

Green's-function approach to the hyperfine problem in atoms and molecules

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To avoid the shortcomings of conventional methods such as the symmetry dilemma and the subtraction of large numbers of roughly equal magnitude, a Green's-function method is extended to the study of hyperfine splitting in atoms and molecules. With this method the hyperfine coupling constants are calculated for the ground and excited states of the molecule by a self-consistent equation, starting from the Hartree-Fock level of a closed-shell system. In this approach the one-particle picture is retained, and it is possible to study the hyperfine problem from a different physical point of view. The theory is applied to the calculation of the ground-state and some excited-state hyperfine coupling constants of Li and CH₃. It is shown that those terms of the perturbation expansion which are essential to explain the constant of the atom are unessential in the case of the methyl radical and vice versa. This result is generalized. The computational effort to evaluate the coupling constants has been found to be very small.

I. INTRODUCTION

Much work has been done to calculate hyperfine coupling constants (hfs) for atoms and molecules by an *ab initio* approach.¹⁻²⁰ Many results obtained so far depend strongly on the method used for calculating the wave function of the system, and there is no general agreement on the relative advantages and shortcomings of the different methods. Actually there are two main reasons responsible for the difficulties arising when calculating hyperfine splitting. First the splitting is proportional to the spin density of the electrons at the nuclei and it is usually obtained as a small difference of comparatively large numbers, i.e., the difference of the spin densities of spin-up and spin-down electrons. Furthermore, the hyperfine splitting arises only in open-shell systems which are difficult to handle compared to closed-shell systems with approximately the same number of electrons. In this work we investigate a method which avoids the above difficulties, but before elaborating on it in detail other approaches to the hfs problem are briefly discussed.

It is convenient to start with an expression for the hfs. Because of the fast rotation of free molecules the hyperfine splittings arise only from the Fermi contact operator which for *S* states is given by^{21,22}

$$F = \sum_N F^N, \quad (1)$$

$$F^N = \frac{8}{3} \pi g \beta g_N \beta_N \sum_k \delta(r_k - r_N) \vec{S}_k \cdot \vec{I}_N,$$

where g , β , g_N , β_N are the electronic g factor, the Bohr magneton, the nuclear g factor, and the nuclear magneton for the N th nucleus, respectively.

\vec{S}_k and \vec{I}_N are the spin operators for the k th electron and the N th nucleus. Experimental results are expressed in terms of a coupling constant²³ a^N

$$F^N = a^N \vec{S} \cdot \vec{I}_N, \quad (2)$$

where \vec{S} is the total electron spin operator. Equating Eq. (1) and Eq. (2) leads to an explicit expression for the hfs as an expectation value in the state described by the wave function Ψ :

$$a^N = \frac{16}{3} \pi g \beta g_N \beta_N \sum_k \langle \Psi | \delta(r_k - r_N) S_k^z | \Psi \rangle. \quad (3)$$

When states which are not *S* states are considered (*L-S* coupling) the above coupling constant is to be divided by $2J$ and Ψ must be understood as $\Psi(J=L+S, M_J=J)$. Equation (3) is the usual starting point for *ab initio* calculations of the hfs.

Most of the calculations are based on the Hartree-Fock (HF) approximation or on extensions of it. In the restricted HF (RHF) scheme the assumption is made that the spatial parts of the HF orbitals are independent of the electron spin. Thus, only the unpaired valence electron contributes to the hfs, and when this electron has a vanishing density at the nucleus, no splitting is expected, in contradiction to experiment. No core polarization or higher correlation effects are included in the RHF hfs. To include core polarization the unrestricted HF (UHF) scheme is used whereby the assumption made in the RHF approximation is omitted. However, the wave function Ψ calculated in the UHF approximation is not an eigenfunction of S^2 , which is very unsatisfactory especially when calculating spin-dependent observables. In addition it is difficult to estimate the amount of correlation included in this approximation. From extensive calculations on atoms Bagus *et al.*⁷ have

concluded that the UHF method should be used with extreme caution for the prediction of spin densities at the nucleus.

From the UHF wave function one obtains an eigenfunction of S^2 by applying a projection operator introduced by Löwdin.²⁴ The hfs obtained with this method (PUHF) are often better than those obtained with the UHF calculation,⁵ but they lead sometimes to worse results than UHF.²⁵ There is also the serious objection that the projection is performed after the variation, leading to a wave function which does not minimize the energy. It is of course reasonable to minimize the energy after projection. This has been attempted by Goddard.^{26,6} The spin density obtained with this method for nitrogen represents an improvement over the UHF value, but the oxygen and fluorine values are in poorer agreement with experiment than the UHF values. It is here also the case that the amount of correlation included is uncertain.²⁷

Another extension of the RHF method which has also been used to calculate atomic hfs⁹ is the so-called spin-optimized HF method.^{31,32} Such an approach is extremely complicated, since it abandons orbital orthogonality. The expense in computer time is large and increases enormously with the number of electrons.

There are still other methods which have been applied to calculate hfs. The configuration-interaction (CI) approach which is, in principle, adequate for calculating many-electron wave functions has been used with varying success.^{2,5,28-30,10-12} The main reason for this is that, especially for larger systems, the selections of configurations is arbitrary. A more complete CI calculation requires a high computational effort. In addition it is difficult to interpret the results physically because of the many-configuration character of Ψ . Meyer⁵ has proposed an approximate extended HF method (AEHF) for evaluating hfs. With this method one uses a many-determinant wave function Ψ with a limited number of single- and double-excited configurations, which describes polarization effects. This method avoids some of the shortcomings of the previously used methods. Indeed the results obtained with AEHF give for the first-row atoms a more consistent agreement with experiment than the methods using a single-determinant wave function. Because of the large contributions of second-order effects in the polarization parameters, some doubts may arise concerning the reliability of the perturbation theory used in this method.⁵

Two other limited types of CI wave functions, referred to as polarization¹⁰ and first-order¹¹ wave functions, have been used to determine atomic hfs. The spin densities obtained with these meth-

ods are also in more consistent agreement with experiment than the values obtained with a single-determinant wave function. For the atoms B to F the spin densities resulting from UHF calculations are about twice as large as the experimental values. The polarization and first-order wave functions indeed lead to smaller spin densities. These are, however, in several cases too small compared with experiment. Larsson *et al.*¹³ have discussed the main reasons for the above behavior of the first-order spin densities by analyzing the corresponding wave functions in terms of natural spin orbitals.³³ Such an analysis is of general importance, since it may help answer the question about which type of correlation and polarization effects contribute to hyperfine structure.

The Brueckner-Goldstone (BG) method has also been applied to the hyperfine splitting problem.¹⁶ In this approach the ground-state expectation value of the Fermi contact operator is calculated starting from an unperturbed Hamiltonian which includes the V^{N-1} potential introduced by Kelly.³⁴ For the Li atom this choice of potential is suitable to avoid the symmetry dilemma²⁴ which arises in the UHF scheme. In addition the BG approach has the advantage that one deals directly with small numbers.

A hierarchy of n -particle variational Bethe-Goldstone equations defined in terms of configurational excitations of a HF reference state has been used by Nesbet¹⁷ to calculate atomic hyperfine coupling constants. The method leads to good results, but requires a considerable amount of computer time.

The present paper investigates an approach to calculate hfs which is completely different from previous methods. As a closed-shell molecule (neutral or ionic) does not exhibit a hyperfine splitting, we may use the Green's function formalism to evaluate the hfs of diverse states of the molecule obtained by removing one electron from the closed shell. In principle, we can also study the effect of removing two or more electrons from the molecule by considering the appropriate many-body Green's functions. Thus, we are able to calculate hfs for ions which are difficult to measure and which might be of interest, e.g., in astrophysics, as well as hfs of radicals and many different open-shell systems. This approach also has the main formal advantages of the BG approach. Further advantages are that the hfs for excited states can be calculated starting from the same closed-shell HF calculation and that the number of terms which contribute to the hfs is strongly reduced due to the properties of closed-shell systems [see Sec. IV, Fig. 2)]. We have chosen the HF potential as a starting point because

of the general availability of HF calculations. The theory can easily be extended to other types of suitable single-particle potentials.

With the present approach it is possible to study the hyperfine problem from a physically different point of view making it a complementary method to those previously applied.

As examples we calculate in Sec. VI the ground-state and some excited-state hfs of Li and CH₃. We do not intend to calculate highly accurate hfs. To do this more adequate basis sets for the HF calculations should be used, especially for the values of the orbitals at the nuclei. Our present aims are to find the important terms of the perturbation expansion, to look at the mutual compensation of correlation and reorganization effects, to assess the computational effort needed to obtain results in reasonable agreement with experiment, and to demonstrate the feasibility of the approach in general.

II. THE HAMILTONIAN AND THE ONE-PARTICLE GREEN'S FUNCTION

The nonrelativistic Hamiltonian of an atom or molecule is given as a sum of a one-particle operator $h(r)$ and a two-particle operator $V(r, r')$. To evaluate the Green's function, this Hamiltonian should be written in the notation of the occupation number formalism, where a_i and a_i^\dagger are annihilation and creation operators for a particle in the one-particle state specified by i . As already mentioned, we choose $h(r)$ to be the HF operator and the one-particle states become the HF spin orbitals. When the Fermi contact operator is included, we find

$$\begin{aligned}
 H &= H_0 + H_V + H_F, \\
 H_0 &= \sum_i \epsilon_i a_i^\dagger a_i, \\
 H_F &= \sum_N H_F^N, \\
 H_F^N &= \sum_{m,n}^N F_{mn}^N a_m^\dagger a_n, \\
 H_V &= \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \\
 &\quad - \sum_{i,j} \sum_{k \in \mathfrak{F}} (V_{ikjk} - V_{ikkj}) a_i^\dagger a_j,
 \end{aligned} \tag{4}$$

where ϵ_i , F_{mn}^N , and V_{ijkl} are the matrix elements of the operators h , F^N , and $|r - r'|^{-1}$, respectively, and \mathfrak{F} is the set of orbitals occupied in the HF ground state of the atom or molecule.

As already mentioned in the Introduction, we attempt to calculate the hfs by a Green's-function method. For this purpose we consider a closed-

shell system of M interacting electrons with a ground-state wave function Ψ_0^M . Then the one-particle Green's function is defined by

$$G_{ij}^{\text{hfs}}(t, t') = -i \langle \Psi_0^M | T \{ a_i(t) a_j^\dagger(t') \} | \Psi_0^M \rangle, \tag{5}$$

where the $a_i(t) = e^{iHt} a_i e^{-iHt}$ are in the Heisenberg representation and T is the Wick time-ordering operator. Of more interest to us is the Fourier transform

$$\begin{aligned}
 G_{ij}^{\text{hfs}}(\omega) &= \int e^{i\omega(t-t')} d(t-t') G_{ij}^{\text{hfs}}(t, t') \\
 &= \sum_n \frac{\langle \Psi_0^M | a_i | \Psi_n^{M+1} \rangle \langle \Psi_n^{M+1} | a_j^\dagger | \Psi_0^M \rangle}{\omega + (E_0^M - E_n^{M+1}) + i0^+} \\
 &\quad + \sum_n \frac{\langle \Psi_0^M | a_j^\dagger | \Psi_n^{M-1} \rangle \langle \Psi_n^{M-1} | a_i | \Psi_0^M \rangle}{\omega + (E_n^{M-1} - E_0^M) - i0^+},
 \end{aligned} \tag{6}$$

where Ψ_n^U and E_n^U are the wave function and the corresponding energy of the n th state of the system having U electrons. Thus by calculating the poles of the Green's functions, one obtains the ionization energies and electron affinities which include the hyperfine structure. Since Fermi contact splitting occurs only in open-shell systems, one can obtain the hfs for the diverse states of the $(M \pm 1)$ -electron systems.

III. A FORMULA FOR THE HYPERFINE SPLITTING

To demonstrate how the hfs can be calculated, we start from the Dyson equation in matrix notation:

$$\underline{G}^{\text{hfs}}(\omega) = \underline{G}^0(\omega) + \underline{G}^0(\omega) \underline{\Sigma}^{\text{hfs}}(\omega) \underline{G}^{\text{hfs}}(\omega), \tag{7}$$

where $\underline{\Sigma}^{\text{hfs}}$ denotes the self-energy part and \underline{G}^0 is the free Green's function,

$$G_{ij}^0(\omega) = \frac{\delta_{ij}}{\omega - \epsilon_i + ai0^+}, \quad a = \begin{cases} +1, & i \notin \mathfrak{F}, \\ -1, & i \in \mathfrak{F}. \end{cases} \tag{8}$$

In addition to the above Green's-function matrix $\underline{G}^{\text{hfs}}$ we consider an analogous function \underline{G}^V which is calculated with $H = H_0 + H_V$ and thus does not include any hyperfine structure:

$$\underline{G}^V = \underline{G}^0 + \underline{G}^0 \underline{\Sigma}^V \underline{G}^V. \tag{9}$$

While the self-energy part $\underline{\Sigma}^{\text{hfs}}$ contains the interaction between the HF particles as well as the Fermi contact interaction, $\underline{\Sigma}^V$ contains only the former interaction. We may write

$$\underline{\Sigma}^{\text{hfs}} = \underline{\Sigma}^V + \underline{\Sigma}^{V,F}, \tag{10}$$

where each term (diagram) of $\underline{\Sigma}^{V,F}$ must contain both interactions. The hfs can be calculated directly from

$$(\underline{G}^V)^{-1} - (\underline{G}^{\text{hfs}})^{-1} = \underline{\Sigma}^{V,F}. \tag{11}$$

Considering only diagonal elements, the Green's

functions may be written as

$$G_{ii}^V = \frac{p_i^V}{\omega + I_i} + f_i^V(\omega) \quad (12a)$$

and

$$G_{ii}^{\text{hfs}} = \frac{p_i^{\text{hfs}}}{\omega + I_i - \Delta_i} + f_i^{\text{hfs}}(\omega), \quad (12b)$$

where p_i^V and p_i^{hfs} are the pole strengths of the corresponding Green's functions and are given by

$$p_i^V = \left[1 - \left(\frac{\partial \Sigma_{ii}^V}{\partial \omega} \right)_{-I_i} \right]^{-1}, \quad (13a)$$

$$p_i^{\text{hfs}} = \left[1 - \left(\frac{\partial \Sigma_{ii}^{\text{hfs}}}{\partial \omega} \right)_{-I_i + \Delta_i} \right]^{-1}. \quad (13b)$$

Δ_i is the hyperfine splitting in the state specified by i and the f_i are correction functions^{35,36} which are smooth around the pole of G_{ii} and vanish at this pole, i.e.,

$$f_i^V(-I_i) = f_i^{\text{hfs}}(-I_i + \Delta_i) = 0.$$

Inserting Eqs. (12a) and (12b) into Eq. (11), one obtains for the hyperfine splitting

$$\Delta_i = p_i^V \Sigma_{ii}^{V,F}(-I_i + \Delta_i) + O(\Delta_i^2); \quad (14)$$

$O(\Delta_i^2)$ denotes a term of the order of Δ_i^2 and is negligible. Equation (14) is a self-consistent equation for the hyperfine splitting in the state $|i, M \pm 1\rangle$. Usually we are not very near a pole of the self-energy part, which means, with $|\Delta_i| \ll I_i$, that we may neglect Δ_i on the right-hand side of Eq. (14). When calculating the hfs for a state i which corresponds to the removal of an outer electron from the ground state of the M electron system, $-I_i$ is far away from poles of $\Sigma_{ii}^{V,F}$,¹⁹ and we may furthermore substitute the ionization potential I_i by $-\epsilon_i$ according to Koopmans' theorem³⁷:

$$\Delta_i = p_i^V \Sigma_{ii}^{V,F}(\epsilon_i). \quad (15)$$

Equation (15) is the basic formula we use in our calculations of Δ_i . It should be mentioned that for obtaining a higher accuracy, G_{ii} and Σ_{ii} in Eqs. (12) and (13) should be replaced by the i th eigenvalue of G and $\epsilon + \Sigma$, respectively, where ϵ is the diagonal matrix of the one-particle energies. However, the eigenvector matrices of the Green's function matrices are usually well approximated by unit matrices³⁸ and Eq. (15) can be used.

$$D = (-1)^2 \sum_{\substack{i_1, i_2, i_3 \neq \mp \\ k \in \mp}} \frac{V_{ikl_2l_3} V_{l_1l_3jk} F_{l_2l_1}^N}{(+\omega - \epsilon_{l_2} - \epsilon_{l_3} + \epsilon_k)(+\omega - \epsilon_{l_1} - \epsilon_{l_3} + \epsilon_k)}, \quad (16)$$

where D is the diagram shown in Fig. 1. In the following we consider three arguments which lead to a strong reduction of the number of diagrams which have to be taken into account and to a sim-

IV. EVALUATION OF $\Sigma^{V,F}$

To complete the calculation of the hfs we have to determine the combined self-energy part $\Sigma^{V,F}$. This is done within the framework of a known perturbation theory.³⁹ It is convenient to use a diagrammatic method which provides us with a straightforward expansion of the self-energy part. For the special case of evaluating $\Sigma^{V,F}$, the rules to draw and evaluate the functions are briefly introduced.

We first introduce some definitions. All diagrams are drawn on a vertical time scale on the page. A solid line pointing upwards represents $iG_{kk}^0(t, t')$ with $t > t'$ and when pointing downwards it represents $iG_{kk}^0(t, t')$ with $t \leq t'$. A wavy line represents the matrix element of the Coulomb interaction and a wavy line attached to F^N inside a circle stands for a matrix element of F^N .

The rules for drawing the diagrams of n th order in V_{ijk} and m th order in F_{ij} are the following: (i) Draw n horizontal V_{ijk} lines and m (≥ 1) horizontal F_{ij} lines and connect them by $2n + m - 1$ G^0 lines. All topologically nonequivalent linked diagrams should be drawn. (ii) Diagrams which split into two unlinked parts by removing a single solid line as well as diagrams with solid lines which start and end at the same wavy line have to be omitted.

It is convenient for us to evaluate the diagrams directly in ω space. The following rules hold: (i) Connect the free indices occurring in each diagram by an $\exp[i\omega(t - t')]$ line, which is pointing from t to t' . (ii) Draw horizontal lines between two successive wavy lines. Any part of a diagram between two successive wavy lines is called a block. (iii) Each G^0 or $\exp[i\omega(t - t')]$ line cut by a horizontal line makes an additive contribution to the denominator of the block: $-\epsilon_i$ and $-\omega$ for G_{ii}^0 and $\exp[i\omega(t - t')]$ pointing upwards and ϵ_i, ω when pointing downwards. (iv) All interactions V_{ijk} and F_{ij} , the contributions of the blocks and a factor $(-1)^{a+b}$ (where a is the number of hole lines and b is the number of closed loops) are multiplied and the sum over the internal indices is taken.

As an example a diagram of second order in V_{ijk} and first order in F_{ij} is obtained by these rules:

plification of the expressions involved. First it is clear that we need only consider the diagrams of first order in F_{ij} . The diagrams of second order in F_{ij} are much smaller but actually contribute to

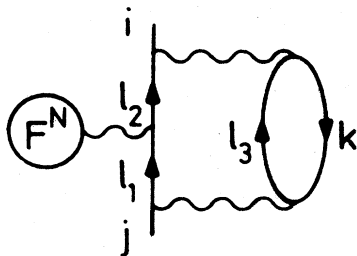


FIG. 1. Diagram of second order in V_{ijkl} and first order in F_{ij} . In the text this diagram is referred to as D .

the nuclear coupling constants describing the nuclear-spin-resonance experiments. The second point is that for closed-shell systems the matrix elements F_{nm} obey simple rules (real spin orbitals are considered):

$$\begin{aligned} F_{mn} &= F_{nm}, \\ F_{m_\sigma n_{\sigma'}} &= F_{m_\sigma n_\sigma} \delta_{\sigma\sigma'}, \\ F_{m_\alpha n_\alpha} &= -F_{m_\beta n_\beta}. \end{aligned} \quad (17)$$

With these rules it can be seen that many diagrams vanish. We obtain the simple rule that diagrams where the Fermi contact wavy line is located at a closed loop ("direct diagrams") do not contribute to $\Sigma_{ij}^{V,F}$, e.g., see Fig. 2. It follows that only "exchange diagrams," i.e., diagrams where the Fermi contact wavy line is located at the solid line going from j to i , contribute to $\Sigma_{ij}^{V,F}$.

This fact may easily be interpreted physically. Consider an unpaired π electron outside the closed shell of doubly occupied orbitals. This electron does not contribute to the hfs since its spin density at the nucleus vanishes. From the diagrams which contribute to $\Sigma_{\pi\pi}^{V,F}$ (see Fig. 3) we conclude that this electron prefers the interaction with other electrons having the same spin than with those of different spin. This is easily seen by considering that

$$V_{i\sigma_i^j\sigma_j^k\sigma_k^l\sigma_l} = V_{ijkl} \delta_{\sigma_i\sigma_k} \delta_{\sigma_j\sigma_l}.$$

Thus, as some of the other electrons have a finite spin density at the nucleus, these diagrams describe the mechanism of core polarization and higher correlation effects contributing to a non-vanishing hfs.

Since we are calculating the hfs of an open-shell system starting from a closed-shell calculation, we may perform the summation over the spin variables and thus simplify the expressions for the diagrams. The rule of performing the spin summation is simple: instead of summing over spin orbitals as in Eq. (16), we may sum over doubly occupied and empty orbitals only and multiply each diagram by 2^b , where b is the number of closed loops.

The nonvanishing diagrams of first order in F_{ij}^N and up to second order in V_{ijkl} are shown in Fig. 3. It should be mentioned that the hfs for each nucleus of the molecule can be calculated separately.

hfs in first-order perturbation theory

In the lowest-order approximation [Fig. 3(a)] we obtain for the hyperfine splitting due to the N th nucleus

$${}^{(1)}\Delta_i^N = p_i F_{ii}^N. \quad (18)$$

The corresponding hfs is simply

$$a_i^N = \frac{8}{3} \pi g \beta g_N \beta_N p_i |\varphi_i(\gamma_N)|^2, \quad (19)$$

where $\varphi_i(\gamma_N)$ is the i th HF orbital of the closed-shell system taken at the N th nucleus. Here the main difference between the present method and the usual methods becomes clear. When the hfs of a radical or an ion is calculated by the RHF approach, one obtains $a_i^N = \frac{8}{3} \pi g \beta g_N \beta_N |\bar{\varphi}_i(\gamma_N)|^2$, where $\bar{\varphi}_i$ is the corresponding RHF orbital of the system. In the present approach we start from the HF calculation of a closed-shell system, the ionization of which leads to the radical or ionic state of interest, and the effective spin density obtained in this case is $p_i |\varphi_i(\gamma_N)|^2$. In a pure one-particle picture p_i is equal to 1, and when many-body effects are included p_i becomes less than 1. Thus, the hfs of Eq. (19) already contains many-body effects.

It has been found³⁸ that for the ionization of the outer electrons the p_i do not vary strongly for different orbitals and have values ≈ 0.9 . Therefore, Eq. (19) provides a simple expression for hfs of s -type unpaired electrons. The efficiency of this formula should be examined by numerical calculations and, if possible, by estimating the contributions of higher orders.

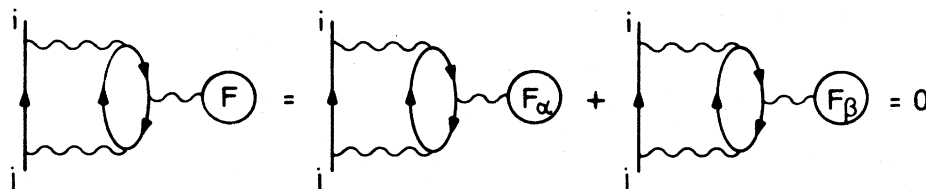


FIG. 2. Example for the cancellation of "direct diagrams."

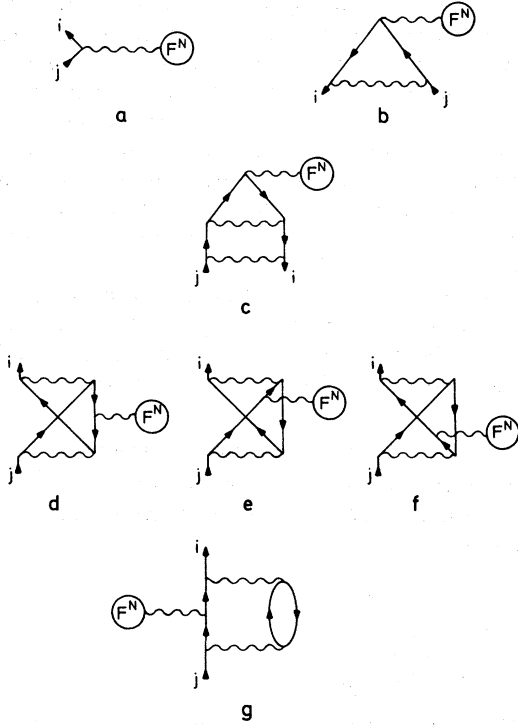


FIG. 3. Feynman diagrams contributing to the hfs of the N th nucleus. (a) Bare vertex; (b) diagram of first order in Coulomb interaction; (c) diagram of second order and independent of ω ; (d)–(g) diagrams of second order which depend on ω .

For completeness we consider also the hyperfine splitting up to first order in V_{ijkl} [Fig. 3(a) + 3(b)]:

$$\Delta_i^N p_i^{-1} = F_{ii}^N + 2 \sum_{k,l} \frac{V_{ilki} F_{k,l}^N}{\epsilon_l - \epsilon_k}. \quad (20)$$

Here k runs over all doubly occupied and l over all empty orbitals (not spin orbitals). Δ_i^N in Eq. (20) already contains spin-polarization effects and also gives an essential contribution towards the hfs of electron systems with an unpaired electron which has a vanishing spin density at the nucleus.

V. RENORMALIZED VERTEX

In Sec. IV the hyperfine splitting has been shown to be proportional to that part of the self-energy which contains one F_{ij}^N line per diagram. Especially in first order Δ_i^N is proportional to the bare vertex F_{ii}^N itself. As is customary in many-body theories, one attempts to arrive at a compact expression for the final result by renormalizing the bare vertex. The symbol we use for the renormalized vertex \mathfrak{F}_{ij}^N is shown in Fig. 4(a).

The renormalized vertex is constructed from

the bare vertex by a self-consistent equation of the type shown in Fig. 4(b), where the block symbolized by A is not yet specified. As commonly done, the block A is connected to \mathfrak{F}^N by one-particle Green's functions. The only requirement we have is that \mathfrak{F}_{ij}^N should contain all the diagrams involved in $\Sigma_{ij}^{V,F}$. This can be done by introducing the interaction operator⁴⁰ γ which is the sum of all linked diagrams which have four free ends and which are still linked when one free Green's function is removed. In a simplified way of writing, where indices and summation symbols are omitted, one obtains

$$\Sigma^{V,F} = F + \gamma G^V G^V F. \quad (21)$$

On the other hand, we may use the Bethe-Salpeter equation which relates γ to its irreducible particle-hole part⁴⁰ I :

$$\gamma = I + IG^V G^V \gamma. \quad (22)$$

It is simply the sum of all diagrams of γ which do not split into two unlinked parts when one-particle and one-hole lines are simultaneously removed. By inserting Eq. (22) into Eq. (21) one obtains $A = I$.

We have thus arrived at a self-consistent equation for the renormalized vertex. Already a finite number of diagrams belonging to A lead, with the equation of Fig. 4(b), to an infinite number of diagrams belonging to $\Sigma^{V,F}$. By renormalizing the bare vertex we have also retained the one-particle picture with its simple physical interpretation. We do not have to deal, as in most other methods, with difficult-to-interpret and difficult-to-calculate many-particle wave functions. This is of course also true for the approach given in Sec. IV, since both approaches are essentially equivalent.

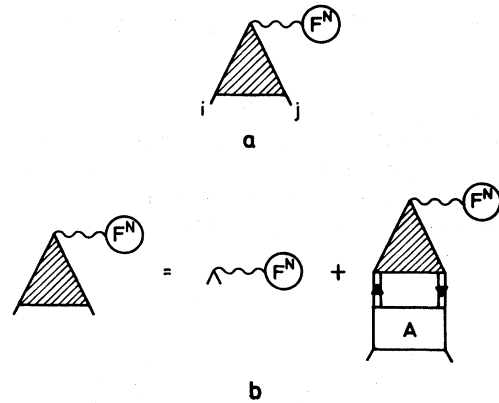


FIG. 4. (a) Renormalized vertex; (b) self-consistent equation for the renormalized vertex. The double solid lines are one-particle Green's functions. The block A is discussed in the text.

Expanding A up to first order in the Coulomb interaction yields the simple result $A = iV_{abcd}$. Inserting this result into the self-consistent equation for \mathcal{F}_{ij}^N and approximating \underline{G}^Y by its first-order expression, one obtains

$$\mathcal{F}_{ij}^N = F_{ij}^N + i \sum_{k,l} \int G_k^{(1)}(-t) G_l^{(1)}(t) V_{iikj} \mathcal{F}_{kl}^N dt \quad (23a)$$

or after integrating over time

$$\mathcal{F}_{ij}^N = F_{ij}^N + \sum_{k,l} \frac{V_{iikj}}{\epsilon_l - \epsilon_k} (n_k - n_l) \mathcal{F}_{kl}^N, \quad (23b)$$

where $n_k = 1$ for $k \in \mathcal{F}$ and 0 otherwise. It can easily be seen that this \mathcal{F}_{ij}^N contains the diagrams in Figs. 3(a), 3(b), and 3(c) as well as analogous terms up to infinite order. It should be mentioned that the direct diagrams which do not contribute to $\Sigma^{V,F}$ have already been omitted from Eqs. (23a) and (23b).

VI. APPLICATION TO Li and CH₃

The zeroth-order term (in the Coulomb interaction) for a hfs is represented by a bare vertex, and the exact value may be obtained by a vertex renormalization. To investigate the question as to whether the bare vertex calculation, which is most easy to perform, may be an adequate approximation for the hfs of a system with an unpaired electron having a nonvanishing density at the nucleus, we shall discuss the well studied Li atom as an example. It is equally important to study a system with an unpaired electron having a vanishing density at the nucleus. For this purpose the hfs of the CH₃ radical are also calculated. In addition the hfs of some excited states of these systems are evaluated.

A. SCF calculations

It is well known that the choice of the basis functions is very important. Gaussian functions are very flexible and have computational advantages over Slater-type functions. For calculating orbital polarizations a much larger basis set of Slater functions is needed in order to obtain comparable results to those obtained with a set of Gaussian functions. However, hfs depends strongly on the $\varphi_i(r_N)$, i.e. on the values of the orbitals at the nuclei, and Gaussian functions have the disadvantage of having a vanishing derivative at the nuclei which is contradictory to reality. This disadvantage can be removed by properly preparing the Gaussian functions.⁵ We also use a basis set of Gaussian functions, but without this method of preparation.

The wave function for the ions Li⁻ and CH₃⁻ have been calculated using Roothaan's finite-

expansion method⁴¹ as implemented in the program system MUNICH.⁴² The basis set of Cartesian Gaussian functions used for the calculation on the Li⁻ ion consists of 11 functions of s -type,⁴³ 3 of p -type (exponential parameters $\alpha_1 = 2.0$, $\alpha_2 = 0.2$, $\alpha_3 = 0.03$) and a set of d -type functions (exponential parameter $\alpha_d = 1.0$) with the s -type functions contracted to 10 functions. The total SCF energy is computed to $E^{\text{SCF}} = -7.427187$ a.u.

The wave function for the CH₃⁻ ion has been calculated using the experimental geometry of the CH₃ radical (planar structure with $R_{\text{CH}} = 2.067$ a.u.) and employing the same basis set (10s/7p/1d on the C atom and 5s/1p on each H atom) as determined by Driessler *et al.*²⁰ with the only difference that Cartesian Gaussian functions have been used instead of Gaussian lobe functions. The total SCF energy is computed to be $E^{\text{SCF}} = -39.516186$ a.u.

B. hfs for the ground state of ⁷Li

In zeroth order in the Coulomb interaction, the hfs for the ground state of Li is given by

$$a^{\text{Li}} = \frac{8}{3} \pi g \beta g_{\text{Li}} \beta_{\text{Li}} p_{2s} |\varphi_{2s}(r_{\text{Li}})|^2, \quad (24)$$

where φ_{2s} is the 2s orbital of Li⁻, p_{2s} is the pole strength corresponding to the ionization of the 2s electron of Li⁻. We have calculated p_{2s} to be 0.91 in second-order perturbation theory. With $\varphi_{2s}(r_{\text{Li}}) = -0.27959$ one obtains $a^{\text{Li}} = 2.84$ a.u. compared with the experimental value⁴⁴ $a^{\text{Li}} = 2.90$ a.u. The excellent agreement of this zeroth-order value with the experimental one is however fortuitous, since the numerical value of a Gaussian-type orbital at the nucleus is smaller than the exact value.^{45,46} Roothaan *et al.*⁴⁷ have performed a highly accurate SCF calculation on Li⁻ with a Slater-type basis set. With their value for φ_{2s} we obtain $a^{\text{Li}} = 3.03$ a.u. with the aid of Eq. (24). For such a simple formula as in Eq. (24) the agreement with experiment is astonishing. This means that for the ground-state hfs of Li, Eq. (24) is much more adequate compared with the restricted HF calculation for Li which leads to a value of⁴⁸ $a^{\text{Li}} = 2.07$ a.u. It should be mentioned that for Li the UHF method also leads to a good result: $a^{\text{Li}} = 2.81$ a.u.⁴⁸

The diagrams which contribute to the renormalized vertex can be divided into two classes. The diagrams of the first class are energy dependent (ω diagrams) in contrast to the diagrams of the second class (constant diagrams). When calculating the constant diagrams up to second order, one obtains $a^{\text{Li}} = 3.14$ a.u. Adding the ω diagrams up to second order leads to a hfs $a^{\text{Li}} = 2.77$ a.u. which is in good agreement with the experimental hfs.

Thus, it is unreasonable to use a renormalized

vertex equation which contains only constant diagrams for calculating the hfs of Li. For a more complete discussion of this point see Sec. VI E.

C. hfs for the ground state of $^{13}\text{CH}_3$

The situation in the case of the methyl radical is completely different from the case of Li. Since the unpaired electron of CH_3 has nodes at the nuclei, Eq. (19) leads to a vanishing hfs. In first-order perturbation theory one obtains the hfs $a^C = 0.32$ a.u. and $a^H = -0.14$ a.u. The pole strength has been calculated in second order to be $p_{1a_2'} = 0.85$. The experimental values are⁴⁹ $a^C = 0.83$ a.u. and $a^H = -0.46$ a.u.

Considering all constant diagrams up to second order yields $a^C = 0.80$ a.u. and $a^H = -0.26$ a.u. In contrast to Li the constant diagrams are of essential importance for CH_3 . The contributions of the ω diagrams are very small. The final results in second order are $a^C = 0.76$ a.u., $a^H = -0.24$ a.u. From Bishop's^{45,46} investigation on Gaussian- and Slater-type orbitals for the hydrogen atom and molecule, we may conclude that the absolute value of the hfs for the proton in CH_3 would increase considerably when the wave function is properly prepared to obtain a more exact cusp at the proton. For carbon in the methyl radical such a preparation is considered to be of little influence on the hfs.

D. hfs for some excited states

With Eq. (14) and Sec. V one obtains for the hyperfine splitting Δ_i for a state specified by i the simple expression

$$\Delta_i = p_i \mathcal{F}_i(-I_i), \quad (25a)$$

where \mathcal{F}_i is the renormalized vertex and I_i is the ionization potential for the i th state of the reference system. In Secs. VI B and VI C we have discussed the case where i stands for the ground state of the molecule, i.e. I_i is the ionization potential of the outermost electron of the reference system.

When an electron is added to the reference system (closed-shell), then the hfs of the states of the resulting negative ion are analogously given by

$$\Delta_j = p_j \mathcal{F}_j(-A_j), \quad (25b)$$

where A_j is the j th electron affinity of the reference system.

The same expressions for the hfs hold even in cases where one electron is removed from the reference system and simultaneously other electrons are excited and in cases where one electron is added and other are excited. In such cases p_i is small ($p_i \lesssim 0.1$) and $-I_i$ is near a pole of $\mathcal{F}_i(\omega)$.⁵⁰

This means that the ω diagrams will lead to the most important contributions to Δ_i . Therefore, it is necessary to evaluate the vertex starting from an irreducible particle-hole part⁴⁰ I of the interaction operator which is explicitly dependent on time.

For Li we have calculated the hfs of the state $1s^1 2s^2$ where a $1s$ electron has been excited to the $2s$ state. The pole strength has been calculated in second order $p_{1s} = 0.78$. The final hfs is $a_{1s} = 302.6$ a.u.

Adding a $2p$ electron to the reference system Li^- leads to a $p_{2p} = 0.93$ and to a hfs $a_{2p}(1s^2 2s^2 2p^1) = 0.51$ a.u.

For the methyl radical one obtains in second order the pole strengths $p_{1e'} = 0.80$ and $p_{2e'} = 0.99$. The corresponding hfs are $a_{1e'}^C [(1a_1')^2 (2a_1')^2 (1e')^3 (1a_2')^2] = -0.17$ a.u. and $a_{2e'}^C [(1a_1')^2 (2a_1')^2 (1e')^4 (1a_2')^3 (2e')^1] = 2.10^{-4}$ a.u. for the carbon nucleus and $a_{1e'}^H = -0.15$ a.u., $a_{2e'}^H = 2.10^{-3}$ a.u. for the protons.

E. The problem of different behavior of perturbation expansions for Li and CH_3

The bare vertex has been found to be an excellent zeroth-order approximation for the hfs of Li. In higher orders the constant diagrams have smaller contributions to the hfs than the ω diagrams. The situation is completely different for CH_3 . Here the ω diagrams have nearly negligible contributions both to a^H and a^C . It is of great importance to know whether these results are accidental or whether systems with an unpaired electron with a finite spin density at the nucleus behave like Li and the other like CH_3 . In case the latter is true, we may use Eq. (23b) for estimating the constant diagrams up to infinite order for systems like CH_3 and an analogous, or more simply a geometric⁵¹ type of approximation for the ω diagrams for systems like Li.

To answer this question, the ω diagrams are considered in some detail. In second order only the seven time-ordered diagrams shown in Fig. 5 are of importance. Some of the diagrams are equal to one another: (a) = (b), (d) = (e), (f) = (g). The diagrams are ordered according to their significance; (a) and (b) have the largest contributions, etc. With the rules given in Sec. IV to evaluate such diagrams one easily understands why these diagrams have large contributions for a system such as Li. The main contribution to diagram (a) comes from $K1 = K2$ and $K3 = i$, especially when $K1 = K2 = K3 = i$. This term does not have a contribution to the hfs of CH_3 , since the orbital i ($= 1a_2'$) has a node at the nuclei and F_{ii}^N is zero. The largest contribution to (c) arises when $K1 = K2 = i$, in the case of (d) when $i = K1 = K3$

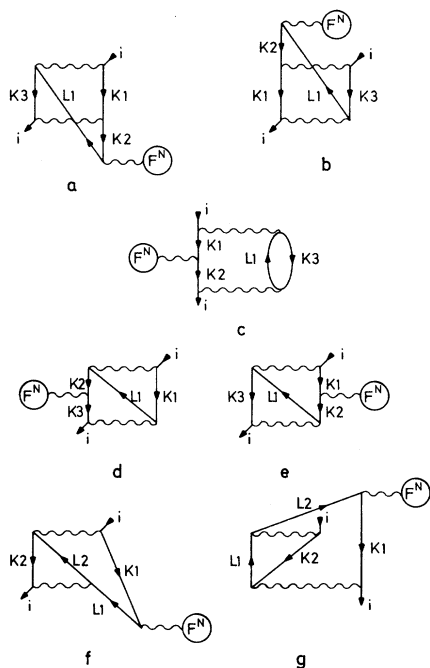


FIG. 5. Seven time-ordered diagrams which lead to the main contribution to the renormalized vertex in second-order perturbation theory in the case of Li.

and for (f) when $K1 = i$. Again these terms do not contribute to the hfs of CH_3 and of similar systems. For molecules with heavier atoms where the unpaired electron has a node at the nucleus the ω diagrams are even less important than for CH_3 , since the molecular integrals of interest, e.g. V_{i,K_2,K_3,K_1} in (a), are smaller for the large $F^N[F^N_{L_1,K_2}]$ in (a), K_2 an inner orbital] and the denominators involved are larger than for CH_3 .

VII. DISCUSSION

To calculate the hfs of a molecule one usually has to construct a many-particle wave function describing the ground state of the system under consideration. By starting with a RHF wave function, a well defined one-particle picture is introduced. To proceed further, configuration interaction must be taken into account. The contributions due to configuration interaction are often subdivided into contributions due to core polarization and to higher correlation effects.

In the present approach it has been demonstrated that the hfs of ions and radicals can be calculated considering the Green's function of a closed-shell system. The main technical advantages of this approach have already been discussed in the Introduction. In principle, it is also possible to investigate the different contributions to the hfs with respect to core polarization and higher cor-

relation effects. Moreover, the mathematically completely different approach attempted in this paper gives us the opportunity to study the hyperfine problem from a different physical point of view discussed in the following.

When ionization potentials are calculated with Green's functions one obtains Koopmans' theorem³⁷ as the first-order approximation. The correction terms to the value obtained by Koopmans' theorem are due to relaxation (or reorganization) and correlation effects.^{52,53} We have the same picture when calculating the hfs by Green's functions. The situation here is even somewhat simpler, since a closed-shell system has a vanishing hfs. The contribution of relaxation effects to the ionization potentials are determined as the difference between the ionization potential obtained from two HF calculations, one on the molecule and one on the ion, and the ionization potential obtained from Koopmans' theorem. The contribution of relaxation effects to the hfs is obtained by subtracting the value calculated with an RHF calculation on the system having hyperfine structure from the value obtained with the aid of Eq. (19). All additional contributions to the hfs arise due to pure correlation effects. It is well known that Koopmans' theorem leads to valence ionization potentials which are close to the experimental values because correlation and relaxation effects often tend to compensate each other.⁵²⁻⁵⁴ If it is also the case for calculating hfs, then Eq. (19) is a good starting point for obtaining accurate hfs for s-type systems.

However, as Koopmans' theorem leads to a first-order (in V_{ijkl}) approximation, one should include the first-order diagram which is shown in Fig. 1(b) in order to obtain an equivalent approximation for the hfs. Inclusion of this diagram makes this "analog to Koopmans' theorem" also applicable for non-s-type systems.

It is possible to collect diagrams according to their physical significance. Thus the time-ordered diagram shown in Fig. 6 for the ionization of the $2s_\alpha$ electron of Li^- describes the $1s_\alpha$ state interacting with the $2s_\alpha$ state through the exchange potential and becoming an excited state which interacts with the Fermi contact operator to return to the $1s_\alpha$ state. The mechanism involved is of the spin-polarization type. To distinguish between the terms corresponding to correlation and those which correspond to relaxation effects in the renormalized vertex, one can employ the method suggested in Ref. 53.

The present approach seems to be very efficient when one considers the computational effort involved. The number of diagrams up to second order is greatly reduced because all direct diagrams cancel out. In addition, many of the re-

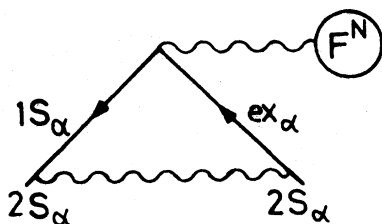


FIG. 6. Diagram of first order in the Coulomb interaction contributing to spin-polarization in Li. ex_α are excited HF states with spin α and a nonvanishing spin density at the nucleus.

maining diagrams have equal contributions; the summation over the spin can be easily performed; and the number of orbitals involved in a diagram is relatively small because of $F_{kk}^N = 0$ for $\varphi_k(r_N)$ or $\varphi_k(r_N)$ equal to zero. The computer time

needed to evaluate one hfs was about 2 sec on the IBM 360/91 with an unoptimized program.

Finally it should be mentioned that the approach discussed in the present paper can, in principle, also be applied to calculate the hfs of those states which are characterized by an ionization with a simultaneous excitation and that more complicated open-shell systems can be treated in an analogous way with many-body Green's functions.

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