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Some Properties of Correlation Functions of Irreducible Tensor Operators*

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(Received 23 December 1968)

Properties of quantum-mechanical time-dependent correlation functions of pairs of irreducible tensor operators are derived from the transformation properties of the tensor operators under rotations, the assumed rotational invariance of the Hamiltonian of the system, and the Wigner-Eckart theorem. It is shown that many of the possible correlation functions are zero, and that the nonzero correlation functions can be expressed in terms of reduced matrix elements. Some examples of irreducible tensor operators which occur in applications are given, and their reduced matrix elements are calculated.

I. INTRODUCTION

Quantum-mechanical time-dependent correlation functions of pairs of operators occur in the theory of magnetic resonance and relaxation,¹ and also in the theories of other phenomena, such as microwave resonance, Raman light scattering, and neutron scattering.² The operators whose correlation functions are to be calculated are irreducible tensor operators, or they can be expressed as linear combinations of irreducible tensor operators. However, the properties of irreducible tensor operators do not seem to have been exploited fully in previous calculations of correlation functions.

Some general properties of correlation functions of irreducible tensor operators are derived in Sec. II, and it is shown how such correlation functions can be expressed in terms of reduced matrix elements. In Sec. III correlation functions of tensor operators pertaining to a single molecule in the system are considered. Section IV is concerned with symmetry properties, symmetrized correlation functions, and their Fourier transforms. In Sec. V some examples of irre-

ducible tensor operators are given, and their reduced matrix elements calculated.

II. GENERAL PROPERTIES

An irreducible tensor operator of rank k can be defined³ as a set of $2k+1$ operators T_{km} , $m = -k, -k+1, \dots, k$, which transform under rotations of the coordinate system in the following manner. The operator T_{km} in a coordinate system S' is equal to the operator

$$RT_{km}R^{-1} = \sum_{m'=-k}^k D_{m'm}^k(\alpha\beta\gamma)T_{km'} \quad (1)$$

in a coordinate system S , where $\alpha\beta\gamma$ are the Euler angles specifying the orientation of S' with respect to S . R is the unitary rotation operator

$$R = \exp(-i\alpha L_z) \exp(-i\beta L_y) \exp(-i\gamma L_z), \quad (2)$$

where $\hbar L_y$ and $\hbar L_z$ are, respectively, the y and z components in S of the total angular momentum $\hbar\vec{L}$ of the system. The unitary matrix $\underline{D}^L(\alpha\beta\gamma)$ has elements

$$D_{M'M}^L(\alpha\beta\gamma) = \langle LM' | R | LM \rangle, \quad (3)$$

where $|LM\rangle$ is an eigenket of \vec{L}^2 and L_z , with eigenvalues $L(L+1)$ and M , respectively.

Consider a system consisting in general of many atoms and molecules. Let the Hamiltonian of the system be denoted by $\hbar F$. The density operator describing the system in thermal equilibrium at temperature T is

$$\rho = e^{-\beta F} / \text{Tr}[e^{-\beta F}], \quad \beta \equiv \hbar/kT, \quad (4)$$

where the k in β is the Boltzmann constant.

The quantum-mechanical correlation function of two irreducible tensor operators T_{km} and $S_{k'm'}$ associated with the system is defined by

$$\langle T_{km}(t) S_{k'm'} \rangle \equiv \text{Tr}[\rho T_{km}(t) S_{k'm'}], \quad (5)$$

where $T_{km}(t)$ is the Heisenberg time-dependent operator

$$T_{km}(t) = e^{iFt} T_{km} e^{-iFt}. \quad (6)$$

Since the trace of a product of operators is unchanged by a cyclic permutation of the operators, it follows that

$$\langle T_{km}(t) S_{k'm'} \rangle = \text{Tr}[T_{km} W_{k'm'}(t)], \quad (7)$$

$$\text{where } W_{k'm'}(t) \equiv e^{-iFt} S_{k'm'} \rho e^{iFt}. \quad (8)$$

The important terms in the Hamiltonian $\hbar F$ are in many cases invariant under rotations of the coordinate system; for example, the terms representing the kinetic energies of the particles in a liquid or gas, and the interactions between particles. If electromagnetic fields are applied to the system, there are interactions which are not invariant under rotations of the coordinate system; however, these interactions are usually negligible compared with the terms in $\hbar F$ which are rotationally invariant. Hence, it will be assumed here that $\hbar F$ is invariant under rotations. In this connection, it is worth noting that when correlation functions arise in the theory of the line shape of a resonance produced by the application of an oscillating electromagnetic field, the Hamiltonian $\hbar F$ that occurs in the correlation functions usually does not contain the interaction with the oscillating field.

Since $\hbar F$ is invariant under rotations, it follows that $\exp(\pm iFt)$ and ρ commute with the rotation operator R and its inverse. Therefore

$$R W_{k'm'}(t) R^{-1} = e^{-iFt} R S_{k'm'} R^{-1} \rho e^{iFt}. \quad (9)$$

Hence $W_{k'm'}(t)$ transforms under rotations in the same manner as $S_{k'm'}$. Therefore $W_{k'm'}(t)$ is an irreducible tensor operator of rank k' .

Let $|LbM\rangle$ be an eigenket of \vec{L}^2 with eigenvalue $L(L+1)$, of L_z with eigenvalue M , and of other operators which commute with each other and with \vec{L}^2 and L_z ; the eigenvalues of the other operators are represented by b . According to the Wigner-Eckart theorem, the matrix element of an irreducible tensor operator T_{km} between two such states is of the form^{3,4}

$$\begin{aligned} \langle L_2 b_2 M_2 | T_{km} | L_1 b_1 M_1 \rangle \\ = C(L_1 k L_2; M_1 m M_2) \langle L_2 b_2 || T_k || L_1 b_1 \rangle, \end{aligned} \quad (10)$$

where $C(L_1 k L_2; M_1 m M_2)$ is a Clebsch-Gordan coefficient, and $\langle L_2 b_2 || T_k || L_1 b_1 \rangle$ is a quantity called the reduced matrix element, which is independent of M_1 and M_2 . Similarly, since $W_{k'm'}(t)$ is an irreducible tensor operator, its matrix elements are of the form

$$\begin{aligned} \langle L_1 b_1 M_1 | W_{k'm'}(t) | L_2 b_2 M_2 \rangle \\ = C(L_2 k' L_1; M_2 m' M_1) \langle L_1 b_1 || W_{k'}(t) || L_2 b_2 \rangle. \end{aligned} \quad (11)$$

If the trace in Eq. (7) is evaluated in the representation $|LbM\rangle$, use is made of Eqs. (10) and (11), the fact that

$$\begin{aligned} C(L_1 k L_2; M_1 m M_2) \\ = \delta_{M_2, M_1 + m} C(L_1 k L_2; M_1 m), \end{aligned}$$

the symmetry properties of the Clebsch-Gordan coefficients⁵ and the relation⁶

$$\begin{aligned} \sum_{m_1} C(j_1 j_2 j; m_1, m - m_1) C(j_1 j_2 j'; m_1, m - m_1) \\ = \delta_{jj'} \Delta(j_1 j_2 j), \end{aligned} \quad (12)$$

where $\Delta(j_1 j_2 j)$ equals unity if j_1 , j_2 , and j can form the sides of a triangle, and is zero otherwise, one obtains the result

$$\begin{aligned} \langle T_{km}(t) S_{k'm'} \rangle \\ = \delta_{k'k} \delta_{m', -m} (-1)^m \langle T_{k0}(t) S_{k0} \rangle, \end{aligned} \quad (13)$$

and

$$\begin{aligned} \langle T_{k0}(t) S_{k0} \rangle = (2k+1)^{-1} \sum_{L_1 b_1} \sum_{L_2 b_2} \Delta(L_1 L_2 k) \\ \times (-1)^{L_1 + L_2} [(2L_2 + 1)(2L_1 + 1)]^{\frac{1}{2}} \end{aligned}$$

$$\times \langle L_2 b_2 \| T_k \| L_1 b_1 \rangle \langle L_1 b_1 \| W_k(t) \| L_2 b_2 \rangle. \quad (14)$$

Equations (13) and (14) have been derived by using just the transformation properties of T_{km} and F under rotations. They show that many of the correlation functions are zero, and that only reduced matrix elements are needed to evaluate the nonzero correlation functions.

III. TENSOR OPERATORS OF A SINGLE MOLECULE

Consider a system containing N molecules. Let T_{km} and $S_{k'm'}$ now be irreducible tensor operators involving just the motion of the particles in a single molecule with respect to its center of mass. This molecule will be designated the first molecule, and its angular momentum with respect to its center of mass will be denoted $\hbar \vec{J}$.

Since the angular momentum operator $\hbar \vec{L}$ of the entire system can be expressed as the sum of the angular momentum operators of the molecules with respect to their centers of mass, plus the sum of the angular momentum operators of the centers of mass, it follows that the rotation operator R for the entire system can be expressed as $R = R' R_1$, where R_1 is a rotation operator of the form of Eq. (2) except that the components of \vec{L} are replaced by the components of \vec{J} , and R' is a rotation operator involving the components of $\vec{L} - \vec{J}$. Since R' and R_1 commute, and R' commutes with T_{km} , it follows that T_{km} transforms under rotations according to Eq. (1), and that equation is also valid with R and R^{-1} replaced by R_1 and R_1^{-1} , respectively.

The correlation function of T_{km} and $S_{k'm'}$ is defined as before by Eq. (5) and can be expressed by Eq. (7). It should be noted that $W_{k'm'}(t)$ is an operator involving all the variables of the system, even though $S_{k'm'}$ involves just the motion of the particles of the first molecule with respect to its center of mass.

The trace over all the variables of the system can be expressed as $\text{Tr} = \text{Tr}_1 \text{Tr}' = \text{Tr}' \text{Tr}_1$, where Tr_1 indicates a trace over the variables describing the motion of the particles in the first molecule with respect to its center of mass, and Tr' denotes a trace over the remaining variables of the system. Hence it follows from Eq. (7) that

$$\langle T_{km}(t) S_{k'm'} \rangle = \text{Tr}'_1 [T_{km} x_{k'm'}(t)], \quad (15)$$

where $x_{k'm'}(t)$, as well as T_{km} , is an operator involving just the motion with respect to the center of mass of the first molecule defined by

$$x_{k'm'}(t) \equiv \text{Tr}' [W_{k'm'}(t)]. \quad (16)$$

Since $W_{k'm'}$ is a tensor operator transforming

according to Eq. (1), it follows that

$$\begin{aligned} R x_{k'm'}(t) R^{-1} &= R_1 x_{k'm'}(t) R_1^{-1} \\ &= \text{Tr}' [R_1 W_{k'm'}(t) R_1^{-1}] \\ &= \text{Tr}' [R' R_1 W_{k'm'}(t) R_1^{-1} R'^{-1}] \\ &= \text{Tr}' [R W_{k'm'}(t) R^{-1}] \\ &= \sum_{m=-k'}^{k'} D_{mm'}^{k'}(\alpha\beta\gamma) \\ &\quad \times \text{Tr}' [W_{k'm'}(t)] \\ &= \sum_{m=-k'}^{k'} D_{mm'}^{k'}(\alpha\beta\gamma) x_{k'm'}(t). \end{aligned} \quad (17)$$

Therefore, $x_{k'm'}(t)$ is an irreducible tensor operator with respect to \vec{L} or \vec{J} .

Let $|JbM\rangle$ be an eigenket of the \vec{J}^2 with eigenvalue $J(J+1)$, of J_z with eigenvalue M , and of a sufficient number of other commuting operators to form a complete set for the first molecule; the eigenvalues of the other operators are represented by b . According to the Wigner-Eckart theorem,^{3,4} the matrix elements of T_{km} and $x_{k'm'}(t)$ in the $|JbM\rangle$ representation are given by Eqs. (10) and (11), respectively, with L_1 and L_2 replaced by J_1 and J_2 . The derivation of Eq. (13) can then be carried out as before, where the T_{km} and $S_{k'm'}$ are now the tensor operators for the first molecule, and where

$$\begin{aligned} \langle T_{k0}(t) S_{k0} \rangle &= (2k+1)^{-1} \sum_{J_1 b_1} \sum_{J_2 b_2} \Delta(J_1 J_2 k) \\ &\quad \times (-1)^{J_1 + J_2} [(2J_2 + 1)(2J_1 + 1)]^{\frac{1}{2}} \\ &\quad \times \langle J_2 b_2 \| T_k \| J_1 b_1 \rangle \langle J_1 b_1 \| x_k(t) \| J_2 b_2 \rangle. \end{aligned} \quad (18)$$

IV. SYMMETRY PROPERTIES, SYMMETRIZED CORRELATION FUNCTIONS, AND FOURIER TRANSFORMS

If, in analogy with Eq. (5), one defines

$$\langle T_{km} S_{k'm'}(t) \rangle \equiv \text{Tr} [\rho T_{km} S_{k'm'}(t)], \quad (19)$$

where $S_{k'm'}(t) \equiv e^{iFt} S_{k'm'} e^{-iFt}$,

then the relation

$$\langle T_{km} S_{k'm'}(t) \rangle = \langle T_{km}(-t) S_{k'm'} \rangle \quad (20)$$

can be obtained by cyclic permutation of the operators in the trace.

It is a consequence of Eq. (13) that

$$\langle T_{km}(t) S_{k'm'} \rangle = \langle T_{k'm'}(t) S_{km} \rangle. \quad (21)$$

The Hermitian adjoints of the irreducible tensor operators considered here are given by⁷

$$T_{km}^\dagger = (-1)^m T_{k, -m}. \quad (22)$$

Therefore T_{k0} and S_{k0} are Hermitian. Hence, it follows from Eqs. (5) and (13), and the fact that F is Hermitian, that

$$\langle T_{km}(t) S_{k'm'} \rangle^* = \langle S_{k'm'} T_{km}(t) \rangle. \quad (23)$$

In some theories,¹ there occur symmetrized correlation functions, defined by

$$\langle \{ T_{km}(t) S_{k'm'} \} \rangle \equiv \text{Tr}[\rho \{ T_{km}(t) S_{k'm'} \}] \quad (24)$$

in terms of the symmetrized product

$$\begin{aligned} & \{ T_{km}(t) S_{k'm'} \} \\ & \equiv \frac{1}{2} [T_{km}(t) S_{k'm'} + S_{k'm'} T_{km}(t)]. \end{aligned} \quad (25)$$

By use of Eqs. (5), (13), and (20), the symmetrized correlation function can be expressed as

$$\begin{aligned} & \langle \{ T_{km}(t) S_{k'm'} \} \rangle \\ & = \frac{1}{2} \langle T_{km}(t) S_{k'm'} \rangle + \frac{1}{2} \langle S_{k'm'} T_{km}(t) \rangle \\ & = \delta_{k'k} \delta_{m'm} (-1)^m \\ & \quad \times \frac{1}{2} [\langle T_{k0}(t) S_{k0} \rangle + \langle S_{k0} T_{k0}(t) \rangle]. \end{aligned} \quad (26)$$

It follows from Eq. (23) that

$$\langle \{ T_{km}(t) S_{k'm'} \} \rangle = \text{Re} \langle T_{km}(t) S_{k'm'} \rangle, \quad (27)$$

so the symmetrized correlation functions of irreducible tensor operators are real. Also, from Eqs. (26), (20), and (21),

$$\langle \{ T_{km}(-t) S_{k'm'} \} \rangle = \langle \{ S_{k'm'}(t) T_{k'm'} \} \rangle. \quad (28)$$

Therefore $\langle \{ T_{km}(t) T_{k'm'} \} \rangle$ is an even function of t .

It is usually the Fourier transforms of correlation functions that occur in applications, rather than the correlation functions themselves.^{1,2} The two-sided Fourier transform of the symmetrized

correlation function of two irreducible tensor operators can be expressed in terms of the one-sided Fourier transforms of unsymmetrized correlation functions as follows:

$$\begin{aligned} & \int_{-\infty}^{\infty} \langle \{ T_{km}(t) S_{k'm'} \} \rangle e^{i\omega t} dt \\ & = \delta_{k'k} \delta_{m'm} (-1)^m \\ & \quad \times \frac{1}{2} \{ \int_0^{\infty} \langle T_{k0}(t) S_{k0} \rangle e^{i\omega t} dt \\ & \quad + \int_0^{\infty} \langle S_{k0}(t) T_{k0} \rangle e^{-i\omega t} dt \\ & \quad + [\int_0^{\infty} \langle T_{k0}(t) S_{k0} \rangle e^{-i\omega t} dt \\ & \quad + \int_0^{\infty} \langle S_{k0}(t) T_{k0} \rangle e^{i\omega t} dt]^* \}. \end{aligned} \quad (29)$$

Use has been made of Eqs. (20), (23), and (13) in deriving Eq. (29). If ω is replaced by $-\omega$ in Eq. (29), one obtains the complex conjugate of expression (29). In the special case that $S_{k'm'} = T_{k'm'}$, Eq. (29) reduces to

$$\begin{aligned} & \int_{-\infty}^{\infty} \langle \{ T_{km}(t) T_{k'm'} \} \rangle e^{i\omega t} dt \\ & = \delta_{k'k} \delta_{m'm} (-1)^m \\ & \quad \times \text{Re} \{ \int_0^{\infty} \langle T_{k0}(t) T_{k0} \rangle e^{i\omega t} dt \\ & \quad + \int_0^{\infty} \langle T_{k0}(t) T_{k0} \rangle e^{-i\omega t} dt \}, \end{aligned} \quad (30)$$

which is a real, even function of ω .

V. EXAMPLES

In this section several examples are given of irreducible tensor operators whose correlation functions occur in practice, and reduced matrix elements of the operators are calculated.

1. Angular Momentum

The spherical components L_m , $m = -1, 0, 1$, of the angular momentum $\hbar \vec{L}$ of a system, defined by

$$L_{\pm 1} \equiv \mp (2)^{-1/2} (L_x \pm iL_y), \quad L_0 \equiv L_z, \quad (31)$$

are the components of an irreducible tensor operator of rank one.⁸ As before, let $|LbM\rangle$ be an eigenket of \vec{L}^2 with eigenvalue $L(L+1)$, of L_z with eigenvalue M , and of other commuting operators whose eigenvalues are represented by b . The matrix elements of the L_m in this representation are⁹

$$\langle L_2 b_2 M_2 | L_m | L_1 b_1 M_1 \rangle = \delta_{b_2 b_1} \delta_{L_2 L_1}$$

$$\times [L_1(L_1+1)]^{1/2} C(L_1, 1, L_2; M_1, m, M_2), \quad (32)$$

which is in the form given by the Wigner-Eckart theorem, Eq. (10), with reduced matrix element

$$\langle L_2 B_2 \| L \| L_1 b_1 \rangle = \delta_{b_2 b_1} \delta_{L_2 L_1} [L_1(L_1+1)]^{1/2}. \quad (33)$$

Similarly, the spherical components, J_m , of the angular momentum of a single molecule of the system are the components of an irreducible tensor operator of rank one with respect to the angular momentum \vec{J} of the molecule. Hence the matrix elements of the operators J_m between eigenstates $|JbM\rangle$ of \vec{J}^2 and J_z , and the reduced matrix element, are given respectively by Eqs. (32) and (33) with the L 's replaced by J 's.

Correlation functions of the spherical components of the angular momentum of a molecule occur in the theory of nuclear magnetic relaxation by spin-rotational interactions of nuclei in linear molecules.²

2. Spherical Harmonics

Consider some vector \vec{r} associated with a system having angular momentum $\hbar \vec{L}$. Let $\Omega \equiv \theta, \phi$ be the polar and azimuthal angles specifying the direction of \vec{r} in a coordinate system S , and $\Omega' \equiv \theta', \phi'$ the polar angles specifying the direction of the same vector in a coordinate system S' the Euler angles of which are $g \equiv \alpha\beta\gamma$ with respect to S . Since spherical harmonics Y_{km} with arguments Ω and Ω' are related by¹⁰

$$Y_{km}(\Omega') = \sum_{m'=-k}^k Y_{km'}(\Omega) D_{m'm}^k(g), \quad (34)$$

the spherical harmonics are irreducible tensor operators.

In the special case that \vec{r} is a vector fixed in a single molecule of the system, the spherical harmonics $Y_{km}(\Omega)$, where Ω represents the polar angles of \vec{r} in the laboratory coordinate system S , are the components of an irreducible tensor operator with respect to the angular momentum \vec{J} of the molecule. Let S_1 be a coordinate system fixed in the molecule. Let g_1 represent the Euler angles of S_1 with respect to S , and Ω_1 the fixed polar angles of \vec{r} in S_1 . From Eq. (34) and the fact that $\underline{D}^l(g_1)$ is a unitary matrix, it follows that

$$Y_{km}(\Omega) = \sum_{m'=-k}^k D_{mm'}^{k*}(g_1) Y_{km'}(\Omega_1). \quad (35)$$

Hence the matrix element of $Y_{km}(\Omega)$ between rotational eigenstates of the molecule can be calculated from

$$\begin{aligned} & \langle J_2 b_2 M_2 | Y_{km}(\Omega) | J_1 b_1 M_1 \rangle \\ &= \sum_{m'=-k}^k \langle J_2 b_2 M_2 | D_{mm'}^{k*}(g_1) | J_1 b_1 M_1 \rangle \\ & \times Y_{km'}(\Omega_1), \end{aligned} \quad (36)$$

since the rotational eigenstates are functions of g_1 . The result must be of the form given by the Wigner-Eckart theorem; that is, Eq. (10) with the L replaced by J .

The right-hand side of Eq. (36) can be evaluated easily if the molecule is a symmetric top. If S_1 is chosen to be the principal body-coordinate system, the normalized rotational eigenstates for a symmetric top are

$$|JKM\rangle = [(2J+1)/8\pi^2]^{1/2} D_{MK}^{J*}(g_1). \quad (37)$$

The $|JKM\rangle$ are eigenstates not only of \vec{J}^2 and J_z , but also of the z component in S_1 of the angular momentum \vec{J} , with eigenvalue K .¹¹ Hence¹²

$$\begin{aligned} & \langle J_2 K_2 M_2 | D_{mm'}^{k*}(g_1) | J_1 K_1 M_1 \rangle \\ &= [(2J_1+1)/(2J_2+1)]^{1/2} C(J_1 k J_2; M_1 m M_2) \\ & \times C(J_1 k J_2; K_1 m' K_2), \end{aligned} \quad (38)$$

where the C are Clebsch-Gordan coefficients, which have the property that

$$C(J_1 k J_2; K_1 m' K_2) = \delta_{K_2, K_1+m} C(J_1 k J_2; K_1 m').$$

Hence as predicted by the Wigner-Eckart theorem

$$\begin{aligned} & \langle J_2 K_2 M_2 | Y_{km}(\Omega) | J_1 K_1 M_1 \rangle \\ &= C(J_1 k J_2; M_1 m M_2) \langle J_2 K_2 \| Y_k(\Omega) \| J_1 K_1 \rangle, \end{aligned} \quad (39)$$

where the reduced matrix element is

$$\begin{aligned} & \langle J_2 K_2 \| Y_k(\Omega) \| J_1 K_1 \rangle = [(2J_1+1)/(2J_2+1)]^{1/2} \\ & \times C(J_1 k J_2; K_1, K_2 - K_1) Y_{k, K_2 - K_1}(\Omega_1). \end{aligned} \quad (40)$$

If the molecule is linear, with rotational eigenstates $|JM\rangle$, and if Ω represents the polar angles specifying the orientation of the molecule in the laboratory coordinate system S , then it can be shown that¹³

$$\begin{aligned} & \langle J_2 M_2 | Y_{km}(\Omega) | J_1 M_1 \rangle \\ &= C(J_1 k J_2; M_1 m M_2) \langle J_2 \| Y_k \| J_1 \rangle, \end{aligned} \quad (41)$$

where the reduced matrix element is

$$\langle J_2 \| Y_k \| J_1 \rangle = C(J_1 k J_2; 00) \\ \times [(2J_1 + 1)/(2J_2 + 1)]^{1/2} [(2k + 1)/4\pi]^{1/2}. \quad (42)$$

As might be expected, the result for a linear molecule can be obtained as a special case of the result for a symmetric top by putting $K_1 = K_2 = 0$ and $\Omega_1 = 0, 0$ in Eqs. (39) and (40).

Correlation functions of second-rank spherical harmonics occur in the theory of spin relaxation by dipole-dipole interactions.¹

3. Spin-Rotational Interaction

The Hamiltonian of the spin-rotational interaction of a nucleus with spin $\hbar \vec{I}$ in a molecule with angular momentum $\hbar \vec{J}$ can be expressed as

$$\mathcal{H}_{sr} = \hbar \vec{I} \cdot \underline{c} \cdot \vec{J} = \hbar \vec{I} \cdot \vec{h}, \quad (43)$$

where \underline{c} is the spin-rotational dyadic, whose elements have constant values c_{xx}, c_{xy}, c_{xz} , etc., in a coordinate system S_1 attached to the molecule, and $\vec{h} \equiv \underline{c} \cdot \vec{J}$ is proportional to the magnetic field produced at the position of the nucleus by the rotation of the molecule.

If spherical components of \vec{I} and \vec{h} , defined as in Eq. (31), are introduced, \mathcal{H}_{sr} can be expressed as

$$\mathcal{H}_{sr} = \hbar \sum_{m=-1}^1 (-1)^m I_{-m} h_m. \quad (44)$$

Since \mathcal{H}_{sr} is invariant under rotations of the laboratory coordinate system, since the I_m are elements of a tensor operator of rank one, and since Eq. (44) is in the form of the scalar product of two tensor operators of rank one, it follows that the h_m are the elements of an irreducible tensor operator of rank one.

Let $g_1 = \alpha_1 \beta_1 \gamma_1$ be the Euler angles of the body-coordinate system S_1 with respect to the laboratory-coordinate system S . Then the spherical components of \vec{h} in S , denoted by h_m , are related to the spherical component in S_1 , denoted by h'_m , according to

$$h_m = \sum_{m'=-1}^1 D_{mm'}^{1*}(g_1) h'_{m'}, \quad (45)$$

since they transform in the same manner as the spherical harmonics in Eq. (35). But since $\vec{h} \equiv \underline{c} \cdot \vec{J}$, it follows that h'_m can be expressed as

$$h'_{m'} = \sum_{n'=-1}^1 a_{m'n'}^{J'_n} J'_{n'}, \quad (46)$$

where the J'_n are the spherical components of \vec{J} in S_1 , and the $a_{m'n'}$ can be expressed in terms of the constant elements of \underline{c} in S_1 . It is easily shown that

$$a_{\pm 1, -1} = \frac{1}{2}(c_{yy} \mp c_{xx}) - \frac{1}{2}i(c_{yx} \pm c_{xy}), \\ a_{\pm 1, 0} = \mp (2)^{-1/2}(c_{xz} \pm ic_{yz}), \\ a_{\pm 1, 1} = \frac{1}{2}(c_{yy} \pm c_{xx}) + \frac{1}{2}i(c_{yx} \mp c_{xy}), \\ a_{0, \pm 1} = \mp (2)^{-1/2}(c_{zx} \mp ic_{zy}), \quad a_{00} = c_{zz}. \quad (47)$$

It follows from the fact that \mathcal{H}_{sr} is Hermitian that

$$a_{mn} = (-1)^{m+n} a_{-m, -n}^*, \quad (48)$$

which is satisfied by the expressions (47).

Substitution of Eq. (46) in Eq. (45) gives

$$h_m = \sum_{m', n'=-1}^1 a_{m'n'} D_{mm'}^{1*}(g_1) J'_{n'}. \quad (49)$$

Since the spherical components J'_n in S_1 are related to the spherical components J_n in S by

$$J'_n = \sum_{n=-1}^1 D_{nn'}^1(g_1) J_n, \quad (50)$$

h_m can be expressed in terms of J_n by use of Eq. (50) in Eq. (49).

Matrix elements in the $|JbM\rangle$ representation can, in principle, be calculated by use of Eqs. (49) and (50). We consider here the special case of a symmetric top molecule, and choose S_1 to be a principal body-coordinate system. The matrix elements of J'_n can be calculated by use of Eqs. (50), (32), (38), and (12), the fact that

$$D_{nn'}^1(g_1) = (-1)^{n-n'} D_{-n, -n'}^{1*}(g_1),$$

and the symmetry properties of the Clebsch-Gordan coefficients.⁵ The result is

$$\langle J_2 K_2 M_2 | J'_n | J_1 K_1 M_1 \rangle = \delta_{M_1 M_2} \delta_{J_1 J_2} \\ \times [J_1(J_1 + 1)]^{1/2} C(J_1 1 J_1; K_2 n' K_1). \quad (51)$$

Use of this expression and Eq. (38) to calculate the matrix elements of expression (49) for h_m gives the following result:

$$\langle J_2 K_2 M_2 | h_m | J_1 K_1 M_1 \rangle \\ = C(J_1 1 J_2; M_1 m M_2) \langle J_2 K_2 || h || J_1 K_1 \rangle, \quad (52)$$

as predicted by the Wigner-Eckart theorem, with reduced matrix element

$$\begin{aligned} & \langle J_2 K_2 \| h \| J_1 K_1 \rangle \\ &= [J_1(J_1 + 1)(2J_1 + 1)/(2J_2 + 1)]^{1/2} \\ & \times \sum_{m', n' = -1}^1 a_{m' n'} \delta_{K_2 - K_1, m' - n'} \\ & \times C(J_1 1 J_1; K_1 - n', n') C(J_1 1 J_2; K_1 - n', m'). \end{aligned} \quad (53)$$

Correlation functions of the quantities h_m occur in the theory of nuclear magnetic relaxation by spin-rotational interactions.¹⁴

4. Nuclear Electric Quadrupole Interaction

The interaction of a nucleus having spin angular momentum $\hbar I$ and quadrupole moment Q with the other charges in a molecule containing the nucleus has the Hamiltonian¹⁵

$$\mathcal{H}_Q = \sum_{m = -2}^2 (-1)^m F_{-m} Q_m. \quad (54)$$

The quantities F_m and Q_m transform under rotations of the coordinate system as second-rank spherical harmonics, and hence are irreducible tensor operators of rank two.

The Q_m involve the nucleus; they can be expressed as

$$Q_0 = [eQ/2I(2I - 1)] [3I_z^2 - I(I + 1)], \quad (55a)$$

$$Q_{\pm 1} = \mp \frac{1}{2}(6)^{1/2} [eQ/2I(2I - 1)] [I_z I_{\pm} + I_{\pm} I_z], \quad (55b)$$

$$Q_{\pm 2} = \frac{1}{2}(6)^{1/2} [eQ/2I(2I - 1)] I_{\pm}^2, \quad (55c)$$

where $I_{\pm} = I_x \pm iI_y$. The F_m are given in terms of the second partial derivatives of the electric potential V of the other charges in the molecule, evaluated at the position of the centroid of the nucleus, by

$$F_0 = \frac{1}{2} V_{zz}, \quad (56a)$$

$$F_{\pm} = \mp (6)^{-1/2} (V_{zx} \pm iV_{zy}), \quad (56b)$$

$$F_{\pm 2} = \frac{1}{2}(6)^{-1/2} (V_{xx} - V_{yy} \pm i2V_{xy}), \quad (56c)$$

where the subscripts on V denote partial derivatives. If elements of the tensor in the laboratory coordinate system S are denoted by F_m , and elements in a principal body-coordinate system S_1 of the molecule are denoted by $F'_{m'}$, then

$$F_m = \sum_{m' = -2}^2 D_{mm'}^{2*}(g_1) F'_{m'}, \quad (57)$$

where g_1 denotes the Euler angles of S_1 with respect to S . The elements $F'_{m'}$ in the body-coordinate system are constants. Since V_{ij} is a real symmetric tensor, there is a body-coordinate system, say S'' , in which V_{ij} is diagonal, the only nonzero elements being V_{XX} , V_{YY} , and V_{ZZ} . The axes of S'' are labeled so that $|V_{ZZ}| \geq |V_{XX}| \geq |V_{YY}|$. Quantities eq and η are defined by

$$eq \equiv V_{ZZ}, \quad \text{and } \eta \equiv (V_{XX} - V_{YY})/V_{ZZ}. \quad (58)$$

The constant elements $F''_{m''}$ of F in S'' are then

$$F''_0 = \frac{1}{2} eq, \quad F''_{\pm 1} = 0, \quad F''_{\pm 2} = \frac{1}{2}(6)^{-1/2} \eta eq. \quad (59)$$

Let $g'' = \alpha''\beta''\gamma''$ be the Euler angles of S'' with respect to S_1 . Since the $F''_{m''}$ are given in terms of the $F'_{m'}$ by an equation similar to Eq. (57), it follows that

$$F_m = \sum_{m', m'' = -2}^2 D_{mm'}^{2*}(g_1) D_{m'm''}^{2*}(g'') F''_{m''}. \quad (60)$$

The matrix elements in the $|JbM\rangle$ representation can be obtained from Eq. (60). In the special case of a symmetric top molecule, the following result is obtained by use of Eq. (38):

$$\begin{aligned} & \langle J_2 K_2 M_2 \| F_m \| J_1 K_1 M_1 \rangle \\ &= C(J_1 2 J_2; M_1 m M_2) \langle J_2 K_2 \| F \| J_1 K_1 \rangle, \end{aligned} \quad (61)$$

in agreement with the Wigner-Eckart theorem, with reduced matrix element

$$\begin{aligned} & \langle J_2 K_2 \| F \| J_1 K_1 \rangle \\ &= [(2J_1 + 1)/(2J_2 + 1)]^{1/2} C(J_1 2 J_2; K_1, K_2 - K_1) \\ & \times \sum_{m'' = -2}^2 D_{K_2 - K_1, m''}^{2*}(g'') F''_{m''} \\ &= [(2J_1 + 1)/(2J_2 + 1)]^{1/2} C(J_1 2 J_2; K_1, K_2 - K_1) \\ & \times \left\{ \frac{1}{2} eq D_{K_2 - K_1, 0}^{2*}(g'') + \frac{1}{2}(6)^{-1/2} \eta eq \right. \\ & \left. \times [D_{K_2 - K_1, -2}^{2*}(g'') + D_{K_2 - K_1, 2}^{2*}(g'')] \right\}. \end{aligned} \quad (62)$$

Correlation functions of the quantities F_m occur in the theory of nuclear magnetic relaxation by quadrupolar interactions.¹⁶

VI. REMARKS

The principal results of this paper, Eqs. (13), (14), and (18), have been derived by use of just the transformation properties of irreducible tensor operators under rotations, the assumed invariance of the Hamiltonian under rotations, and the Wigner-Eckart theorem. Equation (13) shows that many of the possible correlation functions are zero, and Eqs. (14) and (18) show that the nonzero correlation functions can be expressed in terms of reduced matrix elements.

The form of the correlation functions given by Eq. (13) is, in itself, of importance in applications, since it sometimes can be used to reduce the number of unknown quantities in a theoretical expression sufficiently that the remaining unknown quantities can be evaluated by comparison of the theory with experimental results.

The calculation of the nonzero correlation functions remains a formidable task. However, the fact that only reduced matrix elements are required may facilitate the solution of this difficult problem. If so, the examples of reduced matrix elements given in Sec. V should be of use.

*This research was supported in part by a grant to the author from the National Science Foundation.

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⁴D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon Press, Oxford, England, 1962).

⁵Equations (3.16) and (3.17) of Ref. 3.

⁶Equation (12) is Eq. (3.7) of Ref. 3, corrected by insertion of $\Delta(j_1 j_2 j)$ in the right-hand side.

⁷Reference 4, p. 59.

⁸Reference 3, Sec. 18.

⁹Reference 3, Eq. (5.19c).

¹⁰Reference 3, Eq. (4.28a).

¹¹The expression (37) for the rotational eigenfunction of a symmetric top is derived in Sec. 2.5 of Ref. 4. The result quoted on p. 55 of Ref. 3 is not in agreement with this expression, and is apparently incorrect.

¹²Equation (38) is obtained from Eq. (4.62) of Ref. 3, corrected by inserting a factor of $4\pi^2$ in the right-hand side.

¹³Reference 3, Eqs. (5.19).

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