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## Fermi Contact Hyperfine Constants for Rare-Earth Atoms and Ions from Moment-Perturbed Calculations\*

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Moment-perturbed calculations were carried out for the Fermi contact hyperfine constant for a selection of rare-earth atoms and ions. In the cases of neutral and divalent europium, a value that has the same sign as the experimental value but is larger in magnitude, was found. This is in disagreement with earlier published works of Bagus and Picart who, using an unrestricted Hartree-Fock approach, found a result of opposite sign compared to the experimental results. Results will be presented for divalent, trivalent, and neutral ions and atoms, and trends will be discussed.

### I. INTRODUCTION

Theoretical calculations of the Fermi contact hyperfine interaction ( $a_{FC}$ ) in atoms and ions has been of interest over the past decade as a severe test of the accuracy of atomic wave functions and as a reference point for consideration of hyperfine effects in solids. Considerable progress has been made in these respects, especially for the atoms where many-body calculations have been performed. In order to obtain good agreement with experiment, it was necessary in some cases to include such many-body correlation effects, most notably for phosphorus<sup>1</sup> where obtaining even the correct sign is impossible without correlation.

However, in most cases one-electron theory has proved sufficient for a quite adequate qualitative understanding. Such a situation exists for the transition-metal atoms and ions where the pioneering work of Watson and Freeman<sup>2</sup> using the unrestricted Hartree-Fock method (UHF) predicted the correct trend of  $a_{FC}$  for 3d-series atoms and ions before experimental techniques were accurate

enough to show the rather smooth variation of  $\chi = (2\pi/S) |\psi(0)|^2$  now obtained.<sup>3</sup> The situation is quite different, however, for the rare-earth series of atoms and ions where very little work has been published. Watson and Freeman<sup>4</sup> mention, without giving the results, that for the rare-earth ions their UHF calculations for Gd<sup>+++</sup>, and more accurate ones of Bagus for Sm<sup>+++</sup>, Gd<sup>+++</sup>, Dy<sup>+++</sup>, and Tm<sup>+++</sup>, are in striking agreement with the experimental value for Eu<sup>++</sup>. However, in the only published work by Bagus and Picart<sup>5</sup> it is concluded from UHF calculations of Eu and Eu<sup>++</sup> that relativistic effects must be evoked to obtain agreement with experiment and without such, even the correct sign does not result. The differences in the two sets of results referred to above is probably due to the fact that results referred to by Watson and Freeman use analytical basis sets and the recent calculation of Bagus and Picart obtain numerical solutions of the requisite equations.<sup>6</sup> The numerical results should be near the "exact" UHF results, while the analytic solution may not be close to the "exact" solution owing to limitations of the basis set.

It would be interesting if europium was like phosphorus in that one-electron theory gives the wrong sign compared to experiment. Of all the atoms, phosphorus is the only one presently known for which this situation exists. In order to help answer this question we have calculated  $a_{FC}$  for several rare-earth atoms and ions by the moment-perturbation (MP) procedure.<sup>7</sup> It has the advantage of treating the difference of up- and down-spin densities directly as a perturbation rather than finding  $|\delta\psi(0)|^2$  as the difference of the total up- and down-spin densities,  $|\psi_+(0)|^2 - |\psi_-(0)|^2$ , as is done in the UHF calculation. The MP procedure on the other hand suffers from lack of self-consistency, which UHF calculations include, and many-body correlation effects, which UHF calculations include in part, but an uncertain part. Our MP results correspond to the (0, 1) diagram in Brueckner-Goldstone (BG) theory,<sup>8</sup> and it is a good number pending full BG calculations. The MP value<sup>9</sup> compared to within 20% of the total BG (0, 1) diagram in Li, N, Na, P, B, Mn, and Fe. In addition it should be pointed out that the MP method was developed and has been used for calculation of  $a_{FC}$  in the solid state,<sup>10</sup> and the wave function so generated here may be used for that purpose. The MP method was capable of giving the correct quantitative picture of hyperfine effects at  $\text{Li}^+$  and  $\text{F}^-$  ion nuclei surrounding the  $V_K(\text{F}_2^-)$  center in  $\text{LiF}$ , a moderately complex task.<sup>11</sup>

A brief review of the MP method will be given in Sec. II, followed by results and conclusions in Sec. III.

## II. OUTLINE OF MP METHOD

The MP method is only briefly outlined in this section and for details the reader is referred to Ref. 7. Basically, the MP method is the same as the more common exchange-polarization (EP) method<sup>12</sup> except it reverses the order in which the two perturbations  $H_N$  and  $H_{EX}$  are treated.

$$\begin{aligned} \mathcal{H}_N &= (8\pi/3)\mu_B\mu_N\delta(r)\vec{I}\cdot\vec{S}, \\ \mathcal{H}_{EX} &= -\frac{\psi_{\text{val}}(1)}{\psi_{\text{core}}(1)}\int\psi_{\text{val}}(2)\frac{e^2}{r_{12}}\psi_{\text{core}}(2)d\tau_{12}. \end{aligned} \quad (1)$$

For systems such as the rare-earth atoms where there are no unpaired  $s$  states, but where there are unpaired states of higher angular momentum, the entire contribution to  $a_{FC}$  is due to the interaction of  $H_N$  and  $H_{EX}$ . Following the MP approach,  $H_N$  perturbs the paired core  $s$  states  $\psi_s$  to  $\psi_s + \delta\psi_s$ .  $H_{EX}$  then acts as the exchange potential, the unpaired valence states  $\psi_{4f}$  exchanging with  $\psi_s + \delta\psi_s$  to give a finite contribution to  $a_{FC}$ . The utility of this approach over the EP method is in solid-state and other interacting-atom applications, since it has been demonstrated<sup>11</sup> that  $\delta\psi_s$  is often not greatly altered by the configuration of the outer valence

electron, and hence, the same  $\delta\psi_s$  solved from the free atoms or ions can be used in a variety of situations. A further simplification that is gained is that we only have to evaluate multicenter integrals rather than solve a multicenter differential equation, as would have to be done for the EP function. The possibility of these further applications is the reason we used the MP rather than the EP approach for the rare-earth atoms and ions. Here, of course, either would have been as easy to apply as the other, the important point being that we are using a perturbation approach.

The MP functions are determined by solving the integrodifferential equation

$$\begin{aligned} (\mathcal{H}_{ns} - \epsilon_{ns})\delta\psi_{ns} &= \sum_{n's} (\epsilon_{n's} - \epsilon_{ns}) \langle \psi_{n's} | \delta\psi_{ns} \rangle \psi_{n's} \\ &\quad - \mathcal{H}_N \psi_{ns} + \sum_{n's} \langle \psi_{n's} | \mathcal{H}_N | \psi_{ns} \rangle \psi_{n's}, \end{aligned} \quad (2)$$

where this equation must be solved for all occupied core  $ns$  states. In solving we have used the following approximation:

$$(V_{ns} - \epsilon_{ns}) \simeq \nabla^2 \psi_{ns} / \psi_{ns}, \quad (3)$$

which is an identity only if the operators are allowed to act on the zero-order wave functions  $\psi_{ns}$ . Substitution of (3) into (2) gives

$$\begin{aligned} (-\nabla^2 + \nabla^2 \psi_{ns} / \psi_{ns}) \delta\psi_{ns} &= \sum_{n's} (\epsilon_{n's} - \epsilon_{ns}) \langle \psi_{n's} | \delta\psi_{ns} \rangle \psi_{n's} \\ &\quad - \mathcal{H}_N \psi_{ns} + \sum_{n's} \langle \psi_{n's} | \mathcal{H}_N | \psi_{ns} \rangle \psi_{n's}. \end{aligned} \quad (4)$$

The best justification for the use of Eq. (3) in (4) is that when results are compared with the proper diagram of BG many-body perturbation theory, quite satisfactory agreement is obtained.

The final expression for  $a_{FC}$  is

$$a_{FC} = E_{eN} / IJ2\pi\hbar, \quad (5)$$

which is in units of MHZ, and

$$\begin{aligned} E_{eN} &= -2 \sum_n \left[ \int \psi_{\text{val}}(1) \delta\psi_{ns}(1) | e^2 / r_{12} | \right. \\ &\quad \times \psi_{\text{val}}(1) \psi_{ns}(2) \psi_{ns}(2) d\tau_{12} \\ &\quad \left. - \sum_{n'} \int \psi_{\text{val}}(1) \psi_{ns}(1) | e^2 / r_{12} | \right. \\ &\quad \left. \times \psi_{\text{val}}(2) \psi_{n's}(2) d\tau_{12} \int \psi_{n's} \delta\psi_{ns} d\tau \right]. \end{aligned} \quad (6)$$

## III. RESULTS

The hyperfine field at the nuclei of rare-earth ions in the crystalline state has its dominant contribution from orbital effects from the  $4f$  electrons, except for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  which are predominantly in the  $^8S$  state. The same holds true in the atomic cases except for the  $^8S$  ground state of the Eu atom. Thus, let us first concentrate on  $\text{Eu}^{2+}$  ion and Eu atom where the dominant contribution is from  $a_{FC}$  and where we may compare our theoretical calculations for  $a_{FC}$  directly with experiment.

TABLE I.  $a_{FC}$  for Eu and  $\text{Eu}^{++}$  in MHz.

	1s	2s	3s	4s	5s	6s	Total
$\text{Eu}^{153}$	0	3	-182	-181	275	50	-35
$\text{Eu}^{153^{++}}$	0	3	-184	-183	312	...	-51
Experiment <sup>a</sup>							
( $\text{Eu}^{153}$ )		-8.85					
( $\text{Eu}^{153^{++}}$ )		-45					
Reference 5							
( $\text{Eu}^{153}$ )		+17.5 ± 9					
( $\text{Eu}^{153^{++}}$ )		+2.0 ± 9					

<sup>a</sup>J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) A267, 283 (1967).

The unperturbed wave functions for Eu and  $\text{Eu}^{++}$ , as well as for all the other rare-earth atoms and ions, were solved for in the same manner as those described in Ref. 13. Table I gives the results broken into individual contributions from each core.

The first point that is evident immediately is that there is a severe cancellation between the predominantly negative inner cores and positive outer cores. The final  $a_{FC}$  for  $\text{Eu}^{153}$  is only 20% of the contribution from the 5s state alone. Hence, theoretical calculation of this sort must be considered only qualitative in nature until a full many-body calculation is carried out. The contributions listed for the various *ns* cores include both diagonal and nondiagonal terms in Eq. (6). A second feature as seen in Table I is that the 1s and 2s contributions to  $a_{FC}$  in the Eu atom or  $\text{Eu}^{++}$  ion are negligible.

The result for  $\text{Eu}^{++}$  is in quite good agreement with experiment although it must be pointed out that the experimental result is for  $\text{Eu}^{++}$  in crystal, and covalency effects might influence the experimental value as compared to free  $\text{Eu}^{++}$ . If, however, the situation follows that of  $\text{Mn}^{++}$ , the agreement would in general improve.<sup>14</sup>

The atomic result is in reasonable agreement with experiment only when the amount of cancellation among cores is considered. Reasons for the discrepancy could be self-consistency and correlation effects such as are found in Fe and Mn atoms, where MP results are also larger than experiment.<sup>15,16</sup> Correlation contributions calculated from many-body methods are shown to be the main correction to one-electron exchange core polarization. It is interesting to note in these two cases (Fe and Mn) UHF calculations<sup>2</sup> give results on the opposite side of experiment from those of MP, just as they do for the Eu atom. For comparison, the results of Bagus and Picart are presented in Table I.

Another point of interest was the study of the variation of  $a_{FC}$  over the rare-earth series. Figure 1 gives such results for a selection of atoms

and ions. The quantity presented here is  $\chi = (2\pi/S) \times |\delta\psi(0)|^2$ , which represents the unpaired density per spin. As can be seen, there is a significant although smooth variation of  $\chi$  in going across the rare-earth series both for the ++ and +++ ions. Also, the unpaired density per spin is larger in magnitude for the triple-plus ions than for the double-plus ions. The variation of  $\chi$  is somewhat in disagreement with comments<sup>4</sup> made by Watson and Freeman about Bagus's unpublished calculation for  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Tm}^{3+}$ , where an apparently constant  $\chi$  value of -1.2 was found. Our value varies from -1.28 for  $\text{Ce}^{3+}$  to -1.67 for  $\text{Yb}^{3+}$ . This variation is similar to that found for the double-plus 3*d*-series ions.

In summary, it should be said that our MP calculations of  $a_{FC}$  for rare-earth atoms and ions are of the same sign as experiment and reasonably close in magnitude when the severe cancellation between cores is considered. The MP calculation considers the direct one-electron exchange polarization of the *s* cores by the unpaired valence electrons, and results obtained here suggest that correlation contributions to  $a_{FC}$  for rare-earth atoms are necessary and must contribute a positive sign. The conclusion reached above concerning the relative sign of theoretical one-electron calculation results and experiment for the rare-earth series is the same as had previously been found for all other atoms and ions where calculations have been carried out, in particular, for 3*d*-series atoms

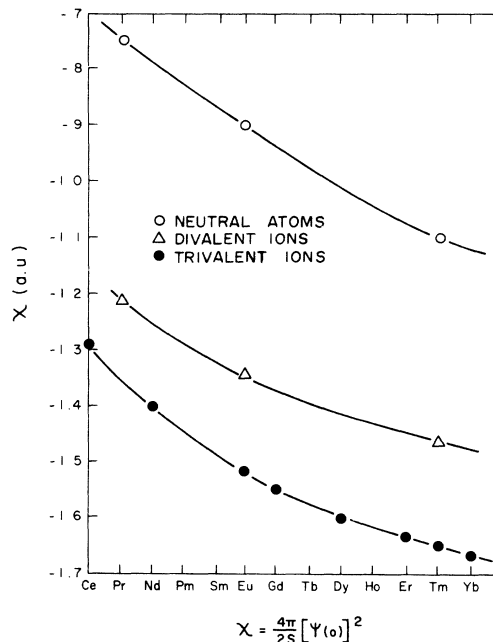


FIG. 1. Unpaired density per spin.

and ions, except for the notable case of the phosphorus atom. The above conclusion is also somewhat different from what is suggested by the work of Bagus and Picart on  $\text{Eu}^{++}$  and Eu atom where a phosphoruslike situation exists. It is the only UHF result that is different in sign from experiment, except, again, for phosphorus. UHF calculations include, in addition to the direct exchange polarization considered by the MP approach, indirect one-electron polarization ( $4f-3d-ns$ , for example) and an uncertain amount of correlation. This additional contribution could explain the difference between MP and UHF results. However, it should be reiterated that UHF calculation takes the difference of large up- and down-spin densities to obtain  $a_{\text{FC}}$  and there is more chance of error

than in using an approach that treats small differences by perturbation, such as the MP method.

Finally, it should be remembered for atoms of this size that relativistic effects are probably quite important and must be considered, as was commented on by Bagus and Picart. Present one-electron relativistic calculations<sup>17,18</sup> predict a negative sign for such contributions to  $a_{\text{FC}}$  in Eu and  $\text{Eu}^{++}$ . From our point of view, this means that correlation effects are required to be somewhat larger than they would be without relativistic considerations. However, we would like to suggest that, in fact, correlation effects could also be important in relativistic calculations and must be included. This would be possible if the BG procedure were reformulated to include relativistic effects.

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## Explicit Formulas in Degenerate Rayleigh-Schrödinger Perturbation Theory for the Energy and Wave Function, Based on a Formula of Lagrange\*

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The solution for the energy and wave function in degenerate Rayleigh-Schrödinger perturbation theory is obtained via a formula of Lagrange. The derivation involves manipulation of the Brillouin-Wigner formulas in a manner similar to the "repeated-partitioning" technique.

### I. INTRODUCTION

Only recently have formal solutions for the energy and wave function in *degenerate* Rayleigh-Schrödinger (RS) perturbation theory been available. Hirschfelder,<sup>1</sup> via recursively defined operators

$Q_i^{(n)}$ , derived what is in essence the degenerate generalization of the standard textbook recursive solution for the nondegenerate case. Choi,<sup>2</sup> following a suggestion by Löwdin,<sup>3</sup> applied a "repeated-partitioning" technique to obtain the energy and wave function in terms of "effective" Hamiltonians