On the perturbation–variational calculation of the nuclear spin–spin coupling in HD

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The interaction energy of the isotropic indirect nuclear spin–spin coupling in nuclear magnetic resonance is

$$E_{AB} = h J_{AB} \mathbf{I}_A . \mathbf{I}_B, \tag{1}$$

where J_{AB} is the coupling constant between the nuclei A and B. The theoretical formulation has been given by Ramsey [1], who showed that E_{AB} can be written as a second-order energy

$$E_{AB} = \sum_n{}' (E_0 - E_n)^{-1} \langle \psi_0 | F_A | \psi_n \rangle \langle \psi_n | F_B | \psi_0 \rangle. \tag{2}$$

The summation over n includes an integration over the continuum. For proton–proton coupling the most important contribution to F is the Fermi-contact interaction [2, 3]

$$F_N = \lambda_N \sum_k \delta(\mathbf{r}_{kN}) \mathbf{S}_k . \mathbf{I}_N, \tag{3}$$

where $\lambda_N = 8\beta h \gamma_N / 3$, and the symbols have their usual meaning. We need a complete knowledge of the wave functions of the ground state as well as the excited states (including the continuum) in order to apply equation (2). Three methods have been used in order to overcome this difficulty:

(*a*) In the simplest calculations $E_n - E_0$ is replaced by a constant energy ΔE, simplifying equation (2) to

$$E_{AB} = -\Delta E^{-1} \langle \psi_0 | F_A F_B | \psi_0 \rangle. \tag{4}$$

Although ΔE is defined exactly by this procedure, the usual interpretation as an average *excitation* energy is only correct if $\langle \psi_0 | F_A | \psi_n \rangle \langle \psi_n | F_B | \psi_0 \rangle$ has the same sign for all n, which is often not true. Consequently no criterion exists for choosing ΔE, and negative values might even be necessary [4, 5]. Therefore this approach has been abandoned almost completely nowadays.

(*b*) When approximation (*a*) is avoided the excited states are usually represented by a finite set of discrete levels, constructed from the virtual orbitals that are obtained with an approximate solution for the ground state of a molecule [6–9]. The only justification for such a procedure would be that these excited states were a very good set for expanding the first-order perturbed wave function. However, extensive calculations on the HF molecule indicate that large contributions of opposite sign arise from even the highest excited states [10, 11]. This casts serious doubts on the theoretical justification of the usual schemes and their success must depend heavily on empirical parametrization.

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(c) A third alternative is to solve equation (2) variationally [5, 12–16]. We shall start with the Hylleraas functional for the second-order energy [5, 17]

$$W^{(2)} = 2\langle \tilde{\psi}^{(1)} | F | \psi_0 \rangle + \langle \tilde{\psi}^{(1)} | \mathcal{H}_0 - E_0 | \tilde{\psi}^{(1)} \rangle, \tag{5}$$

where $\tilde{\psi}^{(1)}$ is the trial first-order perturbed wave function and $F = F_A + F_B$. By expanding

$$F = V_A I_A + V_B I_B \tag{6a}$$

and

$$\tilde{\psi}^{(1)} = \tilde{\psi}_A I_A + \tilde{\psi}_B I_B \tag{6b}$$

we can write $W^{(2)}$ as the sum of three terms:

$$W^{(2)} = W_{AA} I_A{}^2 + W_{BB} I_B{}^2 + W_{AB} \mathbf{I}_A \cdot \mathbf{I}_B. \tag{7}$$

The cross term W_{AB} is a variational approximation to hJ_{AB} and is given by

$$W_{AB} = 2\langle \tilde{\psi}_A | V_B | \psi_0 \rangle + 2\langle \tilde{\psi}_B | V_A | \psi_0 \rangle + 2\langle \tilde{\psi}_A | \mathcal{H}_0 - E_0 | \tilde{\psi}_B \rangle. \tag{8}$$

By making W_{AB} stationary the first-order perturbation equations for $\tilde{\psi}_A$ and $\tilde{\psi}_B$ are satisfied. However, just as in the case of the chemical shift [18] we cannot make a decision about the sign of the second-order variation, because W_{AB} is a cross product. Consequently there is only a stationary principle for W_{AB} and no minimum principle. Taking $\tilde{\psi}_A$ as a linear combination of known functions ψ_{Ai} we get a linear variation problem that leads to the final formula

$$J_{AB} = -(2/h) \sum_i \sum_j \langle \psi_0 | V_B | \psi_{Ai} \rangle \langle \psi_{Ai} | (\mathcal{H}_0 - E_0)^{-1} | \psi_{Bj} \rangle \langle \psi_{Bj} | V_A | \psi_0 \rangle, \tag{9}$$

which is similar to that of Armour and Stone [19]. Applied to a specific molecule the integration over the electron spins can be carried out explicitly.

An alternative approach has been advocated [14] in which one of the self-coupling terms W_{AA} or W_{BB} is minimized. From this also a stationary value for W_{AB} can be calculated but again this is not a bound to hJ_{AB}. Moreover, the form (3) of the Fermi-contact term is a simple approximation to the real relativistic equations and is valid only *up to the first order* in perturbation theory [3, 5]. Consequently the perturbation series for W_{AA} and W_{BB} do not converge [5, 14] and the values obtained for these quantities are meaningless. Nevertheless it might be argued that minimizing W_{AA} or W_{BB} is still a valid technical procedure to get a stationary W_{AB} [14]. W_{AB} itself contains the product of two *different* δ functions and so is acceptable. Therefore we shall restrict our attention to W_{AB}.

The fact that we have only a stationary principle for the coupling constant and no minimum principle has some important consequences: (a) It is possible to get the right answer accidentally. Consequently agreement with experiment is no criterion for the accuracy of the wave function. (b). Increasing the size of the basis does not necessarily improve the result, and might lead to oscillations around the correct value. Only when there are clear indications of convergence can one be confident of the results.

Despite this gloomy situation we tried to calculate variationally the coupling constant in HD. In this case we can use information about $\psi^{(1)}$ from the hydrogen atom. The first-order perturbation equation for the hydrogen atom in the presence of a δ function,

$$(\mathcal{H}_0 - E_0)\psi^{(1)} = -(\delta(r)/r^2 - E^{(1)})\psi_0, \tag{10}$$

can be integrated directly to give [20]

$$\psi^{(1)} = (2/\sqrt{\pi})(2 \ln r - 1/r + 2r + C) \exp(-r), \tag{11}$$

where C is a constant. So besides the normal 1s and 2s-type functions two singular functions occur which we shall denote by 0s and lns. The second-order energy evaluated with this wave function and a δ function is clearly $-\infty$, which confirms our previous statement that the self-coupling energy should be redefined. However, it may be essential to include these singular functions in the basis for a variational calculation of J_{HD}.

For the HD molecule we took an orbital exponent of 1.2. In order to decide about the basis functions describing the spin polarization at the other atom (e.g. the deuterium atom when the Femi-contact term is situated on hydrogen) we did some preliminary calculations. As expected the inclusion in $\tilde{\psi}_H$ of a 1s function on deuterium is essential, while the addition of a 2s function seems to be unimportant. Therefore the best simple basis for $\tilde{\psi}_H$ is probably: $1s_H$, $2s_H$, $0s_H$, lns_H and $1s_D$. A similar basis is used for $\tilde{\psi}_D$. The necessary new one and two-electron integrals with the 0s function can be evaluated using standard methods [21, 22]. However, the lns function leads to complications. For the ground state we shall use the first three functions from table 1. Two properties of ψ_0 are important for the coupling constant: the probability of an electron being at a nucleus and the amount of electron correlation [16]. As the first quantity is about constant the differences in coupling can be attributed to differences in electron correlation.

	E_{tot} (A.U.)	E_{bond} (ev)	$\langle \delta(r) \rangle$ (A.U.)
Coulson MO ($\zeta = 1 \cdot 19$)	$-1 \cdot 1282$	$3 \cdot 488$	$0 \cdot 4517$
Wang VB ($\zeta = 1 \cdot 17$)	$-1 \cdot 1390$	$3 \cdot 784$	$0 \cdot 4520$
James and Coolidge (13 terms)	$-1 \cdot 1735$	$4 \cdot 721$	$0 \cdot 4502$
Kołos and Roothaan (50 terms) (a)	$-1 \cdot 1744$ (b)	$4 \cdot 747$ (b)	$0 \cdot 4571$ (c)

(a) At $R = 1 \cdot 4009$ A.U.

(b) Equal to the experimental value.

(c) One should be careful in interpreting this as the exact value as the Kołos–Roothaan function does not satisfy Schrödinger's equation at the origin (ref. [16]).

Table 1. Some ground-state wave functions of H_2 ($R = 1 \cdot 4$ A.U.).

The results for various sizes of the basis are given in table 2. We see that a basis of 1s and 2s gives a reasonable, though somewhat high, result. Unfortunately this is vitiated when the 0s function is included. As the value for J_{HD} is now too low there are two possibilities when the lns function is added. Either we get a further decrease and a worse result, or the lns function compensates more or less for the decrease caused by the 0s function. In the latter case, however we cannot say that there are any indications of convergence on extension of the basis. So even if basis III plus lns gave perfect agreement with experiment, we could not draw any conclusions because of the oscillatory behaviour of the results. Therefore we did not continue with the lns function for which no result is given. Extension of the basis of 1s and 2s with normal 3s and 2p-type functions leads also to a poorer result.

Basis for ψ_H ($\zeta = 1\cdot 2$)		Ground state		JC (13 terms)
		MO ($\zeta = 1\cdot 19$)	VB ($\zeta = 1\cdot 17$)	
I	$1s_H, 1s_D$	104·2	132·8	110·8
II	$1s_H, 2s_H, 1s_D$	39·8	65·4	45·8
III	$1s_H, 2s_H, 0s_H, 1s_D$	18·2	31·2	21·4
IV	$1s_H, 2s_H, 3s_H, 2p\sigma_H, 2p\pi_H,$			53·7 (a)
	$1s_D, 2s_D, 3s_D, 2p\sigma_D, 2p\pi_D$			
	Experimental			43·0 (b)

(a) Ref. [16].

(b) T. F. Wimmett, 1953, *Phys. Rev.*, **91**, 476.

Table 2.   Variational results for J_{HD} (Hz).

Thus at present there would seem to be no satisfactory method for an *ab initio* calculation of a nuclear spin–spin coupling constant. The approximation of the perturbation series using a finite series of excited states gives convergence problems [11], while the variation method leads to unreliable results because of the existence of a stationary principle and not a minimum principle.

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