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An Evaluation of the Accuracy of Calculating Hyperfine Interactions for *f* Electrons Using the "Point-Dipole Approximation"

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An exact calculation of the hyperfine interaction tensor between a ligand nucleus and f electrons was carried out for: an f^7 ion, an f^{13} ion in a crystal field environment of octahedral symmetry for the two twofold degenerate states, and for an f^{13} and an f^1 ion in a crystal field environment with a tetragonal component. Comparison of the calculated hyperfine tensor to the tensor calculated for a "point magnetic dipole" show small but significant differences for distances > 0.2 nm. The deviations produce a pseudoisotropic term which for nearest neighbors is small in magnitude (~6%) to that found experimentally but for next nearest neighbors is equal in magnitude to that reported experimentally. It was shown that errors of 1 to 2 pm in position coordinates are likely to result whenever hyperfine interactions plus the "point-dipole" equations are used to measure coordinates of nuclei relative to any lanthanide ion (except an f^7 ion).

INTRODUCTION

In ENDOR and EPR analyses of the hyperfine interaction between a lanthanide ion and a nearby ligand nucleus the results are generally expressed in terms of a spin Hamiltonian of the form

$$\mathscr{H} = \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S} - g_N\mu_N\mathbf{B}\cdot\mathbf{I}, \qquad [1]$$

where μ_B and μ_N are the Bohr and nuclear magnetons, respectively, $\mathbf{B}$ is the magnetic field vector, $\mathbf{I}$ is the nuclear spin operator in units of $\hbar$, and $\mathbf{S}$ is the fictitious spin operator in units of $\hbar$. The quantities $\mathbf{g}$ and $\mathbf{A}$ are, in principle, nonsymmetric tensors. Most lanthanide systems studied by ENDOR and EPR have a Kramer doublet for a ground state and these systems are considered to have a fictitious spin of 1/2. In the special case of Gd^{3+} and Eu^{2+}, which have the f^7 configuration, S is taken to be 7/2.

The largest part of the A tensor comes from the dipolar interaction between the nuclear spin and the spin and angular momentum of an electron in an f orbital centered on the lanthanide ion. It has been an "article of faith" in all analyses of

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experimental hyperfine results involving lanthanides that the dipolar contribution to **A** can be calculated with high accuracy using the "point-dipole approximation." In this approximation the *f* electron is regarded as a point magnet with anisotropies in the magnetic moment represented by the *g* tensor. Thus the dipolar contribution to **A** is given by the equation

$$A_{\alpha\beta} = (g_N \mu_N \mu_B R^{-3}) g_{\alpha\beta}(3n_\alpha n_\beta - \delta_{\alpha\beta}), \qquad [2]$$

where R is the distance between nucleus and lanthanide ion, n_α is the direction cosine for the R vector, and $g_{\alpha\beta}$ is an element in the g tensor.

Analytical methods have been recently developed (*1–3*) to calculate the dipolar contribution exactly. These methods have been used to calculate NMR shifts for *d* electrons in transition metal complexes and the results vary significantly from the "point-dipole" values for distance up to 0.7 nm. It might be expected that *f* orbitals will produce less significant deviations but this needs to be checked. The significance of such a check can be appreciated when it is realized that ENDOR (*4–6*) and NMR (*7–10*) studies are appearing in which nuclear coordinates are being obtained from hyperfine interactions using the "point-dipole" equations. Accuracies of 5 pm are quoted in the NMR studies and of 0.5 pm or better in the ENDOR studies. It appears essential that the accuracy of the "point-dipole approximation" used in these studies be critically examined for *f* electrons. This we have undertaken and the results are reported herein.

THEORY

General Procedure

The hyperfine interaction between a nuclear spin **I** and an electron consists of two terms: (1) a dipolar interaction with electron spin **s** and (2) an interaction with the orbital angular momentum **l** of the electron. It can be written in the form (*2*)

$$\mathscr{H}_{\mathrm{IS}} = \sum_i P'\{\mathbf{I}\cdot\mathbf{T}(i)\mathbf{s}_i + r_{\mathrm{N}i}^{-3}\mathbf{I}\cdot\mathbf{l}_i\}, \qquad [3]$$

$$T_{\alpha\beta} = (3r_{\mathrm{N}\alpha}r_{\mathrm{N}\beta} - r_{\mathrm{N}}^2\delta_{\alpha\beta})/r_{\mathrm{N}}^5, \qquad [4]$$

$$P' = 2g_{\mathrm{N}}\mu_e\mu_{\mathrm{N}}. \qquad [5]$$

For calculating hyperfine terms it is convenient to rewrite Eq. [3] as

$$\mathscr{H}_{\mathrm{IS}} = \mathbf{I}\cdot\mathbf{P}, \qquad [6]$$

$$P_\alpha = P' \sum_i \{T_{\alpha x}(i)s_{xi} + T_{\alpha y}(i)s_{yi} + T_{\alpha z}(i)s_{zi} + r_{\mathrm{N}}^{-3}l_{\alpha i}\}. \qquad [7]$$

In calculating the hyperfine parameters, we start with a ground state of $(2S + 1)$ functions which we label as $|M_S\rangle$, where M_S is the approximate azimuthal quantum number of fictitious spin S. By comparing matrix elements of Eq. [1] with those of Eq. [6] we can obtain the expressions

$$A_{\alpha z} = \langle M_S|P_\alpha|M_S\rangle/M_S, \qquad [8]$$

$$A_{\alpha x} = \{\langle M_S + 1|P_\alpha|M_S\rangle + \langle M_S|P_\alpha|M_S + 1\rangle\}/(S^2 + S - M_S^2 - M_S)^{1/2}, \qquad [9]$$

$$A_{\alpha y} = i\{\langle M_S + 1|P_\alpha|M_S) - \langle M_S|P_\alpha|M_S + 1\rangle\}/(S^2 + S - M_S^2 - M_S)^{1/2}. \qquad [10]$$

Equations [8] to [10] are used to obtain the hyperfine parameters in the spin Hamiltonian given in Eq. [1].

The electronic wave functions $|M_S\rangle$ are expressed in terms of single f orbitals f_m which we will write as Slater orbitals

$$f_m = \{(2\beta)^9/8!\}^{1/2} r^3 e^{-\beta r} Y_{3m}(\theta, \phi), \qquad [11]$$

where $Y_{3m}(\theta, \phi)$ are the spherical harmonics.

The integrals in Eqs. [8] to [10] are two center integrals with $T_{\alpha\beta}$ and l_α given in a coordinate system centered at the nucleus and f_m expressed in a coordinate system on the lanthanide ion. These integrals were evaluated exactly using methods developed by Golding and Stubbs (*1*) in which the f_m functions are transformed onto the nuclear coordinate system.

Configuration of f^7

The method of calculation can be illustrated, in part, by giving some details for the rather simple ^8S state of f^7. The $|M_S\rangle$ functions for the ground state are of the form

$$|7/2\rangle = (7!)^{-1/2} \det |f_3^+ f_2^+ f_1^+ f_0^+ f_{-1}^+ f_{-2}^+ f_{-3}^+|, \qquad [12]$$

$$|5/2\rangle = (7\cdot 7!)^{-1/2}\{\det |f_3^- f_2^+ f_1^+ f_0^+ f_{-1}^+ f_{-2}^+ f_{-3}^+| + \det |f_3^+ f_2^- f_1^+ f_0^+ f_{-1}^+ f_{-2}^+ f_{-3}^+| + \cdots\}, \qquad [13]$$

where superscripts + and − refer to the spin state. Since P_α is a sum of one-electron operators, we obtain

$$A_{\alpha z} = \frac{2}{7} \sum_m \langle f_m^+ | P_\alpha | f_m^+ \rangle, \qquad [14]$$

$$A_{\alpha x} = \frac{1}{7} \sum_m \{\langle f_m^+ | P_\alpha | f_m^- \rangle + \langle f_m^- | P_\alpha | f_m^+ \rangle\}, \qquad [15]$$

$$A_{\alpha y} = \frac{i}{7} \sum_m \{\langle f_m^+ | P_\alpha | f_m^- \rangle - \langle f_m^- | P_\alpha | f_m^+ \rangle\}. \qquad [16]$$

We have found it convenient to use real functions. For $m \neq 0$ all f_m functions can be written

$$f_m = (2)^{-1/2}\{\phi_j + i\phi_k\}, \qquad [17]$$

where ϕ_j and ϕ_k are real functions. We now define the terms

$$T_{\alpha\beta}^{jk} = \langle \phi_j | T_{\alpha\beta} | \phi_k \rangle, \qquad [18]$$

$$L_\alpha^{jk} = \langle \phi_j | r_N^{-3} l_\alpha | \phi_k \rangle. \qquad [19]$$

Since $T_{\alpha\beta}^{jk} = T_{\alpha\beta}^{kj}$ and $L_\alpha^{jk} = -L_\alpha^{kj}$, we find

$$\langle f_m | T_{\alpha\beta} | f_m \rangle = (T_{\alpha\beta}^{jj} + T_{\alpha\beta}^{kk})/2, \qquad [20]$$

$$\langle f_m | r_N^{-3} l_\alpha | f_m \rangle = iL_\alpha^{jk} = -\langle f_{-m} | r_N^{-3} l_\alpha | f_{-m} \rangle. \qquad [21]$$

Equation [21] causes the summation over L_α terms to drop out giving

$$A_{\alpha\beta} = \frac{1}{7} \sum_{j=0}^{6} T_{\alpha\beta}^{jj} = \{(2\beta)^9/(8!)4\pi\} \int r^6 T_{\alpha\beta} e^{-2\beta r} d\tau. \qquad [22]$$

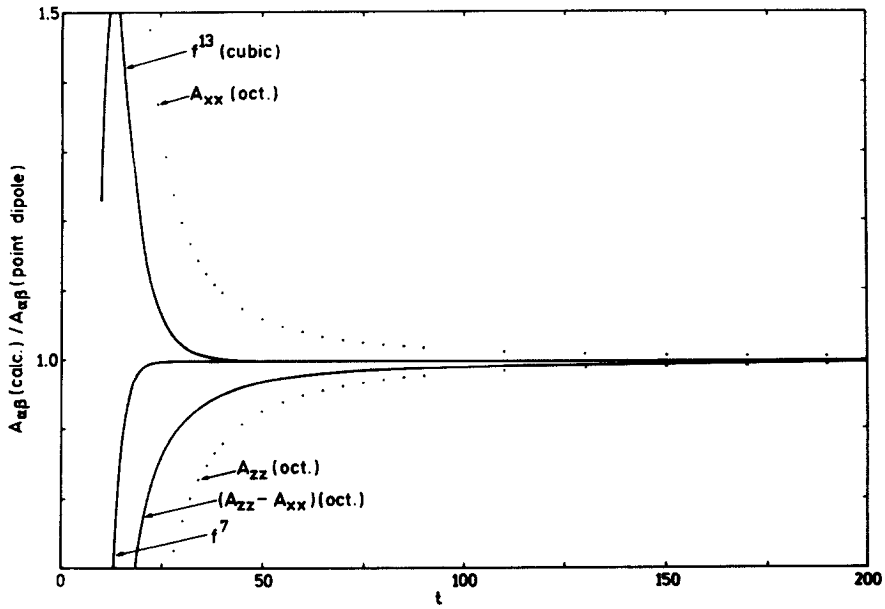

FIG. 1. Plot of the ratio of $A_{\alpha\beta}$ calculated exactly to that calculated from the "point-dipole" model as a function of t (which is defined in text). Ratio is plotted for f^{13} in a cubic crystal field, f^{13} in an octahedral crystal field, and for f^7.

From Eq. [22] we see that the trace ($\sum A_{\alpha\alpha}$) of the hyperfine tensor is zero because $\sum T_{\alpha\alpha} = 0$. Thus no isotropic component will appear at any separation. This results from the spherical symmetry of the f^7 configuration of ^8S state and is not a general property. We shall find that for configurations of lower symmetry the trace will not be zero.

Following Golding and Stubbs (*1*) we now transform r^6 and $e^{-2\beta r}$ onto the nuclear coordinate system and evaluate the various integrals. This can be quite laborious when determined by hand but we now have a computer program that computes this part of the calculation in an analytical form. The spherical symmetry of f^7 makes it unnecessary to evaluate all nine hyperfine parameters. We shall take the z axis to be the line connecting the nucleus to the lanthanide ion and will evaluate only A_{zz} and A_{xx}. The following equations result,

$$A_{zz} = (3\cos^2\theta - 1)P'R^{-3}T_2, \qquad [23]$$

$$A_{xx} = \left\{-\frac{1}{2}(3\cos^2\theta - 1) + \frac{3}{2}\sin^2\theta\cos 2\phi\right\}P'R^{-3}T_2, \qquad [24]$$

$$T_2 = 1 - e^{-t}\left\{\sum_{n=0}^{8}\frac{t^n}{(n!)} + \frac{3t^9}{9!}\right\}, \qquad [25]$$

$$t = 2\beta R, \qquad [26]$$

where θ, ϕ are polar coordinates for **R**. The ratio of the calculated hyperfine constant to that obtained from the "point-dipole approximation" is given by the function T_2 which is plotted as a function of t in Fig. 1.

Configuration f^{13}

Using the hole formulation, the f^{13} configuration can be treated as a one-electron problem. For the symmetries treated here, the resulting equations are much more complex and would make the paper quite cumbersome if they were included. We have therefore chosen to present the results in graphical form. The relevant equations are stored in small computer programs a copy of which may be obtained from the authors upon request.

In general each of the nine hyperfine tensor components is a summation of a series of terms of the form

$$P'R^{-3}Y_{lm}(\theta, \phi)T_{lm}(t),$$

where the summation is over $l = 0, 2, 4, 6$, and 8 and all possible m values. Value $T_{lm}(t)$ is a function of t similar in nature to T_2 in Eq. [25] except that for $l \neq 2$ the limiting value is zero for large values of t. Equation [2] is always the limiting form for large t values.

It is convenient to plot our results as the ratio $A_{\alpha\beta}$ (calculated)/$A_{\alpha\beta}$ (point-dipole) because the ratio will be a function of t, θ, and ϕ only. The pseudoisotropic portion of the hyperfine constant (hereafter called A_s) obtained from the average of the diagonal elements will be plotted as $(A_s \times R^3)/P'$ because this is a dimensionless quantity depending again on only t, θ, and ϕ, making for easier comparisons between different systems and configurations.

1. Cubic f^{13}. We shall consider here the system of a rare earth ion in a cubic site of a CaF_2-type crystal in which there are eight nearest-neighbor F^- ions located along the (111) axes of the crystal. If we take the xyz coordinate system to be the

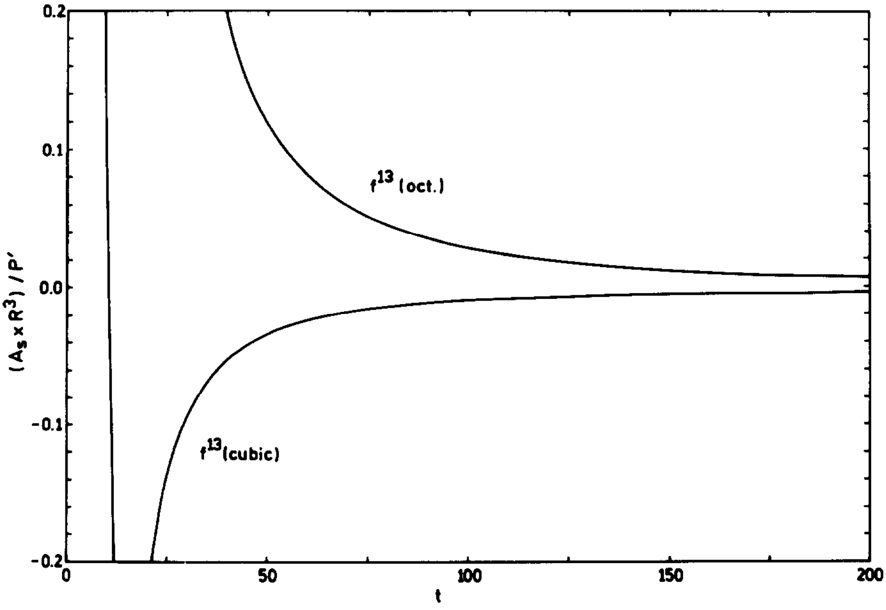

FIG. 2. Plot of the dimensionless $(A_s \times R^3)/P'$ versus t for f^{13} in both a cubic and octahedral crystal field.

cubic axes, the Γ_7 ground state of the $J = 7/2$ state for f^{13} can be written as

$$\left|\pm\frac{1}{2}\right\rangle = \pm\frac{3^{1/2}}{2}\left|\frac{7}{2}, \pm\frac{5}{2}\right\rangle \mp \frac{1}{2}\left|\frac{7}{2}, \mp\frac{3}{2}\right\rangle$$

$$= \pm\frac{3}{(14)^{1/2}} f^{\pm}_{\pm 2} \pm \frac{1}{2}\left(\frac{3}{7}\right)^{1/2} f^{\mp}_{\pm 3} \mp \frac{1}{(14)^{1/2}} f^{\pm}_{\mp 2} \mp \frac{1}{2}\left(\frac{5}{7}\right)^{1/2} f^{\mp}_{\mp 1}. \qquad [27]$$

The g tensor is isotropic with $g = 24/7$. Following the procedures outlined above for f^7 we have obtained equations for all nine hyperfine components.

The nearest-neighbor nuclei are at $\theta = \cos^{-1}(1/3^{1/2}) = 54.7°$. At this orientation all off-diagonal elements are identical and all diagonal elements are the same. The ratio of the off-diagonal element to that predicted by the "point-dipole" equations is plotted versus t in Fig. 1. The value of $(A_S \times R^3)/P'$ is plotted in Fig. 2. Value A_S would be zero for a point dipole.

2. *Octahedral* f^{13}. If an f^{13} ion replaces a Mg^{2+} ion in $KMgF_3$, it is in an octahedral site with six nearest-neighbor F^- ions. In this case it has a Γ_6 ground state which is written as

$$\left|\pm\frac{1}{2}\right\rangle = \pm\frac{1}{2}\left(\frac{5}{3}\right)^{1/2}\left|\frac{7}{2}, \mp\frac{7}{2}\right\rangle \pm \frac{1}{2}\left(\frac{7}{3}\right)^{1/2}\left|\frac{7}{2}, \pm\frac{1}{2}\right\rangle$$

$$= \pm\frac{1}{2}\left(\frac{5}{3}\right)^{1/2} f^{\mp}_{\mp 3} \pm \frac{1}{2} f^{\mp}_{\pm 1} \pm \frac{1}{3^{1/2}} f^{\pm}_{0} \qquad [28]$$

and has an isotropic g of $-8/3$.

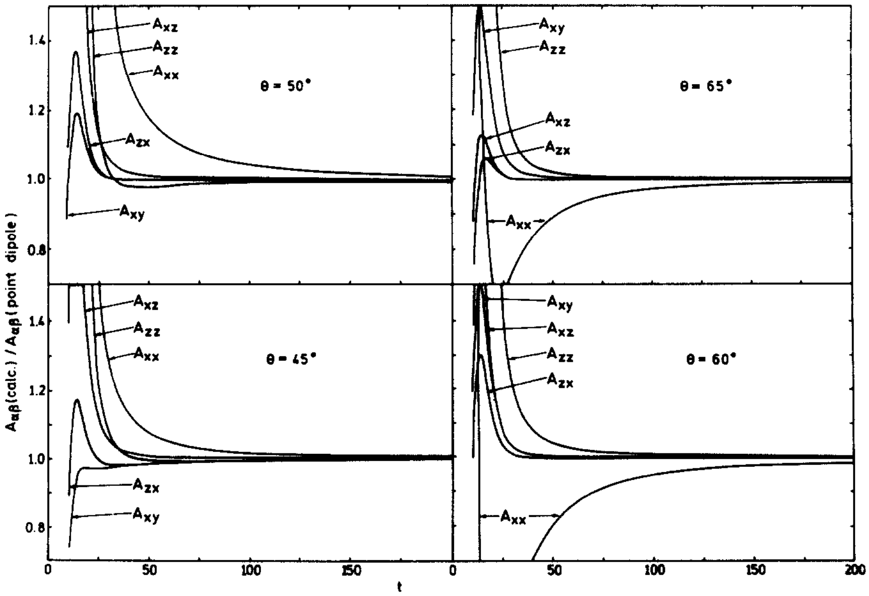

FIG. 3. Plot of the ratio of $A_{\alpha\beta}$ calculated exactly to that calculated from the "point-dipole" model as a function of t for f^{13} in a tetragonally distorted cubic field for different values of θ.

One of the nearest-neighbor fluorides has $\theta = 0°$ and $\phi = 0°$. For this orientation all off-diagonal elements are zero and $A_{xx} = A_{yy}$. Therefore $A_s = (A_{zz} + 2A_{xx})/3$. In this system we have two methods of comparing with the "point-dipole approximation." One is to individually calculate the ratios for A_{zz} and A_{xx} and this is plotted in Fig. 1. The second method is to take the ratio of $(A_{zz} - A_{xx})$ to the "point-dipole" value and this is also plotted in Fig. 1. The second method drops out A_s and is the normal way experimental data would be treated. It is seen to give a smaller deviation from unity in the ratio. The value of $(A_s \times R^3)/P'$ as a function of t is plotted in Fig. 2.

3. Tetragonally distorted f^{13}. If the cubic site in CaF_2 is distorted by the presence of an interstitial F^- ion along the z axis the ground state becomes

$$\left|\pm\frac{1}{2}\right\rangle = \pm a\left|\frac{7}{2}, \pm\frac{5}{2}\right\rangle \mp b\left|\frac{7}{2}, \mp\frac{3}{2}\right\rangle \qquad [29]$$

and

$$g_\parallel = \frac{8}{7}(5a^2 - 3b^2), \qquad [30]$$

$$g_\perp = \frac{32}{7}3^{1/2}ab. \qquad [31]$$

We have done the calculation using

$$a = 0.79926, \qquad b = 0.60099,$$

which are obtained from the experimental g values reported by Kirton and McLaughlan (*11*) for Yb^{3+} in CaF_2. For this site the F^- nuclei are at values of θ different from 54.7° but $\phi = 45°$. Symmetry requires that $A_{xx} = A_{yy}$, $A_{xy} = A_{yx}$, $A_{xz} = A_{yz}$, and $A_{zx} = A_{zy}$. We need, therefore, report on only five of the nine hyperfine terms. The ratio of these five parameters to the "point-dipole" value are plotted in Fig. 3 for $\theta = 45$, 50, 60, and 65°.

The isotropic portion of the tensor, A_s, can be compared in several ways for this system. Since the "point-dipole" equations predict A_s to be nonzero for values of other than 54.7° we can plot the ratio of A_s to the "point-dipole" value of

$$(P'/6R^3)(g_\parallel - g_\perp)(3\cos^2\theta - 1) \qquad [32]$$

as a function of t. This is shown in Fig. 4 for several angles. The reason for the large deviations from unity for this ratio when θ approaches 54.7° is found by examining the difference between A_s(calculated) and A_s(point dipole). In Fig. 5 is plotted this difference multiplied by R^3. It will be noted that the difference changes little with θ. Since A_s(point dipole) goes to zero as θ approaches 54.7° we can understand why the ratios plotted in Fig. 4 diverge from unity as θ becomes close to 54.7°.

A third way of looking at A_s has been suggested by Hutchinson and McKay (*4*). They define a new hyperfine tensor A' in which $A'_{\alpha\beta} = A_{\alpha\beta}/g_{\alpha\beta}$. The trace of A' will be zero if it is pure "point dipole" in origin. A plot of tr $(A' \times R^3)/P'$ versus t is given for various angles in Fig. 6.

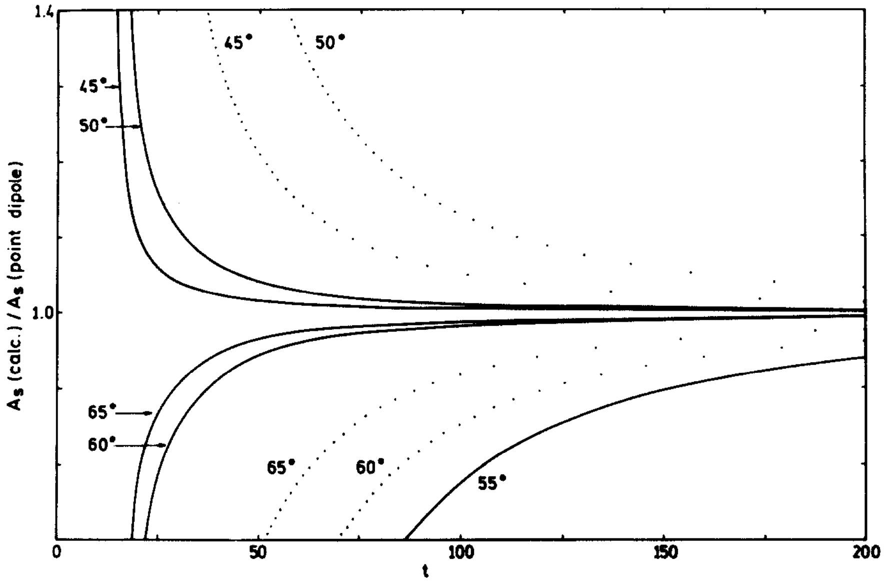

FIG. 4. Ratio of A_s calculated exactly to that calculated from "point-dipole" model as a function of t for both f^{13} and f^1 in a tetragonally distorted cubic field for different values of θ. Solid line is for f^{13} and dotted line for f^1.

Configuration f^1

In a purely cubic environment f^1 has a fourfold degenerate ground state which makes EPR detection impossible. ENDOR measurements, therefore, have only

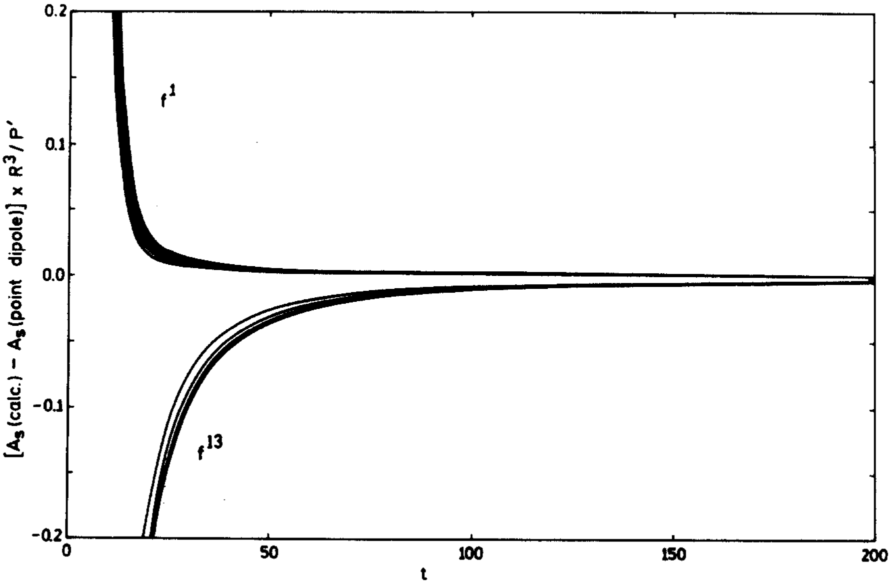

FIG. 5. Difference between $(A_s \times R^3)/P'$ calculated exactly and that calculated from the "point-dipole" model versus t for f^{13} and f^1 in a tetragonally distorted crystal field. θ = 45, 50, 55, 60, and 65° from left to right for each set of curves.

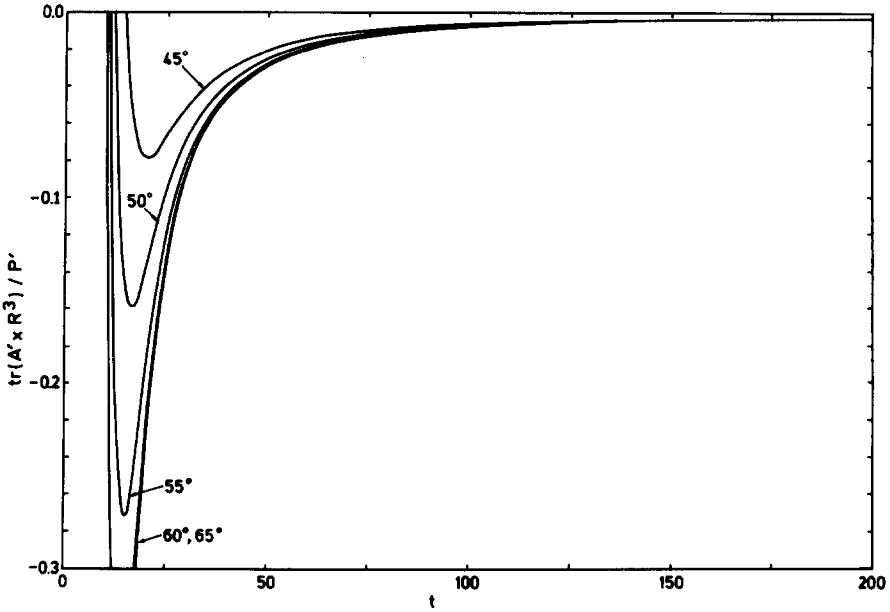

FIG. 6. Trace of $(A' \times R^3)/P'$ versus t for f^{13} in a tetragonally distorted cubic field for different values of θ. Value A' is defined in text.

been reported for distorted systems. Hyperfine values for nearest-neighbor fluorides and interstitial fluorides have been reported (*12–14*) for a tetragonally distorted site in CaF_2 containing Ce^{3+}. Baker *et al.* (*15*) have measured the g tensor and propose the Kramer's doublet ground state of

$$\left|\pm\frac{1}{2}\right\rangle = a\left|\frac{5}{2}, \pm\frac{5}{2}\right\rangle + b\left|\frac{5}{2}, \mp\frac{3}{2}\right\rangle \qquad [33]$$

with $a = 0.91$. A better fit to the g values can be obtained by including a small admixture of $|5/2, \pm 1/2\rangle$ but we have chosen the simpler Eq. [33] for our sample calculation. The g values are

$$g_{\parallel} = \frac{6}{7}(5a^2 - 3b^2), \qquad [34]$$

$$g_{\perp} = \frac{12}{7}5^{1/2}ab. \qquad [35]$$

A plot of the ratio for the five independent hyperfine parameters to the "point-dipole" value is given in Fig. 7 for $\theta = 45°, 50°, 60°$, and $65°$. The ratio of A_s to "point-dipole" value is plotted in Fig. 4 and the difference times R^3 is plotted in Fig. 5. The trace of $(A' \times R^3)/P'$ is plotted in Fig. 8.

DISCUSSION

To discuss these results intelligently we must know the ranges of t that are applicable to real systems. Clementi *et al.* (*16*) have given values of β for neutral

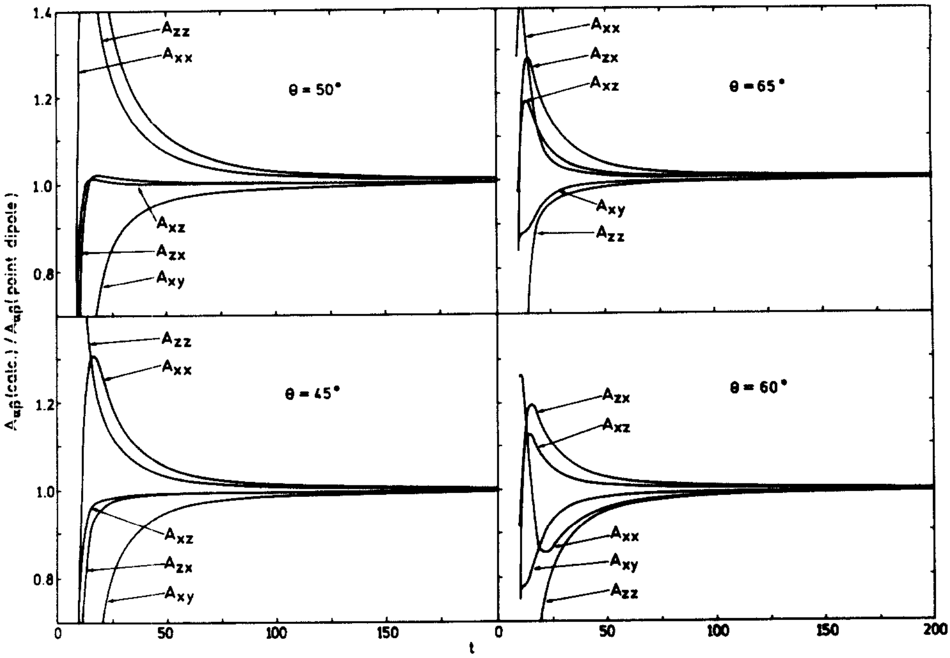

FIG. 7. Ratio of $A_{\alpha\beta}$ calculated exactly to that calculated from the "point-dipole" model as a function of t for f^1 in a tetragonally distorted cubic field for different values of θ.

lanthanide atoms. They report that β varies from $(5.3/a_0)$ for Pr to $(7.4/a_0)$ for Yb. Since we might expect a small increase in β for +3 ions, it seems reasonable to choose $\beta = (5/a_0)$ for f^1, $\beta = (7/a_0)$ for f^7, and $\beta = (8/a_0)$ for f^{13}. Except for metallic hydrides, it is unlikely to find R to be less than 0.2 nm so that the smallest possible values of t would be 37 for f^1, 53 for f^7, and 60 for f^{13}. Examination of the figures show that large deviations from the "point-dipole" values occur generally below $t = 30$ but significant deviations can occur as far as $t = 100$.

One of the surprising results is the magnitude of A_s at fairly large distances. For cubic f^{13}, $A_s = -0.101$ MHz for ^{19}F at 0.23 nm and for octahedral f^{13}, $A_s = 0.577$ MHz for ^{19}F at 0.21 nm. These are significant values experimentally but they are still only about 6% or less (in magnitude) of the values found experimentally. For example, $A_s = 1.67$ MHz (*7*, *17*, *18*) for Yb^{3+} in CaF_2 and $A_s = 22.67$ MHz for Yb^{3+} in $KMgF_3$ (*19*), the large values being attributable to direct spin transfer into the s and p orbitals of the nearest-neighbor fluoride ion. For next nearest neighbors, however, the A_s values calculated here are similar in magnitude to those found experimentally. Hutchison and McKay (*4*) have measured tr A' for protons on water molecules attached to Nd^{3+} ions in which $R > 0.3$ nm. They report values of −0.130, 0.017, 0.010, and 0.039 MHz for tr A' for the four closest protons. We have calculated tr A' for ^1H at 0.3 nm for both cubic and octahedral f^{13} as a function of θ, keeping $\phi = 45°$. The results are plotted in Fig. 9. It can be seen that tr A' varies dramatically with θ and the range of values encompasses the experimental values reported by Hutchison and McKay (*4*).

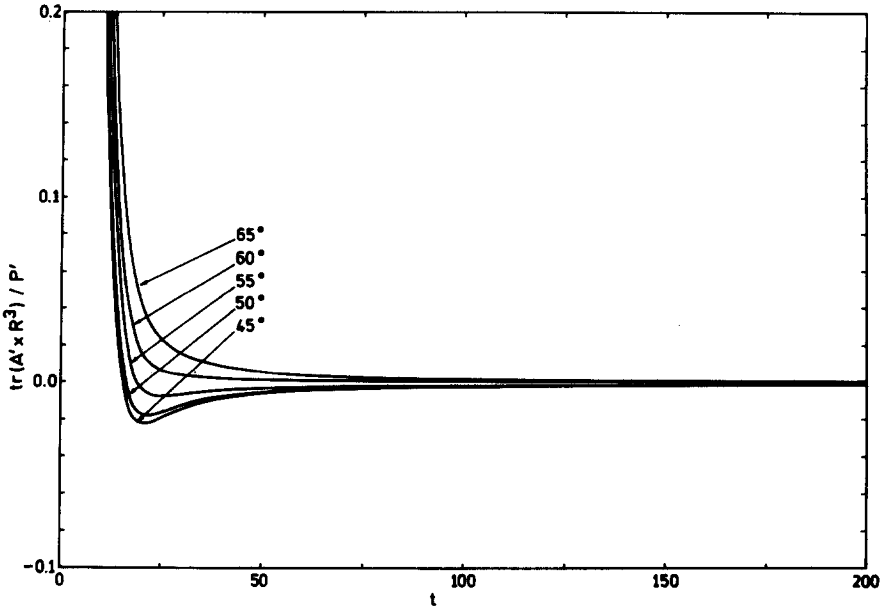

FIG. 8. Trace of $(A' \times R^3)/P'$ versus t for f^1 in a tetragonally distorted cubic field for different values of θ. A' is defined in the text.

Although we have not carried out the calculation for Nd^{3+} itself (which can be accomplished, given enough time and patience), it appears very likely that the small isotropic terms reported in the ENDOR and NMR literature for next nearest neighbors could be attributable to deviations from the "point-dipole" model rather than to Fermi contact interactions on transferred spin.

The deviation of individual hyperfine parameters from the "point-dipole" model is very much dependent on the configuration, the ground state wave function, the θ and ϕ values, and the value of R. For f^7 the ratio plotted in Fig. 1 approaches unity rapidly, differing only in the 10th significant figure at $t = 40$. Thus f^7 can be treated as a point dipole for any reasonable value of R. This is not true for the other systems considered, in which deviations better than 1% were found at $t = 1000$ in some instances. To obtain an estimate of what errors can be generated when R is calculated from hyperfine measurements using the "point-dipole" equations, we have calculated a ΔR for each of the five hyperfine parameters in the tetragonal f^1 and f^{13} cases using the equation

$$\Delta R = R(X^{-1/3} - 1),$$
$$X = A_{\alpha\beta}(\text{calc})/A_{\alpha\beta}(\text{point dipole}). \quad [36]$$

The average of the absolute values of the five ΔR's is given in Table 1 for $R = 0.2$, 0.3, and 0.4 nm at different values of θ. From these calculations it would appear that errors of ±(1 to 2) pm are possible in determining position coordinates of nuclei from hyperfine interactions when the "point-dipole" equations are used. This is larger than the errors quoted in some ENDOR (*4*, *5*) experiments. Any improvement in accuracy will require using exact calculations of the type carried

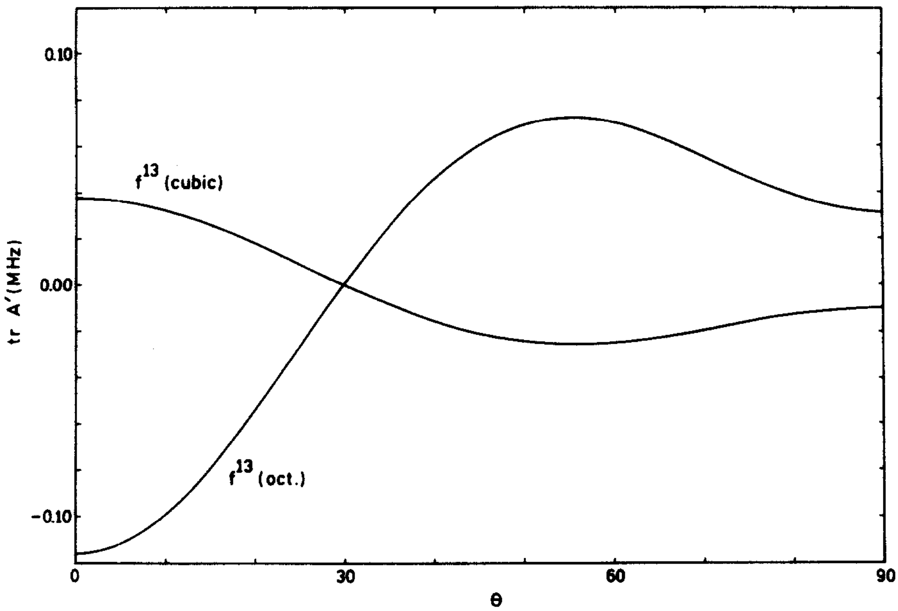

FIG. 9. Trace of A' (MHz) for a proton at $R = 0.3$ nm for an f^{13} ion in either a cubic or octahedral field. Trace is plotted versus θ keeping $\phi = 45°$. Value $\theta = 0$ when nucleus is along a (100) axis of crystal and $\theta = 90°$ when nucleus is along a (110) axis of crystal.

out in this work; of course, use of the f^7 ions (Gd^{3+} and Eu^{2+}) would make such corrections unnecessary.

CONCLUSIONS

It has been shown in this work that differences in the hyperfine interaction for an f electron calculated exactly and that calculated by the "point-dipole" model are small at distances greater than 0.2 nm but the difference is larger than most

TABLE 1

AVERAGE ERROR (ΔR) IN COMPUTED DISTANCE RESULTING FROM "POINT-DIPOLE APPROXIMATION" (ΔR IN PM)

θ (°)	f^{13} (tetragonal distortion)			f^1 (tetragonal distortion)		
R (nm):	0.2	0.3	0.4	0.2	0.3	0.4
10	0.99	0.63	0.46	6.76	4.30	3.18
20	0.82	0.52	0.38	5.50	3.51	2.60
30	0.63	0.37	0.28	3.57	2.28	1.69
40	0.71	0.47	0.35	3.12	2.07	1.55
50	1.97	1.35	1.02	4.89	3.46	2.66
60	2.37	1.52	1.12	3.33	2.23	1.68
70	0.97	0.62	0.46	2.16	1.49	1.14
80	0.87	0.54	0.40	3.48	2.42	1.84

workers in the field have assumed. Errors in nuclear coordinates determined by using the "point-dipole" equations are negligible for the spherical f^7 ions but can be as large as ±2 pm for ions with less symmetrical wave functions. Further it has been shown that the exact dipolar interaction is not traceless and produces a measurable isotropic term in the hyperfine interaction. For nearest neighbor ligands ($R \sim 0.2$ nm) this isotropic term is less than 6% of the isotropic term found experimentally but for next nearest ligand atoms ($R \sim 0.3$ nm) the magnitude is similar to that found experimentally.

We, therefore, urge caution when the "point-dipole" equations are used to analyze hyperfine data whose precision is better than 1%. Also we urge extreme caution in interpreting isotropic terms for next nearest neighbors as "Fermi contact" interactions since they could be wholly or partly attributable to inadequacies in the "point-dipole" equations used to interpret the data. It should be pointed out that the A_s term we have calculated is not related to the "pseudo-contact" shift often discussed in the NMR literature. The "pseudo-contact" term arises from the fact that the "point-dipole" equation, Eq. [2], is not traceless when the g tensor is not isotropic.

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