Gauge-Invariant Method for Calculating the Electric Current Density Induced in Molecules and Solids by an External Magnetic Field

G. W. Parker
Department of Physics, North Carolina State University, Raleigh, North Carolina 27650

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In the approximation in which the nuclei are fixed in space, the electric current density induced in a molecule or solid by a uniform external magnetic field $\vec{B}$ is shown to have the form $\vec{J}=\nabla\times\vec{k}$ where, to first order in $\vec{B}$, $\vec{k}=(e^2\vec{B}/2mc)\sum_i g_i(\vec{r})$. There is one function g_i for each electron. These functions are independent of the gauge of the vector potential, and they are determined by the zero-field configuration-space probability density.

Turning on a uniform magnetic field $\vec{B}$ produces a nonconservative electric field perpendicular to $\vec{B}$. Electrons moving relative to fixed nuclei and experiencing this field would be expected to acquire an induced current which is also perpendicular to $\vec{B}$. A stationary state of this system of electrons would then be characterized by an electric current density satisfying $\vec{j}\cdot\vec{B}=0$ as well as $\nabla\cdot\vec{j}=0$. In this Letter this conjecture is shown to hold when $\vec{j}$ is computed to first order in $\vec{B}$.

The calculation of magnetic susceptibilities and chemical shielding constants has been of interest for some time.[1-9] These quantities are usually calculated from perturbation theory as a sum of two terms, one from first order which involves an unperturbed eigenfunction and the other from second order which involves the first-order change in the corresponding eigenfunction. Although each of these terms is separately gauge dependent, their sum is not, provided that an exact first-order eigenfunction is used. In practice, therefore, actual calculations of magnetic properties have been gauge dependent.[5-8,10,11] An alternative approach is to evaluate the induced current density to first order in $\vec{B}$ and from it calculate the magnetic property of interest. Of course, this approach also requires the solution of the first-order perturbation equation. However, by exploiting the properties $\vec{j}\cdot\vec{B}=0$ and $\nabla\cdot\vec{j}=0$, I have found that this problem can be cast in a different form. A new and gauge-invariant equation is found whose solution determines $\vec{j}$. By use of this formulation, magnetic properties can now be calculated in a gauge-invariant manner.

The Hamiltonian of N electrons moving about fixed nuclei in a uniform magnetic field $\vec{B}$ can be written in the general form

$$H=\sum_{j=1}^{N}\frac{1}{2m}\left(\vec{p}_j+\frac{e\vec{A}_j}{c}\right)^2+V(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N),$$

where $-e$ is the charge on an electron of mass m. The vector potential $\vec{A}_j=\vec{A}(\vec{r}_j)$ satisfies $\nabla_j\times\vec{A}_j=\vec{B}$ and I leave $\nabla_j\cdot\vec{A}_j$ unspecified. Spin-dependent terms have not been included in H since the coupling between the total spin $\vec{S}$ and the field shifts the energy but does not affect the calculation of the induced current density. Furthermore, the induced current density is important when the expectation value of $\vec{S}$ is zero so that the spin current density[12] is also zero.

The general equation for conservation of probability density in configuration space is

$$\partial P/\partial t+\sum_j\nabla_j\circ\vec{J}_j=0, \tag{1}$$

where $P=|\Psi|^2$, $\int P\,d^3r_1\,d^3r_2\cdots d^3r_N=\int P(d^{3N}r)=1$, and

$$\vec{J}_j=\mathrm{Re}(\Psi^*\vec{v}_j\Psi), \tag{2}$$

with $\vec{v}_j=(\vec{p}_j+e\vec{A}_j/c)/m$. Only stationary states are considered here so that $\partial P/\partial t=0$ and $\sum_j\nabla_j\circ\vec{J}_j=0$. The electric current density is then[13]

$$\vec{j}(\vec{r})=\sum_j\int(-e\vec{J}_J)\delta(\vec{r}-\vec{r}_J)(d^{3N}r). \tag{3}$$

Eigenfunctions of H including spin should satisfy the exclusion principle and be eigenfunctions of both the square of the total spin angular momentum and its component along $\vec{B}$. The form taken by such an eigenfunction is[14]

$$\Psi_{S,M}=(\lambda_S)^{-1/2}\sum_{l=1}^{\lambda_S}\psi_l{}^S\Theta_{S,M,l}, \tag{4}$$

where $\psi_l{}^S=\psi_l{}^S(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ and its associated spin function $\Theta_{S,M,l}$ are basis functions of a particular irreducible representation of the symmetric group which are characterized by the spin quantum numbers S and M, the number of electrons, and the orthogonality relation

$$\langle\Theta_{S,M,l}|\Theta_{S,M,k}\rangle=\delta_{lk}. \tag{5}$$

It follows that

$$H\psi_l{}^S=E\psi_l{}^S,\quad l=1,2,\ldots,\lambda_S, \tag{6}$$

where λ_S is the dimension of the irreducible representation for spin S. The expectation values of the permutation-invariant operators for current density and electron charge density then reduce to expressions requiring any one of the spatial eigenfunctions ψ_l^S. For example, the electron charge density is

$$\rho(\vec{r}) = \langle \Psi_{S,M} | \sum_{j=1}^{N} (-e)\delta(\vec{r} - \vec{r}_j) | \Psi_{S,M} \rangle$$
$$= (-e) \sum_{j=1}^{N} \int (P)_{\vec{r}_j = \vec{r}} (d^{3N-3}r)_j ,$$

where $P = |\psi_l^S|^2$, $\int P(d^{3N}r) = 1$, and $(d^{3N-3}r)_j = d^3r_1 \circ\circ\circ d^3r_{j-1} d^3r_{j+1} \circ\circ\circ d^3r_N$. Similarly, in Eq. (2) we should use one of the ψ_l^S to calculate $\vec{j}(\vec{r})$.

To calculate $\vec{j}$ to first order we must solve the first-order perturbation equation

$$(H_0 - E_0)\Psi_1 + H_1\Psi_0 = E_1\Psi_0 , \qquad (7)$$

where $H_0\Psi_0 = E_0\Psi_0$,

$$H_0 = -\sum_j (\hbar^2/2m)\nabla_j^2 + V,$$

and

$$H_1 = -\sum_j (ie\hbar/mc)\vec{A}_j \cdot \nabla_j - \sum_j (ie\hbar/2mc)(\nabla_j \cdot \vec{A}_j).$$

Appropriate zero-field eigenfunctions are $(\Psi_l^S)_{B=0}$. The external field does not split the permutation degeneracy described by Eq. (6), and so only one of these functions is required. Hence $\Psi_0 = (\Psi_l^S)_{B=0}$. I assume that there is no other degeneracy so that Ψ_0 is a real function. The first-order energy then vanishes, i.e., $E_1 = \langle \Psi_0 | H_1 | \Psi_0 \rangle = 0$.[15] If we write $\Psi_1 = F\Psi_0$, Eq. (7) becomes $[H_0, F]\Psi_0 + H_1\Psi_0 = 0$. On evaluating the commutator and introducing the normalized zero-field configuration-space probability density

$$P_0 = \Psi_0^2, \quad \int P_0(d^{3N}r) = 1 ,$$

the first-order equation reduces to

$$\sum_j (\hbar/m)[\nabla_j^2 F + \nabla_j F \cdot \nabla_j(\ln P_0) + (ie/\hbar c)\vec{A}_j \circ \nabla_j(\ln P_0) + (ie/\hbar c)\nabla_j \cdot \vec{A}_j)] = 0 . \qquad (8)$$

This equation is solved in terms of a set of auxiliary functions f_j, one for each particle, by writing

$$\nabla_j F = (-ie/2\hbar c)[2\vec{A}_j + \nabla_j f_j \times \vec{B} + f_j \nabla_j(\ln P_0) \times \vec{B}] . \qquad (9)$$

Calculating $\nabla_j^2 F$ we find[16]

$$\nabla_j^2 F = (-ie/2\hbar c)[2\nabla_j \cdot \vec{A}_j + \nabla_j f_j \cdot \nabla_j(\ln P_0) \times \vec{B}] . \qquad (10)$$

Substituting Eqs. (9) and (10) into Eq. (8) and using cyclic permutations like $\vec{a} \times \vec{b} \circ \vec{c} = \vec{c} \times \vec{a} \circ \vec{b}$ we find it to to be identically satisfied. The functions f_j are then determined by the requirement that $\nabla_j F$ is indeed the gradient of a scalar function, i.e., that

$$\nabla_j \times \nabla_j F = 0, \quad j = 1, 2, \ldots, N.$$

Since $\nabla_j \times \vec{A}_j = \vec{B}$, these conditions take the general form

$$2\vec{B} + \nabla_j \times (\nabla_j f_j \times \vec{B}) + \nabla_j \times [f_j \nabla_j(\ln P_0) \times \vec{B}] = 0 . \qquad (11)$$

I will subsequently show that Eq. (11) and its associated boundary conditions determine the f_j uniquely. Since Eq. (11) involves only $\nabla_j \times \vec{A}_j = \vec{B}$ and not $\vec{A}_j$ itself, *the solution f_j are independent of the gauge of the vector potential.* This is in contrast to the function F in Eq. (9) which depends on the gauge.[17]

The probability current density in first order is evaluated from Eq. (2) as

$$-e\vec{J}_j = (ie\hbar/2m)(\Psi^*\nabla_j\Psi - \Psi\nabla_j\Psi^*) - (e^2/mc)\vec{A}_j |\Psi|^2$$
$$= (ie\hbar/m)P_0\nabla_j F - (e^2/mc)\vec{A}_j P_0 . \qquad (12)$$

Using $\nabla_j F$ from Eq. (9) we find[18]

$$-e\vec{J}_j = (e^2/2mc)\nabla_j \times (P_0 f_j \vec{B}) . \qquad (13)$$

It is clear that $\sum_j \nabla_j \cdot \vec{J}_j = 0$ as required. The electric current density obtained from Eqs. (3) and (13) is then

$$\vec{j}(\vec{r}) = \nabla \times \vec{k}(\vec{r}) , \qquad (14)$$

where

$$\vec{\mathrm{k}}(\vec{\mathrm{r}}) = (e^2\vec{\mathrm{B}}/2mc) \sum_{j=1}^{N} g_j(\vec{\mathrm{r}}), \quad g_j(\vec{\mathrm{r}}) = \int (P_0 f_j)_{\vec{\mathrm{r}}_j=\vec{\mathrm{r}}} (d^{3N-3}r)_j. \tag{15}$$

The current density $\vec{\mathrm{j}}(\vec{\mathrm{r}})$ explicitly satisfies $\nabla\cdot\vec{\mathrm{j}}=0$ and $\vec{\mathrm{j}}\cdot\vec{\mathrm{B}}=0$. Since the f_j are independent of the gauge of the vector potential, so are the g_j and the current density itself. This development can be considered as an independent proof of this well known fact.[19] From Eq. (14) and Stokes's theorem we obtain a useful relation for the electric current I flowing through any closed curve as

$$I = \oint \vec{\mathrm{k}}\circ d\vec{\mathrm{l}} = (e^2/2mc)\sum_{j=1}^{N} \oint g_j(\vec{\mathrm{B}}\circ d\vec{\mathrm{l}}). \tag{16}$$

The boundary conditions on the f_i are determined by their relation to $\vec{\mathrm{j}}$. Since the electric current density must be a finite, continuous, and single-valued function then $\int (P_0 f_j)(d^{3N-3}r)_j$ and $\int \nabla_j (P_0 f_j)(d^{3N-3}r)_j$ must be finite, continuous, and single-valued functions of (x_j, y_j, z_j) for all j. Furthermore, $\vec{\mathrm{j}}(\vec{\mathrm{r}})$ must vanish as $r\to\infty$ so that, for all j,

$$\int (P_0 f_j)(d^{3N-3}r)_j \text{ and } \int \nabla_j (P_0 f_j)(d^{3N-3}r)_j \to 0 \text{ as } r_j \to \infty. \tag{17}$$

For a field in the z direction, $\vec{\mathrm{B}} = B\vec{\mathrm{e}}_z$, Eq. (11) becomes

$$(\partial^2 f_j/\partial x_j^2 + \partial^2 f_j/\partial y_j^2) + (\partial f_j/\partial x_j)\partial(\ln P_0)/\partial x_j + (\partial f_j/\partial y_j)\partial(\ln P_0)/\partial y_j + f_j(\partial^2/\partial x_j^2 + \partial^2/\partial y_j^2)\ln P_0 = 2. \tag{18a}$$

If we define the transverse gradient $\nabla_{tj} = (\partial/\partial x_j)\vec{\mathrm{e}}_x + (\partial/\partial y_j)\vec{\mathrm{e}}_y$, Eq. (18a) is given by

$$\nabla_{tj}^2 f_j + \nabla_{tj} f_j \circ \nabla_{tj}(\ln P_0) + f_j \nabla_{tj}^2(\ln P_0) = 2. \tag{18b}$$

The function F is determined from Eq. (9) as

$$\nabla_j F = (-ieB/2\hbar c)[x_j\vec{\mathrm{e}}_y - y_j\vec{\mathrm{e}}_x - (\partial f_j/\partial x_j)\vec{\mathrm{e}}_y + (\partial f_j/\partial y_j)\vec{\mathrm{e}}_x - f_j\vec{\mathrm{e}}_y\partial(\ln P_0)/\partial x_j + f_j\vec{\mathrm{e}}_x\partial(\ln P_0)/\partial y_j], \tag{19}$$

where I have used $\vec{\mathrm{A}}_j = \frac{1}{2}\vec{\mathrm{B}}\times\vec{\mathrm{r}}_j$. To demonstrate uniqueness consider the integral $\int P_0^{-1}[\nabla_{tj}(h_j P_0)]^2(d^{3N}r)$ where $h_j = f_{j1} - f_{j2}$ is the difference between two assumed solutions of Eq. (18). Integration by parts in the coordinates x_j and y_j using a slightly modifed version of Eq. (17) gives

$$\begin{aligned}\int P_0^{-1}[\nabla_{tj}(h_j P_0)]^2(d^{3N}r) &= -\int h_j P_0 \nabla_{tj}\circ[P_0^{-1}\nabla_{tj}(h_j P_0)](d^{3N}r)\\ &= -\int (d^{3N}r) h_j P_0[\nabla_{tj}^2 h_j + \nabla_{tj} h_j \cdot \nabla_{tj}(\ln P_0) + h_j \nabla_{tj}^2(\ln P_0)] = 0,\end{aligned}$$

since h_j must satisfy the homogeneous part of Eq. (18). Since $P_0 \geqslant 0$, I conclude that $\nabla_{tj}(h_j P_0) = 0$ for all j making the current density unique. Furthermore, since $\vec{\mathrm{j}}_1 = \vec{\mathrm{j}}_2$, $I_1 = I_2$ must also obtain so that, from Eq. (16), the only solution is $h_j = 0$. Some examples will now be given.

Example 1.—An anisotropic oscillator in its ground state has $\ln P_0 = -2\alpha x^2 - 2\beta y^2 - 2\gamma z^2 + \text{const.}$ The solution of Eq. (18) for this P_0 is $f = -\frac{1}{2}(\alpha+\beta)^{-1}$. Using Eq. (19), we find that $F = (ieB/2\hbar c)(\alpha-\beta)(\alpha+\beta)^{-1}xy$. Finally, $g(r) = -\frac{1}{2}(\alpha+\beta)^{-1}P_0(r)$ where $\int P_0 d^3r = 1$.

Example 2.—A particular excited state of an anisotropic oscillator has $\ln P_0 = \ln(x^2) - 2\alpha x^2 - 2\beta y^2 - 2\gamma z^2 + \text{const.}$ The nodal surfaces $x=0$ introduces a singularity into Eq. (18). The solution is $f = -(2\alpha+2\beta)^{-1} - [4(\alpha^2-\beta^2)x^2]^{-1}$, and it contains a term in $1/x^2$. The second-order energy for this state, which is useful for α not too close to β, is

$$E_2 = (e^2B^2/8mc^2)[2/(\alpha+\beta) + 1/(\alpha-\beta)] \quad (\alpha\neq\beta).$$

E_2 exhibits a different magnetic response for different relative values of α and β. When $\beta<\alpha$, we have $E_2>0$, corresponding to diamagnetism. This behavior is also revealed by the current density whose lines circulate about the origin in accordance with Lenz's law. When $\beta>\alpha$, however, the lines of $\vec{\mathrm{j}}$ change dramatically. For example, near the origin there is a paramagnetic circulation. When $\alpha<\beta<3\alpha$ these contributions dominate and $E_2<0$ corresponding to paramagnetism. When $\beta=3\alpha$, we find $E_2=0$ showing that this state is nonmagnetic to second order. Finally, for $\beta>3\alpha$, E_2 is positive again. From Eq. (19) it is found that

$$F = \frac{ieB}{2\hbar c}[(\alpha-\beta)(\alpha+\beta)^{-1}xy + \beta(\alpha^2-\beta^2)^{-1}yx^{-1}].$$

Example 3.—The 1s ground state of the hydrogen atom has $\ln P_0 = -\lambda r + \text{const.}$, where $\lambda = 2/a_0$ (a_0 = Bohr radius). The solution of Eq. (18) for this density function is $f = -(1+\lambda r)/\lambda^2$. Equation (19) gives $\nabla F = 0$ and so I choose $F = 0$. Thus $g(r) = -\lambda^{-2}(1+\lambda r)P_0(r)$ where $\int P_0 d^3r = 1$. The current density obtained from Eq. (14) agrees with Lamb's expression.[2]

Approximate solutions of Eq. (18) may be obtained by utilizing the corresponding variational principle $\delta L(f) = 0$ where

$$L(f_j) = \int (d^{3N}r)\{\tfrac{1}{2}P_0[(\partial f_j/\partial x_j)^2 + (\partial f_j/\partial y_j)^2] + 2f_jP_0 - \tfrac{1}{2}f_j^2P_0(\partial^2/\partial x_j^2 + \partial^2/\partial y_j^2)\ln P_0\}.$$

In conclusion, I emphasize the advantages of this approach to the calculation of magnetic properties. First, because of its explicit form, Eqs. (14) and (15), the current density will always satisfy $\nabla\cdot\vec{j} = 0$ and $\vec{j}\cdot\vec{B} = 0$. Second, since the f_j equations are independent of the gauge of the vector potential, magnetic properties calculated from $\vec{j}$ will be gauge invariant. Both these advantages pertain to the current calculated from approximate solutions to Eqs. (18) or (11) as well as exact solutions.

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[15] For electrons in molecules and solids this condition is called quenching of the angular momentum (Refs. 1 and 9).

[16] The following identities were used: $\nabla\cdot(\vec{a}\times\vec{b}) = \vec{b}\cdot(\nabla\times\vec{a}) - \vec{a}\cdot(\nabla\times\vec{b})$, $\nabla\cdot(\varphi\vec{a}) = \nabla\varphi\cdot\vec{a} + \varphi\nabla\cdot\vec{a}$, $\nabla\times\nabla\varphi = 0$, and $\nabla\cdot(\nabla\times\vec{a}) = 0$.

[17] Gauge invariance of the Schrödinger equation requires an eigenfunction in a new gauge, $\vec{A}' = \vec{A} + \nabla\theta$, to be related to the corresponding eigenfunction in the original gauge by the transformation $\Psi' = \exp[-i\sum_j(e/\hbar c)\theta(\vec{r}_j)]\Psi$. This gives to first order, using $\Psi_1 = F\Psi_0$, $F' = F - \sum_j(ie/\hbar c)\theta(\vec{r}_j)$.

[18] The identity $\nabla\times(\varphi\vec{a}) = \nabla\times\vec{a} + \nabla\varphi\times\vec{a}$ is also used.

[19] By use of the gauge transformation of the eigenfunctions given in Ref. 17 it is easily shown that $\vec{J}_i$ in Eq. (2) are invariant.