

ELECTRON CORRELATIONS IN THE IRON ATOM (*)

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Résumé. — La théorie des perturbations à N Corps est utilisée pour calculer des propriétés de l'atome de fer en tenant compte des effets de corrélation entre électrons. Nous donnons les résultats pour l'interaction de contact de structure hyperfine dans l'état fondamental et aussi pour l'énergie de corrélation. Les corrélations à 3 corps réduisent l'énergie de corrélation de la paire 3 d-3 d de seulement 14 %.

Abstract. — Many-body perturbation theory is used to calculate properties of the iron atom including the effects of electron correlations. Results are given for the hyperfine contact interaction in the ground state and also for the correlation energy. Three-body correlations reduce the 3 d-3 d pair correlation energy by only fourteen percent.

1. Introduction. — In this paper we use the many-body perturbation expansion of Brueckner [1], [2] and Goldstone [3] to calculate the hyperfine contact interaction and correlation energy of the iron atom. In order to apply the Brueckner-Goldstone expansion to atoms, we developed a number of techniques [4-6] which are also applicable to other perturbation expansions. These methods involve (a) explicit calculation of a complete set of numerical radial wave functions for each l -value. (b) choice of a V^{N-1} type potential so that excited single-particle states are good representations of single excitations of the atom [5]. (c) summation over excited states by numerical integration over the continuum and summation over bound excited states first by discrete sums and then by use of the n^{-3} rule [5] to extend the sums to infinity. (d) geometric summation of classes of terms by denominator shifts and approximate summations by ratios of matrix elements.

We have used these methods now in many calculations of various atomic properties [4-11]. Our prescriptions for applying the Brueckner-Goldstone expansion to atoms have also been used recently by the group of Dutta, Das, Pu, and co-workers [12, 13].

One advantage of this approach is that once the complete set of single-particle states has been calculated, one can then calculate many properties with

relative ease. In Fe, after calculating the single-particle states, we first calculated the hyperfine contact interaction and then calculated the correlation energy. These calculations included $l = 0, 1, 2, 3,$ and 4 excited states. All $l = 0$ states were calculated with the Hartree-Fock 4 s equation, and so the 4 s state is described by an Hartree-Fock orbital but the 1 s, 2 s, and 3 s states are not exactly Hartree-Fock states. However, they are extremely close to Hartree-Fock solutions. All $l = 1$ states were calculated with one 4 s electron removed so the 2 p and 3 p states are not Hartree-Fock states but they turned out to be very close to the Hartree-Fock solutions. Also, in calculating diagrams, insertions on the hole lines bring the single-particle energies into extremely close agreement with the Hartree-Fock values. The $l = 2$ states were calculated with the Hartree-Fock equation. The $l = 3$ and $l = 4$ states were calculated with one 3 d electron missing, that is, in the field of

$$(1 s)^2 (2 s)^2 (2 p)^6 (3 s)^2 (3 p)^6 (3 d)^5 (4 s)^2 .$$

2. Hyperfine structure. — The contact contribution to hyperfine splitting is written [14, 15, 16]

$$E_c = CIJ \quad (1)$$

where

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

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and

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (3)$$

We may express C in terms of

$$\chi = \frac{4\pi}{S} \langle LS, M_S = S | \sum_i \delta(r_i) s_{zi} | LS, M_S = S \rangle. \quad (4)$$

The state $|LS, M_S = S\rangle$ is an exact, normalized solution of the Schrödinger equation

$$H|\psi_0\rangle = E|\psi_0\rangle \quad (5)$$

We may use perturbation theory to obtain

$$|LS, M_S = S\rangle.$$

Our single-particle states φ_n are calculated from the equation

$$\left(-\frac{\nabla^2}{2} - \frac{Z}{r} + V(r)\right)\varphi_n = \varepsilon_n \varphi_n. \quad (6)$$

Using the Brueckner-Goldstone perturbation expansion,

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

where

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

and

$$H_0 = \sum_{i=1}^N \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + V(r_i)\right). \quad (9)$$

In eq. (7) the summation is restricted to linked terms [1-3]. We also have

$$E - E_0 = \Delta E = \langle \Phi_0 | H' | \psi_0 \rangle \quad (10)$$

The state $|\Phi_0\rangle$ is the lowest approximation to $|\psi_0\rangle$ and is obtained from

$$H_0 |\Phi_0\rangle = E_0 |\Phi_0\rangle \quad (11)$$

The state $|\Phi_0\rangle$ is normalized to unity, but $|\psi_0\rangle$ as obtained from eq. (7) is not normalized to unity but has the property

$$\langle \Phi_0 | \psi_0 \rangle = 1 \quad (12)$$

In evaluating the expectation value of an operator A , we may directly calculate

$$\langle \psi_0 | A | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle.$$

However, this is equivalent to evaluating all energy diagrams in which there is one and only one interaction with A and any number of interactions with H' . From a diagrammatic point of view, the latter approach is definitely preferable. Extensive discussions of the use of perturbation theory for hyperfine structure calculations have been given by Sandars [17, 18].

The lowest-order diagrams contributing to the hyperfine contact interaction when there are paired

$$l = 0$$

electrons are shown in figure 1(a), (b) and (c). These diagrams also occur inverted as shown in figure 1(d). In figure 1, the triangle represents the hyperfine

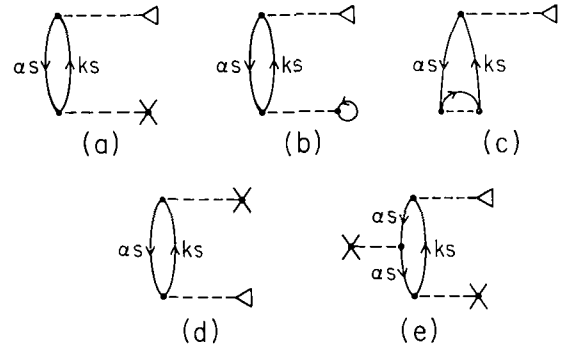


FIG. 1(a)-(d). — Second-order diagrams contributing to hyperfine structure. The hyperfine interaction is indicated by the triangle. These diagrams also occur inverted.

FIG. 1(e). — Insertion on the hole line which modifies the second-order energy.

operators [17, 18]. In figure 1(e) is shown an insertion on the hole line. These interactions may be summed geometrically to shift ε_α by

$$\Delta(\alpha) = \sum_{n=1}^N [\langle \alpha n | v | \alpha n \rangle - \langle \alpha n | v | n \alpha \rangle] - \langle \alpha | V | \alpha \rangle \quad (13)$$

It is found that $\varepsilon_\alpha + \Delta(\alpha)$ is always very close to the Hartree-Fock single-particle energy for the state α . For example, we calculated ε_{3p} to be -3.1017 . However, $\varepsilon_{3p} + \Delta$ is -2.74237 as compared with the Hartree-Fock value -2.74242 .

Contributions to χ from the diagrams of figure 1 are listed in Table I. Continuum contributions were included to $k = 150$ a. u. Our total second-order

TABLE I

Second order contributions to χ	
Excitation	Contribution
4 s \rightarrow k	2.001
4 s \rightarrow n	0.640
3 s \rightarrow k	-0.656
3 s \rightarrow n	-0.030
2 s \rightarrow k	-3.445
2 s \rightarrow n	-0.024
1 s \rightarrow k	0.021
1 s \rightarrow n	0.000
Total	-1.433

result for χ is -1.433 as compared with the experimental value -0.89 obtained by Childs and Goodman [15].

In third-order we have diagrams with two interactions with H' and one interaction with the hyperfine operator as shown in figures 2 and 3. The diagrams of figure 2 include at least one core polarization interaction indicated by the crossed interaction. The

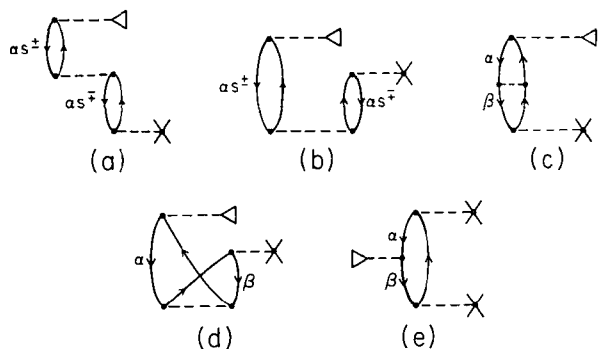


FIG. 2. — (Third-order diagrams involving one or more core-polarization interactions, which are indicated by the cross. Diagrams (a)-(d) also occur inverted.)

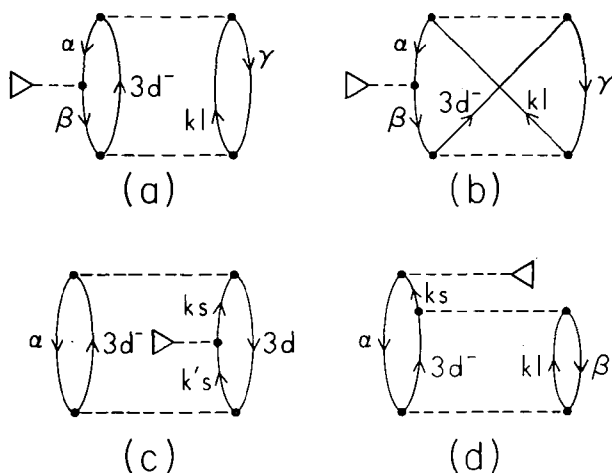


FIG. 3. — Third-order hyperfine diagrams involving correlations. There are also exchange diagrams like (c) and (d). There are exchange diagrams like (d) with $3d^-$ replaced by $k'l'$.

crossed interaction in figure 2 now represents the net effect of interactions with $-V$ and with all passive unexcited states. There are also inverted diagrams corresponding to diagrams (a)-(d) of figure 2. There are also diagrams like 2(b) and 2(c) with the crossed interaction and the hyperfine interaction interchanged. The largest contributions from the diagrams of figure 2 are from diagrams (a) and (b) with $\alpha = 4s$. These contribute 0.486 to χ . The total contribution from all the diagrams of figure 2 was calculated to be 0.641 a.u.

The most important third-order diagrams involving correlations are shown in figure 3. These involve excitation of ns -electrons into unoccupied $3d^-$ states. There are also exchange diagrams corresponding

to 3(d) and other exchange diagrams corresponding to figure 3(d) with $3d^-$ replaced by $k'l'$. We have calculated the contributions from diagrams of figure 3 to be $.001$ a. u. In obtaining this result, there has been considerable cancellation among individual contributions. For example, figure 3(a) with α and β being any of the $4s^-$, $3s^-$, $2s^-$, or $1s^-$ states and $\gamma = 3p$ and $l = 3$ gives a contribution 0.128 a. u. to χ . Our total result for χ from second and third-order diagrams then is -0.792 a. u.

Higher-order diagrams are shown in figure 4. Diagrams 4(a) and 4(b) add to give a product of a correlation energy part times a hyperfine part multi-

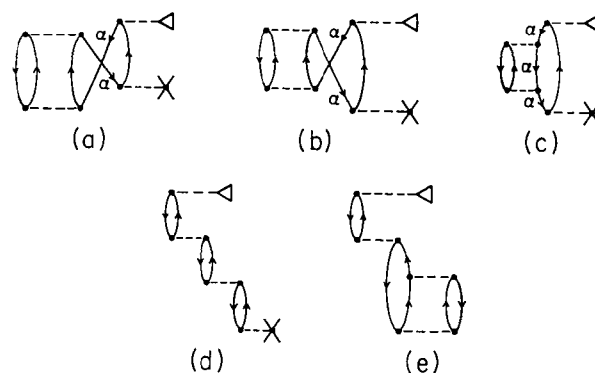


FIG. 4. — Typical higher-order hyperfine structure diagrams.

plied by minus D^{-1} where D is the denominator of the hyperfine part [9]. This result forms the first part of a geometric series which gives the basic diagram of figure 1(a) but with the denominator shifted by

$$\sum_{\beta} E_{\text{corr}}(\alpha, \beta), \quad (14)$$

where $E_{\text{corr}}(\alpha, \beta)$ is the correlation energy of electron in state α with that in state β . Diagram 4(d) represents higher iterations of the diagrams of figure 2, and diagram 4(e) represents similar insertions on the diagram of figure 3(d).

A rough estimate of $E_{\text{corr}}(\alpha, \beta)$ and also of the contributions from diagram 4(c) gave the result -0.262 from diagrams 4(a), (b), and (c). Diagrams 4(d) and 4(e) were estimated geometrically from the results for the diagrams of figure 2. Diagrams 4(d) and 4(e) then contribute 0.175 a. u. and -0.052 a. u. to χ , respectively. Our estimate for fourth-order and higher-order diagrams is -0.139 a. u.

The results for χ are summarized in Table II and compared to experiment and other calculations. The relativistic correction factor 1.07 was taken from Kopfermann [19]. The analytic unrestricted Hartree-Fock (UHF) result was calculated by Bagus and Liu [14]. More accurate UHF results were obtained numerically by Bagus et al. [20] and by Fischer [21] who obtained -0.648 a. u. for χ . C. Froese Fischer has also recently calculated χ in a multi-determinant UHF calculation allowing for $(4s)^2 - (4p)^2$ interaction and obtained -1.062 a. u. for χ .

TABLE II

Results for χ in atomic units

Second-order	- 1.433
Second and third-order	- 0.792
Second and third-order incl. rel. correction	- 0.847
including higher orders	- 0.931
including higher orders and relativistic corrections.....	- 0.996
analytic UHF.....	- 0.768
numerical UHF	- 0.648
multi-determinant UHF	- 1.062
experiment	- 0.89

3. **Correlation Energy.** — Over the past decade there has been great interest in correlation energies of atoms, and we have seen in eq. (14) the importance of correlation energy in calculating high-order hyperfine structure diagrams. In Fe we have carried out explicit calculations of the correlation energy among the outer $(3s)^2 (3p)^6 (3d)^6 (4s)^2$ electrons. The correlation interactions of these outer electrons with the inner $(1s)^2 (2s)^2 (2p)^6$ core are expected to be small and may be estimated from semi-empirical results [22]. Also, the correlation energy among the $(1s)^2 (2s)^2 (2p)^6$ electrons may be obtained from experiment [22].

Our calculations included $l = 0, 1, 2, 3$ and 4 angular momentum excited states. The single excitations and the pair correlations were calculated in second-order perturbation theory. We would expect the second-order pair correlation results to give the pair correlation to within 5-10 % accuracy based on previous calculations [6]. The second-order diagrams are shown in figure 5. Diagram 5(c) represents effects from single excitations. Corresponding to 5(c) there

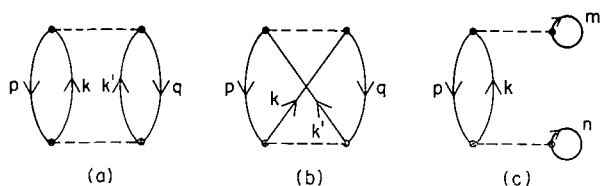


FIG. 5. — Second-order energy diagrams. Diagram (c) also occurs with exchange interactions with passive unexcited state and also with interactions with $-V$.

are also diagrams with exchange interactions with passive unexcited states and also interactions with $-V$ replacing the direct interactions shown in 5(c). Contributions from single excitations are shown in Table III. Results from pair correlations are given in Table IV. As expected, the correlation energy decreases as the spatial separation increases. This is quite clear, for example, for the 4 s-3 s correlation energy.

There is still the question of three-body contributions. In our oxygen correlation energy calculation,

TABLE III

Single excitation contributions to the correlation energy

4 s	- .001 6
3 d	- .003 8
3 p	- .001 5
3 s	- .000 2
Total	- .007 1

TABLE IV

Pair contributions to the correlation energy in a. u.

Pair	Direct	Exchange	Total
—	—	—	—
4 s-4 s	- 0.050 16	0.000 00	- 0.050 16 ^(a)
4 s-3 d	- 0.060 33	0.010 23	- 0.050 10
4 s-3 p	- 0.019 89	0.001 75	- 0.018 14
4 s-3 s	- 0.002 05	0.000 55	- 0.001 51
3 d-3 d	- 0.211 19	0.038 42	- 0.172 77
3 d-3 p	- 0.348 85	0.072 10	- 0.276 75
3 d-3 s	- 0.067 44	0.018 44	- 0.049 00
3 p-3 p	- 0.132 47	0.023 71	- 0.108 76
3 p-3 s	- 0.081 72	0.033 51	- 0.048 21
3 s-3 s	- 0.006 62	0.000 00	- 0.006 62
Total	- 0.980 72	0.198 71	- 0.782 01

^(a) All results of this table are second-order. When higher-order effects are included, the 4 s-4 s pair correlation energy becomes $-0.037 10$ a. u.

pair correlations and single excitations gave 107 % of the experimental correlation energy; and it was then conjectured that three-body effects in oxygen reduce the pair correlation energy by approximately 5 %. Recent configuration interaction calculations on Ne [23, 24] indicate that three-body effects reduce the pair correlation results by approximately 10 %.

In Fe we first examined the three-body correlations among the 3 d electrons where they might be expected to be rather large. The lowest-order three-body diagrams are shown in figure 6. The basic three-body diagram is the ring diagram of figure 6(a). The other diagrams correspond to exchanges of 6(a). In fourth-order there are diagrams like 6(a) with triple excitations. These are expected to be small since the third excitation results from interaction with a particle line or with a hole line and these contribute diagrams of opposite sign and approximately equal magnitude.

In Fe we calculated the ring diagrams of figure 6(a) among 3 d electrons and included excited states with $l = 2$ and $l = 3$ since these gave most of the 3 d-3 d pair correlation energy. From diagrams with $l = 2$ excitations we obtained .021 13 a. u. and 0.003 19 from $l = 3$ excitations. The effects

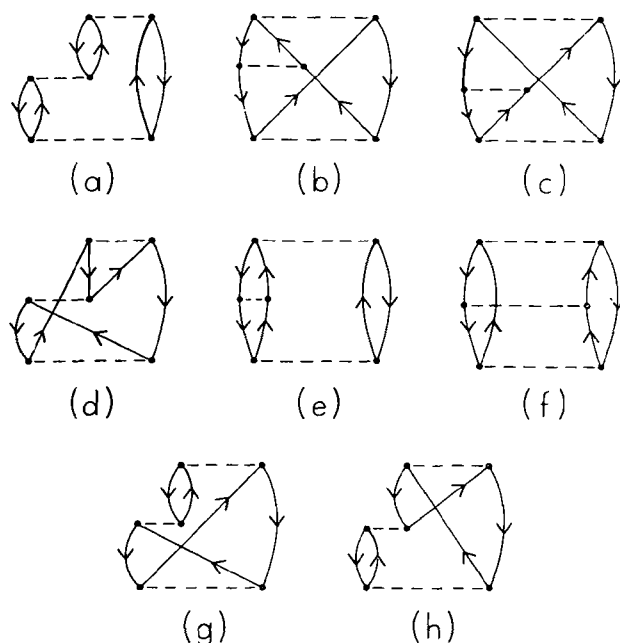


FIG. 6. — Third-order three-body diagrams. (a) ring diagram. (b)-(h) involve one or exchanges of the interactions in (a).

from the exchange diagrams 6(b)-6(h) were estimated to be quite small. This is because each of them involves at least one $K = 2$ term in the Legendre expansion of matrix elements for $l = 2$ excited states. However, in calculating 6(a) for $l = 2$ excited states, these are contributions from three $K = 0$ terms. Our three-body result among 3 d electrons is then 0.024 32 a. u. which is 14 % of the 3 d-3 d pair correlation result.

We have also calculated three-body diagrams like figure 6(a) in which one of the three hole lines is a 3 p state and the other two are 3 d states. We only included 3 d \rightarrow kd and 3 p \rightarrow kp excitations since these gave most of the pair correlation energy. 3 d \rightarrow kd and 3 p \rightarrow kp include both bound and continuum excited states. The 3 d-3 d-3 p result is 0.032 07 a. u. The 3 d-3 p-3 p

$$3 p \rightarrow kp$$

excitations is 0.015 12 a. u. For the 3 p-3 p-3 p ring diagrams with only 3 p \rightarrow kp excitations we obtained 0.001 96 a. u. We believe that our 3 d-3 p-3 p

results and especially our 3 p-3 p-3 p results would be significantly increased by allowance for 3 p \rightarrow kd excitations, particularly excitations into the unoccupied 3 d states. The total of the three-body diagrams which were calculated is 0.073 46 a. u.

Our total result from correlations among the $n = 3$ and $n = 4$ electrons of Fe is then $-0.715 53$ a. u. From the semi-empirical data of Clementi [22], we estimate the correlation energy from interactions of $n = 3$ and $n = 4$ electrons with the $(1 s)^2 (2 s)^2 (2 p)^6$ core as approximately -0.100 a. u. We also have estimated the correlation energy among the

$$(1 s)^2 (2 s)^2 (2 p)^6$$

electrons as approximately -0.500 a. u. This results in a total E_{corr} for Fe equal to -1.316 a. u. This result is probably accurate only to 10-15 %.

In higher orders, if only a fixed pair of electrons pq is considered, many of the higher-order terms may be included by shifting the second-order denominator by $E_{\text{corr}}(p, q)$ which is the pair correlation energy for pq . If one carries out a configuration interaction calculation allowing only for single and double excitations, then one has a Brillouin-Wigner type situation in which the denominator is effectively shifted by E_{corr} , the total correlation energy. The most correct shift of this type is given by [25]

$$\sum_{\alpha} E_{\text{corr}}(p, \alpha) + \sum_{\beta \neq p} E_{\text{corr}}(q, \beta). \quad (15)$$

In order to obtain the shift of eq. (15) in configuration interaction calculations, it is necessary to include four-fold excitations [25]. We have recalculated the 4 s-4 s pair correlation energy with these shifts. We obtained $-0.043 24$ a. u. with the pair shift $E_{\text{corr}}(4 s, 4 s)$. We obtained $-0.012 13$ a. u. with the shift E_{corr} . Using the correct shift of eq. (15), we obtained

$$-0.037 10$$

for the 4 s-4 s pair correlation energy. We do not expect such large differences for the other pairs since the energy denominators are then larger. Nevertheless, these results indicate the importance of including four-fold excitations in configuration interaction calculations in certain cases.

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