

## Currents, kinetic energy, and molecular magnetism

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**Abstract.** Definitions of current density and kinetic energy density, for a general many-electron system in the presence of an external magnetic field, are carefully discussed and various results are established. In particular, the electronic energy expression has a purely classical interpretation in which every element of the 'charge cloud' behaves like a small magnet, the magnetization depending on the circulation of the induced currents.

**Keywords.** Quantum mechanics; current density; property densities; magnetic effects.

### 1. Introduction

In the discussion of molecular electronic structure and properties, the *electron density*  $P(\mathbf{r})$  has always played a central role. For example, as a consequence of the Hellmann-Feynman theorem,  $P(\mathbf{r})$  determines the forces exerted on the nuclei by the electron distribution and hence determines the equilibrium geometry of the molecule; it also determines all spin- and velocity-independent first-order properties† and provides a rigorous basis for classical models in which the electron distribution is regarded as a smeared out 'charge cloud' of density  $-eP(\mathbf{r})$ . Thus, the dipole, quadrupole and higher electric moments, the field gradient at the nuclei, the scattering of x-rays, the electric potential 'seen' by an attacking species at a point outside the molecule can all be calculated *classically* once  $P(\mathbf{r})$  is known.

When *spin* is involved (McWeeny 1970), as in the discussion of interactions between the magnetic dipole of the electron and an applied magnetic field, it is useful to introduce a *spin density*. Unlike  $P(\mathbf{r})$ , which is a scalar density, the spin density is a three-component vector density‡ ( $Q_x, Q_y, Q_z$ ) such that, for example,  $Q_z(\mathbf{r})d\mathbf{r}$  is the contribution to the z-component of total spin angular momentum arising from the volume element  $d\mathbf{r}$  at point  $\mathbf{r}$ . Usually, the z axis is chosen as the direction of an applied magnetic field, and with neglect of spin-orbit coupling effects only one component ( $Q_z$ ) is non-zero; this describes a uniform 'magnetic polarization' of the charge cloud, along the field direction, in which the density of magnetization at point  $\mathbf{r}$  is  $-g\mu_B Q_z(\mathbf{r})$  where  $g$  is the electronic  $g$ -value (2.0023) and  $\mu_B$  is the Bohr magneton. In the presence of spin-orbit coupling, all components may be non-zero and the magnetization is not generally along the field direction (McWeeny 1973, p. 194).

When velocity-dependent effects are considered (e.g. in discussing interactions between spin dipoles and fields produced by motion of the electron through space) it is

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Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

† i.e. properties determined by expectation values of a perturbation operator with respect to the *unperturbed* state of the system.

‡ Strictly, a *pseudo*-vector density, since angular momentum is represented not by a (polar) vector but by an 'axial' or pseudo-vector.

also useful to introduce a (probability) *current density*  $\mathbf{J}$  whose components ( $J_x, J_y, J_z$ ) measure the rate of flow of 'charge' (in electrons per unit volume per unit time), along the three axial directions, at any given point. The corresponding electric current density is simply  $-e\mathbf{J}(\mathbf{r})$ . In a stationary state described by a real wavefunction, the current density is zero everywhere, but imposition of a magnetic field results in a system of circulating 'induced' currents whose presence is associated with molecular diamagnetism.

For many purposes it follows that a molecule may be regarded as a charge distribution of density  $-eP(\mathbf{r})$ , with an intrinsic magnetization (in a non-singlet state,  $S \neq 0$ ) of density  $-g\mu_B\mathbf{Q}(\mathbf{r})$ , containing circulating currents of density  $-e\mathbf{J}(\mathbf{r})$ . These three fundamental density functions, whose role is discussed more fully elsewhere (McWeeny 1984), may be referred to briefly as 'property densities'. Such densities are not usually observed directly but are defined by reference to an integral whose value yields the actual 'observable', and have consequently been described as 'sub-observables' by Hirschfelder (1978). For example,

$$V_{en} = \int V(\mathbf{r}) P(\mathbf{r}) d\mathbf{r} \quad (1)$$

in which  $V(\mathbf{r})$  is the potential energy of an electron of point  $\mathbf{r}$  in the field of the nuclei, yields the total electron-nuclear potential energy and this is consistent with the interpretation of  $P(\mathbf{r}) d\mathbf{r}$  as the number of electrons in volume element  $d\mathbf{r}$ .

The aim of this note is to discuss more fully the current density and in particular its connection with the concept of 'kinetic energy density'; and, since non-vanishing currents normally exist only in the presence of an external magnetic field, we shall have to include from the outset the appropriate vector-potential terms in the Hamiltonian. Thus, we shall start from the Hamiltonian

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i,j}' g(i,j) = \sum_i [(\pi^2(i)/2m) + V(i)] + \frac{1}{2} \sum_{i,j}' e^2/(4\pi\epsilon_0)r_{ij} \quad (2)$$

in which

$$\pi(i) = \mathbf{p}(i) + e\mathbf{A}(i) \quad (3)$$

is the 'gauge-invariant' momentum operator for electron  $i$ ,  $\mathbf{A}$  being the magnetic vector potential of the external field, and the other terms have their usual significance.

## 2. Definitions and difficulties

First we recall that the expectation value of any one-electron quantity, with associated operator  $A = \sum_{i=1}^N A(i)$  say, is given by

$$\langle A \rangle = \langle \Psi | \sum_i A(i) | \Psi \rangle = \int [A(1)\rho(\mathbf{x}_1; \mathbf{x}'_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 \quad (4)$$

where (see, for example, McWeeny and Sutcliffe 1969)

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (5)$$

is the one-electron density matrix, for state  $\Psi$ , and  $\mathbf{x}$  ( $= \mathbf{r}, s$ ) is used to denote space and spin variables collectively.

On taking  $A$  to be a *spinless* operator, the spin integration in (4) is immediate and we obtain

$$\langle A \rangle = \int [A(1)P(\mathbf{r}_1; \mathbf{r}'_1)]_{\mathbf{r}'_1 = \mathbf{r}_1} d\mathbf{r}_1 \quad (A \text{ spinless}) \quad (6)$$

where

$$P(\mathbf{r}_1; \mathbf{r}'_1) = \int [\rho(\mathbf{x}_1; \mathbf{x}'_1)]_{s'_1 = s_1} ds_1 \quad (7)$$

The electron density in (1) is simply the 'diagonal element' ( $\mathbf{r}'_1 = \mathbf{r}_1$ ) of the spinless density matrix defined in (7):  $P(\mathbf{r}) = P(\mathbf{r}; \mathbf{r})$ . Evidently it would be possible to describe the integrand in (1), namely

$$V_{en}(\mathbf{r}) = V(\mathbf{r})P(\mathbf{r}), \quad (8)$$

as a 'potential energy density' for the electrons in the field of the nuclei,  $V_{en}(\mathbf{r}) d\mathbf{r}$  being the contribution to  $V_{en}$  arising from volume element  $d\mathbf{r}$  at point  $\mathbf{r}$ .

We recall that the spin density referred to in §1 plays a similar role in discussing spin properties. Thus, if  $A$  represents the  $z$ -component of total electron spin, (4) yields

$$\langle S_z \rangle = \int Q_z(\mathbf{r}) d\mathbf{r} \quad (9)$$

in which  $Q_z(\mathbf{r})$  is the diagonal element of a *spin density matrix*

$$Q_z(\mathbf{r}_1; \mathbf{r}'_1) = \int [S_z(1)\rho(\mathbf{x}_1; \mathbf{x}'_1)]_{s'_1 = s_1} ds_1 \quad (10)$$

and is evidently the contribution per unit volume, at point  $\mathbf{r}$ , to the spin angular momentum  $z$  component. Components  $Q_x$  and  $Q_y$  are defined similarly.

If now we take  $A(1)$  in (6) to be a component of the velocity operator

$$(1/m)\pi_\alpha = (1/m)(p_\alpha + eA_\alpha) \quad (\alpha = x, y, z) \quad (11)$$

where  $A_\alpha$  is the  $\alpha$ -component of the magnetic vector potential, we obtain from (6) the total *flux* of electron density in the  $\alpha$ -direction in the form

$$\langle \Psi | (1/m) \sum_i \pi_\alpha(i) | \Psi \rangle = \int J_\alpha(\mathbf{r}) d\mathbf{r}. \quad (12)$$

Here  $J_\alpha(\mathbf{r})$  is the diagonal element of a *current density matrix*: noting that the expectation value must be real, we have defined

$$J_\alpha(\mathbf{r}) = (1/m) \text{Re} [\pi_\alpha P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (13)$$

as the *local*  $\alpha$ -flux at point  $\mathbf{r}$ . With this definition (see McWeeny and Sutcliffe 1969, p. 226) it is possible to show that the induced\* magnetic field due to the current distribution may be calculated using the classical Biot-Savart law. The induced flux density is thus

$$B_\alpha^{\text{ind}}(\mathbf{r} = 0) = \left( \frac{\mu_0}{4\pi} \right) \int \frac{[\mathbf{r} \times (-e\mathbf{J}(\mathbf{r}))]_\alpha}{r^3} d\mathbf{r} \quad (14)$$

where  $\mu_0$  is the magnetic permeability of free space and the point at which the field is required has been used as origin.

It would appear that other property densities could be defined similarly. For example, the expectation value of the Hamiltonian (2) contains a kinetic energy term

$$T = (1/2m) \int [\pi^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} d\mathbf{r} = \int T(\mathbf{r}) d\mathbf{r} \quad (15)$$

\* i.e. produced by the field whose vector potential is  $\mathbf{A}$ .

where a kinetic energy density has been introduced as

$$T(\mathbf{r}) = (1/2m) [\pi^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \tag{16}$$

which is analogous to (8). In general, however, there are difficulties with such definitions, as has been stressed in particular by Srebrenik and Bader (1975, 1981), in so far as they lack uniqueness; alternative definitions of a property density, leading to the same expectation value when integrated over all space, may give quite different (and even non-real) values *locally*. An example is the current density (13), in which an imaginary component has been discarded merely because its contribution to the *integral* (12) must vanish,  $\pi_\alpha$  being a Hermitian operator. The root of such difficulties is that the reality of expectation values of Hermitian operators (and even the definition of Hermitian character) requires integration over the whole domain of the variables. To obtain acceptable definitions of *local* properties we should start from the Schrödinger equation itself, which does not contain integrations over all space.

### 3. Point properties. Kinetic energy

Let us start from the time-dependent equation

$$H\Psi = i\hbar(\partial\Psi/\partial t) \tag{17}$$

where, in the presence of the external field, the Hamiltonian (2) may be written

$$H = (1/2m) \sum_i \pi^2(i) + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \tag{18}$$

and  $U$  contains all the potential energy terms.

We adopt the notation (Nakatsuji 1976)

$$\begin{aligned} \langle \Psi | (\dots) | \Psi \rangle_n &= \int (\dots) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n, \mathbf{x}_{n+1}, \dots, \mathbf{x}_N) \\ &\quad \times \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_n, \mathbf{x}_{n+1}, \dots, \mathbf{x}_N) d\mathbf{x}_{n+1} \dots d\mathbf{x}_N, \end{aligned} \tag{19}$$

where  $\Psi^*$  and  $\Psi$  normally contain distinct (primed and unprimed) variables, the last  $(N - n)$  of which are identified before performing the integrations. Thus, for example,

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = N \langle \Psi | \Psi \rangle_1 = ND(\mathbf{x}_1; \mathbf{x}'_1),$$

where  $D(\mathbf{x}_1; \mathbf{x}'_1)$  is the '1-density' with the Coleman (1963) normalization, namely  $\int D(\mathbf{x}_1; \mathbf{x}_1) d\mathbf{x}_1 = 1$ .

On multiplying (17) by  $\Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N)$  and using (19) with  $n = 1$ , we obtain

$$\begin{aligned} \langle \Psi | H | \Psi \rangle_1 &= i\hbar \int \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \frac{\partial \Psi}{\partial t}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N, \end{aligned} \tag{20a}$$

in which the integrand, with  $\mathbf{x}'_1 = \mathbf{x}_1$ , would appear to be an energy density since one further integration would yield the expectation value  $\langle \Psi | H | \Psi \rangle$ . An alternative density, equally acceptable, could be obtained by using the complex conjugate of (17).

Thus,

$$\begin{aligned} \langle H\Psi|\Psi\rangle_1 &= -i\hbar \int \frac{\partial\Psi^*}{\partial t}(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (20b)$$

and the difference of these alternative forms is

$$\langle \Psi|H|\Psi\rangle_1 - \langle H\Psi|\Psi\rangle_1 = i\hbar \frac{\partial D}{\partial t}(\mathbf{x}_1; \mathbf{x}'_1). \quad (21)$$

The two energy densities will thus agree *provided*  $\Psi$  is an *exact* stationary state function, for which  $i\hbar(\partial\Psi/\partial t) = E\Psi$  and  $D$  is time-independent.

Written in full, the first definition (20a) becomes

$$\begin{aligned} \langle \Psi|H|\Psi\rangle_1 &= \int [h(1) + \sum_i g(i, 1) + \sum_j g(1, j)] \\ &\quad \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &\quad + \int \left[ \sum_{i=2}^N h(i) + \frac{1}{2} \sum_{i,j=2}^N g(i, j) \right] \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned} \quad (22)$$

where the second term contains only an  $(N-1)$ -electron Hamiltonian. The second definition (20b) leads to a similar result, but with  $h$  replaced by  $h^\dagger$  throughout, adjoint operators (containing  $-i$  in place of  $i$ ) being understood to work on the *primed* variables of  $\Psi^*$ . At this stage,  $\mathbf{x}_1$  and  $\mathbf{x}'_1$  may be regarded as parameters;  $\Psi$  and  $\Psi^*$  are still antisymmetric functions of all *other* variables and in the domain of these other variables the Hamiltonian in the second integral of (22) is a Hermitian operator. Consequently, in taking the difference in (21) the second integrals are identical and cancel; and the only terms which remain are

$$\begin{aligned} (1/2m) \int [\pi^2(1) - \pi'^2(1')] \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\ \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N = i\hbar \frac{\partial D(\mathbf{x}_1; \mathbf{x}'_1)}{\partial t}. \end{aligned}$$

Since the integrations on the left also yield  $D(\mathbf{x}_1; \mathbf{x}'_1)$  this result gives, with the more usual normalization,

$$(1/2m) [\pi^2 \rho(\mathbf{x}; \mathbf{x}') - \pi'^2 \rho(\mathbf{x}; \mathbf{x}')]_{\mathbf{x}'=\mathbf{x}} = i\hbar \frac{\partial \rho(\mathbf{x})}{\partial t} \quad (23)$$

In the absence of spin operators, a further spin integration gives

$$(1/2m) [\pi^2 p(\mathbf{r}; \mathbf{r}') - \pi'^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}} = i\hbar \frac{\partial P(\mathbf{r})}{\partial t}. \quad (24)$$

It now appears, remembering (16), that the difference between the two energy densities in (21) arises from a difference of two *kinetic-energy* densities: for an exact stationary

state the time derivative in (24) vanishes and the two definitions

$$T(\mathbf{r}) = (1/2m)[\pi^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (25a)$$

$$T'(\mathbf{r}) = (1/2m)[\pi'^2 P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} \quad (25b)$$

yield identical densities at all points in space.

Let us now expand the density matrices in (25) in terms of any complete set of one-electron functions  $\{\chi_r\}$ . Thus

$$P(\mathbf{r}; \mathbf{r}') = \sum_{r,s} P_{rs} \chi_r(\mathbf{r}) \chi_s^*(\mathbf{r}') \quad (P_{sr} = P_{rs}^*) \quad (26)$$

and the two kinetic-energy densities become

$$T(\mathbf{r}) = (1/2m) \sum_{r,s} P_{rs} \chi_s^*(\mathbf{r}) \pi^2 \chi_r(\mathbf{r}) \quad (27a)$$

$$T'(\mathbf{r}) = (1/2m) \sum_{r,s} P_{rs} [\pi^2 \chi_s(\mathbf{r})]^* \chi_r(\mathbf{r}) \quad (27b)$$

The difference between these two expressions may now be written in terms of the current density by using appropriate identities.

First we note that a 'generalized current', of which (13) is the real part, may be defined as

$$\mathbf{J}(\mathbf{r}) = (1/2m)[\pi P(\mathbf{r}; \mathbf{r}')]_{\mathbf{r}' = \mathbf{r}} = \mathbf{J}_R(\mathbf{r}) + i\mathbf{J}_I(\mathbf{r}) \quad (28)$$

where, on using (26), it follows that

$$\mathbf{J}_R(\mathbf{r}) = (\hbar/2mi) \sum_{r,s} P_{rs} [(\nabla \chi_r) \chi_s^* - \chi_r (\nabla \chi_s)^*] + (e/m) \mathbf{A} \sum_{r,s} P_{rs} \chi_r \chi_s^* \quad (29a)$$

$$\mathbf{J}_I(\mathbf{r}) = -(\hbar/2m) \sum_{r,s} P_{rs} [(\nabla \chi_r) \chi_s^* + \chi_r (\nabla \chi_s)^*] = -(\hbar/2m) \nabla P(\mathbf{r}). \quad (29b)$$

Then, in (27), we write

$$\chi_s^* \pi^2 \chi_r = (\hbar/i)^2 \chi_s^* \nabla^2 \chi_r + (e\hbar/i) [2\mathbf{A} \cdot (\chi_s^* \nabla \chi_r) + \chi_s^* \chi_r (\nabla \cdot \mathbf{A})] + e^2 A^2 \chi_s^* \chi_r \quad (30a)$$

$$\chi_r (\pi^2 \chi_s)^* = (\hbar/i)^2 \chi_r \nabla^2 \chi_s^* - (e\hbar/i) [2\mathbf{A} \cdot (\chi_r \nabla \chi_s^*) + \chi_r \chi_s^* (\nabla \cdot \mathbf{A})] + e^2 A^2 \chi_r \chi_s^* \quad (30b)$$

and make use of the identities

$$\nabla \cdot (\chi_r \nabla \chi_s^*) = (\nabla \chi_r) \cdot (\nabla \chi_s^*) + \chi_r \nabla^2 \chi_s^*,$$

and

$$\nabla \cdot (\chi_s^* \nabla \chi_r) = (\nabla \chi_s^*) \cdot (\nabla \chi_r) + \chi_s^* \nabla^2 \chi_r,$$

which give on subtraction

$$\nabla \cdot [\chi_r \nabla \chi_s^* - \chi_s^* \nabla \chi_r] = \chi_r \nabla^2 \chi_s^* - \chi_s^* \nabla^2 \chi_r. \quad (31)$$

On putting (30a,b) into (27a,b) and using (31) we obtain, after rearranging and introducing  $\mathbf{J}_R$  defined in (29a),

$$T(\mathbf{r}) - T'(\mathbf{r}) = (\hbar/i) \nabla \cdot \mathbf{J}_R(\mathbf{r}). \quad (32)$$

Equation (24) is thus equivalent to a conservation condition for the current density:

$$\operatorname{div} \mathbf{J}_R(\mathbf{r}) = -\frac{\partial P(\mathbf{r})}{\partial t}. \quad (33)$$

The flux of probability density out of any region, computed using the *real* current  $\mathbf{J}_R$ , is equal to the rate of decrease of the probability of finding an electron in that region.

The above results apply to any exact solution of the many-electron Schrödinger equation (17). For a stationary state, in particular,  $P$  is time-independent, the divergence of  $\mathbf{J}_R$  is everywhere zero, and the two kinetic-energy densities become real and coincident. Evidently, the physical interpretation of  $\mathbf{J}_R$  (with components defined in (13)) is entirely justified; and the agreement of (27a, b) shows that the kinetic energy density defined in (14) has at least a degree of uniqueness, *provided* the wavefunction represents an exact stationary state.

More generally, with non-exact or time-dependent wavefunctions, there remains the problem of how to define a unique and real kinetic-energy density. The most obvious proposal would be to adopt the *mean* of the two forms in (27a, b), which is evidently the real part of a complex density; and it then readily follows (using identities such as (30)) that

$$\bar{T} = (T + T')/2 = T_0 + (\hbar/2) \operatorname{div} \mathbf{J}_I + e\mathbf{A} \cdot \mathbf{J}_R - (e^2/2m) A^2 P \quad (34)$$

where the imaginary component of the generalized current density is given in (29b), while

$$T_0(\mathbf{r}) = (1/2m) [\mathbf{p} \cdot \mathbf{p}^\dagger P(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}} \quad (35)$$

where the dagger as usual indicates that the second operator works on the primed variables. The density  $T_0(\mathbf{r})$ , integrated over any domain  $\Omega$ , gives the kinetic energy expression introduced by Srebrenik and Bader (1975, 1981) for assigning an energy content to a finite 'subspace'. Thus, with the convention that the  $\mathbf{x}_i$  integration extends only over the domain  $\Omega$ ,

$$\langle T_0 \rangle_\Omega = (1/2m) \int_\Omega \sum_i \mathbf{p}^\dagger(i) \Psi^* \cdot \mathbf{p}(i) \Psi \, dx_1 \dots dx_N. \quad (36)$$

As noted by Srebrenik and Bader, however, even in the field-free case which they considered, integration of the density  $\bar{T}$  provisionally defined in (34) does not yield the same result (36); for the  $\operatorname{div} \mathbf{J}_I$  term in (34) also gives a contribution which is generally non-zero. Thus (using  $\sigma$  to denote the surface of  $\Omega$  and  $dS$  for a surface element)

$$(\hbar/2) \int_\Omega \operatorname{div} \mathbf{J}_I d\mathbf{r} = -(\hbar^2/4m) \int_\Omega \nabla^2 P d\mathbf{r} = -(\hbar^2/4m) \int_\sigma (\nabla P) \cdot dS. \quad (37)$$

This quantity vanishes when  $\Omega$  is the whole of space, since  $P$  and its derivatives go to zero at infinity; and it also vanishes for the 'zero-flux surfaces' used extensively by Bader and co-workers. But it is not at all clear whether (34) or (35) provides the more 'correct' definition from an interpretive point of view, even when  $\mathbf{A} = \mathbf{0}$ , and there are further difficulties when the field-dependent terms are admitted.

Equation (35) suggests the way to proceed. In the presence of the field, we make the usual substitution  $\mathbf{P} \rightarrow \boldsymbol{\pi}$  and consider the eligibility of the quantity

$$T_A(\mathbf{r}) = (1/2m) [\boldsymbol{\pi} \cdot \boldsymbol{\pi}^\dagger P(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}} \quad (38)$$

so that (35) corresponds to the field-free case  $\mathbf{A} = \mathbf{0}$ . To obtain a more illuminating form we may start from (26) and use the identity

$$\begin{aligned} (\boldsymbol{\pi}\chi_r) \cdot (\boldsymbol{\pi}\chi_s) &= \hbar^2(\nabla\chi_r) \cdot (\nabla\chi_s^*) + i\hbar(e\mathbf{A}\chi_r) \cdot (\nabla\chi_s^*) - i\hbar(\nabla\chi_r) \cdot (e\mathbf{A}\chi_s) + e^2 A^2 \chi_r \chi_s^* \\ &= \hbar^2(\nabla\chi_r) \cdot (\nabla\chi_s^*) + (e\hbar/i)\mathbf{A} \cdot [\chi_s^* \nabla\chi_r - \chi_r \nabla\chi_s^* + (ie/\hbar)\mathbf{A}\chi_r \chi_s^*]. \end{aligned}$$

On multiplying both sides by  $(1/2m)P_{rs}$  and summing over  $r$  and  $s$ , the result will clearly be  $T_A(\mathbf{r})$ . The square-bracket term in the identity would lead to  $\mathbf{J}_R$  of (29a) if the imaginary part were doubled; we therefore add and subtract an extra term  $(ie/\hbar)\mathbf{A}\chi_r \chi_s^*$  and, on proceeding as indicated find

$$T_A(\mathbf{r}) = T_0(\mathbf{r}) + e\mathbf{A} \cdot \mathbf{J}_R(\mathbf{r}) - (e^2/2m)A^2 P(\mathbf{r}). \quad (39)$$

The dependence on the field and on the induced current density is exactly as in (34), but the term  $(\hbar/2) \operatorname{div} \mathbf{J}_I$  which leads to the surface term (37) is absent.

To summarize:  $T_A(\mathbf{r})$  is real everywhere, yields the usual kinetic energy when integrated over all space [in agreement with that given by (16)], and shows a correct dependence on current density, electron density and vector potential at all points. Expression (38) appears to offer the most useful definition of a kinetic-energy density for a system in the presence of a magnetic field, described by a wavefunction which is not necessarily exact.

#### 4. Physical interpretations. Discussion

It remains only to discuss the interpretation and status of (39) and the significance of its disagreement with the mean-value definition (34), both forms being consistent with the principles of quantum mechanics as usually stated. The difference between the two expressions is

$$T_f(\mathbf{r}) = T(\mathbf{r}) - T_A(\mathbf{r}) = (\hbar/2) \operatorname{div} \mathbf{J}_I(\mathbf{r}) = -(\hbar^2/4m)\nabla^2 P(\mathbf{r}), \quad (40)$$

which may be regarded as a 'fictitious' kinetic-energy density. This quantity has no observational significance and its presence results only from the use of a *variational* expression for the kinetic energy (i.e. from integrations over all space or a finite domain): in this sense its origin is purely mathematical and has nothing to do with electronic *motion*. The justification for this view is, in essence, contained in the work of Bader and collaborators (Srebrenik and Bader 1980). The kinetic energy of the whole system is obtained by integrating  $\bar{T}$  in (34) over the infinite domain, in which case the term (37) vanishes and both  $\bar{T}$  and  $T_A$  lead to the correct result. The contribution from  $T_f$  does not in fact arise *within* the domain, finite or infinite, but only at the *surface*. It is only when the Schrödinger equation (17) is viewed as the Euler equation for a variational principle that the question of the surface terms arises; when the Lagrangian density is written in a form which contains the usual kinetic energy operator, the stationary value condition *even for a finite region* leads to the Schrödinger equation *provided the surface terms are included*. Whereas for an infinite region the surface terms automatically vanish (and may thus be disregarded) their presence generally ensures that the variational principle, applied to a *finite* region, would yield the same results as direct solution of the Schrödinger equation. The feasibility of using regional variational principles has been demonstrated by Bader and co-workers, who eliminate the surface

terms by choosing *particular* regions bounded by zero-flux surfaces. From the point of view of physical interpretations, however, there seems to be no case for treating the boundary terms as part of the kinetic energy itself; and we therefore adopt  $T_A$ , as given in (38) and (39), as the kinetic-energy density.

The  $A$ -dependent terms in (39) have an interesting physical significance; they yield, on integrating over all space, the exact energy contribution arising from imposition of the magnetic field (up to terms quadratic in field components). To show this, we assume that the wavefunction in the absence of the field is  $\Psi_0$  (for  $A = 0$ ) and that in switching on the field  $H_0 \rightarrow H = H_0 + \lambda H'$  and

$$\Psi_0 \rightarrow \Psi = \Psi_0 + \lambda \Psi' + \dots \quad (\lambda \rightarrow 1) \quad (41)$$

where  $\Psi'$  is exact to first order in field. It is well known that the function  $\Psi$ , which is *not normalized*, does not give the true second-order energy as an expectation value of the Hamiltonian; the correct second-order part of the energy is  $\langle \Psi_0 | H' | \Psi' \rangle$ , or alternatively  $\langle \Psi' | H' | \Psi_0 \rangle$ , whereas  $\langle \Psi | H | \Psi \rangle$  with  $\Psi$  given in (41) gives a second-order term  $\langle \Psi_0 | H' | \Psi' \rangle + \langle \Psi' | H' | \Psi_0 \rangle$  which is too large by a factor of 2. The correct result could, however, be obtained by using, instead of (41), the function

$$\tilde{\Psi} = \Psi_0 + \frac{1}{2} \lambda \Psi', \quad (42)$$

which yields (noting that  $\langle \Psi_0 | H_0 | \Psi' \rangle = 0$ )

$$\begin{aligned} E &= \langle \tilde{\Psi} | (H_0 + \lambda H') | \tilde{\Psi} \rangle \\ &= \langle \Psi_0 | H_0 | \Psi_0 \rangle + \lambda \langle \Psi_0 | H' | \Psi_0 \rangle + \frac{1}{2} \lambda^2 [\langle \Psi_0 | H' | \Psi' \rangle \\ &\quad + \langle \Psi' | H' | \Psi_0 \rangle], \end{aligned} \quad (43a)$$

or in other words

$$E = E_0 + \lambda E' + \lambda^2 E''. \quad (43b)$$

This result may be justified by renormalizing (41) to *second* order, using the renormalized function to compute the energy, and eliminating the  $\langle \Psi' | \Psi' \rangle$  term by reference to the perturbation equations.

The advantage of introducing (42) is that the energy may then be written in terms of densities associated with the function  $\tilde{\Psi}$ : and in particular,

$$\tilde{P} = P_0 + \frac{1}{2} \lambda P' \quad (44)$$

( $P'$  being the true *first-order* density change) will yield the correct expectation value, to *second* order, of the one-electron terms in the Hamiltonian.

Let us now express (43b) in terms of the 'renormalized' density. The leading term is simply  $E_0 = T_0 + V_0$ , where  $V_0$  is the potential energy of the unperturbed system while  $T_0$ , also referring to the unperturbed system and therefore depending only on  $P_0$ , is evidently the first term in the expression (39) for the kinetic energy in the presence of the field. The total electronic energy may thus be written  $E = V_0 + T_A$  where  $T_A$  contains the field dependent terms (linear and quadratic) which appear in (43a). The result is (putting  $\lambda = 1$  from now on and remembering that field components serve to separate the orders)

$$E = E_0 + e \int \mathbf{A} \cdot \mathbf{J}(\mathbf{r}) \, d\mathbf{r} - (e^2/2m) \int A^2 P(\mathbf{r}) \, d\mathbf{r}. \quad (45)$$

In this expression the components of  $\mathbf{J}$  are derived from (44) using (13); but in the last term we may put  $P = P_0$  since  $\mathbf{A}$  is already of first order in field components and inclusion of the second term in (44) would therefore lead to third-order effects. On separating  $\mathbf{J}$  into its two parts we thus obtain

$$E = E_0 + e \int \mathbf{A} \cdot \mathbf{J}_0(\mathbf{r}) \, d\mathbf{r} + e \int \mathbf{A} \cdot \mathbf{J}_1(\mathbf{r}) \, d\mathbf{r} - (e^2/2m) \int A^2 P_0(\mathbf{r}) \, d\mathbf{r} \quad (46)$$

where

$$\mathbf{J}_0(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p}P_0(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}}, \quad (47a)$$

$$\mathbf{J}_1(\mathbf{r}) = (1/m) \operatorname{Re} [e\mathbf{A}P_0(\mathbf{r}; \mathbf{r}') + \mathbf{p}P'(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}}. \quad (47b)$$

Clearly,  $\mathbf{J}_0(\mathbf{r})$  is the current density in the zero-field limit and leads to a 'permanent' magnetic moment i.e. to true paramagnetism; it is non-zero only for atoms and other systems of high symmetry in which there may be unquenched angular momentum.  $\mathbf{J}_1(\mathbf{r})$ , on the other hand, is linear in field components ( $P'$  being of first order) and is therefore connected with *induced* currents; but it is *not* the field proportional part of the true current density, which would be obtained using  $P = P_0 + \lambda P' + \lambda^2 P'' + \dots$ , instead of (44), in the expression (13).

To obtain a more transparent form of (46) it is sufficient to combine the last two terms. The result may be written

$$E = E_0 - \int \mathbf{A} \cdot (-e\mathbf{J}_0(\mathbf{r})) \, d\mathbf{r} - (1/2) \int \mathbf{A} \cdot (-e\mathbf{J}_{\text{ind}}(\mathbf{r})) \, d\mathbf{r} \quad (48)$$

in which  $\mathbf{J}_0(\mathbf{r})$  is defined in (47) while  $\mathbf{J}_{\text{ind}}(\mathbf{r})$  is the field-proportional part of the current density derived from the exact density matrix  $P = P_0 + P' + P'' + \dots$ , according to (13): thus

$$\mathbf{J}_0(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p}P_0(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}}, \quad (49a)$$

$$\mathbf{J}_{\text{ind}}(\mathbf{r}) = (1/m) \operatorname{Re} [\mathbf{p}P'(\mathbf{r}; \mathbf{r}') + e\mathbf{A}P_0(\mathbf{r}; \mathbf{r}')]_{r'=\mathbf{r}}, \quad (49b)$$

and describes the system of induced currents produced by application of the field. The two field-dependent terms in (48) represent, respectively, the potential energy of a system of 'permanent' currents of density  $-e\mathbf{J}_0(\mathbf{r})$ , and that of a system of induced currents of density  $-e\mathbf{J}_{\text{ind}}(\mathbf{r})$ , in a magnetic field of vector potential  $\mathbf{A}$ . Both terms are entirely classical in form, even though the currents themselves are calculated from quantum mechanics. It is also worth remarking that there is no 'gauge problem': the complete current

$$\mathbf{J}(\mathbf{r}) = \mathbf{J}_0(\mathbf{r}) + \mathbf{J}_{\text{ind}}(\mathbf{r}) \quad (50)$$

contains the gauge invariant operator  $\pi$  and is invariant against change of origin of the vector potential; and this property is shared by the separate terms in (49) and by the energy contributions to which they lead in (48). This is not the case in the traditional approach (see for example Davies 1967) where magnetic properties are almost invariably calculated as a difference of 'diamagnetic' and 'paramagnetic' contributions which individually have no invariant physical interpretation.

When the applied field is uniform, the first- and second-order terms take a very familiar form. On putting  $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$ , the  $\mathbf{J}_0$ -term in (48) immediately becomes

$$E' = -\mathbf{B} \cdot \boldsymbol{\mu}_m^0 \quad (51)$$

where  $\mu_m^0$  is the (permanent) magnetic dipole moment, with components

$$\mu_{m\lambda}^0 = -\mu_B \int \text{Re}[L_\lambda P(\mathbf{r}; \mathbf{r}')]_{r'=r} d\mathbf{r} \quad (52)$$

in which  $L_\lambda$  is a (dimensionless) angular momentum component.

The corresponding form of the second-order energy term is

$$E'' = -\frac{1}{2} \mathbf{B} \cdot \mu_m^{\text{ind}} = \frac{1}{2} \mathbf{B} \cdot \alpha^m \cdot \mathbf{B} \quad (53)$$

where

$$\mu_{m\lambda}^{\text{ind}} = \sum_{\mu} \alpha_{\lambda\mu}^m B_{\mu} \quad (54)$$

and represents an *induced* magnetic moment whose components are related to the field components through the magnetic polarizability tensor  $\alpha^m$ . Expressions for the tensor components are easily found on writing  $P$  in the more explicit form

$$P = P_0 + P' = P_0 + B_x P_x + B_y P_y + B_z P_z \quad (55)$$

where  $P_x$ , for example, is the density change per unit applied field in the  $x$  direction, and may be calculated by any appropriate form of perturbation theory. On putting (55) in (49) and using the result to evaluate the final term in (48) we at once find (53), with

$$\alpha_{\lambda\mu}^m = -\mu_B \int \text{Re}[L_\lambda P_\mu(\mathbf{r}; \mathbf{r}')]_{r'=r} d\mathbf{r}. \quad (56)$$

By comparison with (52) it is clear that  $\alpha_{\lambda\mu}^m$  is the  $\lambda$ -component of the magnetic dipole associated with the density change  $P_\mu$  due to unit field in the  $\mu$  direction. The interpretation of the factor 1/2 in (53) is also classical: with  $\mu^{\text{ind}} = \mu^{\text{ind}}(\mathbf{B})$ , the energy change in a field increase  $d\mathbf{B}$  is  $d\mathbf{B} \cdot \mu^{\text{ind}}(\mathbf{B})$  and on allowing the field to increase from zero to its final value integration at once gives (53).

In conclusion, it is worth remarking that realistic *ab initio* calculations of current density, at least at the Hartree-Fock level, are now computationally feasible and provide valuable insight into the magnetic properties of molecules (Lazzeretti and Zanasi 1981).

## References

- Coleman A J 1963 *Rev. Mod. Phys.* **35** 668  
 Davies D W 1967 *The theory of the electric and magnetic properties of molecules* (London: Wiley)  
 Deb B M (ed.) 1981 *The force concept in chemistry* (New York: van Nostrand-Reinhold)  
 Hirschfelder J 1978 *J. Chem. Phys.* **68** 5151  
 Lazzeretti P and Zanasi R 1981 *Chem. Phys. Lett.* **80** 533  
 McWeeny R 1970 *Spins in chemistry* (New York: Academic Press)  
 McWeeny R 1973 *Quantum mechanics: methods and basic application* (Oxford: Pergamon)  
 McWeeny R 1984 *Int. J. Quantum Chem.* **26** 693  
 McWeeny R and Sutcliffe B T 1969 *Methods of molecular quantum mechanics* (London: Academic Press)  
 Srebnik S and Bader R F W 1975 *J. Chem. Phys.* **63** 3945  
 Srebnik S and Bader R F W 1981 *Adv. Quantum Chem.* **14** 63  
 Nakatsuji H 1976 *Phys. Rev.* **A14** 41