

# MANY-BODY PERTURBATION STUDY OF ELECTRON CORRELATION EFFECTS ON NMR PARAMETERS\*

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## I. INTRODUCTION

NMR is routinely used as an indispensable research tool in present-day chemical laboratories because a wide variety of parameters can be extracted from the response of an ensemble of nuclear spins to a resonant excitation. Among them, the chemical shift in nuclear magnetic shielding and the electron-coupled nuclear spin-spin coupling are direct measures of the change in chemical environment around the nuclei concerned. Consequently, the accumulation of shift and coupling data allows us to use the shift and nuclear spin-spin coupling as empirical parameters in rapid identification of the molecular species present. Theoretically, they can be expressed as a sum of first- and second-order properties, thus reflecting the details of the static and dynamic electronic structure of molecules.

In this review, we wish to report on electron correlation effects on these magnetic properties. Diagrammatic many-body perturbation theory (MBPT) (1,2) is employed to analyze the effects since the method is most unbiased, allowing us to make order-by-order evaluation of the correlation effects.

## II. NUCLEAR SPIN-SPIN COUPLING

To begin with, we will discuss the nuclear spin-spin coupling, since it is expected to be more sensitive to electron correlation and involves more problems. In the early days, Ramsey (3), followed by many others, resorted to a "mean excitation energy" approximation. When the numerator changes sign with each excitation in the second-order perturbation formula, however, the approximation may give erroneous results. In fact some coupling constants were calculated with wrong signs. Later, Pople and Santry (4) took explicit account of excited states to remedy the defect of the mean excitation energy approximation, but they utilized only the lowest virtual orbital in evaluating the perturbation formula. We then extended the procedure to include higher virtual orbitals with no sense of convergence noted (5), suggesting the necessity of employing amply extended basis sets, particularly for the Fermi contact interaction. Furthermore, the functions of both the ground and the excited states should be equally well correlated one way or another. Since full configuration interaction (CI) calculations to incorporate electron correlation into both states are unlikely to be feasible for molecules of general interest, MBPT may offer some advantages. It gives correlation corrections order by order as Feynman diagrams, each of which is expressed in terms of single-particle states. Thus, the total correlated wave functions of neither the ground nor the

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Table 1. Fermi contact contribution to HD (in Hz).

Contributions	Ordinary MBPT	FF MBPT
Zeroth-order	12.4	54.3 (=CHF)
First-order	9.4	
Second-order	6.3	-15.4
Third-order		-1.7
Total sum	28.1	37.2
Best estimated		40. <sup>a</sup>

<sup>a</sup>Reference 13. SD (single and double excitation) CI in reference 12 gives 41.8 Hz, which is exact in the basis set employed, since SD CI is exact for a two-electron system.

Table 2. Nuclear magnetic shielding (in ppm) of HF.

	Gauge Origin	$F_{\sigma_{\parallel}d}$	$F_{\sigma_{\perp}d}$	$F_{\sigma_{\perp}p}$	$F_{\sigma}$	$H_{\sigma_{\parallel}d}$	$H_{\sigma_{\perp}d}$	$H_{\sigma_{\perp}p}$	$H_{\sigma}$
CHF MBPT		481.8	482.4	-103.1	413.5	44.05	1.56	17.66	27.50
Zeroth order		481.8	482.4	-38.62		44.05	1.56	11.96	
First order				-26.37				3.53	
Second order F				-14.46				1.18	
CHF type				-16.31				1.24	
non-CHF type		-0.54	-0.23	1.85		0.41	1.34	-0.06	
Total sum		481.3	482.2	-79.45	428.9	44.46	2.90	16.67	27.89
CHF MBPT		481.8	467.3	-91.93	410.9	44.05	140.7	-113.8	32.58
Zeroth order		481.8	467.3	-11.00		44.05	140.7	-90.50	
First order				-33.74				-17.75	
Second order H				-22.68				-2.34	
CHF type				-22.20				-4.20	
non-CHF type		-0.54	-0.38	-0.48		0.41	-0.19	1.86	
Total sum		481.3	466.9	-67.42	426.8	44.46	140.5	-110.6	34.75

excited states are required.

An MBPT calculation of the coupling constant with an extended basis set was first performed through first order in correlation for the Fermi contact contribution in the HD molecule by Schulman and Kaufman (6). The calculation was extended to second order by Itagaki and Saika (7), but the result with 62 Gaussian type orbitals was still far from convergence as shown in the first column of Table 1.

In this connection, the finite-field many-body perturbation theory (FF MBPT) (8,9) deserves some consideration. The scheme incorporates effects of external perturbations by finite perturbation theory prior to the estimation of correlation effects. The effects of electron correlation are then calculated diagrammatically in terms of the perturbation-adapted single-particle states. Thus, the perturbation-induced relaxation effects (8,9) are taken into account to infinite order, while the true correlation effects are obtained to a finite order by the MBPT approach. Therefore, it provides an efficient means for cases where the effects of external perturbations are quite notable. Indeed, this technique has been successfully applied to electric field properties, reproducing them with sufficient accuracy (8,9).

On the other hand, the FF MBPT method has not been applied to magnetic field properties, because the imaginary nature of magnetic field perturbations requires a much greater computational effort as compared with a real perturbation. For the Fermi contact contribution to nuclear spin-spin coupling, however, FF MBPT calculations can be performed without involving too much labor. Since finite perturbation theory or equivalently coupled Hartree-Fock (10) (CHF) calculations usually overestimate the magnitude of the Fermi contact contribution to nuclear-spin coupling, and the rather large overestimate is likely to originate mainly from the neglect of electron correlation, it is of particular interest to see whether the MBPT approach based on the field-dependent single-particle states can recover a significant portion of the correlation effects. Thus we examined the validity and the tractability of the FF MBPT scheme for the Fermi contact contribution to nuclear-spin coupling, with an example of the hydrogen molecule (11).

The MBPT calculations were performed by computing the field-dependent energy diagrams through third order in electron correlation. To further improve the convergence with

respect to the Fermi contact perturbation, we relaxed the fixed-basis-set approach by optimizing the scaling factor of the orbital exponents in the presence of the Fermi contact perturbation. Since the basis-set problem is extremely acute in the Fermi contact contribution, requiring an amply extended basis set, this approach appears promising and appealing.

In carrying out numerical differentiations of the interaction energy between nuclear spins  $I_A$  and  $I_B$  expressed as (3)

$$E(I_A, I_B) = h \vec{I}_A \cdot \vec{J}_{AB} \cdot \vec{I}_B, \quad (1)$$

we employed the finite-difference method developed by Kowalewski (12):

$$\begin{aligned} \frac{\partial^2 E(I_A, I_B)}{\partial I_A \partial I_B} \Big|_{I_A, I_B=0} &= \gamma_A \gamma_B \hbar^2 \frac{\partial^2 E(\mu_A, \mu_B)}{\partial \mu_A \partial \mu_B} \Big|_{\mu_A, \mu_B=0} \\ &\approx \gamma_A \gamma_B \hbar^2 \frac{E(\mu_A, \mu_B) - E(\mu_A, -\mu_B)}{2\mu_A \mu_B} \end{aligned} \quad (2)$$

The value of  $\mu_A$  and  $\mu_B$  was chosen so as to bring the zeroth-order FF MBPT value of  $J_{AB}$  into reasonable agreement with the CHF value.

While the uncoupled Hartree-Fock (UCHF) value of 12.4 Hz for the Fermi contact term in HD, corresponding to the zeroth-order value in the ordinary MBPT approach, underestimates the best estimated Fermi contact contribution of 40.0 Hz (13) by 69%, the CHF value of 54.3 Hz, equivalent to the zeroth-order FF MBPT value overestimates it by 36%. This much deviation of even the CHF value is rather unusual in view of small deviations of the CHF values from experiment in the case of the electric dipole polarizability (8,9), magnetizability, and nuclear magnetic shielding (14). Before discussing this point, we shall first analyze the correlation corrections.

We see from the second column of Table 1 that the second-order correction is negative and large, amounting to almost 30% of the zeroth-order value. As for the third-order correction, it is also negative but already fairly small, being only 3% of the zeroth-order value. Furthermore, the final value through third order, 37.2 Hz, is in fair agreement with the best estimated value. This rapid convergence of FF MBPT expansions demonstrates that FF MBPT affords a computationally tractable, efficient scheme of calculating the Fermi contact term. For reasons to be

described in the next section, on the other hand, the CHF method may be a very good approximation in calculating the contributions other than the Fermi contact term.

Finally, we add a transparent physical interpretation of the general overestimate by the CHF method. As given by eqn. 2, the nuclear-spin coupling is proportional to the energy difference between the parallel and antiparallel nuclear-spin states:

$$J_{HD} \propto E(\uparrow\uparrow) - E(\uparrow\downarrow).$$

A positive coupling constant is expected, because the antiparallel nuclear-spin state must be more stable in conjunction with the paired spin state of the bonding electrons. This situation is already realized at the CHF level. Now let us consider the effects of electron correlation. For the parallel nuclear-spin state,  $\alpha$  and  $\beta$  electrons have an equal weight on both nuclei similar to the  $1\sigma_g$  orbital in the absence of the Fermi contact perturbation. The only difference is that the electron of spin parallel to the nuclear spin, say, the  $\beta$  electron, becomes more diffuse. The difference in the polarization is, however, fairly small and consequently both electrons have a considerable overlap. This leads to a large correlation energy for the parallel nuclear-spin state. For the antiparallel nuclear-spin state, on the other hand,  $\alpha$  and  $\beta$  electrons are differently polarized; each electron has a larger density on a proton of opposite spin. Thus, both electrons have a smaller overlap and thereby a smaller correlation energy. The difference in the correlation energies then makes a negative correction

$$(-|E_{\text{corr}}(\uparrow\uparrow)|) - (-|E_{\text{corr}}(\uparrow\downarrow)|) < 0$$

to the overestimated

$$E^{\text{HF}}(\uparrow\uparrow) - E^{\text{HF}}(\uparrow\downarrow),$$

which is ascribable to an unbalance in the left-off electron correlation in the parallel and antiparallel nuclear-spin states. The same argument applies also in cases other than that of directly bonded nuclei.

### III. NUCLEAR MAGNETIC SHIELDING

When a magnetic field is applied to an atom or a molecule, currents proportional to the field are induced. These currents may interact with either the applied field or magnetic

nuclei in the system. The former interaction can be observed as the magnetizability and the latter as the nuclear magnetic shielding. Both of them are due to the same induced current as a linear response to the applied field, only their dependences on the distance from the gauge origin being different. Inclusion of a major portion of electron correlation effects on such linear responses is required for the theory to have any predictability. However, the situation with respect to correlation corrections in magnetic cases is much less satisfactory than in electric cases.

Here, we present a systematic study (14) of correlation effects on the nuclear magnetic shielding for the HF molecule as a prototype example of simple diatomic molecules, using MBPT. The Hartree-Fock potential in the absence of the external field is used for generating one-electron states. The result is compared with CHF calculations to assess the validity of the latter approach. The results are summarized in Table 2 (15). First, we briefly touch upon the diamagnetic term and then concentrate on the paramagnetic term.

The CHF method gives no correction to the diamagnetic term, so the second-order correlation correction to it calculated by MBPT is included in the table. It can be seen that the correction is quite small and consequently its contribution to the total shielding is negligible.

The CHF fluorine shielding value agrees satisfactorily with experiment and appears nearly gauge invariant. On the other hand, the proton shielding value shows poor gauge dependence. The values with the gauge origin at the F nucleus may probably be preferable, since F is closer to the centroid of the electronic charge. The apparent good gauge dependence of the fluorine shielding may be due to a fortuitous cancellation, but the details are not fully appreciated yet.

In order to analyze the effects of electron correlation and assess the validity of the CHF approach to nuclear magnetic shielding, we shall examine the MBPT results. The first-order correlation correction corresponds to the first-iterated correction by the CHF method. As exemplified by the perpendicular component of the paramagnetic fluorine shielding, the particle-hole ladder type diagram makes a dominant contribution of -29.00 ppm. The dominance of ladder-type diagrams for nuclear magnetic shielding continues to hold for higher orders. Diagrams contained in the CHF iteration were termed the

apparent correlation effects by Sadlej (9).

Non-CHF diagrams, which were termed the true correlation effects by Sadlej (9), first appear in second order. Among the second-order non-CHF diagrams, each diagram having two one-electron operators attached to the same loop is large. In magnitude, some of them being even larger than ladder-type diagrams. Those diagrams having large values individually are nearly cancelled by one another's counterpart for  $F_{\sigma_1 P}$ . Although patterns of cancellation are somewhat different depending upon the molecules, it still holds good that the second-order non-CHF diagrams make an inappreciable contribution to nuclear magnetic shielding. Since the nature of operators other than the Fermi contact interaction in nuclear spin-spin coupling is similar to that of the nuclear magnetic shielding operators, non-CHF diagrams are expected to make only a trivial contribution also to nuclear-spin coupling except the Fermi contact term.

The fluorine chemical shift between HF and F<sub>2</sub> is a classic problem of the chemical shift first qualitatively discussed 30 years ago (16). We analyze the problem here in terms of diagonal ladder diagrams. In HF, major contributions to the paramagnetic term come from the interactions of the highest occupied  $1\pi$  orbital with the  $4\sigma$  and  $5\sigma$  orbitals, which correspond to the counterclockwise currents of the  $\pi$  orbital around the angular node precisely at the fluorine nucleus. Excitation from the  $3\sigma$  orbital to the  $2\pi$ ,  $3\pi$ , and  $6\pi$  orbitals gives rise to clockwise currents around F, leading to the diamagnetic term. The above diagrammatic picture is too simplified in the sense that the large off-diagonal contributions are neglected, but may still help our understanding. In the case of F<sub>2</sub>, the  $1\pi_u-3\sigma_u$  pair makes a conspicuous paramagnetic contribution, corresponding to the paramagnetic currents in the simple atomic model (16).

#### IV. CONCLUSIONS

Effects of electron correlation on the nuclear magnetic shielding and the nuclear spin-spin coupling have been analyzed by comparing MBPT and CHF results. MBPT expansion through second order in electron correlation with reference to the Hartree-Fock Hamiltonian in the absence of the external fields shows that diagrams not included by the CHF method make only a small net contribution for these properties except the Fermi contact nuclear-spin coupling. Therefore, the CHF method is

expected to provide a viable and reliable tool for calculating them. However, it generally overestimates the Fermi contact term. The overestimate originating from the unbalanced incorporation of electron correlation can be efficiently and systematically corrected by the FF MBPT approach.

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