PHYSICAL REVIEW B VOLUME 4, NUMBER 7 1 OCTOBER 1971

Spin Hamiltonian of Low-Symmetry Crystalline Systems

K. M. Beem,* E. J. Hornyak,* and P. G. Rasmussen
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104
(Received 29 March 1971)

The spin Hamiltonian has been developed for paramagnetic species found in crystalline sites of low (less than axial) symmetry. A tensorial form of the Hamiltonian has been stressed in order to emphasize its primarily mathematical origin and to clarify symmetry constraints. The treatment of these constraints, due to both Kramers (time-inversion) and spatial symmetry, is general without restrictive assumptions concerning the strength of the applied magnetic field. It is only assumed that the field-dependent interactions of the states described by the spin Hamiltonian with all other states can be treated as small perturbations. It has been shown that the spin Hamiltonian possesses the symmetry of the actual Hamiltonian if and only if the transformation matrices of the actual and fictitious spin states differ by at most a phase for every symmetry operation. Specific applications are to those terms of the spin Hamiltonian usually sufficient to describe the (approximately) orbital singlet states of a transition-metal ion with a fictitious electronic spin $s \leq \frac{5}{2}$. However, the treatment may easily be extended to cover other terms, including those involving external electric fields and nuclear moments. Guidelines for the analysis and solution of the Hamiltonian matrix have been set out. Certain special reference frames of this Hamiltonian have been discussed, including and in particular the one designated by the symmetry axes of the orthorhombic point groups. The form of the Hamiltonian appropriate for this symmetry has been developed in detail. An operational definition of magnetic axes has been given and it has been shown that rotational studies can be effective in differentiating between orthorhombic, monoclinic, and triclinic site symmetries, when the paramagnetic ions substitute into several crystallographically equivalent sites.

INTRODUCTION

Although crystalline hosts have often been used in electron-spin-resonance (ESR) investigations, few attempts have been made to extract the maximum information from the data, at least in the case of the more complex paramagnets [such as Fe(III)] found in sites of low symmetry. Frequently spectra have been analyzed by means of a spin Hamiltonian appropriate for a higher symmetry and involving an insufficient number of parameters. The resulting errors in the analyses have been much larger than the experimental error, and opportunities to determine the site symmetries have been lost. In this work a general theory is presented, emphasizing symmetry constraints on the Hamiltonian, which is applicable to orthorhombic or lower symmetry. Specific applications are to systems described by fictitious electronic spins of $\frac{5}{2}$ or less.

In what follows, the conventions of Rose[1] pertaining to rotations are adopted. Unless indicated otherwise, transformations are passive. Summation over certain repeated indices will be assumed. These indices are the labels of the components of vectors, tensors, matrices, kets, and bras.

FUNDAMENTAL CONCEPTS

In a refined form of the spin-Hamiltonian method, an n-dimensional block of the actual Hamiltonian matrix is duplicated by the action of a function of magnetic field and angular momentum components (the spin Hamiltonian) on a basis of angular momentum eigenkets with $2j+1=n$. This angular momentum is generally referred to as the fictitious spin because it does not necessarily possess any direct relationship to the variables of the system. The spin Hamiltonian is not merely an operator equivalent since actual states, possibly of a very general nature, are replaced by pure spin states.

The problem of a paramagnetic crystal in an applied electromagnetic field may conveniently be treated by separating the total system into three parts: the system for which the spin Hamiltonian is to be defined, the (internal) environment of the system, and the applied field(s). The system is that portion of the crystal whose states contribute to the resonance spectrum. When dilute crystals are employed, the system may consist of the paramagnetic electrons of some unit such as an ion, as long as the energies of the paramagnetic units are independent. It is not necessary to assume that the paramagnetic electrons are restricted to any one nucleus, but only that they do not encounter, to any measurable extent, the electrons of another unit. Necessarily included in the system are all magnetic nuclei encountered by the paramagnetic electrons.

The environment of the system is the remainder of the crystal whose states and variables are assumed to be integrated out of the problem. The symmetry of the environment is the only factor of

importance here. With the use of doped single crystals, this is given by the point group of the paramagnetic site. There is no definite reason for this point group to be identical to the corresponding point group of the pure host crystal, especially if charge compensation is required. Before the external fields are applied, we can presume to have available the eigenkets $|\alpha_i^0\rangle$ of the zero-field Hamiltonian $\mathcal{H}^0$. Because of the complexity of the problem few characteristics of these kets can be determined. However, as will be shown, knowledge of the transformation properties of these kets with respect to the symmetry operators of the system is sufficient to allow a prediction of the gross features of the magnetic resonance spectra.

Magnetic resonance transitions occur between states separated by increments of energy which are small compared to most atomic and molecular parameters. Most states of a paramagnetic system are therefore removed from direct observation. With the introduction of an external magnetic field, excited states cannot be ignored in the most accurate treatment. If these states are removed from the n observable states by energies which are large compared to the field-dependent terms of the Hamiltonian, the interactions in question can be obtained by perturbation theory. Hereafter it will be assumed that n is chosen to include all excited states for which this is not true. These interactions are accounted for by assuming that the observable states are perturbed, giving the general kets

$$|\alpha_i\rangle = |\alpha_i^0\rangle + \sum_{j>n} |\alpha_j^0\rangle a_{ji}(\vec{B}) , \tag{1}$$

with $i = 1, \ldots, n$. The matrix of the real Hamiltonian $\mathcal{H}(\vec{B})$ within these kets is denoted $\underline{H}(\vec{B})$. The problem reduces to solving this matrix.

Kramers Transformation

Time inversion, first investigated by Kramers[2] and treated mathematically by Wigner,[3] among others, occupies a central role in the theory because it leads to an elegant and simple means of deducing general features of the spin Hamiltonian.[4,5] It is shown elsewhere[6,7] that an antilinear operator ($\mathcal{K}$, the Kramers operator) can be found which produces a transformation, for the stationary states of the system, analogous to classical time inversion. The position operators are unchanged, while momenta, including spin, change sign. Since zero-field Hamiltonians of the systems dealt with here are even functions of momenta, they commute with $\mathcal{K}$ and their eigenkets possess well-defined Kramers symmetry. With appropriate choices of phase,[8] the Kramers conjugates of angular momentum eigenkets are

$$\mathcal{K}\,|jm\rangle = (-1)^{j-m}|j-m\rangle . \tag{2}$$

The eigenkets of $\mathcal{H}^0$ belong to one of two possible classes, for which $\mathcal{K}^2 = \pm 1$. The sign depends on whether the system consists of an even or odd number of fermions. Using this property of $\mathcal{K}$, it is a simple matter to show that from any $2j+1$ eigenkets of $\mathcal{H}^0$, an orthonormal basis may be found with the kets possessing the Kramers conjugates of Eq. (2).[9] In general, the j and m are merely labels. An exception to the above occurs when $2j+1$ is even and $\mathcal{K}^2 = +1$.

Since the Hamiltonian $\mathcal{H}(\vec{B})$ is invariant to time inversion while $\vec{B}$ changes sign, the terms in $\mathcal{H}(\vec{B})$ must be even functions of momenta and field and we have $\mathcal{K}\mathcal{H}(\vec{B})\mathcal{K}^\dagger = \mathcal{H}(-\vec{B})$. The elements of the matrix $\underline{H}(\vec{B})$ are

$$H_{ik}(\vec{B}) = \langle\alpha_i|\,\mathcal{H}(\vec{B})\,|\alpha_k\rangle = \langle\alpha_i|\,(\mathcal{K}^\dagger\mathcal{K})\mathcal{H}(\vec{B})\,|\alpha_k\rangle ,$$

and their complex conjugates are

$$H_{ik}(\vec{B})^* = (\langle\alpha_i|\mathcal{K}^\dagger)\mathcal{H}(-\vec{B})(\mathcal{K}\,|\alpha_k\rangle) .$$

Let $\mathcal{K}_f$ be the product of $\mathcal{K}$ with an operator which reverses the direction of the external field. Then $\mathcal{H}(\vec{B})$ commutes with $\mathcal{K}_f$ and we have

$$H_{ik}(-\vec{B})^* = (\langle\alpha_i|\mathcal{K}_f^\dagger)\mathcal{H}(\vec{B})(\mathcal{K}_f\,|\alpha_k\rangle) . \tag{3}$$

The distinction between $\mathcal{K}_f$ and $\mathcal{K}$ is important for the kets of Eq. (1). Since $\mathcal{K}_f^2 = \mathcal{K}^2 = \pm 1$, we can again find an orthonormal basis which possesses standard Kramers conjugates with the same exception as before. Let the kets of such a basis be the

$$|sm\rangle = |\alpha_i\rangle A_{im} . \tag{4}$$

The label s is used instead of j to indicate that these are not necessarily eigenkets of some angular momentum.

The importance of these matters lies in the possibility of having real states behaving the same way with respect to the Kramers transformation as the pure spin states of the spin-Hamiltonian method. If this is true then the spin Hamiltonian must commute with $\mathcal{K}_f$. There is actually considerable freedom in the choice of the A_{im}; however, it will be seen that the choices are limited if it is desired to take advantage of spatial symmetry.

Irreducible Angular Momentum Tensors

The use of angular momentum tensor operators has become widespread in magnetic resonance studies because they provide the means of expressing the spin Hamiltonian in its most convenient form. In this section the operators tabulated by Koster and Statz[10] are presented in order to clarify

their properties. The operators $T_q^k(\vec{J})$ are defined to be irreducible with respect to rotations. Their transforms are

$$T_q^k(\vec{J}') = \mathcal{P}_R(\omega)\, T_q^k(\vec{J})\, \mathcal{P}_R(\omega)^\dagger = T_u^k(\vec{J})\, D_{uq}^k(\omega) \ . \quad (5)$$

They are said to be of the first kind with respect to $\vec{J}$, the total angular momentum of the system. An equivalent definition, involving the commutators of the tensor components with $\vec{J}$, has been given by Racah.[11] Tensors of the second kind commute with $\vec{J}$ and the rotation operators $\mathcal{P}_R(\omega)$. The first-order tensor is chosen to be $\vec{J}$ itself, with the contrastandard (Fano and Racah's definition[12]) irreducible components

$$T_0^1 = J_0 = J_z, \quad T_{\pm 1}^1 = J_{\pm 1} = \mp (2)^{-1/2}(J_x \mp i J_y) \ .$$

The tensors of order k are chosen to be the irreducible polynomials in the components of $\vec{J}$ of degree k and given by the coupling relations

$$T_q^k = T_m^l\, T_r^t \langle lmtr \,|\, kq \rangle \ , \quad (6)$$

for $k = l + t$. The T notation is reserved for tensors of this type. Since the $T_{\pm k}^k = (J_{\pm 1})^k$ are independent of the individual values of l and t, it follows from Racah's relations that the entire set of a given order is unambiguously defined by the above. These operators possess the following properties[13]:

(i) Their Hermitian conjugates are $(T_q^k)^\dagger = (-1)^{-q} T_{-q}^k$.

(ii) Their Kramers conjugates are $(T_q^k)^K = (-1)^{k-q} T_{-q}^k$.

(iii) Their matrices are given by the Wigner-Eckart theorem and are invariant to rotational transformations of the reference frame.

(iv) When the

$$\langle jm \,|\, T_k^k \,|\, j\, m-k \rangle = (2j+1)^{-1/2} \langle jm \,|\, k\, k\, j\, m-k \rangle \langle j \,||\, T^k \,||\, j \rangle$$

are evaluated, the reduced matrix elements are found to be

$$\langle j \,||\, T^k \,||\, j \rangle = 2^{-k} \left[\frac{k!\,(2j+k+1)!}{(2j-k)!\,(2k-1)!!} \right]^{1/2}$$

for $k \neq 0$, and unity for $k = 0$, where $(2k-1)!! = 1 \times 3 \times 5 \times \cdots \times (2k-1)$.

With the use of the Wigner-Eckart theorem and the unitary nature of the coupling coefficients, it can be shown that the $(2j+1)^2$ matrices for which $k \leq 2j$ constitute a complete, linearly independent set. This is the foundation of the spin-Hamiltonian method because a suitable linear combination of these matrices reproduces any square matrix of dimension $2j+1$.

SPIN HAMILTONIAN

The exact form of the n-dimensional matrix $\underline{H}(\vec{B})$ depends not only on the choice of reference frame, but also on the transformation matrix $\underline{A}$ of Eq. (4). In general, the elements $H_{mm'}$ are power series in the B_i and may be conveniently decomposed in terms of irreducible tensor components,

$$H_{mm'} = \sum_{l=0}^{\infty} \sum_{u} F(lu)_{mm'}\, C^{lu}(\vec{B}) \ . \quad (7)$$

The $C^{lu}(\vec{B})$ are the standard components of irreducible tensors of the second kind and are themselves power series in the B_i. If the field-dependent terms of $\mathcal{H}(\vec{B})$ are linear in $\vec{B}$, the C^{lu} result from rth-order perturbations with $r \geq l$ and $r + l$ even. Their rotational transforms and conjugates are given by

$$C^{lu}(\vec{B}') = C^{lv}(\vec{B})\, D_{vu}^l(\omega)^* \ ,$$

$$C^{lu}(\vec{B})^\dagger = (-1)^u\, C^{l-u}(\vec{B}) \ ,$$

$$\mathcal{K}_f\, C^{lu}(\vec{B})\, \mathcal{K}_f^{-1} = (-1)^{l+u} C^{l-u}(\vec{B}) \ .$$

The $F(lu)_{mm'}$ are elements of n-dimensional field-independent matrices and may be expressed as

$$F(lu)_{mm'} = \sum_{k=0}^{2j} b_u^{kl\,q} \langle jm \,|\, T_q^k \,|\, jm' \rangle \ ,$$

as long as n equals $2j+1$. Association of each of the $|sm\rangle$ with the corresponding angular momentum ket defines the spin Hamiltonian $\mathcal{H}_s$. We have

$$H_{mm'} = (H_s)_{mm'} = \langle jm \,|\, \mathcal{H}_s \,|\, jm' \rangle$$

and (8)

$$\mathcal{H}_s = \sum_{k=0}^{2j} \sum_{l=0}^{\infty} b_u^{kl\,q}\, T_q^k(\vec{J})\, C^{lu}(\vec{B}) \ .$$

The Hermitian property of the matrix $\underline{H}(\vec{B})$ requires that the parameters possess the form

$$b_u^{kl\,q} = (-1)^{q-u} (b_{-u}^{k\,l\,-q})^* \ . \quad (9)$$

Although it often happens that $s = j$ coincides with an approximate quantum number of the system, it should be emphasized that $\vec{J}$ may have little physical significance. Hereafter, it will be referred to as the fictitious spin or just spin vector.

A unitary change of basis in spin space generates a similarity transformation upon the spin-Hamiltonian matrix $\underline{H}_s$. For example, substitution of the spin kets of a rotated reference frame gives $\underline{H}_s' = \underline{D}^j(\omega)^\dagger \underline{H}_s \underline{D}^j(\omega)$. Because of the invariance of the $\langle jm \,|\, T_q^k \,|\, jm' \rangle$, this similarity transformation is obtained by substituting the $B_i' = R_{ij}(\omega) B_j$ and the

$$(b_u^{kl\,q})' = D_{pq}^k(\omega)^*\, b_v^{kl\,p}\, D_{vu}^l(\omega) \quad (10)$$

for the B_i and the $b_u^{kl\,q}$. Although we have $\underline{H}' = \underline{H}_s'$, if $\underline{A}' = \underline{A}\,\underline{D}^j(\omega)$ is substituted for $\underline{A}$ in Eq. (4), the $|sm\rangle'$ are not necessarily the appropriate kets of the rotated frame.

Because the matrix $\underline{H}_s(\vec{B})$ is defined for a certain reference frame, it will be useful to have available matrices which are functions of the field components B_i' of rotated frames. Since these matrices describe the same physical situation, they must be similar to $\underline{H}_s(\vec{B})$. Convenient choices are the $\underline{H}_s'$ defined above, which are obtained by rotations in spin and real space, as long as the spin Hamiltonian is assumed invariant to such transformations. In this sense, the reference axes of fictitious spin and real space are always assumed to coincide. The parameters are "double" irreducible tensors with respect to these rotations; their transforms are given by Eq. (10). As will be seen, the advantage obtained by these admittedly arbitrary choices is that possible similarities between fictitious spin and real space are emphasized.

Symmetry Constraints

The general spin Hamiltonian contains $(2j+1)^2$ independent parameters for each $C^{lu}(\vec{B})$. In order to determine to what extent possible environmental symmetry reduces this number, the transformation properties of the real kets $|sm\rangle$ must be established. If the variables of the system are transformed from one reference frame to another, $\mathcal{H}^0$ is unchanged provided that the environment is identical in the related frames. Let the operators which produce these transformations, the spatial symmetry operators of the paramagnetic site, be denoted $\mathcal{P}$. They commute with $\mathcal{H}^0$, but not with $\mathcal{H}(\vec{B})$, since they do not act on the field components. However, $\mathcal{H}(\vec{B})$ will commute with the $\mathcal{P}_f$ which are defined to be products of the $\mathcal{P}$ with operators which transform the field. If the transformed components are $B_i' = P_{ij}B_j$, it must be that $\mathcal{P}\mathcal{H}(\vec{B}) = \mathcal{H}(\underline{P}^{-1}\vec{B})\mathcal{P}$. Consideration of the elements of $\underline{H}(\vec{B})$ gives

$$H_{mm'}(\vec{B}) = \langle sm|\mathcal{H}(\vec{B})|sm'\rangle = \langle sm|(\mathcal{P}^\dagger\mathcal{P})\mathcal{H}(\vec{B})|sm'\rangle$$
$$= (\langle sm|\mathcal{P}^\dagger)\mathcal{H}(\underline{P}^{-1}\vec{B})(\mathcal{P}|sm'\rangle) .$$

Now if the field is reoriented so that the new components equal the B_i', we have

$$H_{mm'}(\vec{B}') = (\langle sm|\mathcal{P}_f^\dagger)\mathcal{H}(\vec{B})(\mathcal{P}_f|sm'\rangle) . \qquad (11)$$

Since the reorientation leaves the physical situation unchanged, $\underline{H}(\vec{B}')$ must at least be similar to $\underline{H}(\vec{B})$, and the transformation

$$\mathcal{P}_f|sm\rangle = |sm'\rangle U_{m'm}$$

must be unitary. From Eq. (1) it is seen that this transformation is the same as that which results from the $\mathcal{P}$ acting on the eigenkets of $\mathcal{H}^0$, as long as the latter follow Eq. (4). Therefore, the perturbed kets span the same irreducible representations (of the group of operators $\mathcal{P}_f$) as do the eigenkets of $\mathcal{H}^0$.

In the following, the $\mathcal{P}_f$ are limited to the rotation operators $\mathcal{P}_{Rf}(\omega)$. Using the same notation for the analogous operators of spin space, which involve the fictitious spin $\vec{J}$ rather than the total angular momentum of the system, we have

$$\mathcal{P}_{Rf}(\omega)|jm\rangle = \mathcal{P}_R(\omega)|jm\rangle = |jm'\rangle D^j_{m'm}(\omega) .$$

There is no reason for the $\underline{D}^j(\omega)$ to equal the transformation matrices $\underline{U}(\omega)$ of the real kets. The symmetry transformations of $\mathcal{H}(\vec{B})$ give the matrices

$$\underline{H}(\vec{B}') = \underline{H}_s(\vec{B}') = \underline{U}(\omega)^\dagger \underline{H}_s(\vec{B})\underline{U}(\omega) ,$$

with elements $(\langle jm|\mathcal{P}_{Rf}^\dagger)\mathcal{H}_s'(\mathcal{P}_{Rf}|jm'\rangle)$, where $\mathcal{P}_{Rf}\mathcal{H}_s = \mathcal{H}_s'\mathcal{P}_{Rf}$. On the other hand, the transformations in spin space chosen in the preceding section give the matrices

$$\underline{H}_s(\vec{B})' = \underline{D}^j(\omega)^\dagger \underline{H}_s(\vec{B})\underline{D}^j(\omega) ,$$

with elements $(\langle jm|\mathcal{P}_{Rf}^\dagger)\mathcal{H}_s(\mathcal{P}_{Rf}|jm'\rangle)$. In order for the spin Hamiltonian to commute with the $\mathcal{P}_{Rf}(\omega)$, the two similarity transformations must be identical $[\underline{H}_s(\vec{B}') = \underline{H}_s(\vec{B})']$ and the matrix $\underline{H}_s(\vec{B})$ must commute with $\underline{D}^j(\omega)\underline{U}(\omega)^\dagger$. A necessary and sufficient condition for this is

$$\underline{U}(\omega) = e^{i\Phi(\omega)}\underline{D}^j(\omega) , \qquad (12)$$

as long as $\mathcal{H}_s$ contains operators of odd k. (It is easily seen that the only matrices which commute with all $2k+1$ matrices having elements $\langle jm|T_q^k|jm'\rangle$, k odd, are multiples of the unit matrix.) If the relation (12) holds for every symmetry operation, then the spin Hamiltonian possesses all the symmetry of the real Hamiltonian. A similar argument indicates that the spin Hamiltonian commutes with the Kramers operator $\mathcal{K}_f$ unless j is a half-odd integer and the system consists of an even number of fermions. In the latter case, $\mathcal{H}_s$ possesses an unusual form.[14]

If the real and spin kets span the same irreducible representations, the $\underline{U}(\omega)$ and $\underline{D}^j(\omega)$ are at least similar and can be made equal with a suitable choice of the A_{im} of Eq. (4). We do not have to check on the validity of relation (12) for all symmetry operations, but only for the generators of the group. The most complex group under discussion is the octahedral group O which possesses two generators.[15] As examples, it can be shown that if the spin states transform as $\Gamma_4(j=1)$ or $\Gamma_6(j=\frac{1}{2})$, relation (12) holds for the entire group even though the real states transform as Γ_5 $(s=1)$ or Γ_7 $(s=\frac{1}{2})$. One notable exception occurs for Γ_7, Γ_8 $(j=\frac{5}{2})$ and Γ_6, Γ_8 $(s=\frac{5}{2})$.

Constraints on the b_u^{klq} are established because the symmetry operators do not transform these field-independent numbers. In order to have $\mathcal{H}_s = \mathcal{K}_f\mathcal{H}_s\mathcal{K}_f^\dagger$, it must be that

$$b_u^{klq} = (-1)^{k+l+q-u}(b_{-u}^{kl-q})^* = (-1)^{k+l}b_u^{klq} . \qquad (13)$$

The field and operator tensors must have the same parity. From symmetry rotations, we obtain

$$b_u^{klq} = D_{pq}^k(\omega)^* b_v^{klp} D_{vu}^l(\omega) = (b_u^{klq})' \ . \tag{14}$$

The Euler angles ($\alpha\beta\gamma \equiv \omega$) of these rotations are simplest when the original reference frame of $\underline{H}(\vec{B})$ is chosen to coincide with symmetry axes. $\underline{A}$ reflection through a plane is equivalent to an inversion followed or preceded by a rotation of π about the plane's normal which passes through the inversion center. The operator and field components are functions of pseudo-(axial)-quantities, and are unchanged by inversion. Therefore, the action of a symmetry reflection on $\mathcal{H}_s$ is equivalent to the rotation. Similarly, the action of an improper rotation is equivalent to that of the corresponding proper rotation, and the possible forms of the spin Hamiltonian of Eq. (8) are determined by the proper point groups.

The details of the system have been left unspecified because the form of the spin Hamiltonian depends only on the number of states involved, and the symmetry of these states and the actual Hamiltonian. When nuclear moments are present, $\vec{J}$ can be considered the total fictitious spin of the system. Alternatively, it is convenient to use "uncoupled" kets (eigenkets of fictitious electronic and nuclear spin), with $\mathcal{H}_s$ being a product of as many different tensor operators as there are independent parts of the system. This introduces a great many additional terms, but without any fundamental difference in treatment. An external electric field $\vec{E}$ is even (odd) with respect to time (space) inversion. If such a field is applied, or if ligand nuclear moments are present, certain constraints must be suitably modified. In particular, the constraints imposed by reflections and improper rotations do not duplicate those of proper rotations for the parameters of terms involving $\vec{E}$ or the ligand operators.

Analysis of Hamiltonian

For the remainder of this work it is assumed that s is the fictitious *electronic* spin label. Treating terms involving nuclear operators as perturbations upon the electronic spin Hamiltonian rarely constitutes a problem. In addition, it is assumed that $\mathcal{H}_s$ is linear in the magnetic field with $C^{00}=1$, $C^{1u}=B^u$, $C^{lu}=0$, $l>1$. The Hamiltonian of Eq. (8) is then

$$\sum_{k=0}^{2s} [\, b^{kq} T_q^k(\vec{J}) + b_u^{klq} T_q^k(\vec{J}) B^u \,] \ . \tag{15}$$

From Kramers symmetry, k must be even in the first part, odd in the second. The Zeeman term ($k=1$) is written in terms of Cartesian components as

$$\beta_0 g_{ij} B_i J_j \ , \tag{16}$$

where $\overleftrightarrow{g}$ is the electronic g tensor. The $k=3,5$ terms are those first postulated by Bleaney.[16] Since their presence has rarely been detected, they will not be included in the treatment. The terms with $k=0,2$ together constitute the quadratic form

$$D_{ij} J_i J_j \ . \tag{17}$$

The quantity $\overleftrightarrow{D}$ is usually referred to as the zero-field splitting tensor. The term with $k=4$ (allowed for $s \geq 2$) is not negligible for Fe(III), given normal experimental accuracy. The quantities $\overleftrightarrow{g}$ and $\overleftrightarrow{D}$ (along with hyperfine tensors) are second-rank Cartesian tensors with respect to the arbitrary transformations defined earlier. With $\overleftrightarrow{g}$ as an example, we have

$$(g_{il})' = R_{ij} g_{jk} R_{lk} \tag{18}$$

as the analog to Eq. (10), where $\underline{R}(\omega)$ is the vector transformation matrix. The rotational symmetry constraints are $\overleftrightarrow{g}' = \overleftrightarrow{g}$.

Computation of the spin-Hamiltonian matrix by use of the Wigner-Eckart theorem is quite simple, amounting to a determination of the appropriate coupling coefficients. The general matrix of zero-field parameters for $s=\frac{5}{2}$ is presented in Table I.

The availability of relatively simple matrix diagonalization computer programs, for real Hermitian matrices, eliminates much of the need for perturbation equations. In conjunction with transformations of the parameters, these programs provide excellent means of fitting magnetic resonance spectra. The g tensor is very nearly isotropic in many problems, particularly those in

TABLE I. The zero-field spin Hamiltonian matrix for $s=\frac{5}{2}$.

	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$
	1	2	4	7	11	16
		3	5	8	12	17
$\underline{H}_s^0 =$			6	9	13	18
				10	14	19
					15	20
						21

(1) = (21) = $3[6^{1/2}b^{20} - \frac{1}{7}(70^{1/2})b^{40}]$

(2) = $-$(20) = $-(20)^{1/2}[b^{21} + \frac{3}{7}(14)^{1/2}b^{41}]$

(3) = (15) = $6^{1/2}b^{20} - \frac{15}{7}(70)^{1/2}b^{42}$

(4) = (19) = $10^{1/2}[b^{22} + \frac{9}{7}(7)^{1/2}b^{42}]$

(5) = $-$(14) = $-(8)^{1/2}b^{21} + \frac{15}{7}(28)^{1/2}b^{41}$

(7) = $-$(18) = $-(180)^{1/2}b^{43}$

(8) = (13) = $18^{1/2}[b^{22} - \frac{5}{7}(7)^{1/2}b^{42}]$

(11) = (17) = $180^{1/2}b^{44}$

(9) = (12) = (16) = 0

(6) = (10) = 0, by choice

which the electronic ground states are approximately orbital singlets. In such cases, it is convenient to assume isotropy at the start. The Zeeman interaction possesses its simplest form when the field direction is taken as the z axis. The diagonal zero-field parameters ($q=0$) of such a reference frame can then be estimated using the high-field transitions. It may be that the transitions of a given orientation do not depend on the off-diagonal b^{kq} to any great extent. However, the diagonal parameters of other orientations are functions of all the b^{kq}. Convenient transformations of parameters are considered in the next section.

If possible, a transformation in spin space is chosen in order to have a real matrix. The operators T_q^k, J_z, and J_x have real matrices. Therefore, if the reference axes are chosen so that the b^{kq} are real and B_y is zero, the Hamiltonian matrix is real. Unfortunately, it is usually necessary to gather data from several orientations of the field. For low symmetry, it will be impossible to have a real matrix in all situations. In order to solve the Hermitian complex matrix $\underline{C}=\underline{A}+i\underline{B}$, note that the supermatrix

$$\underline{M}=\begin{pmatrix}\underline{A} & -\underline{B}\\ \underline{B} & \underline{A}\end{pmatrix}$$

is real and symmetrical. Since the eigenvalues of $\underline{M}$ are those of $\underline{C}$, each repeated once, the problem is solved by diagonalizing the matrix of dimension $4s+2$.

Miscellaneous Transformations

The matrix $\underline{H}(-\vec{B})^*$ of Eq. (3) is similar to $\underline{H}(\vec{B})$ because the Kramers transformation is (anti)-unitary. Since $\underline{H}(\vec{B})^*$ is also a similar matrix, mere reversal of the field's direction is a similarity transformation and magnetic resonance spectra must display 180° periodicity as the field is perpendicularly rotated about *any* axis. Since the Hamiltonians $\mathcal{H}_s$ and $-\mathcal{H}_s$ are equally valid (the parameters are fitted to energy *differences*), the above result indicates that the absolute signs of the zero-field parameters b^{kq} are not directly determinable from the resonance spectra. However, they can be observed by noting changes in relative intensities of fine-structure transitions as the temperature is lowered.

The relative sign of b^{20} and b^{40} (and b^{22} and b^{42}) is always important because these parameters occur in the same matrix elements. With simple Hamiltonians it is easily seen that the absolute sign of b^{22} is inconsequential; the parameter occurs in even powers in an expansion of the secular determinant. One must be careful not to overgeneralize this case; the problem should be approached by considering whether certain sign changes are similarity transformations of the matrix. For example, a rotation of $\frac{1}{2}\pi$ about the z axis gives $(b^{kq})'=(-1)^{(1/2)q}\,b^{kq}$; therefore, the sign of b^{22} is unimportant only if the field is collinear with the z axis and the parameters of odd q vanish. The usual convention is to choose b^{22} positive in a convenient reference frame. A reversal of this sign must be accompanied by any additional changes in $\mathcal{H}_s$ brought on by the interchange of the x and $-y$ axes. A rotation of π about the z axis gives $(b^{kq})'$ equal to $(-1)^q b^{kq}$. Since the part of the Zeeman term involving the operators J_x, J_y also changes sign, a change of sign of all matrix elements of odd Δm is a similarity transformation.

APPLICATIONS TO LOW SYMMETRY

In the remainder of this work, some of the effects due to low-symmetry environments are considered. The spin Hamiltonian, given by Eq. (15), with $s=\frac{5}{2}$, is assumed to possess the symmetry of the true Hamiltonian. If possible, the reference axes of the Hamiltonian are chosen to be symmetry axes with the z the major axis (if any).

Special Reference Frames

Through use of relations such as Eq. (10), the spin Hamiltonian may be expressed in terms of any special reference frame, including those unrelated to symmetry, in which the number of independent parameters is reduced. Ignoring symmetry for the moment, the most useful special frames are the principal axes of second-rank Cartesian tensors.

Symmetric ($D_{ij}=D_{ji}$) and real second-rank tensors always possess principal axes; that is, an orthogonal reference frame may be found in which the off-diagonal components vanish and the diagonal components (principal values) are real. It follows from Kramers symmetry that tensors such as $\overleftrightarrow{D}$ and $\overleftrightarrow{g}$ are real. The Hermitian property of the spin Hamiltonian demands that $\overleftrightarrow{D}$ (but not $\overleftrightarrow{g}$) be symmetric. The D_{ij} are functions of the irreducible parameters b^{00} and the b^{2q}. Since the former is proportional to the isotropic trace of D, it does not affect the spectra and can be ignored. The principal axes belong to the second-order parameters which form the anisotropic part of $\overleftrightarrow{D}$. The two independent parameters of the principal axis frame are b^{20} and $b^{22}=b^{2-2}$, the coefficients of the terms $(\frac{3}{2})^{1/2}[J_z^2-\frac{1}{3}J^2]$ and $J_x^2-J_y^2$, respectively. The utility of this reference frame will become apparent in the next section, where it will be shown that symmetry can designate the location of these axes.

The g tensor is potentially asymmetric and does not necessarily possess principal axes. In the cases in which $\overleftrightarrow{g}$ is found to be nearly isotropic, it seems reasonable to ignore asymmetry. It has been proven that the effects of asymmetry are small as long as the anisotropy of the tensor is small, at least for the simple problem in which the

Hamiltonian consists solely of the Zeeman term.[17]

Orthorhombic Hamiltonian

All point symmetry operations can be expressed as either proper rotations or products of proper rotations with spatial inversion. Because a Hamiltonian such as that given by Eq. (8) is invariant to spatial inversion, the constraints resulting from the products duplicate those of the appropriate proper rotations. Therefore, in order to determine the special forms of such a Hamiltonian, we need consider only the proper point groups O, T, and C_n, D_n, $n=2,3,4,6$.

The unique constraints on the parameters result from a simplest set of generators, the minimum number of symmetry operators which generate the group. This number is 2 for the orthorhombic group D_2 and convenient choices of generators are the twofold rotations about the z and y axes. Using the analog of Eq. (14) for zero-field parameters ($l=0$), we find that an n-fold symmetry rotation about the z axis gives the constraint

$$b^{kq}=e^{i2q\pi/n}b^{kq}\ . \tag{19}$$

Nonvanishing parameters therefore have $|q|/n=0,1,2,\ldots$. The constraint resulting from a twofold rotation about the y axis is

$$b^{kq}=d^k_{pq}(\pi)\,b^{kp}=(-1)^{k-q}b^{k-q}=(b^{kq})^*\ .$$

Equations (9) and (13) have been used. The zero-field parameters appropriate for the group D_2 are real and have $|q|$ even (or zero). It is easily seen that the Cartesian tensors of the spin Hamiltonian are diagonal (with possibly independent principal values) as long as the symmetry axes of the group D_2 are chosen as the reference axes; a twofold rotation about the ξ axis gives

$$g_{\xi\eta}=g'_{\xi\eta}=-g_{\xi\eta}$$

for $\xi\neq\eta$. These symmetry axes are the principal axes of the Cartesian tensors as well as the b^{2q}.

This particular form of the spin Hamiltonian can be called orthorhombic because it depends on the point symmetries D_2, C_{2v}, or D_{2h} which distinguish crystals of the orthorhombic class from the lower monoclinic or triclinic classes. Besides requiring the coincidence of principal axis frames, this form is convenient because the Hamiltonian matrix is real as long as the field lies in the xz plane. Because the Hamiltonian [$k=1,2,4$ in Eq. (15)] contains as many as eight independent parameters, data from several field orientations will be needed for a complete analysis. The most useful orientations are those with the field along a symmetry axis; the Zeeman interaction can be diagonalized without disturbing the form of the Hamiltonian. In order to take advantage of these factors, the transformations of parameters which result from relabeling of the symmetry axes are needed. Let the symmetry axes be labeled as

$$(x,y,z)=(z',x',y')=(-x'',z'',y'')$$

if the b^{kq} are the zero-field parameters of the original frame, the transformed parameters are

$$(b^{kq})'=b^{kp}D^k_{pq}(0,\tfrac{1}{2}\pi,\tfrac{1}{2}\pi)^*=e^{iq(1/2)\pi}b^{kp}d^k_{pq}(\tfrac{1}{2}\pi)$$

and

$$(b^{kq})''=b^{kp}D^k_{pq}(\tfrac{1}{2}\pi,\tfrac{1}{2}\pi,\tfrac{1}{2}\pi)^*=e^{i(1/2)\pi(q+p)}b^{kp}d^k_{pq}(\tfrac{1}{2}\pi)\ .$$

All three sets possess the orthorhombic form. The irrational numbers involved in the transformations can be eliminated (with the original set as an example) by the substitutions $D=(\frac{3}{2})^{1/2}b^{20}$, $E=b^{22}$, $c^0=70^{1/2}b^{40}$, $c^2=7^{1/2}b^{42}$, $c^4=b^{44}$. In all three sets the b^{kq} and b^{k-q} are equal. The quantities D and E are the usual second-order parameters found in the literature, the coefficients of the terms $J_z^2-\frac{1}{3}J^2$ and $J_x^2-J_y^2$. The primed transformations are given in Table II; other transformations differ only by certain signs.

Although the orthorhombic Hamiltonian contains convenient simplifications, these do not justify its use in all low-symmetry problems; this form has occasionally been used when the reference axes of the Hamiltonian were merely not related by symmetry ($x\neq y\neq z$). However, for symmetries less than orthorhombic, certain of the constraints cannot be shown to apply. In particular, if the pertinent point symmetry is C_2 (or C_{2h}, C_s), which can be called monoclinic after the crystal class which cannot possess higher point symmetry, the imaginary parts of the b^{kq} and the xy and yx components of Cartesian tensors do not have to vanish. Additionally, the asymmetry $g_{xy}\neq g_{yx}$ may be present. The other orthorhombic constraints hold as long as the twofold symmetry axis, which is one principal axis of all Cartesian tensors, is retained as the z axis. If the point symmetry of the problem is C_1 or C_i (triclinic), the only constraints on the parameters are those given by the Hermitian and Kramers properties of the spin Hamiltonian.

Spectral Symmetry

Identical spectra are obtained from experiments with field orientations related by symmetry. This spectral symmetry, the observable result of con-

TABLE II. The rhombic transformations for rotations of Euler angles $(0,\frac{1}{2}\pi,\frac{1}{2}\pi)$.

$D'=\frac{3}{2}E-\frac{1}{2}D$
$E'=\frac{1}{2}E-\frac{1}{2}D$
$c^{0\prime}=\frac{1}{8}(3c^0-20c^2+70c^4)$
$c^{2\prime}=\frac{1}{8}(c^0-4c^2-14c^4)$
$c^{4\prime}=\frac{1}{16}(c^0+4c^2+2c^4)$

straints such as Eq. (14), can be different from the environmental symmetry. For example, if the spectrum possesses an angular periodicity of $2\pi/n$ as the field is rotated, the axis of rotation can be either an n-fold proper or the appropriate improper symmetry axis. It may well be that the spectral symmetry is higher than required because certain key parameters are negligible. For example, the trigonal, tetragonal, and hexagonal forms (those dependent on the groups D_3, D_4, D_6) of the spin Hamiltonian are identical for $s \leq 1$. This spin Hamiltonian is axial; the spectrum possesses cylindrical symmetry about the major axis. The above holds true for $s = \frac{3}{2}$ as well when the Zeeman term alone adequately describes the field interactions. In exactly the same situations, the cubic groups O and T demand an isotropic Hamiltonian.

Spectra obtained from the field orientations (θ, ϕ) and $(\theta, \phi + \pi)$ must be identical when the z is a twofold symmetry axis. Therefore, as the field is rotated about any direction in the xy plane, the resonant field strengths of every line in the spectrum must pass through extreme values as the field's direction passes through the twofold axis, which can then be called a magnetic axis of the spin Hamiltonian and the spectrum. The spin Hamiltonians appropriate for the point symmetries D_2, D_4, D_6, O, and T necessarily possess at least one orthogonal set of magnetic axes. This result of twofold symmetry is more useful than the 180° angular periodicity in determining the symmetry of the spin Hamiltonian, since, as we have already observed, spectra always possess the 180° periodicity (due to Kramers symmetry), as long as the field remains perpendicular to the axis of rotation. In the next section, an application of these concepts is presented.

Magnetically Inequivalent Sites

It is quite common to find several paramagnetic sites which are crystallographically equivalent and possess a common crystal axis. Unless the Hamiltonian of each site is axially symmetric about the common axis, the sites are magnetically inequivalent for general orientations of the field, with nonsuperimposed spectra. This can be valuable in determining the individual site symmetry.

The case of six sites with parallel and equivalent z axes is considered here; the treatment also includes two and three equivalent sites and is easily extended to four. When the field orientation with respect to a given site is (θ, ϕ_1), the orientations with respect to the equivalent axes of the other sites are given by (θ, ϕ'), where the ϕ' differ from ϕ_1 by π, $\pm\frac{1}{3}\pi$, or $\pm\frac{2}{3}\pi$. Useful information can be obtained from the following orientations:

(i) $\theta = 0$. All sites are magnetically equivalent in this orientation, giving superimposed spectra. This can be used as an aid in alignment of the crystal.

(ii) $\theta = \frac{1}{2}\pi$. The Hamiltonians of the pairs of sites with $\Delta\phi = \pi$ differ, but only in that the field's direction is reversed. These pairs are then equivalent with three groups of possibly inequivalent sites.

(iii) $0 < \theta < \frac{1}{2}\pi$. For general ϕ, there may be six magnetically inequivalent sites. However, the field orientations for the pairs with $\Delta\phi = \pi$ differ by a rotation of π about the z axis. These pairs are then equivalent as long as the latter is a magnetic axis (a twofold or a normal to a symmetry plane). In this case, as in the second example, resolution of each transition into at most a triplet is possible.

(iv) If the field is aligned along the x axis of the first site ($\theta = \frac{1}{2}\pi$, $\phi_1 = 0$), the sites having $\phi' = \pm\frac{1}{3}\pi$, $\pm\frac{2}{3}\pi$ are all equivalent as long as either the x or the y is a magnetic axis. We then see that if triplets coalesce to doublets, monoclinic symmetry is indicated, with the twofold or normal perpendicular to the common axis of the sites.

(v) With the field lying in the xz or yz plane, doublets will again be observed as long as the x, y, and z axes are magnetic axes. This is a sensitive indication of orthorhombic symmetry.

It should be emphasized that the above results depend only on Kramers symmetry and twofold symmetry axes or symmetry planes. The equivalencies are proven by showing that the field's orientation with respect to one site can be obtained from that with respect to another site by one or a combination of these symmetry transformations.

It is seen that rotational studies can be effective in differentiating between orthorhombic, monoclinic, and triclinic site symmetries, when the paramagnetic ions substitute into several crystallographically equivalent sites. An example for which this is true is ferric iron doped into β-eucryptite ($LiAlSiO_4$).[18,19] The analysis of the ESR spectra of this system will be presented in a later paper.

---

*Present address: Corporate Research Laboratories, Owens-Illinois Technical Center, P. O. Box 1035, Toledo, Ohio 43601.

[1]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957), p. 48.

[2]H. A. Kramers, Proc. Koninkl. Ned. Akad. Wetenschop. 33, 959 (1930).

[3]E. P. Wigner, Gött. Nachr. Math.-Phys. Kl., p. 546 (1932).

[4]J. S. Griffith, *Theory of Transition Metal Ions* (Cambridge U. P., Cambridge, England, 1964), p. 205.

[5]J. S. Griffith, Mol. Phys. 3, 80 (1960).

[6]A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1966), Vol. II, p. 664.

[7]E. P. Wigner, *Group Theory* (Academic, New York, 1959), p. 325.
[8]E. P. Wigner, in Ref. 7, p. 345.
[9]K. M. Beem, Ph.D. dissertation (University of Michigan, 1969), p. 8 (unpublished).
[10]G. F. Koster and H. Statz, Phys. Rev. 113, 445 (1959).
[11]G. Racah, Phys. Rev. 62, 442 (1942).
[12]U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1959), p. 20.
[13]K. M. Beem, in Ref. 9, p. 10.
[14]J. S. Griffith, Phys. Rev. 132, 316 (1963).
[15]J. S. Griffith, *Theory of Transition Metal Ions* (Cambridge U. P., Cambridge, England, 1964), p. 154.
[16]B. Bleaney, Proc. Phys. Soc. (London) A73, 939 (1959).
[17]R. F. Schneider, J. Chem. Phys. 48, 4905 (1968).
[18]K. M. Beem, in Ref. 9.
[19]E. J. Hornyak, Ph.D. dissertation (University of Michigan, 1969) (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 7 1 OCTOBER 1971

Theory of Electron-Surface-Plasmons Interactions in Tunneling, Low-Energy-Electron Diffraction, and Photoemission*

K. L. Ngai
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173
and
E. N. Economou†
James Franck Institute, University of Chicago, Chicago, Illinois 60637
(Received 27 October 1970)

A general theory of surface-plasmon excitation by electrons in the cases of electron tunneling, low-energy-electron diffraction, and photoemission is developed. Particular emphasis has been given to the physical concepts related to the electron-surface-plasmon interaction. The inelastic-tunneling current due to surface-plasmon emission in semiconductor-metal junctions has been calculated in detail. The surface-plasmon contributions to the inelastic spectra in low-energy-electron diffraction and to the energy distribution curves of photoemitted electrons have also been evaluated. The theory involves essentially a single parameter which determines the magnitude of the Landau damping of the surface plasmons. Using the value for this parameter as deduced from Feibelman's theory, we obtain in all cases good agreement with available experimental results, both in magnitude and line shape.

I. INTRODUCTION

A well-known property of an electron gas is its capacity to undergo collective motions, i.e., plasma oscillations (PO). The properties of these oscillations in the case of one material extending over the whole space were the subject of considerable experimental and theoretical work.[1-3] In addition to these bulk plasma oscillations (BPO), the existence of surfaces separating materials with different electronic properties introduces new modes of plasma oscillations localized around the surfaces which are called surface-plasma oscillations[4] (SPO) or surface plasmons (SP). The SPO can interact with electrons (or charged particles in general) and photons and consequently may show a considerable influence on the observable characteristics of many systems. Thus the existence of SPO has been proved experimentally, through measurement of electron energy loss,[5] u.v. radiation,[6] transition radiation,[7,8] low-energy-electron diffraction (LEED),[9,10] photoemission,[11] and superconducting tunneling.[12-14] Recently, excitations of plasmons in a degenerate semiconductor by tunneling electrons have been observed in metal-semiconductor junctions[15,16] although there is some disagreement about the interpretation of the experiments.[15-17]

There are some basic differences between bulk and surface plasmons[4]: (a) In BP, charge density is different from zero inside the material while in SP only surface charge density exists. (b) The BP are accompanied by electrostatic fields [i.e., no coupling to the transverse part of the electromagnetic (em) fields] while the fields created by SP show a mixed character having both transverse and longitudinal components. (c) The dispersion relation for BP is generally determined only by the properties of the material while for SP the geometry plays a dominant role in determining their dispersion relations. (d) The electrostatic fields associated with BP are confined strictly inside the material where the charge oscillations take place while the fields created by SP are extended outside the materials responsible for their existence.

Plasmons exist as well-defined collective excitations as long as the wavelength of the oscillations is longer than a characteristic length of the order of magnitude of the interelectronic separation. For