

## Hyperfine field in metallic iron: An appraisal of the theory

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Recently an experiment has been performed for the first time to measure the contribution to the hyperfine field in metallic iron from each electron shell separately. In view of this measurement, it has become important to study the interrelationship between various theories for studying exchange core polarization contributions to the hyperfine field with the aim of deciding on the appropriate theoretical values that have to be compared with experimental data. Such a comparison is carried out here between the Hartree-Fock perturbation theory, self-consistent-field perturbation theory, linked-cluster many-body perturbation theory (LCMBPT), and the unrestricted Hartree-Fock (UHF) theory. It is concluded that, in principle, the predictions of the self-consistent-field perturbation theory and UHF theory for shell-by-shell contributions should be comparable, although the total hyperfine fields from all the shells should be the same for all four theories. The quantitative accuracies of the various procedures are studied by considering the results for  $\text{Fe}^{+3}$  ion, iron atom, and manganese atom. It is concluded that while the accuracies of results from the Hartree-Fock and self-consistent-field perturbation theory and LCMBPT are comparable, there are some numerical problems in obtaining comparable accuracy with the UHF procedure. Shell-by-shell core contributions and conduction-band contributions to the hyperfine field are compared with the results from internal-conversion experiments. A possible reason for differences between theory and experiment is discussed.

### I. INTRODUCTION

Although the total hyperfine field at nuclear positions has been measured by a variety of techniques, the contributions from the individual electron shells have only recently become accessible to direct observation.<sup>1</sup> Predictions have been made of the individual shell contributions,<sup>2</sup> but in the case of a recent measurement for metallic iron,<sup>1</sup> there appears to be a large discrepancy between the theory and the measurements, and this seems to indicate far-reaching changes are needed in our theoretical understanding of hyperfine fields. It is our purpose in this paper to carefully scrutinize the approximations used in the present theories, in search of a possible origin of the discrepancy.

The quantity provided by the experiment is

$$\delta_{ns} = |\psi_{ns}^\dagger(0)|^2 / |\psi_{ns}(0)|^2 - 1. \quad (1)$$

On the other hand, the quantity most frequently tabulated<sup>2</sup> in theoretical works is

$$\chi_{ns} = (4\pi/2S)(|\psi_{ns}^\dagger(0)|^2 - |\psi_{ns}(0)|^2) \quad (2a)$$

$$= (4\pi/2S)|\psi_{ns}(0)|^2 \delta_{ns}. \quad (2b)$$

In these equations  $\psi_{ns}^\dagger(\vec{r})$ ,  $\psi_{ns}(\vec{r})$  are the  $n$ th orbitals for majority ( $\uparrow$ ) and minority ( $\downarrow$ ) spin  $s$  states. The spatial parts of these functions are not spin independent, and we denote the average of the two states by  $\psi_{ns}(\vec{r})$ .

The factor which converts  $\chi$  to the hyperfine field is  $4.17 \times 10^4 a_0^3$  Oe. In Table I we have listed the experimental values for  $\delta_{ns}$  ( $n=2, 3$ ) and the consequent  $\chi_{ns}$  and  $H_{ns}$ ; these values are taken from Ref. 1.  $\delta_{1s}$  is too small to be measured, and there is theoretical agreement that it may be neglected. We have also listed in Table I values of  $\chi_{ns}$  determined (as described below) from our band wave functions for ferromagnetic iron; these values are typical of those predicted by current theories.

There is no substantial difference between various authors for the factor  $|\psi_{ns}(0)|^2$  in (2); so considerations of  $\chi$  and  $\delta$  are equivalent, and we choose to discuss  $\chi$ . We note that the experimental  $\chi_{ns}$  agree in sign with the theoretical ones but are a factor of 2–3 larger. Thus the core contribution to the hyperfine field deduced from the results of Ref. 1 is much larger than current theory predicts. The total field from core and conduction states is known<sup>3</sup> from many other experiments to be  $-339$  kOe, so that the new experiments need, for consistency with other work, a large compensating contribution ( $\sim 300$ – $1500$  kOe) from the conduction electrons; such fields are at least an order of magnitude larger than current band theory predicts. Theory is therefore presented with the double problem of explaining both the large core contributions, and, by implication, the large band contribution. We intend here to concentrate on the core contribution.

TABLE I. Experimental and theoretical contributions to the hyperfine field in metallic iron.  $\delta_{ns}$  and  $\chi_{ns}$  are defined in the text in Eq. (1) and (2), respectively.

	Experiment		Theory
$10^2\delta_{2s}$	$-0.63 \pm 0.15$		$-0.24$
$\chi_{2s}$	$(-17.8 \pm 4.2)\alpha_0^{-3}$		$-6.77\alpha_0^{-3}$
$H_{2s}$	$-1640 \pm 400$ kOe		$-623$ kOe
$10^2 \left( \delta_{3s} + \delta_{4s} \frac{ \psi_{4s}(0) ^2}{ \delta_{3s}(0) ^2} \right)$	$1.43 \pm 0.68$		
$10^2\delta_{3s}$	$1.16 \pm 0.6$	$1.43 \pm 0.68$	$0.57$
$\chi_{3s}$	$(4.5 \pm 2.3)\alpha_0^{-3}$	$(5.5 \pm 2.6)\alpha_0^{-3}$	$2.22\alpha_0^{-3}$
$H_{3s}$	$400 \pm 200$ kOe	$510 \pm 240$ kOe	$243$ kOe
$H_{4s}$	$\sim 100$ kOe	$0$ kOe	$33$ kOe
$H_{total}$	$-(1140 \pm 640)$ kOe		$-347$ kOe

## II. DESCRIPTION OF THEORETICAL METHODS

Several methods have been used to compute  $\chi_{ns}$ . While these theories are usually in fair agreement with one another for  $\sum_n \chi_{ns}$ , there are some apparent differences in the individual  $\chi_{ns}$  terms, even to differences in sign. To resolve these differences and to delineate the limitations of each method, we will now briefly describe each method.

### A. UHF method

In the (spin) unrestricted Hartree-Fock (UHF) method,<sup>2</sup> the wave functions for the electron orbitals are obtained as self-consistent orthonormal eigenfunctions of the Hartree-Fock equations, without requiring the radial part of the wave function to be spin independent. The values of  $\chi_{ns}$  are computed directly from Eq. (2a); the reason for nonzero values appearing is that majority and minority spin  $s$  electrons have different exchange interactions with the  $d$  electrons. It frequently

occurs that  $\chi_{ns}$  calculated in this manner is derived from small differences between large almost-equal numbers.

Ideally, the UHF method should employ a numerical solution of the Hartree-Fock equations. However, in the interests of computational economy, an analytic-basis set expansion is frequently used, with coefficients determined variationally. The  $\chi_{ns}$  values computed in this manner have been found<sup>2</sup> to be sensitive to the size and quality of the basis set used.

### B. Hartree-Fock perturbation theory

The starting point of Hartree-Fock perturbation theory (HFPT) is the set of orthonormal eigenfunctions obtained by solving the Hartree-Fock equations subject to the requirement that the radial parts of the orbitals be spin independent; such functions are called restricted Hartree-Fock functions. The difference between the exchange interactions experienced by spin-up and spin-down electrons is then employed as a perturbation to find corrections  $\delta\psi$  to the one-electron orbitals.  $\chi$  is then calculated as

$$\chi_{ns} = (4\pi/2S) 2\psi_{ns}(0) \delta\psi_{ns}(0). \quad (3)$$

It should be noted that in the perturbation method, the difference  $\delta\psi$  between spin-up and spin-down orbitals is obtained directly, so that problems in taking the difference of large, almost equal, numbers, are avoided. It is also clear that it does not matter whether the unperturbed  $\psi_{ns}(\vec{r})$  is obtained numerically or variationally. We have obtained the  $\delta\psi_{ns}$  by numerical solution of the differential equations corresponding to the appropriate perturbation equations, derived earlier in the literature,<sup>4</sup> dealing with nonorthogonal Hartree-Fock perturbation theory, namely,

$$\begin{aligned} (h_i - \epsilon_i)\delta\psi_i + h'\psi_i = \sum_j \left( \langle \psi_j | \delta\psi_i \rangle (\epsilon_j - \epsilon_i)\psi_j + \langle \psi_j | h' | \psi_i \rangle \psi_j - \langle \psi_j \psi_i | \cdot | \psi_i \delta\psi_i \rangle \psi_j \right. \\ \left. + \langle \psi_j | \delta\psi_i \rangle \langle \psi_i | \cdot | \psi_j \rangle \psi_i - \sum_k \langle \psi_j | \delta\psi_i \rangle \langle \psi_k \psi_i | \cdot | \psi_j \psi_i \rangle \psi_k \right), \end{aligned} \quad (4)$$

where  $h_i$  and  $\epsilon_i$  refer to the restricted Hartree-Fock one-electron Hamiltonian and energy corresponding to the  $i$ th state.<sup>4</sup> The  $\psi_i$ ,  $\psi_j$ , and  $\psi_k$  refer to the unperturbed core wave functions of up spin in the restricted Hartree-Fock approximation, the state  $i$  referring to core  $ns$  states of up spin. The states  $j$  and  $k$  also refer to up-spin states and include the core  $np$  states as well as  $ns$ .  $h'$  refers to the perturbation Hamiltonian corresponding to the extra exchange interactions ex-

perienced by the up-spin electrons, as compared to the down-spin electrons, due to the effect of the surplus of valence electrons with up spin. Thus

$$h'(1)\psi_i(1) = \sum_v \langle \psi_v(2) | e^2/r_{12} | \psi_i(2) \rangle \psi_v(1), \quad (5)$$

where the states  $v$  refer to the unpaired spin-valence states involving the  $3d$  states in the atom or the band states in the metal. The matrix elements are noted in abbreviation, namely,

$$\begin{aligned} \langle \psi_i | \cdot | \psi_j \rangle \psi_k(1) &= \langle \psi_i(2) | e^2/r_{12} | \psi_j(2) \rangle \\ &\quad \times \psi_k(1) - \langle \psi_i(2) | e^2/r_{12} | \psi_k(2) \rangle \psi_j(1), \\ \langle \psi_j \psi_i | \cdot | \psi_i \delta \psi_i \rangle &= \langle \psi_j(1) \psi_i(2) | e^2/r_{12} | \psi_i(2) \delta \psi_i(1) \rangle \\ &\quad - \langle \psi_j(1) \psi_i(2) | e^2/r_{12} | \delta \psi_i(2) \psi_j(1) \rangle. \end{aligned} \quad (6)$$

It is, of course, desirable to find functions  $\delta \psi_i$ , which, when added to the zero-order functions  $\psi_i$ , produce normalized mutually-orthogonal orbitals. There are infinitely many such sets of functions. One particularly convenient set is found by requiring

$$\langle \delta \psi_i | \psi_j \rangle = 0 \quad (7)$$

for all occupied zero-order orbitals  $\psi_j$ . This set of  $\delta \psi_i$  we will call HFPT solutions. The perturbed orbitals are

$$\psi'_i = \psi_i + \delta \psi_i \quad (8)$$

and satisfy the Hartree-Fock equations

$$H \psi'_i = \sum_j \lambda_{ij} \psi'_j, \quad (9)$$

where  $\lambda_{ij}$  is given by<sup>4</sup>

$$\begin{aligned} \lambda_{ij} &= \langle \psi_j | \psi'_i \rangle (\epsilon_j - \epsilon_i) + \langle \psi_j | h' | \psi_i \rangle \\ &\quad + \sum_k \left( \langle \psi_j \psi'_k | \cdot | \psi_k \psi_i \rangle + \langle \psi_j \psi_k | \cdot | \psi'_k \psi_i \rangle \right). \end{aligned} \quad (10)$$

Another useful set of functions can be found by performing a unitary transformation on the set  $\psi'_i$  to diagonalize the  $\lambda$  matrix of Eq. (6). To first order this transformation merely adds to each  $\delta \psi_i$  some linear combination of the occupied zero-order orbitals; it has been shown in Ref. 4 that the new  $\delta \psi_i$  are still solutions of the perturbation equations. We will call this set of  $\delta \psi_i$  self-

consistent-field perturbation-theory (SCFPT) solutions.

Since the solutions of the HFPT equations are not unique, it is important to clarify their physical meaning and realm of usefulness. In obtaining the HFPT solutions, the orthogonalization procedure [Eq. (7)] is essentially imposing the Pauli principle by requiring that the excitation involve only the higher-energy virtual orbitals. Excitation of, for example, a 3s electron to the 2s level is thereby forbidden, but so is an excitation of a 2s electron to the 3s level. In transforming the HFPT solutions to the SCFPT solutions, we are allowing compensating transitions in each direction. Therefore, the total hyperfine field calculated from the HFPT solutions will be the same as that calculated from the SCFPT solutions; a unitary transformation cannot alter<sup>4</sup> the expectation value of any operator calculated from the *determinantal* wave function.

Since the SCFPT solutions represent eigenfunctions, they should correspond to the UHF solutions. Because the HFPT and SCFPT solutions differ in shell-by-shell contributions to the hyperfine field, but agree in the total, HFPT and UHF predictions will also differ in the shell-by-shell contributions, but (except for computational limitations as mentioned above) agree in the total, as has occurred in published results. As examples, we list in the fourth and fifth columns of Tables II and III the  $\chi_{ns}$  values deduced from HFPT solutions, the corresponding SCFPT solutions, and UHF results for  $\text{Fe}^{+3}$  (Ref. 2) and the Fe atom (Ref. 5). The HFPT solutions were obtained by solving Eq. (4) numerically to obtain  $\delta \psi_{ns}$  and to these adding multiples of  $\psi_{1s}$ ,  $\psi_{2s}$ , and

TABLE II. Contributions to  $\chi$  in  $\text{Fe}^{+3}$  due to both direct-exchange effects ( $d \rightarrow s$ ) and indirect-polarization ( $d \rightarrow np \rightarrow s$ ) effects, as calculated by the several methods<sup>a</sup> described in Sec. II.

		$d \rightarrow s$	$d \rightarrow 2p \rightarrow s$	$d \rightarrow 3p \rightarrow s$	Total	UHF
1s	LCMBPT	0.01	0.06	-0.03	0.04	
	HFPT	0.03	0.17	-0.09	0.10	
	SCFPT	-0.29	0.31	-0.16	-0.14	-0.25
2s	LCMBPT	-4.29	-0.16	0.08	-4.37	
	HFPT	-4.31	-0.23	0.03	-4.50	
	SCFPT	-8.39	-0.45	-0.03	-8.88	-8.51
3s	LCMBPT	0.33	-0.13	0.32	0.52	
	HFPT	0.35	-0.02	0.47	0.79	
	SCFPT	4.75	0.06	0.60	5.41	5.77
Total	LCMBPT	-3.95	-0.23	0.37	-3.81	
	HFPT or SCFPT	-3.94	-0.08	0.41	-3.61	-3.00

<sup>a</sup>The abbreviations LCMBPT, HFPT, and SCFPT stand for linked-cluster many-body perturbation theory, Hartree-Fock perturbation theory, and self-consistent-field perturbation theory, respectively.

$\psi_{3s}$  through the Schmidt orthogonalization procedure to satisfy the orthogonality conditions in Eq. (7). These orthogonalized  $\delta\psi_{ns}$  were then used to obtain  $\psi'_{1s}$ ,  $\psi'_{2s}$ , and  $\psi'_{3s}$  defined by Eq. (8), which were then used in Eq. (10) to get the matrix  $\lambda_{ij}$ . This latter matrix was diagonalized, and from the transformed basis, the SCFPT solutions  $\delta\psi$  were derived, as explained earlier.

We see the SCFPT results are in reasonable (but not exact) agreement, shell by shell, with the UHF results. It may be noted in passing that the major shifts in contributions between HFPT and SCFPT occur in the 2s and 3s shells, 1s and 4s being almost unaffected. The reason for this is twofold: both 2s and 3s electrons have a large density at the nuclear site, and the energy denominators for a 2s-3s interaction are reasonably small.

The question arises as to which set of functions is most appropriate for interpreting the experiment reported in Ref. 1. It is important to note that this experiment is not measuring a static property or expectation value, but instead, a transition ratio or the square of an off-diagonal matrix element. In the sudden approximation, the matrix element is calculated between states in which one electron's wave function changes from that of an atomic orbital to a plane wave, and all other orbitals are unaltered. Thus we need the one-electron *eigenfunctions*, that is, the SCFPT or UHF functions.

We should not minimize the significance of the

HFPT functions. Their usefulness is derived from the fact that they very simply and directly provide us with the importance of any given interaction. That is, they may be given a fairly simple diagrammatic representation (in the Feynman sense), whereas the SCFPT or UHF functions represent the sum of several diagrams among which there is considerable mutual cancellation. Thus, the HFPT functions provide a convenient link between one-electron theory and the more complex but more complete many-body theory.

### C. LCMBPT method

The linked-cluster many-body perturbation-theory method<sup>6-8</sup> (LCMBPT) uses the restricted Hartree-Fock Hamiltonian to generate a complete set of states and then uses the difference between that Hamiltonian and the exact Hamiltonian as a perturbation. The formalism is most conveniently expressed in a diagrammatic expansion, and this facilitates the identification of the importance of specific interactions. The procedure has been applied to a wide variety of problems in atoms, ions, and small molecules, with excellent agreement between predicted and measured quantities. Because of the extensive success of this method and because in principle the method can give a complete theory, we adopt it as the standard by which the UHF and perturbation theories are judged.

The diagrams corresponding to the HFPT method

TABLE III. Contributions to  $\chi$  for the  $3d^64s^2$  configuration of atomic iron due to both direct-exchange ( $d \rightarrow s$ ) and indirect-polarization ( $d \rightarrow np \rightarrow s$ ) effects, as calculated by the several methods<sup>a</sup> described in Sec. II.

		$d \rightarrow s$	$d \rightarrow 2p \rightarrow s$	$d \rightarrow 3p \rightarrow s$	Total	UHF
1s	LCMBPT	0.02				
	HFPT	0.02	0.14	-0.04	0.12	
	SCFPT	-0.25	0.27	-0.09	-0.06	-0.15
2s	LCMBPT	-3.47				
	HFPT	-3.60	-0.19	0.02	-3.78	
	SCFPT	-7.27	-0.39	-0.02	-7.69	-7.99
3s	LCMBPT	-0.69				
	HFPT	-0.64	-0.02	0.24	-0.42	
	SCFPT	3.33	0.05	0.42	3.80	4.48
4s	LCMBPT	2.64				
	HFPT	2.64	-0.00	-0.03	2.61	
	SCFPT	2.61	0.00	-0.13	2.49	2.89
Total	LCMBPT	-1.49	-0.08	0.11	-1.46	
	HFPT or SCFPT	-1.58	-0.07	0.18	-1.47	-0.77

<sup>a</sup>The abbreviations LCMBPT, HFPT, and SCFPT stand for linked-cluster many-body perturbation theory, Hartree-Fock perturbation theory, and self-consistent-field perturbation theory, respectively.

TABLE IV. Direct and indirect core contributions to  $\chi$  and the hyperfine field  $H$  calculated for ferromagnetic iron using the HFPT functions and SCFPT functions described in Sec. II B.

	Direct		Indirect		Total HFPT		Total SCFPT	
	$\chi$	$H$ (kOe)	$\delta\chi$	$\delta H$ (kOe)	$\chi$	$H$ (kOe)	$\chi$	$H$ (kOe)
1s	0.02	2	0.11	10	0.13	12	-0.01	-1
2s	-3.23	-296	-0.16	-15	-3.39	-310	-6.78	-622
3s	-1.49	-137	0.60	55	-0.89	-82	2.65	243
Total Core	-4.70	-431	0.55	50	-4.15	-380	-4.15	-380

are easily identified. Calculations for  $\text{Fe}^{+3}$  (Ref. 7) and the Fe atom (Ref. 8) have been published, and we list the appropriate terms in Tables II and III. There is very good agreement, shell by shell, between the HFPT results and the corresponding terms in the LCMBPT expansion, even though the mathematical techniques involved in the two methods are quite dissimilar. We therefore will adopt the HFPT (or SCFPT) results as a "secondary standard." That this is a better choice than the UHF results is illustrated by the case of the Fe atom (Table III). Here the one-electron contributions to  $\chi$  from both LCMBPT and HFPT or SCFPT are  $-1.47$ , while the UHF result is  $-0.77$  (Ref. 5). (A factor of 2 could be very important for the problem discussed in Sec. I.) We have made a similar comparison for the Mn atom, and we find that here also, the LCMBPT one-electron contributions (Ref. 9) are twice the UHF results (Ref. 2) but in agreement with the HFPT or SCFPT predictions.

### III. $\chi$ FOR METALLIC IRON

Ideally, we would like to be able to use the LCMBPT procedure to calculate  $\chi$  for metallic iron, but this is a formidable problem with the computational facilities available. However, the LCMBPT calculations which have been made for the iron atom and for  $\text{Fe}^{+3}$  can guide us in choosing the interactions which are probably the most important for the core electrons in the metal; some of these can be calculated by the HFPT procedure.

#### A. Polarization by the conduction electrons

The most important contribution to  $\chi$  comes from the exchange interaction between the conduction electrons and the core  $s$  electrons. We have previously calculated<sup>10</sup>  $\sum_n \chi_{ns}$  due to this mechanism using wave functions from a band-structure calculation as the perturbing states. We have now repeated that calculation for  $\chi_{2s}$ . The

results (using HFPT functions) are given in Table IV. The contribution listed for the 1s state is small and is taken from a free-atom calculation. The 3s contribution is determined by the difference of the total  $\sum_n \chi_{ns}$  calculated earlier<sup>10</sup> and the sum of the calculated  $\chi_{1s}$  and  $\chi_{2s}$  from the present work.

#### B. Indirect polarization through $p$ electrons

In Fig. 1, we show the diagram which has proved to be the next most important contributor to the hyperfine field in  $\text{Fe}^{+3}$  and the Fe atom. This can be given the following physical interpretation: the  $d$  (conduction electrons) exchange-polarize the  $p$  electrons, and the resulting  $p$ -spin density is then able to exchange-polarize the  $s$  states. We have not been able to calculate these contributions using the band states; so instead, we have made the corresponding calculation for the free-atom configuration  $3d^7 4s^{1/2} 4s^{1/2}$ , which should approximate the configuration of the metal quite well.<sup>11</sup> The results are listed in Table V. The important terms are  $(d \rightarrow 3p \rightarrow 3s)$ ,  $(d \rightarrow 2p \rightarrow 2s)$ , and  $(d \rightarrow 2p \rightarrow 1s)$ . Curiously, the indirect polarization of the 1s state is more important than the direct polarization. We have used these results to estimate the indirect-polarization terms for the metal, and the changes to be made on going from the HFPT func-

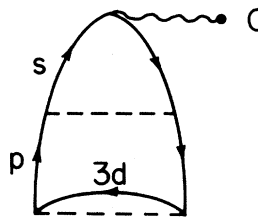


FIG. 1. Diagrammatic representation of the indirect-polarization process in which the 3d electrons exchange polarize the  $p$  states and these subsequently exchange polarize the core  $s$  states which then interact with the contact interaction (wavy line ending with a C).

TABLE V. Contributions to  $\chi$  for the  $3d^7 4s^{1/2} 4s^{1/2}$  configuration of atomic iron due to both direct-exchange ( $d \rightarrow s$ ) and indirect-polarization ( $d \rightarrow np \rightarrow s$ ) effects, as calculated by the perturbation theory<sup>a</sup> described in Sec. II B. The last column lists the hyperfine field which would result from 2.2 unpaired  $d$  spins.

		$d \rightarrow s$	$d \rightarrow 2p \rightarrow s$	$d \rightarrow 3p \rightarrow s$	Total	Hyperfine field for 2.2 spins
1s	HFPT	0.02	0.13	-0.01	0.13	12 kOe
	SCFPT	-0.22	0.24	-0.03	-0.01	-1 kOe
2s	HFPT	-3.23	-0.17	0.01	-3.39	-311 kOe
	SCFPT	-6.45	-0.35	-0.01	-6.81	-625 kOe
3s	HFPT	-1.02	-0.01	0.14	-0.89	-82 kOe
	SCFPT	2.40	0.05	0.20	2.64	243 kOe
4s	HFPT	0.80	-0.00	-0.01	0.79	72 kOe
	SCFPT	0.84	-0.00	-0.03	0.80	74 kOe
Total		-3.43	-0.06	0.13	-3.37	

<sup>a</sup>The abbreviations HFPT and SCFPT stand for Hartree-Fock perturbation theory and self-consistent-field perturbation theory, respectively.

tions to the SCFPT functions, as given in Table IV.

Tables II, III, and V illustrate the importance of careful consideration of each term separately.

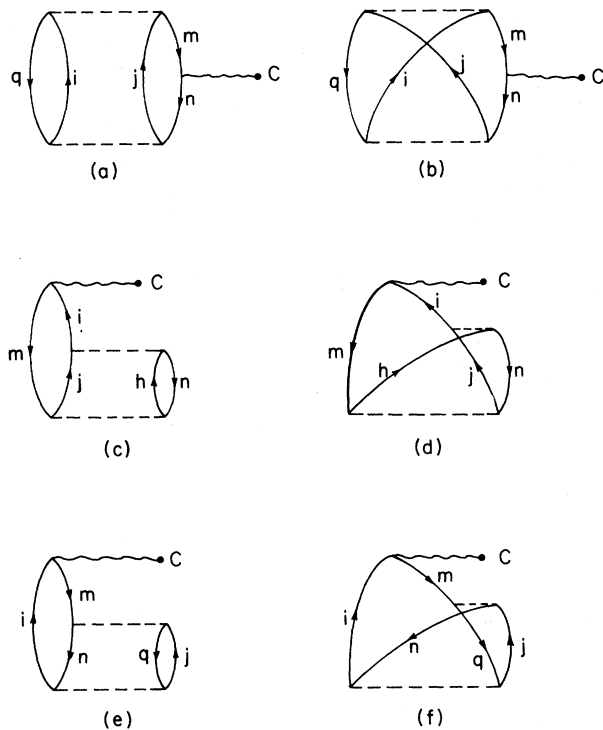


FIG. 2. Diagrammatic representation of the many-body interactions which have been found to make significant contributions to the hyperfine field in  $\text{Fe}^{+3}$  and Fe atom. Solid lines represent electron states; dashed lines, the Coulomb interaction; and wavy line ending with a C, the contact hyperfine interaction.

For  $\text{Fe}^{+3}$ , the  $d \rightarrow 3p \rightarrow 3s$  contribution is 130% of the direct  $d$  polarization. If we had not carried out the corresponding calculation for the pseudo-metal configuration  $3d^7 4s^{1/2} 4s^{1/2}$ , but had simply assumed that the direct and indirect  $3s$  contributions were always in this ratio for iron, we would have erroneously concluded that the indirect  $d \rightarrow 3p \rightarrow 3s$  contribution to  $\chi$  in the metal was  $-1.96a_0^{-3}$  ( $-180\text{kG}$ ). This would give a total core hyperfine field of about  $-610\text{kG}$ , which, as shown by Table I, is sufficient to produce agreement with the experiment of Ref. 1. Thus, the appeal to the  $3d^7 4s^{1/2} 4s^{1/2}$  calculation is insufficient in itself to give us the metal result—it is also necessary to look at the contributions from individual diagrams for other nearby configurations to discern a trend for  $\chi_{ns}$ . In the present case, in the sequence of configurations  $3d^5$ ,  $3d^4 s^2$ ,  $3d^7 4s^{1/2} 4s^{1/2}$ , the following trends are evident: rather rapid change of the direct  $d$  polarization of the  $3s$  electrons, and much slower change in the indirect terms. The magnitudes are such that no reasonable adjustment of an assumed configuration for the metal would produce the desired large fields.

The indirect mechanisms also allow an induced-spin polarization in an  $s$  state to further polarize other  $s$  states. An examination of the LCMBPT contributions for  $\text{Fe}^{+3}$  and Fe atom indicate that these contributions are much smaller than the indirect polarization through the  $p$  states; so we have not calculated these terms for the metal.

### C. Correlation contributions

Figure 2 depicts some diagrams which have proved to make sizable contributions to the hyperfine fields in the atomic systems, for certain

combinations of electron states.

Figure 2(b) is the exchange version of Fig. 2(a), Fig. 2(d) of Fig. 2(c), and Fig. 2(f) of Fig. 2(e). From Refs. 7 and 8 it appears, that in addition to cancellations for each of the diagrams from various choices of one-electron occupied and excited states, there are also cancellations between direct and exchange terms. For example, for Fig. 2(a), the choice  $q=3p$ ,  $m=n=3s^\dagger$  gives for the  $\text{Fe}^{+3}$  ion a contribution to  $\chi$  of  $0.252 a_0^{-3}$ , while the same choice for Fig. 2(b) produces a contribution of  $-0.173 a_0^{-3}$ . Again, with  $q=3p$ ,  $m=3s^\dagger$ ,  $n=2s^\dagger$ , the contributions are  $-0.108 a_0^{-3}$  and  $0.067 a_0^{-3}$ , respectively. For the iron atom, the corresponding contributions are of the same order of magnitude with similar cancellations occurring. The total contributions from these and additional diagrams involving core  $s$  states is found to lead to less than 10% reduction of the core polarization discussed in Sec III A. There is no reason to expect the percentage to be any bigger in the metal, or that the sign of these contributions would reverse to produce reinforcement of the core polarization. We conclude, therefore, that correlation effects are insufficient to explain the large core fields found in Ref. 1.

The conduction-electron contribution can be influenced by conduction-conduction correlation effects, which have been only partially included through their influence on the diagonal elements of the Hamiltonian. The incorporation of correlation in the nondiagonal elements is more difficult. Its quantitative influence on the hyperfine field can however, be significant, but at best, of the order of magnitude of the conduction-electron contribution only. Since this latter quantity is small compared with the net hyperfine field, conduction-conduction correlation contributions are not expected to be of significance relative to the net hyperfine field.

#### IV. CONCLUSION

The work of Ref. 1 represents a very important experimental advance in the understanding of hyperfine fields, and the challenge of the large core fields found therein should not be lightly brushed aside on the grounds that previous UHF calculations have not found such fields. Instead, it is important to assess the accuracy of the theoretical procedures for calculating hyperfine fields to establish whether or not the experimental results are in real disagreement with theory. This is the stance adopted here, and our reasons for adopting it are as follows. (a) There are many contributions to  $\chi_{ns}$ , and there are cancellations between them. The differing contributions do not

have a common scaling factor in going from one atom/ion to another. It is possible, for example, for a particular contribution to change rapidly, even changing sign, as the configuration changes, while other contributions change much more slowly. Thus some near cancellations could be converted into reinforcement, and perhaps, under some suitable conditions, produce the required large field. (b) We believe there are some numerical problems in implementing the UHF procedure (basis set problems and problems in taking the difference of large almost-equal numbers). The evidence supporting this contention consists of the known sensitivity of the theoretical predictions of UHF calculations to the size of the basis set and the difference by a factor of 2 between the UHF results and the LCMBPT one-electron terms for the hyperfine field in transition-metal atoms. These difficulties could mask the changes we are seeking. (c) Some estimate was needed of correlation contributions.

We have attempted to give the best theoretical prediction available by current methods for the core fields. We have enumerated the one-electron effects and examined the contributions from correlation interactions. We have not succeeded in locating a possible source for the large core fields. However, the total hyperfine field which we calculate is in excellent agreement with other experiments.

We therefore feel that experimental confirmation of the results of Ref. 1 is urgently needed. It would be particularly useful to reduce the experimental uncertainties in the measured values of  $\delta$ . If the present experimental results are reaffirmed, then further theoretical work is required. The present work rules out one-electron effects and correlation interactions in the atomic state prior to the emission of the conversion electron. It may be necessary to reexamine the basis of the relationship of the internal-conversion coefficients for different spin states of the electrons to the electronic density at the nucleus for these states. This relationship depends on the assumptions, in the calculation of the transition probability associated with the internal-conversion process, of plane-wave character for the final state of the internal-conversion electron and the neglect of relaxation effects and changes in correlation effects associated with the other core electrons following the emission of the internal-conversion electron. The influence of the latter effects has been shown<sup>12</sup> to be of importance in the explanation of exchange-splitting of core energies as probed by x-ray emission spectra. If the relaxation and correlation effects and/or the departure of the emitted electron from plane-wave character

in the calculation of the transition probability for internal conversion are found to be important for the explanation of the results given in Ref. 1, this would be tantamount to a statement that experiment is not, in fact, measuring  $\delta_{ns}$  as given by

Eq. (1), and there would be no conflict with the measured total hyperfine field.

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