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Two-Dipole Magnetic-Field Density Functional Theory

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We show that, by constructing a magnetic-field density functional theory for the response of many-electron systems to the magnetic field generated by two magnetic dipoles, one can calculate the orbital portion of the indirect spin–spin coupling, nuclear magnetic shielding tensor, and diamagnetic susceptibility of any such system.

Introduction

The lowest order response of many-electron systems to weak magnetic fields is the natural purview of the physical chemist. Indeed, all nuclear magnetic resonance experiments measure just this object, and the wealth of equilibrium and dynamical information obtained thereby is well-known.

But the lowest order response of a closed-shell electronic system to a magnetic field is *second* order in the field,¹ and this makes its theoretical calculation less straightforward than the calculation of lowest order responses to, for example, electric fields. The trouble is illustrated by the perturbation-theory expression for the lowest (second) order change in ground-state energy caused by a weak magnetic field \mathbf{B} ,

$$E^{(2)}(B^2) = \left\langle 0^{(0)} \left| \frac{1}{2c^2} \sum_{i=1}^N A^2(\mathbf{r}_i) \right| 0^{(0)} \right\rangle + \left\langle 0^{(0)} \left| \frac{1}{2c} \sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i) + \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i \right| 0^{(1)}(B) \right\rangle + c.c. \quad (1)$$

where atomic units are used and only the orbital response is considered. \mathbf{p}_i is the momentum operator for the i th electron, and $\mathbf{A}(\mathbf{r})$ is the vector potential. To calculate the second term on the right-hand side of eq 1, the “paramagnetic” contribution to the energy, requires finding $|0^{(1)}(B)\rangle$, the first correction to the zero-field ground electronic eigenstate $|0^{(0)}\rangle$. This is a time-consuming task.^{2–5}

Equation 1 conforms to the general principle that finding second-order responses requires finding the perturbation of the ground state to first order. But actually this general principle can—in principle—be evaded for magnetic responses.⁶ That is, the second-order change in the energy due to a weak magnetic field can be calculated from knowledge of only the unperturbed ground state. (In fact, one does not even need the entire ground-state wave function but only the ground-state density.)

The evasion proceeds by way of magnetic-field density functional theory, which is defined more explicitly in ref 6, and the price of the evasion is that an explicit method of calculation to arbitrary accuracy—i.e. the equivalent of eq 1—is not yet known, although there are a number of approximate methods.^{7–13} What we wish to show here is that construction of only an incomplete magnetic-field density functional theory, that which can predict the responses of an electronic system to only one

specific form of magnetic field, would have wide utility. Specifically, if one constructs a magnetic-field density functional theory for the magnetic field caused by two magnetic dipoles, one can calculate the orbital portion of the indirect spin–spin couplings, nuclear magnetic shielding tensors, and diamagnetic susceptibilities for any electronic system with only the zero-field ground-state density.

Two-Dipole Magnetic-Field Density Functional Theory

We have shown in earlier work that the ground-state electronic energy E of a many-electron system in the presence of a magnetic field can be written as a functional $E[\rho, \mathbf{B}]$ of the magnetic field $\mathbf{B}(\mathbf{r})$ and the ground-state electronic density $\rho(\mathbf{r})$.⁶ We made the comment in ref 6 that there was no obvious purpose in regarding $\mathbf{B}(\mathbf{r})$ in the functional $E[\rho, \mathbf{B}]$ as an independent variable. But this is not quite true. Suppose we make a functional expansion of $E[\rho, \mathbf{B}]$ about the function $\mathbf{B}(\mathbf{r}) = 0$ for a closed-shell system,

$$E[\rho, \mathbf{B}] = E_0[\rho_0, 0] + \int d^3r d^3r' \mathbf{B}(\mathbf{r}) \cdot \left. \frac{\delta^2 E}{\delta \mathbf{B}(\mathbf{r}) \delta \mathbf{B}(\mathbf{r}')} \right|_{\mathbf{B} \rightarrow 0} \cdot \mathbf{B}(\mathbf{r}') + \dots \quad (2)$$

where $\rho_0(\mathbf{r})$ is the ground-state density in the absence of the field. Note that this expansion is made with respect to only the *explicit* dependence of $E[\rho, \mathbf{B}]$ on $\mathbf{B}(\mathbf{r})$. There is also an *implicit* dependence of $E[\rho, \mathbf{B}]$ on $\mathbf{B}(\mathbf{r})$, because $\rho(\mathbf{r})$ itself depends on $\mathbf{B}(\mathbf{r})$. But to order B^2 this implicit dependence of E is proportional to the first variation of E with respect to $\rho(\mathbf{r})$, and the variational theorem requires this variation to vanish for the correct ground-state density. Note also the lack of a term in eq 2 that is first order in B . This is a consequence of our assumption of a closed-shell ground state and the reason why we must go to second order to obtain the lowest order magnetic response of such systems.

We define a generalized susceptibility kernel as the coefficient of the fields in the second term of eq 2,

$$\mathbf{F}[\mathbf{r}, \mathbf{r}'; \rho_0] = \left. \frac{\delta^2 E}{\delta \mathbf{B}(\mathbf{r}) \delta \mathbf{B}(\mathbf{r}')} \right|_{\mathbf{B} \rightarrow 0} \quad (3)$$

\mathbf{F} is a second-rank tensor.

$E[\rho, \mathbf{B}]$ depends only on $\rho(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$. It does not depend explicitly on the potential (due typically to the nuclei) that the electrons find themselves in. Thus it is called “universal” and need be constructed only once for all possible many-electron systems. \mathbf{F} is also “universal” in the same sense. In addition,

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however, since the functional derivative defining it is evaluated at $\mathbf{B}(\mathbf{r}) \rightarrow 0$, \mathbf{F} is independent of $\mathbf{B}(\mathbf{r})$ and can only depend on the unperturbed ($B = 0$) ground-state density $\rho_0(\mathbf{r})$. Thus, remarkably, knowing \mathbf{F} , a function of two variables (\mathbf{r} and \mathbf{r}') and a functional of one ($\rho_0(\mathbf{r})$), would allow the calculation of any orbital second-order magnetic response of any many-electron system from knowledge of only the unperturbed ground-state electronic density.

Unfortunately we don't know \mathbf{F} exactly, and constructing good approximations to it is a difficult task. Furthermore, an approximation to \mathbf{F} would generally have to be constructed directly for each specific form of $\mathbf{B}(\mathbf{r})$, since the general behavior of $E[\rho, \mathbf{B}]$ with $\mathbf{B}(\mathbf{r})$ is unknown. As we pointed out in ref 6, this is not a fatal drawback, simple because the variety of forms of $\mathbf{B}(\mathbf{r})$ that are of wide interest is not large. In fact the magnetic responses most often measured are just those to a constant field and/or one or two magnetic dipoles.

What we wish to point out here, however, is that actually the responses to *all* of these latter forms of $\mathbf{B}(\mathbf{r})$ can be calculated from the \mathbf{F} found by constructing $E[\rho, \mathbf{B}]$ to order B^2 for just *one* particular form of $\mathbf{B}(\mathbf{r})$. This form is that of the magnetic field caused by two nuclear magnetic dipoles,

$$\mathbf{B}(\mathbf{r}; \mu_1, \mu_2) = \mu_1 \cdot \mathbf{M}(\mathbf{r}, \mathbf{R}_1) + \mu_2 \cdot \mathbf{M}(\mathbf{r}, \mathbf{R}_2) \quad (4)$$

$$\mathbf{M}(\mathbf{r}, \mathbf{R}) = -\frac{\mathbf{1}}{|\mathbf{r} - \mathbf{R}|^3} + \frac{3(\mathbf{r} - \mathbf{R})(\mathbf{r} - \mathbf{R})}{|\mathbf{r} - \mathbf{R}|^5}$$

where $\mathbf{1}$ is the unit tensor and the two magnetic dipoles μ_1 and μ_2 are located at \mathbf{R}_1 and \mathbf{R}_2 , respectively.

Suppose we constructed by some (approximate) means $E[\rho, \mathbf{B}]$ to order B^2 for the field in eq 4. If we compared the result to the right-hand side of eq 2, we could pick out \mathbf{F} . This would not generally be the full \mathbf{F} because we presumably used information about the form $\mathbf{B}(\mathbf{r})$ to calculate E . What we would be picking out would really be $\mathbf{F}^{(\mu\mu)}$, the pieces of \mathbf{F} that couple with $\mathbf{B}(\mathbf{r})$ when the latter is the two-dipole field given by eq 4.

Using $\mathbf{F}^{(\mu\mu)}$ we could calculate the orbital magnetic response of any electronic system to two magnetic dipoles. In particular by using eq 4 and eq 2 one can show that the indirect spin-spin coupling constant tensor is given by

$$\mathbf{J}(\mathbf{R}_1 - \mathbf{R}_2) = \int d^3r d^3r' \mathbf{M}(\mathbf{r}, \mathbf{R}_1) \cdot \mathbf{F}^{(\mu\mu)}[\mathbf{r}, \mathbf{r}'; \rho_0] \cdot \mathbf{M}(\mathbf{r}', \mathbf{R}_2) \quad (5)$$

where we would need to supply $\rho_0(\mathbf{r})$, the zero-field ground-state density of the system in question, in order to evaluate the right-hand side.

But as promised we can get more than \mathbf{J} out of $\mathbf{F}^{(\mu\mu)}$. Suppose we take $\mathbf{R}_2 \rightarrow \infty$ in eq 4. The resulting magnetic field, to lowest order in R_2^{-1} , is

$$\mathbf{B}(\mathbf{r}; \mu_1, \mathbf{B}_0) = \mu_1 \cdot \mathbf{M}(\mathbf{r}, \mathbf{R}_1) + \mathbf{B}_0 \quad (6)$$

$$\mathbf{B}_0 = \mu_1 \cdot \left\{ -\frac{\mathbf{1}}{R_2^3} + \frac{3\mathbf{R}_2\mathbf{R}_2}{R_2^5} \right\}$$

which is the field due to a magnetic dipole and a constant external field \mathbf{B}_0 , that is, the fields appearing in a nuclear magnetic resonance experiment.

Since the $\mathbf{B}(\mathbf{r})$ in eq 6 is the first term in the expansion in powers of R_2^{-1} of the $\mathbf{B}(\mathbf{r})$ in eq 4, the energy $E[\rho, \mathbf{B}]$ for $\mathbf{B}(\mathbf{r})$ given by eq 6 must similarly be given by the first term in the expansion in powers of R_2^{-1} of the energy $E[\rho, \mathbf{B}]$ for $\mathbf{B}(\mathbf{r})$ given by eq 4. $\mathbf{F}^{(\mu\mu)}$ must therefore contain all the information required

to construct $E[\rho, \mathbf{B}]$ to second order for *both* fields. We may use $\mathbf{F}^{(\mu\mu)}$, then, to also calculate—after supplying the zero-field ground-state density—the magnetic shielding tensor σ of a nuclear spin magnetic dipole in any electronic system. By using eq 6 in eq 2 this can be shown to be given by

$$\sigma = \int d^3r d^3r' \mathbf{M}'(\mathbf{r}, \mathbf{R}_1) \cdot \mathbf{F}^{(\mu\mu)}[\mathbf{r}, \mathbf{r}'; \rho_0] \quad (7)$$

$$\mathbf{M}' = -\frac{\mathbf{1}}{|\mathbf{r} - \mathbf{R}|^3} + \frac{3(\mathbf{r} - \mathbf{R})(\mathbf{r} - \mathbf{R})}{|\mathbf{r} - \mathbf{R}|^5}$$

Finally, if we take the limit $\mathbf{R}_1 \rightarrow \infty$ in eq 6, we arrive at a field that is constant, and so $\mathbf{F}^{(\mu\mu)}$ must contain all the information necessary to construct $E[\rho, \mathbf{B}]$ for $\mathbf{B}(\mathbf{r}) = \mathbf{B}$ as well. From $\mathbf{F}^{(\mu\mu)}$ we may therefore also obtain the ordinary magnetic susceptibility tensor χ of any electronic system, which by inserting $\mathbf{B}(\mathbf{r}) = \mathbf{B}$ into eq 2 can be shown to be given by

$$-\chi = \int d^3r d^3r' \mathbf{F}^{(\mu\mu)}[\mathbf{r}, \mathbf{r}'; \rho_0] \quad (8)$$

As a final point we note that calculations using any of eqs 5, 7, or 8 would be intrinsically gauge-invariant, since no separation of the energy into diamagnetic and paramagnetic contributions occurs and only observable quantities (density and magnetic field) are used.

Conclusion

Magnetic-field density functional theory holds out the promise of being able to calculate second-order magnetic responses from the zero-order (field-free) electronic density. The present lack of understanding of the general behavior of $E[\rho, \mathbf{B}]$ as a functional of $\mathbf{B}(\mathbf{r})$ means approximations to the energy functionals that enter such a theory must be constructed individually for each form of $\mathbf{B}(\mathbf{r})$. What we have shown here is that constructing an approximation to $E[\rho, \mathbf{B}]$ for only *one* type of $\mathbf{B}(\mathbf{r})$, that due to two magnetic dipoles, allows the calculation, for any electronic system, of indirect spin-spin couplings, nuclear magnetic shielding tensors, and diamagnetic susceptibilities. This lends particular attractiveness to the goal of constructing an approximation to $E[\rho, \mathbf{B}]$ for the two-dipole magnetic field.

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Note Added in Proof: Our theorem has been extended to include the electron spin density coupled to a magnetic field. Hence, we may determine the Fermi contact contribution to J .¹⁴

Concerning Stuart Rice

The articles in this issue of *The Journal of Physical Chemistry* constitute a collective birthday present for Stuart Rice. Like Stuart's scientific work, the research is eclectic in that most aspects of physical chemistry are represented. Whether these pieces of science are as audacious and imaginative and as beautifully explicated as Stuart's remains to be seen. I do not want to write this afterward as a scientific critique. I want to write about my history with Stuart. I have known him almost my entire scientific life. Indeed, if it hadn't been for him, I might not have had a scientific life.

When I first heard of Stuart, I had been at the University of Chicago about two quarters. The chairman of the chemistry department had just given me a warning: I was not narrow and deep in my scientific knowledge—I wasn't even shallow and

broad. I was about to be tossed out of graduate school. Stuart had just arrived, preceded by a tidal wave of rumors of great brilliance, as well as coming from, yes, Harvard—a theorist who did experiments. It had, a little earlier, become eminently clear that I too was to be a theorist, a theorist who carried out no experiments. So I went to see Stuart. The first thing that amazed me was that the blackboard had written on it a list of all the important problems of physical chemistry. Was that list a daily reminder of the problems Stuart needed to solve? Or were they there for his future students to solve? Or was it some mixture of both? The next thing that struck me was, yes, he would let me work with him—take a risk. And I did. He did too. I can say without exaggeration that Stuart Rice changed my life. He gave me the opportunity to carry out independent science. There were no lessons on “how” to carry out scientific research, no “scientific method”, if you will, just doing it. I did it. But while I was “doing it”, I felt enormous support, interest, and active participation, and I was always taken seriously. Those feelings and their reality did not end with graduate school. They have been an essential part of my entire life.

I wasn't the only one.

Robert A. Harris

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