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Notes

Note on Nuclear Spin-Spin Coupling in HD

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In a recent note Pyykkö [1] has given some critical comments on the finite second-order hyperfine self-coupling energy problem arising in variational nuclear spin-spin coupling constant calculations done with contact operators which are less singular than the delta function [2–5] or even nonsingular [6–8].

Thereupon we want to give the following short annotations:

1. It can be shown [8] that the finite self-coupling energy $E_{HH}^{(2)}$ non-relativistically calculated from the nonsingular contact operator $f_m(r, a) = \exp(-r/a)/2a^3$ [6, 7, 8] is not unphysical (too large), if the first-order terms quadratic in the vector potential are included. Thus, variation calculations of $E_{HD}^{(2)}$ influenced by a non-relativistically calculated $E_{HH}^{(2)}$ (case (b) in [1]) are not unphysical if carried out by considering those quadratic terms.
2. The finite second-order self-coupling energies $\tilde{E}_{HH,s}^{(2)}$ and $\tilde{E}_{HH,l}^{(2)}$ calculated from the short-range part

$$\tilde{\Psi}_s^{(1)} = -\lambda a^{-1} \exp(-r/a)[r/a+1]\Psi^{(0)}$$

and the long-range part

$$\tilde{\Psi}_l^{(1)} = +\lambda k_2 r \Psi^{(0)}$$

of the trial first-order wave-function $\tilde{\Psi}^{(1)}$ [1, 6] differ appreciably in their order. This partitioning of energy can be accounted for by linearly varying $\tilde{\Psi}_s^{(1)}$ and $\tilde{\Psi}_l^{(1)}$ independently. The variational procedure [9] then leads to the calculated spin-spin coupling energy $\tilde{E}_{HD}^{(2)}$ according to Das and Bersohn [10] being independent of the short-range part of $\tilde{\Psi}^{(1)}$ and hence of $\tilde{E}_{HH,s}^{(2)}$ (not of $\tilde{E}_{HH,l}^{(2)}$) to the order $O(a)$, $a \approx 10^{-6}$ a.u. (nuclear magnetic extension parameter).

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