Electric Multipole Interactions between Rare-Earth Ions*

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(Received 3 August 1967)

In calculations of electrostatic coupling effects between rare-earth ions, it is generally assumed that the electric quadrupole-quadrupole term is much larger than the corresponding interactions between higher-degree multipole moments. In this paper we point out that the relative importance of the higher-degree terms may be enhanced by electrostatic shielding and induced-moment effects similar to those affecting single-ion crystal-field terms, and we derive the Hamiltonian operators for the l-l' multipole interactions up to sixth degree. Comparison with the observed single-ion crystal fields also suggests that electric multipole interactions might be relatively important throughout the rare-earth series and not only for the larger light ions, as is often assumed. For pairs of Kramers ions at low temperatures ($S'=\frac{1}{2}$), the various multipole interactions will contribute in second order to different terms of an effective spin Hamiltoniam of the form $\mathbf{S}_i' \cdot \mathbf{K} \cdot \mathbf{S}_j'$, and the resulting interaction tensor $\mathbf{K}$ will generally be quite anisotropic, subject only to symmetry. There also a corresponding anisotropic contribution to the magnetic g tensor, whose principal values and axes may thus be different from those of the single ions. Detailed multipole calculations are prohibitively complicated in the general case, and unless it can be shown that the higher-degree terms are in fact negligible, the observable interaction parameters in any particular case must therefore be treated as strictly empirical quantities, restricted only by symmetry.

1. INTRODUCTION

ELECTRIC multipole interactions (EMI) between rare-earth ions are of importance both for optical energy transfer processes[1-4] and for effective spin-spin and Zeeman interactions[5-8] in rare-earth salts and rare-earth metals.[9,10] In the calculations of such effects it has generally been assumed that the successive terms of a given parity are each a factor of the order of $\langle r^2 \rangle / R^2 \approx 1/100$ smaller than the preceding one, (r=radius of $4f$ electron orbit and R=ionic separation), so that no terms beyond the electric quadrupole-quadrupole interaction (EQQ) need be considered. It is well known, however, that if similar considerations are applied to the electrostatic crystal field completely erroneous results are obtained. Indeed, in most low-symmetry cases the sixth-degree terms are found to be of the same order of magnitude as the second-degree terms. In this paper we discuss the probable relative sizes of the different EMI terms in light of recent experimental and theoretical work on crystal fields, and we consider some of the complex effects which could result from appreciable higher-degree terms. In Sec. 2 we derive a general spin Hamiltonian for EMI's up to sixth degree acting within a given J manifold and in Sec. 3 we discuss some of the difficulties in calculating reliable values for the different coefficients. Some of the ob-

servable effects which could result from the higher-degree EMI's are discussed briefly in Sec. 4.

2. ELECTRIC MULTIPOLE INTERACTION HAMILTONIAN

The classical energy of interaction between electric multipoles may readily be found by expanding the Coulomb interaction.[11] Let us consider two charge distributions 1 and 2, centered about origins O_1 and O_2 with coordinate axes (x_1, y_1, z_1) and (x_2, y_2, z_2), chosen to be parallel and such that x_1 and x_2 lie in the bond-axis plane, that is, the plane defined by the z axis and the line joining O_1 and O_2 (see Fig. 1). The distance from O_1 to O_2 is defined as $\mathbf{R}$ and the angle between $\mathbf{R}$ and the z_1 axis as θ_0. The separation between two typical electrons i and j belonging to charge distributions centered around O_1 and O_2, respectively, is defined as r_{ij}. In terms of spherical harmonics centered about O_1 and O_2, respectively, the electrostatic interaction energy

$$V_{12} = \sum_{i,j} (e^2/r_{ij}) \qquad (1)$$

is then given by

$$V_{12} = e^2 \sum_{i,j} \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} \frac{(-)^{l'} r_i{}^l r_j{}^{l'}}{R^{l+l'+1}}$$

$$\times \sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} B_{ll'}{}^{mm'} Y_{l+l'}{}^{-m-m'}(\theta_0, 0)$$

$$\times Y_l{}^m(\theta_i, \phi_i) Y_{l'}{}^{m'}(\theta_j, \phi_j), \qquad (2)$$

where

$$B_{ll'}{}^{mm'} = \frac{(-)^{m+m'}(4\pi)^{3/2}}{[(2l+1)(2l'+1)(2l+2l'+1)]^{1/2}}$$

$$\times \left(\frac{(l+l'+m+m')!(l+l'-m-m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!} \right)^{1/2}$$

* Supported in part by the U.S. Atomic Energy Commission.
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and where the Y_l^m are the same as the $\Theta(l, m)$ $[\exp(im\phi)/(2\pi)^{-1/2}]$ defined by Condon and Shortley.[12] The above expression is based on the assumption that the two charge distributions are well separated so that $r < R$, and it is only valid in that approximation.

The corresponding spin Hamiltonian for V_{12} acting within a J manifold of an f-electron configuration may now be obtained by introducing the transformation

$$\sum_i r_i{}^l (4\pi/2l+1)^{1/2} Y_l^m(\theta_i, \phi_i) \rightarrow \chi_l \langle r^l \rangle \tilde{O}_l^m, \quad (3)$$

where the $\tilde{O}_l^m$ are the Racah operator equivalents defined by Buckmaster[13,14] and the χ_l are the reduced matrix elements as defined by Elliott and Stevens.[15] The corresponding spin Hamiltonian is therefore given by

$$\mathcal{H}_{12} = \sum_{l, l'=2,4,6} A_{ll'} \sum_{m, m'} Q_{ll'}{}^{mm'} \tilde{O}_l^m(1) \tilde{O}_{l'}{}^{m'}(2), \quad (4)$$

where

$$A_{ll'} = \frac{e^2 \chi_l(1) \chi_{l'}(2) \langle r_1{}^l \rangle \langle r_2{}^{l'} \rangle}{\epsilon_{ll'} R^{l+l'+1}}$$

and

$$Q_{ll'}{}^{mm'} = (-)^{m+m'+l'} \left(\frac{4\pi}{2l+2l'+1} \right)^{1/2}$$

$$\times \left(\frac{(l+l'+m+m')!(l+l'-m-m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!} \right)^{1/2}$$

$$\times Y_{l+l'}{}^{-m-m'}(\theta_0, 0).$$

Terms in which l or l' are either odd or greater than 6 will only have matrix elements outside the $4f$ configuration, and we shall neglect them here. This is equivalent to neglecting configuration mixing, which is generally small.

In some cases it is more convenient to choose axes which are not parallel (for example, when the two charge distributions have axial symmetry about different axes) and one may then transform the operators in Eq. (4) using the fact that the Racah operators $\tilde{O}_l^m$ transform under rotations like normalized spherical harmonics.[14]

For the particular simple case in which O_{z1} and O_{z2} are both parallel and collinear, that is, $\theta_0 = 0$, the general Hamiltonian reduces to

$$\mathcal{H}_{12} = \sum_{l, l'=2,4,6} A_{ll'} \sum_m Q_{ll'}{}^{m-m} \tilde{O}_l^m(1) \tilde{O}_{l'}{}^{-m}(2), \quad (5)$$

[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England 1935), p. 52.
[13] H. A. Buckmaster, Can. J. Phys. **40**, 1670 (1962). The $\tilde{O}_l^m$ are related by simple normalizing factors to the more usual O_l^m, which are much less convenient in a problem of the present kind.
[14] For a complete set of matrix elements of the $\tilde{O}_l^m$, see R. J. Birgeneau, Can. J. Phys. **45**, 3761 (1967).
[15] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).
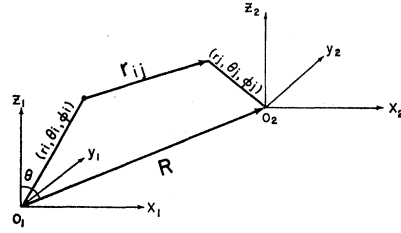

FIG. 1. Orientation of coordinate axes for charge distributions centered around O_1 and O_2.

where

$$Q_{ll'}{}^{m-m} = \frac{(-)^\nu(l+l')!}{\{(l+m)!(l-m)!(l'+m)!(l'-m)!\}^{1/2}}$$

and $A_{ll'}$ is defined as above.

In the expressions for the $A_{ll'}$ we have followed the usual practice of introducing effective dielectric constants $\epsilon_{ll'}$ to represent in the simplest possible way the complex effects of other ions in the solid. This approximation is clearly very crude, since it neglects completely the microscopic nature of the possible shielding and enhancement effects and in particular their spatial anisotropy. However, even in this very simplest form it introduces six essentially independent constants, and any further refinement is quite unwarranted at the present time. In fact, as we shall see in the next section, there are so many other uncertainties in the estimation of the individual coefficients that any present applications of the full Hamiltonian must be restricted to qualitative rather than detailed quantitative predictions. The only really effective improvement would be to treat the set of factors $A_{ll'} Q_{ll'}{}^{mm'}$ as empirical constants, as is commonly done for the $A_l^m \langle r^l \rangle$ in crystal-field calculations, but in the most general case this would here introduce up to 729 different parameters! In cases of high symmetry and low angular momentum the number of constants might perhaps become more tractable. However, for the present, we shall use the scalar dielectric constant approximation and consider some of the other more important factors.

3. ESTIMATES OF THE COUPLING PARAMETERS

A. Relative Magnitudes

Let us first consider the relative sizes of successive terms in Eq. (4) for two charge distributions *in vacuo*. In most cases the different reduced matrix elements will not be very different, and the ratios of successive even parity terms will therefore be approximately $\langle r^{l+2} \rangle / R^2 \langle r^l \rangle$, which may be further approximated by $\langle r^2 \rangle / R^2$, where $\langle r^2 \rangle$ is the mean-square f-electron radius and R is the separation between the two interaction ions. For rare-earth salts R is typically 5 Å, and this ratio is approximately 1/100. On this simple model then one would expect the lowest-degree term in Eq. (4), the electric quadrupole-quadrupole interaction (EQQ), to

completely dominate over the succeeding terms in the series, and indeed most analyses to date have been carried out on that assumption.

In reality, however, the simple *in vacuo* approximation may be a very poor one, as is well known in similar calculations of static crystal fields. For these there exists ample experimental evidence that second-, fourth-, and sixth-degree terms are often comparable and a great deal of theoretical and experimental work has been carried out in an effort to understand the discrepancy from the simple theory. It is probably fair to say that these attempts have so far been only partially successful, but a number of potentially important mechanisms have been identified, and it is of interest to consider whether these same effects might also enhance the higher-degree EMI terms.

1. Linear and Nonlinear Shielding

The $4f$ electrons in rare-earth ions are shielded by the filled $5s$ and $5p$ shells, and a number of workers have considered the effect of this shielding in great detail.[16-21] It is found that the second-degree terms are reduced by 50 to 75%, whereas the fourth- and sixth-degree terms are only slightly affected. The linear shielding effects may be readily incorporated into the EMI scheme by replacing $\langle r^l \rangle$ in Eq. (4) by $\langle r^l \rangle (1-\sigma_l)$, where σ_l is the appropriate linear shielding factor. Linear shielding will therefore change the ratio of successive terms by a factor $(1-\sigma_{l+2})/(1-\sigma_l)$ so that, for example, the ratio of the 2-4 to the 2-2 pole terms is enhanced by a factor of about 3.

The effects of nonlinear shielding are much more difficult to categorize.[20] In general, they will probably also enhance the higher-degree terms somewhat, but as yet neither the theoretical nor the experimental situations are clear enough to make a definite statement.

2. Induced Moments

In insulating crystals it is also necessary to take into account the polarizability of the ligands, since the resultant induced moments may make an important contribution to the net electrostatic interaction.[22-25] The simplest model for calculating these effects is one in which the ligands are approximated by point charges

and induced point dipoles and quadrupoles. It is found, however, that the point-multipole model is not capable of explaining either the relative sizes of the crystal-field terms for a given ion or the systematic trends of the crystal-field terms between the ions.[24] An alternative suggestion has been offered by Burns,[25] who pointed out that it is probably incorrect to treat the ligand polarizability effects by *point* multipoles of low order, and that instead one should treat them as more extended charge distributions. The induced dipole, for example, should thus be approximated by an extended dipole made up of plus and minus charges located at the "surface" of the ligand. Detailed quantitative calculations based on this model seem prohibitively difficult. However, Burns has been able to show that both the relative sizes of the V_4^0 and V_6^0 terms and their variation over the rare-earth series in a given isostructural lattice are reasonably explained on the assumption of extended induced multipoles.

It is clear that induced moment effects will be of equal importance for the EMI. Their main effect will be to enhance the size of the higher multipole interactions relative to the EQQ, since they effectively reduce the separation R, and rough estimates indicate that they could easily make the 4-4, 4-6, and 6-6 multipole interactions approximately equal. The detailed polarizability effects are obviously very complicated, but to a first approximation we can take them into account through the different dielectric constants $\epsilon_{ll'}$, which may be substantially less than unity.

3. Overlap and Covalency

Recently it has been shown that overlap and covalency effects are qualitatively important for the understanding of crystal fields.[26-28] For the EMI, on the other hand, covalency should only enter via the $\langle r^l \rangle$ and this effect should be rather small. Thus, in making any analogy between crystal fields and EMI terms, it is important to assess the importance of covalency. The most complete calculations in a low symmetry case have been carried out for $PrCl_3$. One group, Ellis and Newman,[28] obtain rather remarkable agreement with experiment using a model which takes into account only the contributions from the immediately surrounding ligands, and the validity of this approximation has been discussed in detail by Freeman and Watson.[27] On the other hand, a completely opposite result has been obtained by Ray and co-workers,[24,29] who have carried out calculations in which the effects of overlap (actually only the Coulombic part) are

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[17] C. J. Lenander and E. Y. Wong, J. Chem. Phys. **38**, 2150 (1963).

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[27] See R. E. Watson and R. J. Freeman, Phys. Rev. **156**, 251 (1967), for an extensive list of references on covalency in rare-earth salts.

[28] M. M. Ellis and D. J. Newman, Phys. Letters **21**, 508 (1966).

[29] A. K. Raychaudhuri and D. K. Ray, Proc. Phys. Soc. (London) **90**, 839 (1967).

added to the point-multipole contributions, and they find that the agreement with experiment is actually worsened. Most importantly, in these latter calculations the relative sizes of the successive crystal-field terms are not changed from those predicted by the point-multipole model.

From an experimental point of view there is some evidence for the predominantly ionic electrostatic model, at least for the second-degree terms. Comparisons of the electric field gradients seen by the nuclei and by the $4f$ electrons give values of the ratios close to those calculated on simple electrostatic shielding models, indicating that covalency may not be so important, at least for the lower-degree terms.[20,21,27] However, there is no comparable evidence for the higher-degree crystal-field terms for which the large enhancement is observed experimentally.

The role of overlap and covalency is therefore not at all clear at present. If these effects are in fact responsible for most of the enhancement of the higher-degree crystal-field terms, it would imply that the induced-moment and shielding effects are correspondingly less important, suggesting that they may also be less important for the enhancement of the higher-degree EMI terms. However, for the present there is insufficient evidence to reach any definite conclusions on this.

4. Cancellation Effects

In comparing ratios of crystal-field parameters with ratios of EMI terms it is also important to consider the effects of cancellation of the different contributions to the crystal-field parameters. Point-multipole calculations indicate that the $A_2^0 \langle r^2 \rangle$ term is nearly always the result of a partial cancellation of several large terms even in cases where the symmetry is far from cubic,[16,24] but that this tends to be less important for the higher-degree crystal-field parameters. Thus, even though it is found experimentally that $A_2^0 \langle r^2 \rangle$, $A_4^0 \langle r^4 \rangle$, and $A_6^0 \langle r^6 \rangle$ are all comparable, this does not imply that the individual contributions to these terms are necessarily of the same order of magnitude. In general, an estimate of the EMI terms based on a direct comparison with corresponding crystal-field parameters would thus tend to overestimate the higher-degree EMI terms, but the importance of cancellation effects can only really be assessed from detailed calculations in any particular case.

We see from all this that it is in fact impossible at the present time to make any reliable estimates of the strengths of the different EMI terms, but it does seem fairly clear that the higher-degree terms may well be comparable with the lower-degree (EQQ) terms in some cases. If some of the present controversies concerning the origins of the static crystal-field effects could be resolved by further theoretical or experimental work it might become possible to apply the same considerations to the multipole interaction terms. For the present time, though, we must conclude that the parameters $A_{ll'}$ in Eq. (4) should be treated as parameters to be determined by experiment and that there is no *a priori* reason for considering only the EQQ terms.

B. Absolute Magnitudes

In order to assess the possible observable effects which may result from a general EMI Hamiltonian we can make the very rough estimate that the different $A_{ll'}$ parameters may generally be comparable, and we can estimate the absolute order of magnitude from the EQQ coefficient deduced from EPR measurements on Ce^{3+} in $LaCl_3$.[8] In our notation this gives $A_{22} \approx 0.06$ cm^{-1}, which agrees within a factor of 2 with the value ~ 0.03 cm^{-1} obtained by simple substitution of typical values into Eq. (4), with ϵ_{22} set equal to one. This agreement might be somewhat fortuitous, as the earlier experiments should really be reanalyzed in the light of possible higher-order EMI effects, but it suggests that general order of magnitude is probably correct. If we take into account the Q parameters and the matrix elements of the $\tilde{O}_l^m$ operators we find for the matrix elements of a typical term in Eq. (4) values of the order of 1 to 10 cm^{-1}. Of course there will be considerable variations due to the many factors which contribute to any specific term and in particular many terms will be identically zero by virtue of special symmetry conditions. This is perhaps just as well, as the completely general Hamiltonian contains up to 729 independent terms! However, even in simplest case there will still be very many terms, and unless one can show that most of them are quantitatively negligible one must face a very complex situation.

In the light of all these difficulties it seems somewhat futile to speculate how the EMI terms will vary between different ions, but it is perhaps worth noting that if it should turn out that the analogy with the static crystal field is, in fact, valid, we would expect a relatively slow and smooth variation across an isostructural series such as the rare-earth ethyl sulfates. This would be in contradiction with previous speculations[5] which have postulated that electrostatic interactions (specifically EQQ) should be much more important for the lighter rare earths because of their larger radial extent.

4. OBSERVABLE EFFECTS OF HIGHER-ORDER EMI TERMS

It is clear that the possibility of higher-order EMI terms adds a significant complication to an already difficult problem. Unless it can be proved experimentally or theoretically that all the higher-order terms are in fact negligible, any detailed analysis of their relative strengths becomes extremely difficult. It is most important therefore to consider the *qualitative* effects which they could produce. We consider these separately for optical energy transfer processes, for magnetic

spin-spin coupling, and for their effect on the magnetic g values.

A. Nonradiative Energy Transfer Processes

The higher-degree EMI effects differ from EQQ interactions in two important respects: they have matrix elements between a much wider range of ionic states (ΔL, ΔJ, $\Delta M \leq \pm 6$, against ΔL, ΔJ, $\Delta M \leq \pm 2$) and they vary more rapidly with ionic separation. The first of these increases by a considerable factor the number of channels by which energy-transfer processes can proceed and this in turn would generally shorten lifetimes. Conversely a given energy-transfer rate could be explained by appreciably weaker electric interactions. The second effect would complicate to a considerable extent the interpretation of experiments on the concentration dependence of energy-transfer processes.[3] However, the observable effects do not appear to be very sensitive to the details of the range dependence of the interactions,[4] and it is doubtful whether the higher-order terms would in fact make very noticeable contributions, except perhaps at high concentrations.

From a practical point of view it would appear therefore that the principal effect of higher-order multipole interactions would be to allow relaxation via otherwise forbidden transitions. A possible measure of their importance could thus be obtained from the fluorescence of a mixed system in which the co-dopant is such that the only energy-matched relaxation channels are ones with $\Delta J > 2$.

B. Effective Spin-Spin Interactions

From the point of view of magnetism the EMI terms will have two important effects: In first order they will add to the static crystal field and produce shifts of energy levels relative to an isostructural but magnetically dilute system, and these shifts will vary with temperature according to the thermal population of the interacting ions.[6] The magnitudes of the shifts will depend on the effective number of interacting neighbors and given our above estimate for typical matrix elements it could well amount to between 1 and 10 cm^{-1}. If only the EQQ terms are important the shifts would be correspondingly smaller. Such shifts could be particularly interesting in systems which have two or more low-lying states which are almost degenerate and of the appropriate symmetry, as it is then possible that the interactions could lead to a phase transition similar to that postulated by Blume for the case of UO_2.[6,30]

In second order the different EMI terms will act as an effective spin-spin coupling mechanism between ions with degenerate (Kramers) states, as discussed extensively by various authors for the case of quadrupole-

quadrupole terms.[5-8] Although it might seem initially that the idea of a purely electrostatic coupling mechanism producing spin-spin interactions between time reversed doublets is a violation of Kramers theorem, closer examination reveals that this is not so. Briefly, the effective spin-spin interaction arises from those higher-order processes in which both ions are coupled to excited states. The pair wave function then may not be factorized into a single product of two single-ion wave functions and the pair must therefore be regarded as a single system with an even number of electrons. Kramer's theorem then no longer requires doubly degenerate energy levels. As in the case of the energy-transfer processes, the principal effect of the new higher-order terms arises from the larger number of states which may be coupled by the operators with larger m values. However, in addition to a quantitative difference, this may here also make a qualitative difference, as we may readily see from the form of the second-order expressions for the interaction energies.

Let us consider two interacting ions with ground-state doublets $|\pm G_1\rangle$ and $|\pm G_2\rangle$ and excited doublets $|\pm E_{1i}\rangle$ and $|\pm E_{2j}\rangle$, at energies E_i and E_j. Following earlier EQQ calculations[7,8,31] we write the matrix element for the effective interaction between, say, $|G_1G_2\rangle$ and $|G_1'G_2'\rangle$ in terms of the second-order expression

$$\sum_{E_iE_j} \frac{\langle G_1G_2 | \mathcal{3C}_{12} | E_{1i}E_{2j}\rangle \langle E_{1i}E_{2j} | \mathcal{3C}_{12} | G_1'G_2'\rangle}{-(E_{1i}+E_{2j})}$$

$$\equiv \langle G_1G_z | \mathcal{3C}_{\text{eff}} | G_1'G_2'\rangle, \quad (6)$$

taking proper care of degeneracies, as discussed by Baker.[7] The effective spin Hamiltonian may be expressed in the usual general form

$$\mathcal{3C}_{\text{eff}} = \mathbf{S_1'} \cdot \mathbf{K} \cdot \mathbf{S_2'}, \quad (7)$$

where $\mathbf{S_1'}$ and $\mathbf{S_2'}$ are effective spin-$\frac{1}{2}$ operators which represent the two ground-state doublets. From Eq. (6) it is immediately obvious that the presence of higher-order terms will allow contributions from many more excited states, and in addition it will contribute many new types of *cross terms* between the two factors in the numerator. Since the $\mathcal{3C}_{12}$ in each factor may generally contain up to 729 different terms the number of nonzero cross terms for any given intermediate state $|E_{1i}E_{2j}\rangle$ will usually be considerable! The major effect of the cross terms will thus be to ensure appreciable contributions from most or all of the combinations of $|G_1G_2\rangle$ and $|G_1'G_2'\rangle$ (subject only to symmetry) and in practice this implies that most of the components of the interaction tensor $\mathbf{K}$ will generally be nonzero.

Let us consider, for example, the very simple cases of Ce^{3+} in either $CeCl_3$ or cerium ethyl sulfate for which the ground state is an almost pure $|J=\frac{5}{2}, J_z=\pm\frac{5}{2}\rangle$

[30] M. Blume, Phys. Rev. **141**, 517 (1966). We are grateful to Dr. Blume for pointing out to us the possible similarity to the UO_2 case.

[31] R. J. Birgeneau, thesis, Yale University, 1966 (unpublished).

doublet. The EQQ interaction acting alone can only couple states with $|\Delta M| \leq 2$, and in second order it can therefore give nonzero values only for the diagonal interaction terms corresponding to K_{zz}. In third order other terms become possible but these will generally be quite negligible. If we include higher-degree EMI terms there will be many additional contributions such as, for example,

$$\frac{\langle \tfrac{5}{2}, -\tfrac{5}{2} \mid \tilde{O}_2{}^1 \tilde{O}_2{}^{-1} \mid \tfrac{3}{2}, -\tfrac{3}{2} \rangle \langle \tfrac{3}{2}, -\tfrac{3}{2} \mid \tilde{O}_4{}^4 \tilde{O}_4{}^{-4} \mid -\tfrac{5}{2}, +\tfrac{5}{2} \rangle}{2E_{3/2}},$$

which corresponds to a coupling between the effective spins of the form $[(K_{xx}+K_{yy})/2]S_{1+}'S_{2-}'$. There will generally be many such contributions which may have positive or negative signs, and we must therefore expect the tensor **K** to have a completely general form, subject only to limitations imposed by symmetry. Thus if the pair has at least threefold rotational symmetry about one axis the final interaction spin Hamiltonian must have the form

$$\mathcal{3C}_{\text{eff}}{}^{\text{axial}} = K_{\|} S_{1z}' S_{2z}' + K_{\perp}/2(S_{1+}'S_{2-}' + S_{1-}'S_{2+}')$$
$$+ K_a/2(S_{1x}'S_{2y}' - S_{1y}'S_{2x}'), \quad (8)$$

and since $S_1' = S_2' = \tfrac{1}{2}$ this can be further simplified by a suitable rotation of axes to give

$$\mathcal{3C}_{\text{eff}}{}^{\text{axial}} = K_{\|} S_{1z}' S_{2z}' + K_{\perp}'/2(S_{1+}'S_{2-}' + S_{1-}'S_{2+}'), \quad (9)$$

where $K_{\perp}' = (K_{\perp}^2 + K_a^2)^{1/2}$. If there is a reflection plane or center of symmetry K_a will be zero for all choices of axes. In cases of lower symmetry the tensor **K** can, and generally will, have a generally anisotropic form which can be transformed to

$$\mathcal{3C}_{\text{eff}} = K_{x'x'} S_{1x}' S_{2x}' + K_{y'y'} S_{1y}' S_{2y}' + K_{z'z'} S_{1z}' S_{2z}'$$

by a suitable choice of axes. The interactions in the general case are thus determined by six essentially independent parameters.

The possibility of cross terms can also make significant quantitative differences in cases in which some of the multipole moments are relatively small, if such terms can combine with other larger terms. In particular, if it should turn out that the quadrupole-quadrupole terms are, in fact, somewhat larger than the higher-degree multipole terms it may nevertheless be possible for second-order cross terms involving, say, $O_2{}^m O_2{}^{m'}$ and $O_2{}^{m''} O_4{}^{m'''}$, to be comparable with terms involving products of four $O_2{}^m$ operators. In a similar way it is also possible that weak electric dipole terms, allowed when configuration mixing is included, may contribute significantly to some of the cross terms. Another complication of the same sort is the possibility of cross terms with spin-phonon coupling terms.[7] These generally have the same form as our EMI Hamiltonian and because of time reversal they normally also act only in

second order. However, if it should happen that they are comparable in some particular case with the electric multipole terms, significant cross terms could result. Yet another kind of cross term which may be important in some cases involves the *magnetic* dipole-dipole coupling. This interaction can of course act in first order, but it may also combine in second order with both spin-phonon and EMI terms. In general such effect will be small but in some cases they may not be entirely negligible.

We see from all this that there can be very many different contributions to the **K** tensor, so that reliable estimates of the components can be made only in very special cases. Typical values may range anywhere between plus and minus a few tenths of 1 cm^{-1} and, in general, it is certainly safer to treat all the nonzero components as a set of independent parameters to be determined experimentally.

C. Effective *g*-Value Shifts

In addition to the second-order cross terms involving different interaction terms, there can also be cross terms between some of the EMI terms and the Zeeman terms corresponding to an applied field. These will be qualitatively similar to the cross terms involving the EQQ interactions described by Birgeneau et al.,[8] and they will produce similar shifts in the EPR pair spectra. The effects are proportional to the field and can be described by adding extra terms to the magnetic *g* tensor. In general, these extra terms will be quite anisotropic and for any one particular pair they will have principal axes which are not necessarily related to those of the magnetic *g* tensors of the individual ions. As in the case of the **K** tensor the general situation is therefore quite complicated, but it may again be simplified appreciably by symmetry. The effect of the extra cross terms on the magnetic bulk properties may be further simplified by cancellations, so that the low-field magnetic susceptibility, for example, can still be expressed in terms of three effective *g* values corresponding to fields applied along the principal axes. Like the first-order crystal field shifts, the *g*-shift terms will also depend on temperature, corresponding to the thermal population of excited states which have different multipole moments. This effect will generally be hard to observe since there will usually be a corresponding decrease in the relaxation time which will broaden microwave-resonance transitions, but it may be possible to detect changes using optical measurements and high magnetic fields. However, similar temperature-dependent shifts can also arise from changes in the static crystal field arising from simple lattice expansion and care must be taken in interpreting any such measurements.

5. CONCLUSIONS

The principal point raised by this paper is the question whether higher-degree electric multipole interac-

tions may be important in ionic rare-earth compounds (and perhaps also in other systems). It is found that there are a number of competing effects which may or may not point to a relative enhancement of the higher-degree terms, but there is certainly no clear cut evidence that they are negligible compared with the usually considered electric quadrupole-quadrupole interactions. The effect of higher-degree terms on optical nonradiative energy-transfer processes is shown to be largely quantitative rather than qualitative, any observable effects arising principally from the less stringent selection rules resulting from the extra higher-degree terms. The effects on magnetic properties are also similar to those produced by the lower-degree quadrupole terms, except for the fact that the extra terms may produce appreciable contributions to components of the interaction and g-value tensors which are otherwise zero or very small. Unless it can be shown, therefore, that the higher-degree electric multipole terms are in fact negligible one must expect a completely general form for both the effective spin-spin interaction, $\mathbf{S}_i' \cdot \mathbf{K} \cdot \mathbf{S}_j'$ and the Zeeman interaction $\mu_B \mathbf{H} \cdot (\mathbf{g}_i \cdot \mathbf{S}_i' + \mathbf{g}_j \cdot \mathbf{S}_j')$ describing a pair of $S' = \frac{1}{2}$ ions. We have not considered situations of higher degeneracy or the case of non-Kramers ions but the same sort of complications will apply. The calculation of the components of the $\mathbf{K}$ and $\mathbf{g}$ tensors will generally be very difficult but in favorable cases they may be simplified appreciably by symmetry which, as always, remains as the only reliable guide to the possible anisotropy.

ACKNOWLEDGMENTS

Coherent Field Dynamics in First- and Second-Order Processes

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(Received 5 July 1967)

The problem of the interaction of a beam of radiation in a coherent state and an atomic system is investigated. A complete set of states of the field is introduced, called displaced stationary states, which are found to be particularly convenient in dealing with first- and second-order processes such as dispersion, Raman scattering, single and double emission, and absorption. In this formalism the resonant conditions for the occurrence of processes which have their counterpart in ordinary first- and second-order perturbation theory (where the state of the field is assumed to be a stationary state) are found in a natural way. In addition, a description is indicated of physical situations which are peculiar to coherent field dynamics and thus have no such counterpart. The coherence properties of the displaced stationary states are analyzed. It is shown under which experimental conditions (such as appropriate photon correlation methods) it would appear to be possible to verify whether the displaced stationary states indeed provide a good description of the underlying dynamics. The formalism can readily be extended to higher-order processes.

I. INTRODUCTION

IN quantum optics, with the advent of the laser, one faces the problem of describing elementary first- and second-order processes such as absorption and emission, dispersion and Raman effect, and double absorption and emission. If one treats the output of the laser as a coherent state (in the sense of Glauber[1]) and considers the interaction of such a state with a material system such as an atom or molecule, one is faced with the problem of the coherent state (unlike the stationary state with a definite number of photons) not being an eigenstate of the unperturbed Hamiltonian

of the radiation field. The problem one faces is to find a representation of the Schrödinger equation suitable to convey a physically meaningful description of the atomic system interacting with the coherent field. In Sec. II, we introduce a complete set of states of the radiation field, the displaced stationary states, which we arrive at by carrying out a unitary transformation of the Schrödinger equation and representing the transformed equation in Fock space. In Sec. III, we deal with the problem of absorption and emission when the atomic system is interacting with a coherent field or with a displaced stationary state field. We find that in addition to a description bearing a close resemblance to the usual one prevailing when the initial

[1] R. J. Glauber, Phys. Rev. **131**, 2766 (1963).