Notizen

NMR Spin-Spin Coupling in HD

By W. Sänger and J. Voitländer

Physikalisch-Chemisches Institut der Universität München

The contact contribution to the nuclear spin-spin coupling constant in HD is evaluated variationally by using the nonsingular contact spatial part $f_m(r, a) = \exp(-r/a)/2\, a^3$, $a = O(10^{-6})$ a. u. J_{HD} is calculated to be 39 Hz and is independent of the sharp short-range part of the trial first-order wavefunction to the order $O(a)$.

In recent papers [1,2] a variational calculation of the isotropic nonsingular contact contribution

$$H_1 = \sum_{N,i} \lambda_N f_m^N(i)\, 2\, S_z(i)\, I_z^N ,$$

$$f_m^N(i) = \exp(-r_{iN}/a)/2\, a^3 ,$$
$$\lambda_N = (1/3)\, g_N\, \beta_N\, g\, \beta , \qquad (1)$$
$$N = \text{H, D}, \quad a = O(10^{-6}) \text{ a. u.}$$

to the rotationally averaged nuclear spin-spin coupling constant in the molecule HD

$$J_{HD} = \lambda_H\, \lambda_D\, E_{HD}\, (h\, I_z^H\, I_z^D)^{-1} \qquad (2)$$

has been presented. There, the one-electron Hylleraas functional due to the whole second-order energy E_2 is

$$\tilde{E}_2 = \lambda_H^2\, \tilde{E}_{HH} + \lambda_D^2\, \tilde{E}_{DD} + \lambda_H\, \lambda_D\, \tilde{E}_{HD} \qquad (3)$$
$$= 2 \langle \tilde{1} \,|\, h_0 - \varepsilon_0 \,|\, \tilde{1} \rangle + 4 \langle \tilde{1} \,|\, \sum_N \lambda_N f_m^N I_z^N \,|\, 0 \rangle .$$

In (3) the integration over the electron spins has already been done. In particular, h_0, $|0\rangle$ and ε_0 are the unperturbed approximate one-electron hamiltonian, groundstate Coulson MO and eigenvalue, respectively. $|\tilde{1}\rangle$ is the trial first-order MO of the HD molecule contact perturbed at the centres H and D, i.e.

$$|\tilde{1}\rangle = \sum_N \lambda_N [\tilde{c}_s^N\, |\tilde{N}_s\rangle + \tilde{c}_1^N\, |\tilde{N}_1\rangle]\, I_z^N ,$$

$$|\tilde{H}_s\rangle = |c_1^s\, \varphi_0^H + c_2^s\, \varphi_0^D + \tilde{\varphi}_{1,s}^H\rangle , \qquad (4)$$

$$|\tilde{H}_1\rangle = |c_1^1\, \varphi_0^H + c_2^1\, \varphi_0^D + \tilde{\varphi}_1^{H_1}\rangle .$$

The molecules HD and H_2 are identical with respect to their electronic distribution. By symmetry, the functions $|\tilde{D}_s\rangle$ and $|\tilde{D}_1\rangle$ in $|\tilde{1}\rangle$ result from interchanging H and D in $|\tilde{H}_s\rangle$ and $|\tilde{H}_1\rangle$. $\tilde{c}_s^N$ and $\tilde{c}_1^N$

are linear variational parameters, the physical meaning of which will be explained later. The constants $c_{1,2}^1$ and $c_{1,2}^s$ stem from spatial Schmidt orthogonalization $\langle \tilde{1} \,|\, 0 \rangle = 0$. c_1^S and c_2^S being of the order $O(a^2)$ become negligible in (3). The φ_0^N in (4) are scaled 1s-AOs. They are superimposed by the nonsingular functions

$$\tilde{\varphi}_{1,s}^N = -(1/a) \exp(-k_1\, r_N/a)\, [k_1\, r_N/a + 1]\, \varphi_0^N \quad (5)$$

and

$$\tilde{\varphi}_{1,1}^N = + k_2\, r_N\, \varphi_0^N ,$$

respectively. The sum of these two functions, $\tilde{\varphi}_1^N$, approximates the exact first-order correction to φ_0^N, i.e. the exact nonsingular solution φ_1^N of the atomic first-order perturbation ($= f_m^N$) equation (k_1 and k_2 are fitting constants). Like φ_1^N the approximate function $\tilde{\varphi}_1^N$ is composed of a short-range part $\tilde{\varphi}_{1,s}^N$, rapidly decreasing at very short (subatomic) distances of the order $O(a)$ from the perturbing nucleus N, and a long-range part $\tilde{\varphi}_{1,1}^N$, gradually decreasing at large (atomic) distances. This partitioning follows from using the more realistic nonsingular magnetic moment distribution function f_m^N rather than $\delta(r)/r^2$. $\tilde{\varphi}_{1,s}^N$ can be interpreted as the wavefunction of the electron "entering" the perturbing nucleus (contact) and leading to the non-divergent self-coupling term

$$E_{NN} \sim \langle \tilde{\varphi}_{1,s}^N \,|\, f_m^N\, \varphi_0^N \rangle . \qquad (6)$$

$\tilde{\varphi}_{1,1}^N$ describes the electron carrying its spin polarization away from the perturbing nuclear spin.

Going over to the molecule HD, by intuition one may expect that the sharp short-range part $\tilde{\varphi}_{1,s}^N$ is unaltered. The long-range part now covering the internuclear (chemical) region transfers the electron spin polarization via the chemical bond from one nucleus to the other and enables its interaction with the second nuclear spin thus producing the nuclear spin-spin hetero-coupling energy

$$\lambda_H\, \lambda_D\, E_{HD} = 4\, \lambda_H\, \lambda_D \langle H \,|\, f_m^D \,|\, 0 \rangle I_z^H\, I_z^D$$
$$= 4\, \lambda_D\, \lambda_H \langle D \,|\, f_m^H \,|\, 0 \rangle I_z^D\, I_z^H \qquad (7)$$

to which J_{HD} is proportional. Note that in the variational Ansatz (4) the trial first-order wavefunction of the molecule contact perturbed at the centre N is different from that used in Reference [1,2]. Pyykkö [3] has pointed out that $\tilde{E}_{HD}$ depends on E_{NN} if the trial function [1,2]

$$|\tilde{N}\rangle = \tilde{c}_N\, |\tilde{N}_s + \tilde{N}_1\rangle$$

with only one variational parameter $\tilde{c}_N$ is used. The calculation of E_{NN} from the operator f_m^N including first-order terms in the non-relativistic atomic Pauli hamiltionian that are quadratic in the vector potential $\boldsymbol{A}$ gives a reasonable (not too high) value [4]. Therefore, one has still to find out whether the formally correct E_{NN}-dependent approaches to E_{HD}, i.e. (33) and (37) in Ref. [2] are affected by those A^2-terms [4]. In the following, we prefer the Ansatz (4) of varying $\tilde{c}_s^N$ and $\tilde{c}_l^N$ independently [3, 5] by physical reasons: The second-order energies calculated from the short- and long-range parts differ greatly in their order and should therefore by varied independently, i.e. the variation must be made more flexible in order to account for the partitioning of energy. Setting

$$\partial \tilde{E}_2 / \partial \tilde{c}_s^N = \partial \tilde{E}_2 / \partial \tilde{c}_l^N = 0 \qquad (8)$$

one obtains the linear inhomogeneous system

$$\begin{aligned}
&[2\,\tilde{c}_s^H H_{1,s} + \tilde{c}_l^H A + 2\,C_{1,s}]\lambda_H I_z^H \\
&+ [c_s^D B + \tilde{c}_l^D A + B]\lambda_D I_z^D = 0, \\
&[2\,\tilde{c}_l^H H_{1,1} + \tilde{c}_s^H A + 2\,C_{1,1}]\lambda_H I_z^H \\
&+ [2\,\tilde{c}_l^D H_{2,1} + \tilde{c}_s^D A + 2\,C_{2,1}]\lambda_D I_z^D = 0,
\end{aligned} \qquad (9)$$

followed by two equations with H and D being interchanged. To save space in (9) the abbreviations

$$\begin{aligned}
H_{1,1(s)} &= \langle \tilde{N}_{1(s)} | h_0 - \varepsilon_0 | \tilde{N}_{1(s)} \rangle, \\
C_{1,1(s)} &= \langle \tilde{N}_{1(s)} | f_m^N | 0 \rangle, \\
H_{2,1} &= \langle \tilde{H}_1 | h_0 - \varepsilon_0 | \tilde{D}_1 \rangle = \langle \tilde{D}_1 | h_0 - \varepsilon_0 | \tilde{H}_1 \rangle, \\
C_{2,1} &= \langle \tilde{H}_1 | f_m^D | 0 \rangle = \langle \tilde{D}_1 | f_m^H | 0 \rangle
\end{aligned}$$

are introduced. The terms A and B are of the order

$$A = O(a), \quad B = O\left(\exp(-1/a)\right).$$

Neglecting these small corrections one evaluates

$$\begin{aligned}
\tilde{c}_s^H &= \tilde{c}_s^D = -C_{1,s}/H_{1,s}, \\
\tilde{C}_l^H &= (H_{1,1}C_{2,1} - H_{2,1}C_{1,1})\lambda_H I_z^H \\
&+ (H_{1,1}C_{1,1} - H_{2,1}C_{2,1})\lambda_D I_z^D / (H_{2,l}^2 - H_{1,l}^2)\lambda_D I_z^D
\end{aligned} \qquad (10)$$

(ln $\tilde{c}_l^D$ H and D are interchanged). With the parameters $\tilde{c}_s^N$ and $\tilde{c}_l^N$ thus fixed the hetero-coupling energy

$$\begin{aligned}
\lambda_H \lambda_D \tilde{E}_{HD}(\tilde{c}_l^H, \tilde{c}_l^D) \\
= 4\,\lambda_H\lambda_D I_z^H I_z^D \;[(2\,H_{1,1}C_{1,1}C_{2,1} \\
- H_{2,1}(C_{1,l}^2 + C_{2,l}^2)]/(H_{2,l}^2 - H_{1,l}^2)
\end{aligned} \qquad (11)$$

appears to be independent of the $\tilde{c}_s^N$ and hence of the (short-range) self-coupling term $C_{1,s}$ (see (6)) to the order $O(a)$. Summarizing the above results we deduce the following statements:

a) The independent variations of $\tilde{c}_l^N$ and c_s^N in (4) are justified physically by the partitioning of the whole second-order energy due to the long and short-range parts of the first-order perturbed wavefunction.

b) The Ansatz (4) leads to a variational nuclear spin-spin coupling energy which is independent of the sharp short-range part (near the perturbing nucleus) of the first-order trial function to the order $O(a)$.

c) By using the same numerical values for the molecular parameters as in Ref. [1] from (11) we find $\tilde{J}_{HD} = 39$ Hz (the experimental value [5] is 42.94 ± 0.10 Hz). Varying the cross-terms of (3) alone [see (38) in Ref. [2]] leads to the same numerical result. This approach is equivalent to setting $H_{1,1}$ and $C_{1,1}$ in (10) and (11) equal to zero. Thirdly, varying one of the self-coupling terms of (3) proportional to $(I_z^N)^2$ and employing only the long-range parts defined in (4) gives $J_{HD} = 39$ Hz as well. This approach is equivalent to setting $H_{2,1}$ and $C_{2,1}$ in (10) equal to zero.

d) The three possible approaches of varying either the whole second-order energy (physically reasonable) or the cross-term or one of the self-coupling energy terms due to $|\tilde{N}_1\rangle$ become equivalent in the case of

$$H_{1,1} = -C_{1,1}, \quad H_{2,1} = -C_{2,1}. \qquad (12)$$

With our $|\tilde{N}_1\rangle$ we find (12) well satisfied and hence $\tilde{J}_{HD} = 39$ Hz for each of the three variational approaches.

From using the nonsingular contact spatial part $f_m^N(r, a)$ and the Ansatz (4) we conclude that the long-range part $|\tilde{N}_1\rangle$ of the trial first-order wavefunction spatially accounts for the NMR spin-spin coupling constant in HD to the order $O(a)$.

[1] W. Sänger and J. Voitländer, Z. Naturforsch. **28 a**, 1866 [1973], ibid. **29 a**, 364 [1974].
[2] W. Sänger and J. Voitländer, Chem. Phys. **9**, 183 [1975].
[3] P. Pyykkö, Theor. Chim. Acta, **39**, 185 [1975], private communication [1975].
[4] E. A. Moore and R. E. Moss, Mol. Phys., in press, private communication [1975].
[5] J. Paviot, J. Hoarau, Theor. Chim. Acta **35**, 251 [1974].
[6] H. Benoit and P. Piejus, C. R. Acad. Sci. Paris **265 B**, 101 [1967].