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Relationes

Comments on Calculations of Nuclear Spin-Spin Coupling Constants Using the Blinder Operator

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It is pointed out that the finite second-order hyperfine self-coupling energies, obtained by the Blinder operator, are unphysical and 10^2 times too large. The additional terms in the first-order matrix element are also unphysical. Therefore the Blinder operator gives no improvement over the simple delta function. The consequences on the recent calculations by Paviot and Hoarau and by Sänger and Voitländer are discussed.

Key word: Nuclear spin-spin coupling constants

In 1960 Blinder [1] published an interesting derivation of the Fermi contact hyperfine Hamiltonian

$$\mathscr{H}_3 = -\frac{8\pi}{3} g g_n \beta \beta_n \boldsymbol{I} \cdot \boldsymbol{S} \delta(\boldsymbol{r}) . \tag{1}$$

He stated explicitly that the derivation "differs solely in matters of manipulation". Schwartz [13] showed that the second-order energies $E^{(2)}$ calculated with $\mathscr{H}_3$ diverge. Gregson *et al.* [4] showed in 1970 that a finite $E^{(2)}$ could be obtained by using the approximation

$$\delta(\boldsymbol{r}) = r^{-2} \delta(r) \cong r^{-2} r_0^{-1} \exp(-r/r_0) , \tag{2}$$

$$r_0 = \tfrac{1}{2} Z \alpha^2 \text{ (a.u.)} \tag{3}$$

for the function

$$\delta(r) \cong r_0 r^{-2} (r + r_0)^{-2} , \tag{4}$$

appearing in Blinder's derivation. The $E^{(2)}$ calculated by them for the hydrogen atom ground state was $8 \cdot 10^6$ Hz. Latvamaa *et al.* [7] considered the same problem using four-component Dirac states and also repeated the fully covariant quantum electrodynamical calculation. They found that the correct second-order contribution to the ground state hyperfine splitting is about $4 \cdot 10^4$ Hz. The total theoretical splitting agrees with experiment within 3 ppm or $4 \cdot 10^3$ Hz. Thus the Gregson result for the self-coupling energy is unphysical and over two orders of magnitude too large.

As the recent calculations of nuclear spin-spin coupling constants in molecules by Sänger and Voitländer [12] and by Hoarau and Paviot [5, 8] use the Gregson self-coupling energy $E^{(2)}_{\mathrm{HH}}$, it seems worthwhile to point out that only the following possibilities exist:

(a) the calculated $E^{(2)}_{\mathrm{HH}}$ has no effect on the calculated spin-spin coupling energy $E^{(2)}_{\mathrm{HD}}$ and may therefore be omitted, or

(b) the calculated $E^{(2)}_{\mathrm{HH}}$ does influence the calculated $E^{(2)}_{\mathrm{HD}}$ and the latter quantity is also unphysical.

Consider as an illustrative example a hydrogen atom, perturbed by its own nucleus

$$\mathscr{H}^{(0)} = -\frac{1}{2}\nabla^2 - \frac{1}{r}, \tag{5}$$

$$\mathscr{H}^{(1)}_{\mathrm{H}} = \lambda_{\mathrm{H}} r^{-2} r_0^{-1} \exp(-r/r_0), \tag{6}$$

$$\Psi^{(0)} = \pi^{-1/2} \exp(-r), \tag{7}$$

$$\Psi^{(1)} = \lambda a_0[-r_0^{-1} \exp(-a_1 r/r_0)(a_1 r/r_0 + 1) + a_2 r]\Psi^{(0)}. \tag{8}$$

The Ansatz (8) is taken from Ref. [12]. a_0, a_1, and a_2 are variational parameters. Using the perturbation (6) in the Hylleraas functional

$$\tilde{E}_2 = \langle \Psi^{(1)} | \mathscr{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle + 2\langle \Psi^{(1)} | \mathscr{H}^{(1)}_{\mathrm{H}} | \Psi^{(0)} \rangle, \tag{9}$$

we fix the parameters a_i from the condition

$$d\tilde{E}_2/da_i = 0. \tag{10}$$

The spin-spin coupling energy between the nuclei H and D in a molecule is given by the equation

$$E^{(2)}_{\mathrm{HD}} = \langle \Psi^{(0)} | \mathscr{H}^{(1)}_{\mathrm{H}} | \Psi^{(1)}_{\mathrm{D}} \rangle + \langle \Psi^{(0)} | \mathscr{H}^{(1)}_{\mathrm{D}} | \Psi^{(1)}_{\mathrm{H}} \rangle, \tag{11}$$

deduced from perturbation theory, and is proportional to the product $a_0 a_2$.

Putting $a_0 = 1$ and varying a_1 and a_2 independently as done in Ref. [8] we find, as they do, that a_2 is independent of the self-coupling energy to the order $O(r_0)$. Thus the work of Paviot and Hoarau seems to belong to case (a). On the other hand, if a_0 is determined from Eq. (10), the value of $a_0 a_2$ will depend on $E^{(2)}_{\mathrm{HH}}$. As Sänger and Voitländer permit variations of their $\tilde{c}_N$ (the equivalent of a_0), their work appears to belong to case (b).

As the $E^{(2)}_{\mathrm{HH}}$, calculated using the Blinder operator (4) is unphysical, one may ask whether its additional terms for first-order matrix elements

$$E^{(1)} = \langle \Psi^{(0)} | \mathscr{H}^{(1)} | \Psi^{(0)} \rangle \tag{12}$$

would be meaningful. Defining a relativistic correction factor

$$B = E^{(1)}(c = \alpha^{-1})/E^{(1)}(c = \infty) \tag{13}$$

the Blinder operator gives for a 1*s* state

$$B(\text{Blinder}) = 1 + 2(\alpha Z)^2 \ln(\alpha Z) + C(\alpha Z)^2 + \dots, \tag{14}$$

where C is the Euler constant, and Z the nuclear charge.

The correct result [2, 11] is

$$B(\text{Breit}) = 1 + \tfrac{3}{2}(\alpha Z)^2 + O((\alpha Z)^4)\,. \tag{15}$$

Thus the Blinder operator gives no improvement over the usual delta function in first-order theory, either.

The $1/r$ singularity appearing in the $\Psi^{(1)}$ of Schwartz [13] can be removed [9] but the $\ln r$ singularity cannot. As sharp structure in $\Psi^{(1)}$ amounts to mixing in high-energy intermediate states, one may ask how large this contribution to the spin-spin coupling constant will be. The relative contribution to the spin-spin coupling constant from the momentum region $k > 10^2$ a.u. turns out [6, 10] to be less than 10^{-3} of the total. We conclude that "the wave function, which is incorrect at very short distances and gives an incorrect, indeed infinite, value for the self-coupling, will nevertheless be correct at large distances and give the correct value for the spin coupling constants" [3].

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