Equivalence of the Variational Criteria in the Calculation of the Nuclear Spin-Spin Coupling Constant of HD

H. P. Trivedi *

Physical Chemistry Laboratory, South Parks Road,
Oxford OX1 3OZ, England

Z. Naturforsch. **35a**, 1108–1109 (1980);
received May 27, 1980

Using symmetry arguments it is shown that the variation of the self coupling, the cross coupling and the total second order energy are equivalent criteria for the calculation of the nuclear spin-spin coupling constant of HD and larger symmetric molecules. A previously given condition guaranteeing this equivalence is shown to be unnecessarily restrictive.

A wide variety of perturbation-variation methods have been applied to the study of the nuclear spin-spin coupling constant of the simplest system, the molecule HD. Distinction has been routinely made [1–5] between the results obtained using three variational criteria-namely, the variation of (i) the self coupling energy, (ii) the cross coupling energy, and (iii) the total second order energy. It has been stated [6] that the three criteria become equivalent if, and only if, the perturbed wavefunctions $\tilde{\psi}_{\mathrm{H}}^{(1)}$ and $\tilde{\psi}_{\mathrm{D}}^{(1)}$ are expanded over the same bases [7]. As it stands, this condition appears somewhat arbitrary and physically unsatisfactory because of its bases dependence. In this letter we seek a physical basis for it and find that it implies a certain unnecessary restriction on the form of the perturbed wavefunction $\psi^{(1)}$. We also point out that the charge symmetry of the nuclear framework directly guarantees a unique result and hence the equivalence of the three variational criteria for HD. This result is subsequently generalised to larger symmetric molecules.

The proof is trivial and goes as follows. We rewrite the contact perturbation

$$\sum_i [\lambda_{\mathrm{H},i} f(r_{\mathrm{H},i}) + \lambda_{\mathrm{D},i} f(r_{\mathrm{D},i})] \tag{1}$$

as

$$\sum_i [\lambda_{+,i} h_{+,i} + \lambda_{-,i} h_{-,i}] \equiv \bar{h}_+ + \bar{h}_- , \tag{2}$$

where

$$\lambda_{\pm,i} = (\lambda_{\mathrm{H},i} \pm \lambda_{\mathrm{D},i})/2 \quad \text{and}$$
$$h_{\pm,i} = f(r_{\mathrm{H},i}) \pm f(r_{\mathrm{D},i}) .$$

Here i labels the electron, $f(r_{\mathrm{N},i})$ is a short range function (which can be a delta function) centred on the nucleus N(=H, D), $\lambda_{\mathrm{N},i}$ is the strength of the interaction and $r_{\mathrm{N},i}$ measures the distance of electron i from the nucleus N. (The abbreviations $\bar{h}_\pm$ stand for $\sum_i \lambda_{\pm,i} h_{\pm,i}$.)

By virtue of the *gerade* symmetry of the Σ_g ground state wavefunction the perturbed wavefunction $\psi_+^{(1)}$ ($\psi_-^{(1)}$) corresponding to $\bar{h}_+$ ($\bar{h}_-$) necessarily has *gerade* (*ungerade*) symmetry. Applying the double perturbation theory to (2) rather than (1) and taking into consideration the symmetry of $\psi_\pm^{(1)}$ quite simply and directly leads to the following consequences:

(a) Variation of the new cross term $\lambda_+ \lambda_-$ yields the inconsequential identity $0 = 0$.

(b) Variation of the new self coupling terms $\lambda_\pm{}^2$ decouples the calculation for $\bar{h}_+$ and $\bar{h}_-$. Both terms now independently contribute to E_{HD} and their individual contributions must be added together to obtain the total heterocoupling energy from which the coupling constant is obtained.

(c) Variation of the total second order energy yields (a) + (b) above.

This type of argument readily generalises to include larger molecules *if* the unperturbed electronic wavefunction is an eigenfunction of a symmetry operation which has the net effect only of interchanging the two nuclei in question. For this purpose, interchanges between nuclei having the same charge (except for the two nuclei in question) are considered indistinguishable. Example are the proton-proton couplings in H_2O, NH_3, CH_4, C_2H_4 (cis and trans); proton-deuteron couplings in the deuterated versions of the above molecules, boron-boron and nitrogen-nitrogen couplings in Borazine, and countless others.

This result (viz., the equivalence of the three variational criteria) is a direct consequence of the symmetry properties of the molecules. To our knowledge, it cannot be proved for a general case (i.e., in the absence of any symmetry). Expanding

---

* Present address and reprint request to: Institut für Chemie, Universität Regensburg, D-8400 Regensburg 2.

0340-4811 / 80 / 1000-1108 $ 01.00/0. — Please order a reprint rather than making your own copy.

the trial perturbed wavefunction $\tilde{\psi}^{(1)} = \lambda_{\mathrm{H}} \tilde{\psi}_{\mathrm{H}}^{(1)} + \lambda_{\mathrm{D}} \tilde{\psi}_{\mathrm{D}}^{(1)}$ for HD over identical bases centred around H and D serves to ensure that it automatically obeys appropriate symmetry conditions.

Writing $\psi_{+}^{(1)} = \varphi_{\mathrm{H}} + \varphi_{\mathrm{D}}$ and $\psi_{-}^{(1)} = \chi_{\mathrm{H}} - \chi_{\mathrm{D}}$ (where φ_{N} and χ_{N} ($\mathrm{N} = \mathrm{H}, \mathrm{D}$) are functions centred about N) it is readily apparent that

$$\begin{aligned} \psi^{(1)} &= \lambda_{+} \psi_{+}^{(1)} + \lambda_{-} \psi_{-}^{(1)} = \lambda_{\mathrm{H}} \psi_{\mathrm{H}}^{(1)} + \lambda_{\mathrm{D}} \psi_{\mathrm{D}}^{(1)} \\ &= \lambda_{\mathrm{H}} (\tfrac{1}{2}(\varphi_{\mathrm{H}} + \chi_{\mathrm{H}}) + \tfrac{1}{2}(\varphi_{\mathrm{D}} - \chi_{\mathrm{D}})) \\ &\quad + \lambda_{\mathrm{D}} (\tfrac{1}{2}(\varphi_{\mathrm{D}} + \chi_{\mathrm{D}}) + \tfrac{1}{2}(\varphi_{\mathrm{H}} - \chi_{\mathrm{H}})) \end{aligned}$$

contains, in general, *terms proportional to* $\lambda_{\mathrm{H}} (\lambda_{\mathrm{D}})$ *which are centred around* D(H) *in addition to those centred around* H(D). It is not difficult to see that the occurrence of terms involving the ratio $\lambda_{\mathrm{D}}/\lambda_{\mathrm{H}} (\lambda_{\mathrm{H}}/\lambda_{\mathrm{D}})$ in $\psi_{\mathrm{H}}^{(1)} (\tilde{\psi}_{\mathrm{D}}^{(1)})$ in [4] and [7] in course of varying the total second order energy points to this very fact. That $\tilde{\psi}^{(1)} (= \lambda_{\mathrm{H}} \tilde{\psi}_{\mathrm{H}}^{(1)} + \lambda_{\mathrm{D}} \tilde{\psi}_{\mathrm{D}}^{(1)})$, the perturbed wavefunction expanded over identical bases centred about H and D, is already symmetry adapted can be seen by rewriting

$$\psi^{(1)} = \lambda_{+} (\tilde{\psi}_{\mathrm{H}}^{(1)} + \tilde{\psi}_{\mathrm{D}}^{(1)}) + \lambda_{-} (\tilde{\psi}_{\mathrm{H}}^{(1)} - \psi_{\mathrm{D}}^{(1)}) .$$

This is only a special case of the more general symmetry adapted $\psi^{(1)}$ in which $\varphi_{\mathrm{N}} = \chi_{\mathrm{N}}$, $\mathrm{N} = \mathrm{H}, \mathrm{D}$. This is an unnecessary restriction and it is implicit in [2—4], for example.

The author wishes to thank the S.R.C.(U.K.) for financial support.

[1] T. P. Das and R. Bersohn, Phys. Rev. **115**, 897 (1959).
[2] J. Paviot and J. Hoarau, Theor. Chim. Acta (Berlin) **35**, 251 (1974).
[3] A. Delpuech, J. Paviot, and J. Hoarau, Theor. Chim. Acta Berlin **42**, 345 (1976).
[4] W. Sänger and J. Voitländer, (a) Chem. Phys. **9**, 183 (1975); (b) Z. Naturforsch. **30a**, 1491 (1975).
[5] J. Schaefer and R. Yaris, J. Chem. Phys. **46**, 948 (1967).
[6] J. Kowalewski, Prog. N.M.R. Spectry. **11**, 1 (1977).
[7] J. Hoarau and J. Paviot, Theor. Chim. Acta Berlin **35**, 243 (1974).