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LETTER TO THE EDITOR

The contact hyperfine interaction: an ill-defined problem

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Abstract. It is pointed out that the standard derivation of the contact hyperfine interaction contains an unwarranted assumption. When making away with this assumption the problem becomes indeterminate unless a more detailed description of the nuclear magnetisation is given.

The coupling of the nuclear and electronic magnetic moments—the hyperfine interaction—is a well known effect in magnetic resonance experiments (Abragam 1961, Abragam and Bleaney 1970). The singular part of this interaction, the so-called contact hyperfine interaction (Fermi 1930, Bethe and Salpeter 1957, Tinkham 1964), provides a sensitive probe of the value over the nucleus of the electronic wave function. In nuclear magnetic resonance experiments in metals, for instance, this part gives the main contribution to the Knight shift (Knight 1956). Although it was first derived by Fermi from Dirac's equation, the contact hyperfine interaction may be obtained in a purely classical fashion (Ferrell 1960, Milford 1960, Jackson 1975). If one carefully examines the different derivations, one finds that in all cases an integral is evaluated over a spherically symmetric region. In what follows it will be shown that the value of the aforementioned integral depends on the shape of the region of integration, and therefore the problem does not have a unique answer. This ambiguity turns out to be related to a lack of specification of the precise distribution of nuclear angular momentum that gives rise to the measured nuclear magnetic dipole moment.

In order to make our point in the simplest possible way, we will take the classical approach. The magnetostatic energy U of interaction between an electronic magnetic dipole moment $\boldsymbol{m}$ at point $\boldsymbol{r}$ and a nuclear magnetic moment $\boldsymbol{\mu}$ at $\boldsymbol{r}'$ is given by

$$U = -\,\boldsymbol{m}\,.\,\boldsymbol{B}(\boldsymbol{r}, \boldsymbol{r}') \tag{1}$$

where

$$\boldsymbol{B}(\boldsymbol{r}, \boldsymbol{r}') = \nabla \times \left(\frac{\boldsymbol{\mu} \times (\boldsymbol{r} - \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\right) = \nabla \times \nabla \times \left(\frac{\boldsymbol{\mu}}{|\boldsymbol{r} - \boldsymbol{r}'|}\right) \tag{2}$$

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is the nuclear magnetic induction. A quantum mechanical derivation gives an identical expression but in terms of operators. As all the operators involved commute among themselves, no error arises if one uses the standard rules of calculus.

The field equation (2) is everywhere well defined and gives

$$\boldsymbol{B}(\boldsymbol{r}, \boldsymbol{r}') = \frac{3(\boldsymbol{r} - \boldsymbol{r}')[\boldsymbol{\mu}.(\boldsymbol{r} - \boldsymbol{r}')]}{|\boldsymbol{r} - \boldsymbol{r}'|^5} - \frac{\boldsymbol{\mu}}{|\boldsymbol{r} - \boldsymbol{r}'|^3} \tag{3}$$

except at $\boldsymbol{r} = \boldsymbol{r}'$ where it is singular. Using some general properties of operator ∇ (Korn and Korn 1968) it is found that

$$\begin{aligned} \nabla \times \nabla \times \left(\frac{\boldsymbol{\mu}}{|\boldsymbol{r} - \boldsymbol{r}'|}\right) &= \nabla\left[\nabla.\left(\frac{\boldsymbol{\mu}}{|\boldsymbol{r} - \boldsymbol{r}'|}\right)\right] - \nabla^2\left(\frac{\boldsymbol{\mu}}{|\boldsymbol{r} - \boldsymbol{r}'|}\right) \\ &= \nabla\left[\boldsymbol{\mu}.\nabla\left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right)\right] - \boldsymbol{\mu}\nabla^2\left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right). \end{aligned} \tag{4}$$

The last member of equation (4) exhibits the well known integrable singularity

$$\nabla^2\left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right) = -4\pi\delta(\boldsymbol{r} - \boldsymbol{r}') \tag{5}$$

where δ is the Dirac delta function. It is known that the previous term also has an integrable singularity. This singularity, which to our knowledge has never been correctly analysed, originates the ambiguity mentioned at the beginning. In order to expose the singularity we take the product of that term with a smooth function $f(\boldsymbol{r})$, we integrate over a volume V enclosing $\boldsymbol{r}'$, and we then let V go to zero. That is, we evaluate the expression

$$I(\boldsymbol{r}') = \lim_{V \to 0} \int_V f(\boldsymbol{r})\, \nabla\left[\boldsymbol{\mu}.\nabla\left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right)\right] \mathrm{d}^3\boldsymbol{r}' \tag{6}$$

where $\boldsymbol{r}'$ is always inside V. We first notice that

$$\nabla\left[\boldsymbol{\mu}.\nabla\left(\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right)\right] = -4\pi\mathbf{d}(\boldsymbol{r} - \boldsymbol{r}').\boldsymbol{\mu} \tag{7}$$

where $\mathbf{d}(x)$ is the symmetric tensor of rank 2 given by

$$d_{jk}(\boldsymbol{x}) = -\frac{1}{4\pi}\frac{\partial^2}{\partial x_j \partial x_k}\frac{1}{|\boldsymbol{x}|} \tag{8}$$

If $f(\boldsymbol{r})$ is everywhere smooth we can write

$$I(\boldsymbol{r}') = -4\pi f(\boldsymbol{r}')\boldsymbol{C}(\boldsymbol{r}').\boldsymbol{\mu} \tag{9}$$

where

$$\boldsymbol{C}(\boldsymbol{r}') = \lim_{V \to 0} \int_V \mathbf{d}(\boldsymbol{r} - \boldsymbol{r}')\, \mathrm{d}^3\boldsymbol{r}. \tag{10}$$

It is easy to see that C_{jk} may be rewritten in the following form:

$$C_{jk}(\boldsymbol{r}') = \lim_{V \to 0} D_{jk}(\boldsymbol{r}') \tag{11}$$

where

$$D_{jk}(\boldsymbol{r}') = -\frac{1}{4\pi}\frac{\partial^2}{\partial x'_j \partial x'_k}\int_V \frac{\mathrm{d}^3\boldsymbol{r}}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{12}$$

is the demagnetising tensor (Moskowitz and Della Torre 1966), whose principal values are the standard demagnetising coefficients. We may now write the full expression for the magnetostatic energy equation (1):

$$U = \frac{\boldsymbol{m}.\boldsymbol{\mu}}{|\boldsymbol{r}-\boldsymbol{r}'|^3} - 3\frac{[\boldsymbol{m}.(\boldsymbol{r}-\boldsymbol{r}')][\boldsymbol{\mu}.(\boldsymbol{r}-\boldsymbol{r}')]}{|\boldsymbol{r}-\boldsymbol{r}'|^5} + 4\pi\boldsymbol{m}.(\boldsymbol{C}(\boldsymbol{r}')-\boldsymbol{1}).\boldsymbol{\mu}\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{13}$$

where the last term is the contact hyperfine interaction. It is known that the value of the demagnetising tensor **D** depends on the shape of the region V of integration. Therefore the contact term is not defined unless one specifies how to take the limit in equation (11). In the particular case of a spherical volume V we obtain

$$D_{jk}(\boldsymbol{r}') = \tfrac{1}{3}\delta_{jk} \tag{14}$$

where δ_{jk} is the Kronecker delta, and the components are constant as long as $\boldsymbol{r}'$ is inside V regardless of the size of V. The ensuing particular value

$$U_c = -\frac{8\pi}{3}\boldsymbol{m}.\boldsymbol{\mu}\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{15}$$

for the contact term is the one always quoted in the literature.

From a purely mathematical point of view the contact term is not defined, but it may be seen that this indetermination is inherent in the point dipole model. Indeed, a point dipole may be thought of as the limit of a bounded current distribution when its volume goes to zero. In the limit the fields outside different distributions will be the same as long as their dipole moments are equal. But there is no reason why the interaction of a magnetisation with the field inside the distribution should be the same for different distributions.

It therefore seems that the only possible way of removing the indetermination in the contact hyperfine interaction is to give a more detailed model for the nuclear magnetic dipole moment, that is to consider fully the problem of the nuclear angular momentum.

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