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A density functional theory of the Fermi contact contribution to the nuclear spin–spin coupling constant

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Abstract

The authors' magnetic field density functional theory is extended to include electron spin-dependent interactions. Coupling the new theory with traditional spin density functional theory in the local limit yields a linear differential equation for the net spin density. The coefficients in the equation are functions of the electron density in the absence of a nuclear spin.

A little while ago we proved that the ground state energy of an inhomogeneous many-electron system in the presence of a vector potential, $A(r)$, is a universal functional of the electron density *and* the magnetic field, $B(r)$ [1,2]. Through the use of time reversal arguments and the variational principle, we found that second-order properties have a particularly simple form. In particular, the orbital portion of the nuclear spin–spin coupling, the chemical shielding tensor, and the magnetic susceptibility tensor, may be related to one universal functional of the density in the *absence* of the magnetic field.

Although our theorem as it stands allows us to obtain the orbital portion of the nuclear spin–spin coupling tensor, the electron spin terms were excluded. The Fermi contact term is generally the most important contribution to the coupling constant [3–5], hence we must rectify our omission. In this note we show that the contact coupling is a universal functional of the electron density in the absence of the perturbing nuclear spins. We also point out that unlike the orbital case where useful functionals are

only now being obtained [6], useful spin density functionals appear to exist [7–10].

The proof of our theorem is identical to that developed before. The many-electron Hamiltonian in the presence of an inhomogeneous magnetic field, $B(r)$, is

$$H = H_0 + \mu_B \int B(r) \cdot s(r) \, d^3r, \qquad (1)$$

where H_0 contains the nonmagnetic portions of the Hamiltonian. $s(r)$ is the spin density operator, and μ_B is the Bohr magneton. Although the orbital contribution to the Hamiltonian, and therefore the energy, may readily be included, we neglect it. The neglect is justified because we are interested in second-order properties where spin and orbital effects are additive. We now fix the magnetic field just like we fix the electron–electron interaction in ordinary density functional theory. The Hohenberg–Kohn theorem states that the ground state energy is a universal functional of the density. The proof is identical to that used before [1]. The magnetic field

must appear explicitly in the functional. Hence we have,

$$E = G(\rho, \boldsymbol{B}) - \int \nu(\boldsymbol{r})\rho(\boldsymbol{r})\, d^3r$$

$$+ \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, d^3r\, d^3r', \qquad (2)$$

where we have separated out the contributions to the energy due to the external field, $\nu(\boldsymbol{r})$, and the classical electron–electron interaction. $\boldsymbol{B}$ denotes the explicit field dependence of the functional. The density also depends upon the field.

Of interest to us are the responses to weak fields. Symmetry under time reversal requires that the energy and density be even functions of the magnetic field for a nondegenerate ground state. Hence, the lowest-order correction in the presence of a magnetic field to the zero-field energy, E_0, and density, ρ_0, is $\mathscr{O}(B^2)$. The energy depends on the magnetic field explicitly and also implicitly through the density, hence the correction of $\mathscr{O}(B^2)$ to E_0 has two terms. The coefficient of B^2 in the first is just (d^2E/dB^2) $(B = 0)$. The coefficient of B^2 in the second is $\rho^{(2)}$, the first correction to the density, multiplied by $(\delta E/\delta\rho)(\rho = \rho_0)$, the first variation of the energy with respect to the density *evaluated at the equilibrium zero-field density*. However the variational principles requires this term to be equal to zero. Therefore only the explicit dependence on B of $E[\rho, B]$ contributes to the first correction to E_0. Hence we may write the second-order energy which we denote as $E^{(2)}$, as

$$E^{(2)} = \int \boldsymbol{B}(\boldsymbol{r}) \cdot \tilde{F}(\rho_0, \boldsymbol{r}, \boldsymbol{r}') \cdot \boldsymbol{B}(\boldsymbol{r}')\, d^3r\, d^3r', \qquad (3)$$

where the functional, $\tilde{F}(\rho_0, \boldsymbol{r}, \boldsymbol{r}')$, depends only on the zeroth-order density. To calculate the Fermi contact contribution to the coupling we take the magnetic field in Eq. (3) to be,

$$\boldsymbol{B}(\boldsymbol{r}) = \sum_{\alpha = a,b} \tfrac{4}{3}\pi\delta^3(\boldsymbol{r} - \boldsymbol{R}_\alpha)\boldsymbol{\mu}_\alpha, \qquad (4)$$

where $\boldsymbol{R}_\alpha$ and $\boldsymbol{\mu}_\alpha$ are the position and magnetic moment operator respectively of nuclear spin α.

Then the spin–spin coupling constant is

$$J_{ab} = \tfrac{8}{3}\pi\, \text{Tr}\, \tilde{F}(\rho, \boldsymbol{R}_a, \boldsymbol{R}_b). \qquad (5)$$

This completes the proof. Thus, were the universal functional, $\tilde{F}(\rho_0, \boldsymbol{r}, \boldsymbol{r}')$, known, one could compute the contact contribution to J in any system from knowledge of the zero-field ground-state density. Our previous work [2] identifies another similar functional from which the orbital contribution may be calculated.

We now turn to the second point of this work: a method by which Eq. (3) may be used to obtain J without explicit knowledge of F. This can be done by taking advantage of recent developments in spin density functional theory [7–10]. That theory states, assuming that there is only one direction for the magnetic field, that the ground state energy is a universal functional of the spin density deviation, $\xi(\boldsymbol{r})$, where

$$\xi(\boldsymbol{r}) = \rho_\uparrow(\boldsymbol{r}) - \rho_\downarrow(\boldsymbol{r}) \qquad (6)$$

and the total density, $\rho(\boldsymbol{r})$. Thus, in the weak field limit Eq. (3) is replaced by

$$E^{(2)} = \int \xi(\boldsymbol{r})F'(\rho_0, \boldsymbol{r}, \boldsymbol{r}')\xi(\boldsymbol{r}')\, d^3r\, d^3r'. \qquad (7)$$

This form has a real advantage over the form given by Eq. (3). There is a $\xi(\boldsymbol{r})$ variational principle. That is, $\xi(\boldsymbol{r})$ satisfies

$$\frac{\delta E^{(2)}}{\delta\xi(\boldsymbol{r})} = 0. \qquad (8)$$

Hence, as is well known, we may determine $\xi(\boldsymbol{r})$ for one nuclear spin, say "a", and determine the energy and coupling at the other spin, b, through use of the Hellman–Feynman theorem [3,4]. That is, we have,

$$\boldsymbol{\mu}_a \cdot \boldsymbol{\mu}_b J_{ab} = \mu_b \xi_a(\boldsymbol{R}_b)\tfrac{4}{3}\pi\mu_B, \qquad (9)$$

where $\xi_a(\boldsymbol{R}_b)$ is the spin deviation at $\boldsymbol{R}_b$ due to a nuclear spin at $\boldsymbol{R}_a$.

Although we may proceed in general, let us consider the very recent developments in spin density functional theory. These developments take the form of exchange–correlation energy functionals, as well as kinetic energy functionals, of unprecedented accu-

racy and simplicity [9–11]. To take advantage of these functionals we first write the energy as

$$E(\rho_0, \xi) = T_0\left(\tfrac{1}{2}(\rho_0 + \xi)\right) + T_0\left(\tfrac{1}{2}(\rho_0 - \xi)\right)$$

$$+ E_x\left(\tfrac{1}{2}(\rho_0 + \xi)\right) + E_x\left(\tfrac{1}{2}(\rho_0 - \xi)\right)$$

$$+ E_c(\rho_0, \xi) - \int \nu(r)\rho_0(r)\,d^3r$$

$$+ \frac{1}{2}\int\int \frac{\rho_0(r)\rho_0(r')}{|r - r'|}\,d^3r\,d^3r'$$

$$+ \mu_B \int \xi(r)\delta^3(r - R_a)\,d^3r\,d^3r',$$
$$(10)$$

where T_0, E_x, and E_c are the kinetic energy, exchange, and kinetic energy corrected correlation spin density functionals, respectively.

We have already included the fact that only ρ_0 appears to second order. Now we assume that both the kinetic energy and exchange–correlation functionals are local functions of $\rho_0 \pm \xi$ and $|\nabla(\rho_0 \pm \xi)|$. We now expand the energy to second order in ξ. The most general form of the energy function is,

$$E = E_0(\rho_0) + \int\int\int \Big\{\xi(r)^2 A_1(\rho_0)$$

$$+ \xi(r)\nabla\xi(r)\cdot\nabla\rho_0(r)A_2(\rho_0)$$

$$+ [\nabla\xi(r)]^2 A_3(\rho_0)$$

$$+ [\nabla\rho_0(r)]^2 A_4(\rho_0)\Big\}\,d^3r$$

$$- \xi(r)\left[A_1 + \tfrac{1}{2}\nabla\cdot(A_2)\nabla\rho_0(r)\right]$$

$$+ \tfrac{1}{2}\mu_B\mu_a\int \xi(r)\delta^3(r - R_a)\,d^3r.   (11)$$

The coefficients, $A_1 \ldots A_4$, depend on the particular form of the kinetic energy, exchange, and correlation functions. Minimizing Eq. (11) with respect to $\xi(r)$ yields

$$\nabla\cdot A_3\nabla\xi(r) + \nabla\cdot\left[(\nabla\xi(r)\cdot\nabla\rho_0(r))A_4\nabla\rho_0(r)\right]$$

$$- \xi(r)\left[A_1 + \tfrac{1}{2}\nabla\cdot(A_2)\nabla\rho_0(r)\right]$$

$$= \tfrac{1}{2}\mu_B\mu_a\delta^3(r - R_a)   (12)$$

In a sense Eq. (12) is a density functional generalization of the Dalgarno–Schwartz equation for the

hyperfine coupling in one electron atoms [12–14]. In the latter case the one electron $\xi(r)$ satisfies

$$-\nabla^2\xi(r) + \frac{1}{\rho_0}\nabla\rho_0(r)\cdot\nabla\xi(r)$$

$$+ \left(\frac{\nabla^2\rho_0(r)}{\rho_0(r)} - \frac{5}{2}\frac{[\nabla\rho_0(r)]^2}{\rho_0(r)^2}\right)\xi(r)$$

$$= \tfrac{4}{3}\pi\mu_B\mu_z\rho_0(r)\delta^3(r - R).   (13)$$

Here the nuclear spin is at R.

In conclusion, we have generalized our magnetic field density functional theory to include the Fermi contact contribution to the nuclear spin–spin coupling constant. We have also related our theory to traditional spin density functional theory. Combining the variational principle with time reversal arguments, we have shown that in the local limit the net spin density, $\xi(r)$, satisfies a linear partial differential equation. The coefficients of this equation are functions of the unperturbed density. For all density functionals currently in use, the functions may be written explicitly. An example is given in the Appendix.

Unlike a recent Kohn–Sham theory of coupling constants [15], the new equation is a pure density functional theory. One needs only solve one linear differential equation. Hopefully the new equation will provide a new way of calculation of spin–spin couplings. Hopefully too, the theory may be used as a stringent test of density functionals.

Appendix

In the appendix we relate A_1 to A_4 to the Lee, Lee and Parr 'G' function [10]. With 'y' given by

$$y = 2^{1/3}\frac{|\nabla\rho_0(r)|}{\rho_0(r)},   (A.1)$$

we have

$$A_1 = \tfrac{5}{9}C_F\rho_0^{-1/3}\Big[1 + \alpha\big(G - \tfrac{6}{2}yG' + \tfrac{8}{5}y^2G''\big)\Big]$$
$$+ \tfrac{2}{9}C_X\rho_0^{-2/3}\Big[1 + \beta\big(G - yG' + y^2G''\big)\Big].$$

$$(A.2)$$

$$A_2 = \tfrac{4}{3}C_F\alpha\rho_0^{5/3} + \tfrac{4}{3}C_X\beta\rho_0^{4/3}\frac{yG' + y^2G''}{\nabla\rho_0(r)^2}, \quad (A.3)$$

$$A_3 = \big(C_F\alpha\rho_0^{5/3} + C_X\beta\rho_0^{4/3}\big)\frac{yG'}{\nabla\rho_0(r)^2}, \qquad (A.4)$$

and

$$A_4 = -\big(C_F\alpha\rho_0^{5/3} + C_X\beta\rho_0^{4/3}\big)\frac{yG' - y^2G''}{\nabla\rho_0(r)^42}.$$

$$(A.5)$$

When the LLP and Becke functions are used [9–11], G is given by

$$G = \frac{y^2}{1 + \gamma\,\sinh^{-1}y}, \qquad (A.6)$$

where γ is a constant. LLP suggest the values $\alpha \approx \beta = 4.5135 \times 10^{-3}$, and $\gamma = 0.0253$.

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