\begin{aligned} &UJ_+U^\dagger = -J_-, \quad UJ_-U^\dagger = -J_+, \quad UJ_3U^\dagger = -J_3, \\ &KJ_+K = J_+, \quad KJ_-K = J_-, \quad KJ_3K = J_3. \end{aligned} \tag{A6}$$

Because of the linear property of U and the antilinear property of K, properties (A6) may also be written

$$\begin{aligned} &UJ_1U^\dagger = -J_1, \quad UJ_2U^\dagger = J_2, \quad UJ_3U^\dagger = -J_3, \\ &KJ_1K = J_1, \quad KJ_2K = -J_2, \quad KJ_3K = J_3. \end{aligned} \tag{A7}$$

Combining these operations, we obtain

$$\Theta J_i \Theta^{-1} = -J_i, \tag{A8}$$

which is, indeed, the time-reversal operation.

Note that from the first line of Eqs. (A7) it follows that U is equal to one of the operators generated by $\mathcal{R},\mathcal{R}',\mathcal{S}$, and $\mathcal{S}'$. Indeed, from the definition (A5) it follows that [cf. Eqs. (7) and (9)] U is the operator corresponding to

$$\begin{pmatrix} 0 & 1 \\ -1 & 1 \end{pmatrix}, \tag{A9}$$

that is,

$$U = e^{i\pi J_2}. \tag{A10}$$

We are now prepared to examine the consequences of

$$\Theta T_0 \Theta^\dagger = T_0. \tag{A11}$$

Since

$$UT_0U^\dagger = T_0, \tag{A12}$$

we obtain

$$KT_0K = T_0, \tag{A13a}$$

$$T_0K = KT_0. \tag{A13b}$$

Since an eigenstate of T_0 with eigenvalue λ is a linear combination of the form $\sum_m \alpha_m|jm\rangle$, we obtain

$$T_0 \sum_m \alpha_m^*|j_m\rangle = \lambda \sum_m \alpha_m^*|jm\rangle, \tag{A14}$$

since T_0 is Hermitian and its eigenvalues real. Let S_λ denote the space of functions Φ such that $T_0\Phi = \lambda\Phi$. If S_λ is irreducible with respect to $\bar{O}$, then we must have

$$\sum_m \alpha_m^*|jm\rangle = \omega \sum_m \alpha_m|jm\rangle, \tag{A15a}$$

that is,

$$\alpha_m^* = \omega\alpha_m, \quad \omega\omega^* = 1. \tag{A15b}$$

It follows that with appropriate normalization of $\sum_m \alpha_m|jm\rangle$, we can always choose α_m to be real. Moshinsky and Kramer[42] have proved that each eigenspace S_λ is irreducible, a fact which is substantiated by our numerical calculations.

It follows that the consequences of time-reversal invariance of T_0 is contained fully in the statement: the eigenstates of T_0 may be obtained as real linear combinations of the basis vectors $|jm\rangle, m = j, \ldots, -j$. (In the case of the spherical harmonics, one should choose the Biedenharn phase $|lm\rangle = i^l Y_{lm}$.)

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[1]G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, N. J., 1945).

[2]K. Fox, in *Molecular Spectroscopy; Modern Research*, edited by K. Narahari Rao and C. W. Mathews (Academic, New York, 1972); W. C. Maguire and K. Fox, Bull. Am. Astron. Soc. 8, 471 (1976).

[3]K. Fox, J. P. Aldridge, H. J. Flicker, R. F. Holland, R. S. McDowell, and N. G. Nereson, in Proceedings of the Ohio State University Symposium on Molecular Structure and Spectroscopy, 1975 (unpublished).

[4]J. P. Aldridge, H. Filip, H. Flicker, R. F. Holland, R. S. McDowell, N. G. Nereson, and K. Fox, J. Mol. Spectrosc. 58, 165 (1975).

[5]H. W. Galbraith, R. S. McDowell, and C. D. Cantrell (unpublished).

[6]K. Fox, Phys. Rev. Lett. 27, 233 (1971); K. Fox, Phys. Rev. A 6, 907 (1972).

[7]C. W. Holt, M. C. L. Gerry, and I. Ozier, Can. J. Phys. 53, 1791 (1975), and references therein.

[8]F. Michelot, J. Moret-Bailly, and K. Fox, J. Chem. Phys. 60, 2606 (1974); 60, 2610 (1974), and references therein.

[9]The early applications of the Racah-Wigner tensor algebra to the interpretation of the vibration-rotation spectra of spherical top molecules was carried out principally by the following authors: J. D. Louck, thesis (Ohio State University, 1958) (unpublished); K. T. Hecht, J. Mol. Spectrosc. 5, 355 (1960); 5, 390 (1960); J. Moret-Bailly, thesis (University of Paris, 1961) (unpublished); J. Moret-Bailly, Cah. Phys. 15, 237 (1961); J. Moret-Bailly, J. Mol. Spectrosc. 15, 344 (1965); K. Fox, thesis (University of Michigan, 1962) (unpublished); K. Fox, J. Mol. Spectrosc. 9, 381 (1962).

[10]L. C. Biedenharn and A. Gamba, Rev. Bras. Fis. 2, 319 (1972); J. D. Louck, Phys. Rev. A 9, 2273 (1974); E. de Vries and A. J. van Zanten, J. Phys. A 7, 807 (1974).

[11]G. Racah, Phys. Rev. 61, 186 (1942); 62, 438 (1942); 63, 367 (1943). [These papers together with many other original papers contributing to angular momentum theory may be found in *Quantum Theory of Angular Momentum*, edited by L. C. Biedenharn and H. Van Dam (Academic, New York, 1965)].

[12]E. P. Wigner, *Group Theory*, translated by J. J. Griffin (Academic, New York, 1959).

[13]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[14]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957).

[15]U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1959).

[16]Invariance under spatial inversion will be considered subsequently.

[17]While the entire theory could be presented within the framework of SU(2), it is convenient to note explicitly the SO(3) case.

[18]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U.P., London, 1953).

[19]H. Weyl, *The Classical Groups*, (Princeton U.P., Princeton, N.J., 1946), p. 56.

[20]J. D. Louck and H. W. Galbraith, Rev. Mod. Phys. 44, 540 (1972).

[21]J. D. Louck and L. C. Biedenharn, J. Math. Phys. 14, 1336 (1973).

[22]In physical applications only Hermitian tensors of integral rank occur as interactions, but the mathematical theory admits half-integral-rank tensors as well.

[23]C. Eckart, Rev. Mod. Phys. 2, 305 (1930); E. P. Wigner, Ref. 12.

[24]J. Schwinger, in *Quantum Theory of Angular Momentum*, edited by L. C. Biedenharn and H. Van Dam

(Academic, New York, 1965).
[25]J. D. Louck and H. W. Galbraith, Rev. Mod. Phys. 48, 69 (1976).
[26]J. D. Louck, J. Mol. Spectrosc. 61, 107 (1976).
[27]K. T Hecht, J. Mol. Spectrosc. 5, 355 (1960); 5, 390 (1960).
[28]H. Bethe, Ann. Phys. (Leipz.) 3, 133 (1929).
[29]More modern group-theoretical discussions may be found in M. Hamermesh, *Group Theory and Its Application to Physical Problems* (Addison-Wesley, Reading, Mass., 1962), Chap. 9.
[30]See, for example, B. Meyer, Can. J. Math. 6, 135 (1954), and references therein.
[31]L. Michel, in Proceedings of the Fifth International Colloquium on Group Theoretical Methods in Physics, Montreal, 1976 (unpublished).
[32]H. A. Jahn, Proc. R. Soc. A 168, 469 (1938).
[33]T_0 may be expressed in various forms: cf. Ref. 9, and A. J. Dorney and J. K. G. Watson, J. Mol. Spectrosc. 42, 135 (1972).
[34]W. G. Harter has pointed out to us that this realization may be particularly useful for gaining an intuitive understanding of the problem (cf. Ref. 49).
[35]The direct use of solid harmonics has been extensively made by F. Michelot and J. Moret-Bailly, J. Phys. (Paris) 36, 451 (1975).
[36]L. C. Biedenharn, W. Brouwer, and W. T. Sharp, *The Algebra of Representations of Some Finite Groups* (Rice University Studies, Houston, 1968), Vol. 54, No. 2, p. 49.
[37]See Ref. 12, Chap. 26.
[38]For a beautiful development of the essentials of angular momentum theory see V. Bargmann, Rev. Mod. Phys. 34, 829 (1962) (also reprinted in the Biedenharn and Van Dam volume referred to in Ref. 11).
[39]P. Jordan, Z. Phys. 94, 531 (1935).
[40]P. A. M. Dirac, *Principles of Quantum Mechanics*, 4th ed. (Oxford U. P., London, 1958), p. 37.
[41]B. R. Judd, W. Miller, Jr., J. Patera, and P. Winternitz, J. Math. Phys. 15, 1787 (1975); R. T. Sharp, *ibid.* 16, 2050 (1975); A. Peccia and R. T. Sharp, *ibid.* 17, 1313 (1976); see also, J. D. Louck, in Proceedings of the International Symposium on Mathematical Physics, Mexico City, 5–8 January 1976 (unpublished).
[42]P. Kramer and M. Moshinsky [Nucl. Phys. 82, 241 (1966)] used the operator T_0 to characterize uniquely four-particle harmonic-oscillator states having permutational (S_4) symmetry.
[43]Values of the $F^{(4)}$ coefficients have been published up to $j=21$: J. Moret-Bailly, L. Gautier, and J. Montagutelli, J. Mol. Spectrosc. 15, 355 (1965). The relation between the $F^{(4)}$ coefficients and the eigenvalues of the operator T has been noted by J. C. Hilico, J. P. Champion, and G. Pierre, J. Mol. Spectrosc. 60, 422 (1976).
[44]Since there is no multiplicity of irreps, the ratios of the eigenvalues therefore agree, as they must, with the splitting ratios given by Biedenharn and Gamba for integral j (cf. Ref. 10).
[45]Special forms for the Racah coefficients (73c) having repeated arguments are given in L. C. Biedenharn, J. M. Blatt, and M. E. Rose, Rev. Mod. Phys. 24, 249 (1952).
[46]The results obtained here demonstrate that the interesting operator to study for large j is $(2j+1)^{1/2}T$ and not T.
[47]We are indebted to Dr. Morris Klein for suggesting the applicability of this theorem: see E. Isaacson and H. B. Keller, *Analysis of Numerical Methods* (Wiley, New York, 1966), p. 135.
[48]One may calculate these limits directly using Eqs. (2), (32), and (70), or one may refer to Edmonds (Ref. 14), Appendix 2.
[49]W. G. Harter communicated his observation to us after hearing our report about the spectrum of T at the Ohio State Molecular Spectroscopy Symposium, June, 1976 (unpublished). Since then, he and C. W. Patterson have attempted to describe certain qualitative features of the spectrum utilizing these induced representation ideas: W. G. Harter and C. W. Patterson, Phys. Rev. Lett. 38, 224 (1977).
[50]J. S. Lomont, *Applications of Finite Groups* (Academic, New York, 1959), p. 223.
[51]This clockwise and counterclockwise rule would seem to be the analog of $j=\frac{4}{2}n$ ($n=0, 1, \ldots$) and $j=\frac{1}{2}(4n+2)$ ($n=0,1,\ldots$) for the even and odd integral cases.
[52]See, for example, Ref. 29, p. 367.
[53]It is nontrivial to assign the irrep labels to the levels, and since our principal interest was in the integral case, we have not yet checked out these assignments.
[54]References to the computation of the Wigner coefficients for the reduction $D^j \downarrow G$, where G is a finite subgroup of the rotation group, are too numerous to mention here. The procedures followed in our computations have evolved from the following papers: K. Fox and I. Ozier, J. Chem. Phys. 52, 5044 (1970); A. S. Householder and K. Fox, J. Comput. Phys. 8, 292 (1971); K. Fox and B. J. Krohn (unpublished). We refer the reader to these papers for a more complete referencing of the literature. Tables for all integral values $2 \leq j \leq 100$ of the $F^{(4)}$ coefficients are now available upon request: B. J. Krohn, Los Alamos Scientific Laboratory Report No. LA-6554-MS (October, 1976) (unpublished).
[55]W. G. Harter and C. W. Patterson (unpublished); C. W. Patterson and W. G. Harter (unpublished).