

*Work performed under the auspices of a contract between the Département des Recherches Physiques and the Association Euratom-C.E.A. at Fontenay-aux-Roses.

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PHYSICAL REVIEW A

VOLUME 2, NUMBER 4

OCTOBER 1970

Hyperfine Contact Interaction in the Iron Atom Calculated by Many-Body Theory*

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(Received 13 March 1970)

The contribution of the hyperfine contact interaction in the iron atom has been calculated by many-body theory. Terms involving one and two Coulomb interactions have been included, and our result for the contact constant is -4.55 MHz as compared with the experimental result of -5.1 MHz obtained by Childs and Goodman. Inclusion of an approximate relativistic correction changes the calculated value to -4.87 MHz. An estimate of higher-order terms gives a theoretical result -5.35 MHz or -5.72 MHz when the relativistic correction factor is included.

I. INTRODUCTION

The many-body perturbation theory of Brueckner¹ and Goldstone² is used to calculate the hyperfine contact interaction in the iron atom. The methods used to evaluate the diagrams of perturbation theory are taken from our previous work.³⁻⁵ Our methods for applying the Brueckner-Goldstone theory to atoms have also been used in hyperfine calculations by Dutta *et al.*⁶

The effect of the contact interaction in the iron atom has been analyzed previously by Watson and Freeman⁷ who carried out an unrestricted Hartree-Fock (UHF) calculation in an analytic expansion and obtained the value -3.4 MHz for the contact hyperfine-interaction constant C . A more accurate UHF calculation using an analytic expansion was later carried out by Bagus and Liu⁸ who obtained the value -4.4 MHz for C . An experimental value for C equal to -5.1 MHz has been obtained by Childs and Goodman from their measurements of the magnetic dipole hyperfine-interaction constants for the $5d_{4,3,2,1}$ states of the ground term of Fe^{57} in an atomic-beam magnetic-resonance experiment.⁹

The contact contribution to the hyperfine splitting is written⁸⁻¹⁰

$$E_C = C \vec{I} \cdot \vec{J}, \quad (1)$$

where $\vec{I}$ is the nuclear spin and $\vec{J}$ is the electronic angular momentum. The contact constant C may be written^{8,9}

$$C = \frac{8}{3} \pi (g_J - 1) g_e \mu_e g_I (\mu_N / S) \times \langle LS, M_L, M_S = S | \sum_i \delta(\vec{r}_i) s_{zi} | LS, M_L = L, M_S = S \rangle, \quad (2)$$

where

$$g_J = 1 + [J(J+1) + S(S+1) - L(L+1)] / [2J(J+1)]. \quad (3)$$

The usual g factors of the electron and of the nucleus are represented by g_e and g_I , respectively.¹¹ The symbols μ_e and μ_N represent the Bohr magneton and nuclear magneton.¹¹

We may also express C in terms of

$$\chi = \frac{4\pi}{S} \langle LS; M_L, M_S = S | \sum_{i=1}^N \delta(\vec{r}_i) s_{zi} | LS; M_L, M_S = S \rangle. \quad (4)$$

In order to calculate Eq. (4), we require the state

$|LS; M_L, M_S = S\rangle$. For the 5D ground state of iron, we also choose $M_L = L = 2$. The state $|LS; M_L, M_S = S\rangle$ is an exact (normalized to unity) solution of the Schrödinger equation

$$H|\psi_0\rangle = E|\psi_0\rangle,$$

with

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i < j=1}^N r_{ij}^{-1}. \quad (5)$$

Atomic units are used throughout this paper. A first approximation to $|\psi_0\rangle$ may be obtained by replacing $\sum r_{ij}^{-1}$ by $\sum_{i=1}^N V(r_i)$. Then $|\psi_0\rangle$ is approximated by $|\Phi_0\rangle$, where $|\Phi_0\rangle$ is a determinant containing the N single-particle states ϕ_n which are the lowest-energy solutions of

$$\left[-\frac{1}{2} \nabla^2 - Z/r + V(r) \right] \phi_n = \epsilon_n \phi_n. \quad (6)$$

The N states occupied in $|\Phi_0\rangle$ are called unexcited states, and all other solutions of Eq. (6) are called excited states. The unperturbed energy is $E_0 = \sum_{i=1}^N \epsilon_i$. From the Brueckner-Goldstone perturbation expansion,^{1,2} one obtains

$$|\psi_0\rangle = \sum_L [(E_0 - H_0)^{-1} H']^n |\Phi_0\rangle, \quad (7)$$

where $\sum_L$ means that only "linked" terms^{1,2} are to be included. The perturbation one obtains is

$$H' = \sum_{i < j=1}^N r_{ij}^{-1} - \sum_{i=1}^N V(r_i). \quad (8)$$

The energy correction one obtains is

$$\Delta E = E - E_0 = \sum_L \langle \Phi_0 | H' \left(\frac{1}{E_0 - H_0} H' \right)^n | \Phi_0 \rangle, \quad (9)$$

where L' restricts the sum to terms which are linked^{1,2} when the leftmost H' is removed for $n \geq 1$. The state $|\psi_0\rangle$ is an eigenstate of L^2, S^2, L_z , and S_z if $|\Phi_0\rangle$ is an eigenstate of these operators and if $\hat{L}$ and $\hat{S}$ commute with H' .⁵ Since the state $|\psi_0\rangle$ has the normalization $\langle \Phi_0 | \psi_0 \rangle = 1$ and is therefore not normalized to unity, the normalized state is given by

$$|LS; M_L = L, M_S = S\rangle = |\psi_0\rangle / \langle \psi_0 | \psi_0 \rangle^{1/2}, \quad (10)$$

where $|\Phi_0\rangle$ is an eigenstate of L_z and S_z with eigenvalues M_L and M_S , respectively. We could calculate χ by first calculating $|\psi_0\rangle$ and then substituting into Eqs. (4) and (10). We may also use an equivalent approach^{5,12} which is to calculate all energy diagrams in which there is one and only one interaction with $4\pi S^{-1} \sum_i s_{zi} \delta(\vec{r}_i)$ and any number of interactions with H' given by Eq. (8). The latter approach is used in this paper. Extensive discussions of the use of perturbation theory to calculate hyperfine structure may be found in the articles of Sandars.¹³

II. CALCULATIONS

A. Single-Particle States

The lowest-order diagrams contributing to χ are shown in Fig. 1 and involve one Coulomb interaction. We note that χ is zero when $|\psi_0\rangle$ is approximated by $|\Phi_0\rangle$ since the ns electrons with spin up and spin down are paired. In Fig. 1, the triangular symbol represents the hyperfine operator $s_z \delta(\vec{r})$, which is the notation of Sandars.¹³ The cross in Figs. 1(a) and 1(d) represents interaction with $-V(r)$. In Fig. 1(b) there is a direct interaction with a passive unexcited state, and in Fig. 1(c) there is an exchange interaction. The symbol αs refers to $1s^\pm, 2s^\pm, 3s^\pm$, and $4s^\pm$. Because of the factor s_z in the hyperfine interaction, Figs. 1(a) and 1(b) cancel for $\alpha s^\pm$ since αs^+ and αs^- states are calculated in the same potential. There is also cancellation of Fig. 1(c) with all exchange interactions except those involving the $3d$ electrons. The αs^+ electrons have exchange interactions with the five $3d^+$ electrons, and αs^- electrons have an exchange interaction with the single $3d^-$ electron. The net effect is equivalent in this order to four $3d$ exchange interactions with each αs^+ . We must also include the inverted diagrams as shown in Fig. 1(d). An insertion on the hole line is shown in Fig. 1(e). All such diagonal terms may be summed geometrically and result in an effective single-particle energy $\epsilon_{\alpha s}$ shifted by the matrix elements of the insertion.⁴ Diagrams in this calculation were evaluated with these shifts included.

In calculating the single-particle states we have used our V^{n-1} potential^{3,4} in which the excited states represent approximate physical single-particle excitations of the atom. All $l=0$ states were calculated with the Hartree-Fock $4s$ equation for neutral Fe. We then have an orthogonal set of $l=0$ states. However, the $1s, 2s$, and $3s$ states are not Hartree-Fock solutions although they were found numerical-

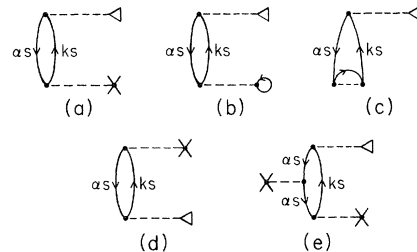


FIG. 1. Lowest-order contributions to χ for Fe. The triangular symbol represents the hyperfine contact operator $s_z \delta(\vec{r})$. Diagrams (a)–(c) also occur inverted as shown in (d). (e) insertion on the hole line. These insertions may be shown to modify the single-particle energies by the shift of Eq. (11).

ly to be very close to the Hartree-Fock solutions, the maximum difference in the radial part of the wave function being 0.001 a.u. As in the case of oxygen,⁴ the single-particle energies $\epsilon_{\alpha s}$ differ appreciably from the Hartree-Fock values. However, when we include the shift for $\epsilon_{\alpha s}$ due to insertions on the hole lines as shown in Fig. 1(e), the single-particle energies are in close agreement with the Hartree-Fock energies.¹⁴ Following the discussion of Ref. 4, the shift for a state α is given by

$$\Delta(\alpha) = \sum_{n=1}^N [\langle \alpha n | v | \alpha n \rangle - \langle \alpha n | v | n \alpha \rangle] - \langle \alpha | V | \alpha \rangle, \quad (11)$$

where the sum over n includes all occupied single-particle states. For $l=0$ states, $\Delta(\alpha)$ equals $\langle \alpha 4s | v | \alpha 4s \rangle - \langle \alpha 4s | v | 4s \alpha \rangle$ plus extremely small correction terms involving differences between our orbitals and the Hartree-Fock orbitals used in our potential V . The shifted and unshifted values for ϵ_{α} are compared in Table I.

For the np states, our previous prescription⁴ would suggest that we use the Hartree-Fock $3p$ equation to calculate all $l=1$ states. However, the complete set of single-particle states generated in a calculation such as this should be applicable to the calculation of many different atomic properties including polarizabilities where the transition $4s \rightarrow 4p$ should be very important. Also, we expect important correlation contributions from $4s \rightarrow 4p$ excitations. As a result, we decided to calculate all $l=1$ states in the field of all Fe electrons except for one $4s$ electron which is removed. Exchange interactions are included so that a given $2p$ electron effectively experiences a field because of interactions with five other $2p$ electrons when the direct and exchange terms are canceled (similarly for the $3p$ electrons). Our $3p$ and $2p$ states now are not Hartree-Fock states; but they were found to be reasonably close to the Hartree-Fock states calculated by Clementi, the maximum difference in the wave functions being 0.004 a.u. We also note that the

TABLE I. Single-particle energies in a.u.

α	ϵ_{α}^a	$\epsilon_{\alpha}'^b$	$\epsilon_{\alpha HF}^c$
1s	-261.757 64	-261.373 41	-261.373 11
2s	-32.311 68	-31.936 32	-31.936 23
3s	-4.524 58	-4.169 83	-4.169 72
4s	-0.258 34	-0.258 34	-0.258 32
2p	-27.792 27	-27.413 73	-27.414 31
3p	-3.101 69	-2.742 37	-2.742 42
3d	-0.647 18	-0.647 18	-0.647 10

^aCalculated with the potential of this paper.

^b $\epsilon_{\alpha} + \Delta(\alpha)$, where Δ is given by Eq. (11).

^cHartree-Fock value calculated by Clementi, Ref. 14.

TABLE II. Second-order contributions to χ .

Excitation	Contribution
4s $\rightarrow$ k	2.001 051 ^a
4s $\rightarrow$ n	0.640 074 ^b
3s $\rightarrow$ k	-0.656 384 ^a
3s $\rightarrow$ n	-0.030 331 ^b
2s $\rightarrow$ k	-3.444 827 ^a
2s $\rightarrow$ n	-0.024 462 ^b
1s $\rightarrow$ k	0.020 844 ^a
1s $\rightarrow$ n	0.000 013 ^b
Total	-1.433 360 ^c

^aContribution from continuum excited states.

^bContribution from bound excited states.

^cThis value for χ corresponds to $C=8.236$ MHz, where C is the contact constant.

necessary wave-function corrections may be calculated by the perturbation expansion. Our values for ϵ_{2p} and ϵ_{3p} are listed in Table I along with values corrected by the shift Δ of Eq. (11). For the $2p$ and $3p$ states, the shift of Eq. (11) is $\langle \alpha 4s | v | \alpha 4s \rangle - \langle \alpha 4s | v | 4s \alpha \rangle$ plus very small corrections due to differences in our $2p$ and $3p$ wave functions and the Hartree-Fock wave functions. The $l=2$ states were all calculated with the Hartree-Fock $3d$ equation. In calculating all of our states, we used the Hartree-Fock orbitals given by Clementi¹⁴ to calculate the direct and exchange terms of our potential. We have also calculated all $l=3$ and $l=4$ states in the field of all Fe electrons with one $3d$ electron removed.

B. Second-Order Results

Contributions from the second-order diagram of Fig. 1(c) and its inverted form are listed in Table II. These results represent the lowest-order contributions to χ from core polarization. The calculations include the hole-hole insertions of Fig. 1(e) since we calculated Fig. 1(c) with the shifted ϵ_{α}' of Table I. All of our calculations include these shifts so that effects as shown in Fig. 1(e) are included in all diagrams. Sums over the infinite number of bound excited states were included by our n^{-3} rule.^{3,4} Continuum states were included by numerical integration.³ We have included continuum contributions out to $k=150$ a.u. However, only the $1s$ excitations to continuum states involve appreciable contributions beyond $k=50$ a.u. We note in Table II that excitations to bound excited states are most important for $4s$ excitations. In order to convert from χ to MHz, we multiply by the factor 5.746 07. The total value for χ in second order corresponds to $C=-8.236$ MHz. We note

that there is much cancellation in the contributions from the different α s excitations.

C. Third-Order Results

In third order there are two interactions with H' . There are diagrams with core-polarization effects as shown in Fig. 2 and also purely-correlation diagrams as shown in Fig. 3. The crossed interaction in Fig. 2 now is generalized to represent the net effect of interactions with $-V$ and with all passive unexcited states. There are also inverted diagrams corresponding to each of the diagrams of Fig. 2. There are also diagrams corresponding to Figs. 2(b) and 2(d), but with the crossed interaction interchanged. Results of the contributions from the diagrams of Fig. 2 to χ are given in Table III. Contributions not explicitly listed in Table III were calculated or estimated to be small.

Among the correlation diagrams there is much cancellation from interactions involving spin-up and spin-down electrons. Most of the net contribution is due to the fact that ns^- electrons may be excited into the unoccupied $3d^-$ states with $m_l = \pm 1, 0, -2$. The basic diagrams of this type are shown in Fig. 3, and contributions from these diagrams are listed in Table IV. There are exchange diagrams for Figs. 3(c) and 3(d), but the exchange diagrams for Fig. 3(c) give zero contribution. There are also exchange diagrams such as Fig. 3(b) with $3d^-$ replaced by kl' . In these diagrams, the hyperfine interaction may also occur on the line labeled kl when $l=0$. Contributions not explicitly listed were calculated or estimated to be small. They will be listed in a future calculation which will include higher-order terms. We note that there is much cancellation among the various contributions of Table IV.

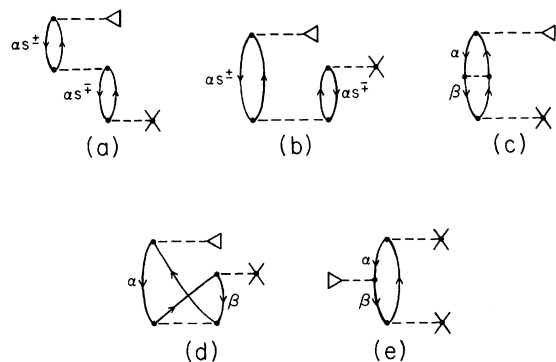


FIG. 2. Third-order core-polarization diagrams. The crossed interaction represents the net effect of interactions with $-V$ and with all passive unexcited states. There are also inverted diagrams corresponding to (a)–(d).

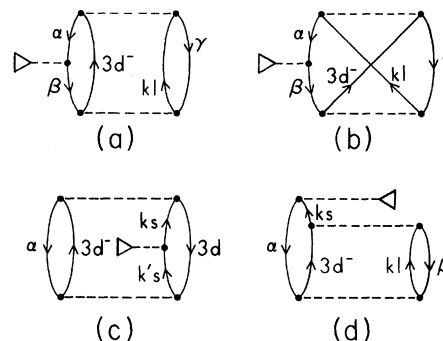


FIG. 3. Third-order correlation diagrams. There are also diagrams such as (b) with $3d^-$ replaced by kl' . The hyperfine interaction also occurs on any particle line of (b) when $l=0$ for that line. The diagram of (d) also occurs inverted.

D. Higher-Order Terms

Our total result for χ from second- and third-order diagrams is given by the total of Tables II–IV, and is equal to -0.792 .

An estimate has been made of some of the higher-order diagrams expected to be important for χ . These diagrams are shown in Fig. 4 and were found to be important in calculating the contact interaction in atomic oxygen.⁵ As discussed in Ref. 5, Figs. 4(a) and 4(b) add to give a product of the second-order hyperfine diagram times a second-order energy diagram divided by the negative of the denominator in the hyperfine diagram. Higher-order terms such as Figs. 4(a) and 4(b) give a geometric series which may be summed⁵ to shift the single-particle energy ϵ_α in the second-order diagram by $\sum_{\beta \neq \alpha} E_{\text{corr}}(\alpha, \beta)$, where $E_{\text{corr}}(\alpha, \beta)$ is the pair correlation energy for electrons in states α and β . Diagrams such as Fig. 4(c) with higher-order interactions may be approximated also by a shifted denominator in the basic diagrams of Fig. 1. A more complete discussion of higher-order terms of these types is given in Ref. 5. In Fig. 4(d) is shown a higher-order diagram involving interactions of the types shown in Fig. 2. Fourth- and higher-order terms involving the interactions of Fig. 2 were estimated geometrically^{3,5} to contribute to χ approximately 0.175 a.u. The interactions of Fig. 2 also modify Fig. 3(d) as shown in Fig. 4(e). This contribution to χ was estimated geometrically to be -0.052 a.u. In order to calculate the contribution of Figs. 4(a) and 4(b) which contribute to the denominator shift $\sum E_{\text{corr}}(\alpha, \beta)$, we must first calculate the pair correlation energy for α with all other electrons. This work is now in progress but is not yet complete. Our estimate of an appropriate denominator shift for the second-order diagram is

TABLE III. Contributions to χ from the diagrams of Fig. 2.

Diagram ^a	Value ^b
(a) $\alpha s = 4s$	0.243 210
(b) $\alpha s = 4s$	0.243 210 ^c
(a) $\alpha s = 3s$	0.002 709 ^c
(b) $\alpha s = 3s$	0.002 709 ^c
(a) $\alpha s = 2s$	-0.032 092
(b) $\alpha s = 2s$	-0.032 092 ^c
(a) $\alpha s = 1s$	0.000 000
(b) $\alpha s = 1s$	0.000 000
(c) $\alpha = 4s; \beta = 3s, 2s, 1s$	-0.000 852
(c) $\alpha = 3s; \beta = 4s, 2s, 1s$	0.087 808
(c) $\alpha = 2s; \beta = 4s, 3s, 1s$	0.027 378
(c) $\alpha = 1s; \beta = 4s, 3s, 2s$	-0.017 709
(d) $\alpha = 4s; \beta = 3s, 2s, 1s$	-0.000 216 ^d
(d) $\alpha = 3s; \beta = 4s, 2s, 1s$	0.075 292 ^d
(d) $\alpha = 2s; \beta = 4s, 3s, 1s$	0.033 489 ^d
(d) $\alpha = 1s; \beta = 4s, 3s, 2s$	-0.012 531 ^d
(c) $\beta = 3d; \alpha = 4s, 3s, 2s, 1s$	0.003 377
(c) $\beta = 3p; \alpha = 4s, 3s, 2s, 1s$	0.104 998
(c) $\beta = 2p; \alpha = 4s, 3s, 2s, 1s$	-0.075 333
(e) $\alpha, \beta = 4s, 3s, 2s, 1s$	-0.012 290
Total	0.641 065

^aLetters refer to the diagrams of Fig. 2.^bInverted diagrams are also included.^cDiagram with the hyperfine interaction and the crossed interaction interchanged is also included.^dDiagram in which the hyperfine interactions occur below the crossed interaction is also included as well as the inverted diagrams.

-0.05 a.u. The diagrams of Fig. 1(a)–1(d) were recalculated with this shift and the change in χ was found to be -0.262 a.u. Most of this result is due to a reduction in the 4s contribution. Our total estimate for χ from higher-order diagrams is then -0.139 a.u.

Our results are summarized in Table V and are compared with other calculations. In Table V we

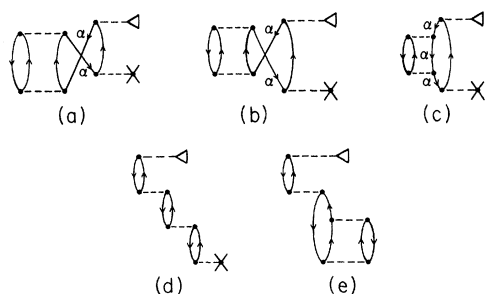


FIG. 4. Typical higher-order diagrams. (a) and (b) contribute to a geometric series which results in a shift in the basic second-order diagram. (d) represents a higher interaction of the core-polarization diagram of Fig. 2(a). (e) illustrates a modification to the basic diagram of Fig. 3(d). Diagrams (a)–(e) also occur inverted.

TABLE IV. Contributions to χ from the diagrams of Fig. 3.

Diagram ^a	Value
(a) $\alpha, \beta = 4s-1s; \gamma = 3d; l = 0$	0.018 232
(a) $\alpha, \beta = 4s-1s; \gamma = 3d; l = 2$	0.082 041
(a) $\alpha, \beta = 4s-1s; \gamma = 3d; l = 4$	0.060 988
(a) $\alpha, \beta = 4s-1s; \gamma = 3p; l = 1$	0.013 471
(a) $\alpha, \beta = 4s-1s; \gamma = 3p; l = 3$	0.128 493
(a) $\alpha, \beta = 4s-1s; \gamma = 2p; l = 1$	0.000 720
(a) $\alpha, \beta = 4s-1s; \gamma = 2p; l = 3$	0.005 086
(b) $\alpha, \beta = 4s-1s; \gamma = 3d; l = 2$	-0.043 360
(b) $\alpha, \beta = 4s-1s; \gamma = 3d; l = 4$	-0.009 198
(b) $\alpha, \beta = 4s-1s; \gamma = 3p; l = 1$	-0.049 664
(b) $\alpha, \beta = 4s-1s; \gamma = 3p; l = 3$	-0.080 266
(b) $\alpha, \beta = 4s-1s; \gamma = 2p; l = 1$	-0.003 055
(b) $\alpha, \beta = 4s-1s; \gamma = 2p; l = 3$	-0.003 647
(c) $\alpha = 4s-1s$	0.045 192
(d) $\alpha = 4s-1s; \beta = 3d; l = 0$	-0.072 554
(d) $\alpha = 4s-1s; \beta = 3d; l = 2$	-0.110 788
(d) $\alpha = 4s-1s; \beta = 3d; l = 4$	0.019 052
Total	0.000 743

^aThe notation 4s-1s means that α, β includes 4s, 3s, 2s and 1s.

have included the effect of multiplying our calculations by a relativistic correction factor 1.07 taken from Kopfermann.¹⁵ An analytic-expansion UHF calculation by Bagus and Liu⁸ resulted in χ equal to -0.768 a.u. Recently Fischer¹⁶ and Bagus, Liu, and Schaefer¹⁷ have carried out numerical UHF calculations for Fe and other atoms, and for Fe they obtained χ equal to -0.648 a.u. Fischer has also carried out a multideterminant UHF calculation in which mixing of the $(3d)^6(4s)^2$ and $(3d)^6(4p)^2$

TABLE V. Results for χ in a.u.

Calculation	
Second order ^a	-1.433
Second and third order ^b	-0.792
Second and third order with relativistic correction ^c	-0.847
Including higher orders ^d	-0.931
Including higher orders plus relativistic correction ^c	-0.996
Analytic UHF ^e	-0.768
Numerical UHF ^f	-0.648
Multideterminant UHF ^g	-1.062
Experiment ^h	-0.89

^aTaken from Table II.^bFrom Tables II–IV.^cRelativistic correction estimated from Ref. 15.^dResults from Tables II–IV plus our estimate of higher-order terms.^eFrom Ref. 8.^fFrom Refs. 16 and 17.^gFrom Ref. 16.^hFrom Ref. 9.

configurations is included. The result is a significant reduction in the $4s$ spin density which is positive, and χ becomes -1.062 a.u. The experimental value for χ (-0.89 a.u.) was obtained from the experimental result of Childs and Goodman⁹ that the contact constant $C = 5.1$ MHz.

III. CONCLUSIONS

Our value for χ through third order is in fairly good agreement with experiment, particularly after multiplication by the approximate relativistic correction factor.¹⁵ Our rough estimate of higher-order terms brings our nonrelativistic result into a little closer agreement with experiment. However, when the relativistic correction factor is included, our result "including higher-order terms" is in worse agreement with experiment than our result through third order. It is desirable that a much more careful study be made of higher-order terms. In estimating some of the higher-order terms, we used a denominator shift -0.05 a.u. for the second-order diagrams, the principal effect of which is the reduction of the $4s$ spin density at the nucleus.

None of the UHF results in Table V include the relativistic correction factor 1.07. The difference between the analytic UHF results and the numeri-

cal UHF results^{16,17} is evidently due to an incomplete basis set for the analytic expansion. The UHF results must be obtained to great accuracy since there are very large cancellations between spin-up and spin-down densities at the nucleus. We also note that in UHF calculations the wave function is no longer exactly an eigenstate of S^2 . In the UHF calculations listed in Table V, S^2 was calculated to be 6.018 for the analytic case,⁸ 6.0185 for the numerical case,^{16,17} and 6.0161 for the numerical multideterminant calculation.¹⁸ In many-body perturbation calculations we note that the wave function is an eigenstate of S^2 since we start from an eigenstate of S^2 , and since the perturbation H' commutes with $\hat{S}$.

Although the results of this calculation are in reasonable agreement with experiment, we see that contributions from terms beyond third order may be large and should be calculated carefully. We plan to investigate the higher-order terms after we have calculated the correlation energy of Fe.

ACKNOWLEDGMENTS

We wish to thank Dr. P. S. Bagus, Professor C. F. Fischer, and Professor G. B. Hess for helpful discussions.

*Research sponsored in part by the Aerospace Research Laboratories, Office of Aerospace Research, U. S. Air Force, Contract No. F 33615-69-C-1048, and by U. S. Atomic Energy Commission.

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