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See note b

1) NA

2) NA

3) NA

4) See note b

5) 40 pgs

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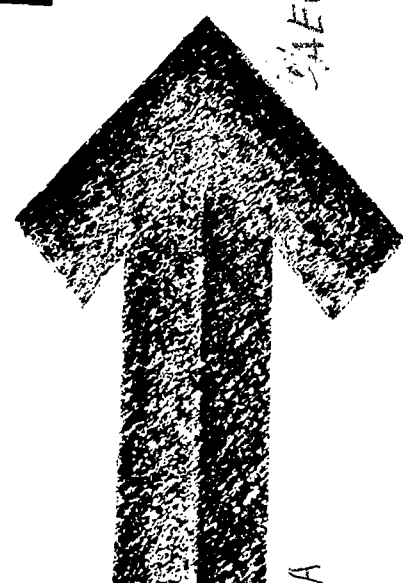
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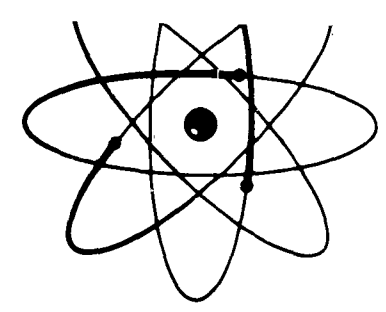
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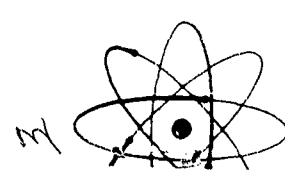
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The coupling of nuclear spins by second-order perturbation mechanisms was first proposed and discussed by Ramsey and Purcell¹ in explanation of experimental results obtained by Hahn and Maxwell.² Invoking an arbitrary "average energy" denominator to compare magnitudes of the several terms for the HD molecule, Ramsey³ showed that the dominant contribution to the indirect spin-spin coupling arises from the second-order perturbation theory energy of the Fermi-contact Hamiltonian,⁴ $\mathcal{H}_F = (16\pi\beta\hbar/3) \sum_{k,N} \gamma_N \delta(r_{kN}) S_k \cdot I_N$, where $r_{kN} = r_k - r_N$ and S_k and I_N are the electron and nuclear spins respectively. Stephen⁵ and others⁶ have since performed variational calculations for this same energy.

A new approximate procedure⁷ for performing perturbation calculations on simple unperturbed molecular wave-functions introducing no arbitrary parameters, enables the relatively facile calculation of some molecular properties.⁸ This procedure is used here to calculate approximately Fermi-contact contribution,

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J_F , to the indirect scalar coupling between the nuclear spins in HD. The scalar coupling constant is written as J , where the coupling energy is $E = \hbar J I_H \cdot I_D + \hbar I_H \cdot g_{ID}$ and g is a traceless tensor whose effect vanishes under the usual experimental conditions. Consider the ground-state described by the Coulson-MO wave-function,⁹ $|0(r_1, r_2), 0(\sigma_1, \sigma_2)\rangle = 2^{-\frac{1}{2}} N^{-2} |(H+D)(1)(H+D)(2)$ [$\alpha(1)\beta(2) - \alpha(2)\beta(1)$] assuming the space- and spin-coordinates be separable for the excited states as well. $|H(1)\rangle$ and $|D(1)\rangle$ are one-electron 1s AO's centered on the proton and the deuteron respectively with, e.g. $|H(1)\rangle = (\alpha^3/\pi)^{\frac{1}{2}} \exp(-\alpha r_{1H})$, $\alpha = 1.197$, $N^2 = 2(1 + \langle A|B\rangle)$ and $R_{HD} = 1.4217 a_0$. J_F can be written, considering both the one-electron and two-electron contributions, as³

$$J_F = 2(2/3\hbar)(16\pi\beta\hbar/3)^2 \gamma_H \gamma_D \sum_i \langle 0, 0 | \delta(r_{1H}) S_i | n, n \rangle \cdot \langle n, n | \delta(r_{1D}) S_i | 0, 0 \rangle + \langle 0, 0 | \delta(r_{2H}) S_2 | n, n \rangle \cdot \langle n, n | \delta(r_{1D}) S_1 | 0, 0 \rangle \quad (1)$$

The "covalent approximation" observes⁷ that if $\mathcal{H}_0 |0, 0\rangle \equiv E_0 |0, 0\rangle$ since $|0, 0\rangle$ is never an exact eigenfunction of \mathcal{H}_0 , then $\mathcal{H}_0 |A(1)(A+B)(2), 0\rangle \approx E_0 |A(1)(A+B)(2), 0\rangle$ and $\mathcal{H}_0 |B(1)(A+B)(2), 0\rangle \approx E_0 |B(1)(A+B)(2), 0\rangle$. Let the function $f_N[\delta(r_{iN'})]$ for each electron i and nuclei N, N' , be defined by the inhomogeneous p.d.e.

$$[\nabla_N^2 - \delta(r_{iN'})] \mathcal{H}_0 |N(1)\rangle = \delta(r_{iN'}) |N(1)\rangle - \langle N(1) | \delta(r_{iN'}) |N(1)\rangle |N(1)\rangle \quad (2)$$

The spatial function for electron $j \neq 1$ and the spin functions have been suppressed, defining $f\{\delta(r_1)\}$ to be independent of r_j . For $N = N'$ the solution to Eq. (2) is¹⁰

$$f_N\{\delta(r_{1N})\} = (2m/4\pi\hbar^2)(-1/r_{1N} + 2\alpha \ln r_{1N} + 2\alpha r_{1N}) \quad (3)$$

We have not succeeded in solving for $f_N\{\delta(r_{1N'})\}$, $N \neq N'$, although these f 's will be small as the inhomogeneities themselves, e.g. $\delta(r_H) | D \rangle \sim \exp(-\alpha R_{HD}) = 0.19$, are small. Their contributions are neglected as argued below. Following Dalgarno¹¹ and Schwartz¹⁰ the commutators of the f 's are substituted into Eq. (1) neglecting the non-orthogonality of $|A\rangle$ and $|B\rangle$ with $|n\rangle$ which gives a small error,⁷ and the sum over $|n\rangle$ is taken, observing that $\langle 0 | S_1^2 | 0 \rangle = -\langle 0 | S_1 \cdot S_2 | 0 \rangle = \frac{3}{4}$ and $\langle 0 | S_1 | 0 \rangle = 0$. J_F then becomes¹²

$$J_F = \hbar^{-1}(16\pi\hbar^2/3)^2 \gamma_H \gamma_D N^{-4} \left\{ N^2 \langle (H+D)(1) | \delta(r_{1H}) f_D \{ \delta(r_{1D}) \} | D(1) \rangle + \langle H(1) | f_H \{ \delta(r_{1H}) \} \delta(r_{1D}) | H(1) \rangle + X_1 \right\} - \left[\langle (H+D)(1)(H+D)(2) | \delta(r_{2H}) f_D \{ \delta(r_{1D}) \} | D(1)(H+D)(2) \rangle + \langle (H+D)(1)H(2) | f_H \{ \delta(r_{2H}) \} \delta(r_{1D}) | H(1)(H+D)(2) \rangle + X_2 \right] \quad (4)$$

with X_1 given by $X_1 = \sum' (E_0 - E_n)^{-1} \langle D(1)(H+D)(2) | \delta(r_{1H}) | n \rangle \langle n | \delta(r_{1D}) | H(1)(H+D)(2) \rangle$ and X_2 analogously. Such terms will clearly be small as both matrix elements involve the value at one nucleus of the AO centered on the other, being of the order of $\exp(-2\alpha R_{HD})$. X_1 and X_2 should each be $\exp(-\alpha R_{HD})$ smaller than the next largest one-electron and two-electron terms respectively,

which are themselves $\exp(-\alpha R)$ smaller than the respective dominant terms. The divergence of the Fermi self-coupling ($J_{F,HH}$ or $J_{F,DD}$), when nuclear size corrections are neglected, is observed trivially.

When the necessary integrals are evaluated, the calculated contribution to J_F from the one-electron terms is 3.0 cps while that from the two-electron terms is -34.5 cps for a total of -29.5 cps. The error from both the method and the wave function (e.g., too much ionic contribution) is probably within 25% and will be discussed elsewhere along with results of other calculations. Experiment¹³ gives $J_{HD} = 43$ cps of indeterminate sign, and the calculated J_F indicates that indeed J_F is a principal contributor to J_{HD} . (The different orbital contributions³ will be discussed elsewhere.) The sign of J_{HD} could, in principle, be determined by ultra-high-resolution molecular beam techniques.

The negative calculated J_F is surprising since the approximation using an "average energy" denominator with the usual positive (and arbitrary) ΔE^* gives³ J_{HD} incorrectly as positive. This exhibits the well-known fallibility¹⁴ of the "average energy" procedure for sums whose numerators are not positive-definite.

The negative J_F can be argued physically. Consider the two-electron term, the energy of which is expressed as proportional to $(I_H \cdot S_1)(I_D \cdot S_2)$ whose dominant contribution has electron 1 on H and electron 2 on D. If H and D have their spins parallel, then by the Pauli principle, either $I_H \cdot S_1$ is positive and $I_D \cdot S_2$ negative, or vice versa, and the energy which is their product is negative. Since, for the scalar coupling, $E = \hbar^2 J_{HD} I_H \cdot I_D$, J_{HD}

is negative. 15 The quantum mechanical argument would observe that most of the lowest coupled triplet states, rather than being "anti-bonding" states, e.g. $|\mathcal{A}(H-D)(1)(H+D)(2)\rangle$, are "bonding" states of higher AO's, e.g. $|\mathcal{A}(H+D)(1)(H'+D')(2)\rangle$ where H', D' are higher S₋ states. For such $|n\rangle$ in the (dominant) two-electron sum, whenever the l.h. matrix element is positive, the r.h. one is negative. The product is therefore negative, which with a negative energy denominator and a negative spin matrix element, gives J_{HD} negative.

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END