On the Convergence of the Calculated Spin-spin Coupling Constant of HD

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It is shown that the concurrence of the results obtained by varying the self coupling energy, the total second order energy and the cross coupling energy independently can be readily accomplished. In addition, it is possible to arrange to obtain any pre-specified value for the coupling constant. On this basis it is suggested that it might be dangerous to construe the concurrence of calculated results as an indication of convergence in practice.

Calculations of the spin-spin coupling constant of the HD molecule have been performed by many authors [1–5] in many different ways. This note deals with the class of calculations involving a less singular contact operator than the delta function. With such an operator and a suitable choice of variational functions it becomes possible to make the cross-coupling energy independent (to within a very small parameter) of the (finite) self-coupling energy [5], the value of which depends on the precise form of the contact operator [1–5]. Delpuech [6] et al. concluded from their study that it is necessary to use variational functions which mimic the true solution both in the immediate vicinity (that is, within a few Fermis) of the perturbing nucleus and in the inter-nuclear domain in order to get convergence. Sänger and Voitländer [2] using a non-singular contact operator did not directly address themselves to the question of convergence but they computed the coupling constant J_{HD} in three different ways — by varying the self coupling energy, the total second order energy and the cross coupling energy — and obtained the same result, 39 Hz, in each case. The question poses itself whether this can be taken as an indication of convergence. In what follows we argue that it would be dangerous to do so. We demonstrate that a class of variational functions can be chosen for which this concurrence can be guaranteed and for which it is possible to obtain any pre-specified value for J_{HD}.

After integrating out the spin the original two electron problems can be reduced to a one electron problem. Having postulated a short range and a long range part for the solution and observed that the cross coupling energy is independent of the self coupling energy [2, 5] the coupling constant can be written down (in terms of quantities which depend on the long range solution alone) as [2]

$$J^{(2)}_{\mathrm{HD}} = (2.95)\,[2\,H_{1,l}\,C_{1,l}\,C_{2,l} - H_{2,l}(C^2{}_{1,l} + C^2{}_{2,l})]/[H^2{}_{2,l} - H^2{}_{1,l}] \quad (1)$$

in Hz. The superscript (2) indicates — as in [1] — that this corresponds to the minimisation of the total second order energy, and 2.95 is the conversion factor to convert atomic units to Hz in the case of HD. Also

$$\begin{aligned} H_{1,l} &\equiv \langle \tilde{H}_l |\, h_0 - \varepsilon_0 \,| \tilde{H}_l \rangle = \langle \tilde{D}_l |\, h_0 - \varepsilon_0 \,| \tilde{D}_l \rangle\,, \\ H_{2,l} &\equiv \langle \tilde{H}_l |\, h_0 - \varepsilon_0 \,| \tilde{D}_l \rangle = \langle \tilde{D}_l |\, h_0 - \varepsilon_0 \,| \tilde{H}_l \rangle\,, \\ C_{1,l} &\equiv \langle \tilde{H}_l |\, f^{\mathrm{H}}_m \,| 0 \rangle = \langle \tilde{D}_l |\, f^{\mathrm{D}}_m \,| 0 \rangle\,, \quad \text{and} \\ C_{2,l} &\equiv \langle \tilde{H}_l |\, f^{\mathrm{D}}_m \,| 0 \rangle = \langle \tilde{D}_l |\, f^{\mathrm{H}}_m \,| 0 \rangle\,. \end{aligned} \quad (2)$$

Here f^{N}_m represents the contact interaction [2, 7] and is a short range function centered on the nucleus N (= H, D). $|\tilde{H}_l\rangle$ ($|\tilde{D}_l\rangle$) is the long range basis function for the variational solution associated with the contact perturbation at H (D).

Varying the self coupling energy alone — denoted by the superscript (1) — yields [1]

$$J^{(1)}_{\mathrm{HD}} = -\,(2.95)\,C_{1,l}\,C_{2,l}/H_{1,l} \quad (3)$$

while varying the cross coupling energy alone — denoted by the superscript (3) — yields [1]

$$J^{(3)}_{\mathrm{HD}} = -\,(2.95)\,C^2_{2,l}/H_{2,l}\,. \quad (4)$$

Sänger and Voitländer [2] point out that all three expressions, i.e., (1), (3) and (5), are equivalent if

$$H_{1,l} = -\,C_{1,l} \quad \text{and} \quad H_{2,l} = -\,C_{2,l}\,. \quad (5)$$

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The equalities above are not invariant under scaling of $|\tilde{H}_l\rangle$ and $|\tilde{D}_l\rangle$ by a constant k since $H_{1,l}$ and $H_{2,l}$ scale as k^2 while $C_{1,l}$ and $C_{2,l}$ scale as k. The expressions (1), (3) and (4) for J_{HD} ought to be and are invariant under such scaling. In fact, the equalities (5) are only a special case of the more general requirement

$$H_{1,l}/H_{2,l} = C_{1,l}/C_{2,l} \tag{6}$$

which would ensure that $J_{\mathrm{HD}}^{(1)} = J_{\mathrm{HD}}^{(2)} = J_{\mathrm{HD}}^{(3)}$. This is readily verified by inserting (6) in (1), (3) and (4). Condition (6) is clearly invariant under scaling of the bases.

We now proceed to construct bases functions which would a priori guarantee (6). Consider the somewhat unusual choice

$$|\tilde{N}_l\rangle = |\tilde{\psi}_N \pm \tilde{\psi}_{N'}\rangle \quad (N' \neq N) \tag{7}$$

where $\tilde{\psi}_N$ is an arbitrary function centred on the nucleus N. For instance, if we choose the negative sign and $\tilde{\psi}_N = \sqrt{\varepsilon^3/\pi}\exp(-\varepsilon\, r_N)$, $|\tilde{N}_l\rangle$ would be just the higher lying (anti-bonding) LCAO orbital in the minimal basis set. It is obvious by symmetry of $|\tilde{N}_l\rangle$ with respect to N and N' that

$$H_{1,l}/H_{2,l} = C_{1,l}/C_{2,l} = \pm 1\,, \tag{8}$$

according as which of the ± signs is chosen in (7). Hence, $J_{\mathrm{HD}}^{(1)} = J_{\mathrm{HD}}^{(2)} = J_{\mathrm{HD}}^{(3)}$.

To be fair, the choice of the perturbed wavefunction (7) does not appear to be a physically reasonable one (compare, for example, with Ref. [6]). It is nevertheless permissible to draw formal conclusions from this analysis.

Further insight can be gained by considering Equation (3). Since ε_0 is the variational upper bound on h_0 it necessarily follows that $H_{1,l}$ must be positive semi-definite. The product $C_{1,l}\,C_{2,l}$ is positive (negative) semi-definite corresponding to the choice of + (−) sign in (7), and J_{HD} is correspondingly negative (positive) semi-definite. To be specific, taking the + (−) sign and choosing $\tilde{\psi}_N = \sqrt{\eta^3/\pi}\exp(-\eta\, r_N)$, it is possible to obtain any pre-specified negative (positive) value for J_{HD} by adjusting η.

We have seen that it is possible to choose a class of variational functions, albeit formally, for which it can be guaranteed that $J_{\mathrm{HD}}^{(1)} = J_{\mathrm{HD}}^{(2)} = J_{\mathrm{HD}}^{(3)} =$ any pre-specified value, under the linear variational procedure as described in [2]. While the variational bases used in [2], unlike (7), do not a priori guarantee the equality (6), it might nevertheless prove dangerous to take the concurrence of the $J_{\mathrm{HD}}^{(1)}$, $J_{\mathrm{HD}}^{(2)}$ and $J_{\mathrm{HD}}^{(3)}$ values to be an indication that they have converged.

To summarise, we have used simple scaling arguments to show that (5) is only a special case of the requirement (6) to ensure that $J_{\mathrm{HD}}^{(1)} = J_{\mathrm{HD}}^{(2)} = J_{\mathrm{HD}}^{(3)}$. Use of the antibonding orbital for HD in the minimal LCAO basis, in particular guarantees such concurrence, and it is possible to obtain any desired (positive) value for J_{HD} with it by suitably adjusting the exponent. It may be misleading to interpret the concurrence as being indicative of convergence.

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