Molecular electronic property density functions: The nuclear magnetic shielding density

Cynthia J. Jameson

Department of Chemistry, University of Illinois at Chicago Circle, Box 4348, Chicago, Illinois 60680

A. D. Buckingham

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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The general concept of a density function for a molecular electronic property is considered. The origin dependence of some electric and magnetic property densities is investigated and the nuclear magnetic shielding density function is used as a typical example. Density difference maps which reflect the changes in this electronic property upon molecule formation and bond extension are shown for the HF molecule and the related systems, the H atom and F⁻ ion.

Molecular charge density maps have been widely used in the physical interpretation of bonding, molecular properties, and reactivities. Charge density difference functions depict charge transfer and polarization, which characterize the bonding in the molecule, or the changes during the course of a chemical reaction, or the facilitation or opposition of nuclear motion. A review of applications of molecular charge distributions by Bader indicates the utility of the charge density function.[1]

In a similar fashion, molecular electronic property density functions may be useful in providing a physical interpretation of gross differences between molecules in the magnitudes of such electronic properties, their dependence on nuclear configuration and conformation, as well as more subtle differences or shifts which have been observed in such properties: hydrogen-bonding effects, intermolecular effects, etc. Density functions will be of special interest for molecular electronic properties which are not approximately the sum of atomic contributions. In this paper we consider the concept of molecular electronic property density functions, discuss the origin dependence of some electric and magnetic property densities, and select for illustration the nuclear magnetic shielding density function. This function is of special interest from the point of view that magnetic shielding is very sensitive to small changes in the molecule and is subject to very accurate measurement.

THEORY

The concept of a property density function is not new. For a charge distribution $\rho_0(\mathbf{r})$ the electric dipole moment is

$$\boldsymbol{\mu} = \int \mathbf{r}\,\rho_0\,d\mathbf{r} \quad . \tag{1}$$

We can define the electric dipole moment density $\boldsymbol{\mu}(\mathbf{r})$ of the charge distribution by writing

$$\boldsymbol{\mu} = \int \boldsymbol{\mu}(\mathbf{r})\,d\mathbf{r} \quad , \tag{2}$$

where

$$\boldsymbol{\mu}(\mathbf{r}) = \mathbf{r}\,\rho_0 \quad . \tag{3}$$

Similarly, the magnetic dipole moment due to a charge distribution with a current density $\mathbf{j}(\mathbf{r})$ is given by

$$\mathbf{m} = \frac{1}{2c}\int \mathbf{r}\times\mathbf{j}(\mathbf{r})\,d\mathbf{r} \quad . \tag{4}$$

Thus, the magnetic dipole moment density $\mathbf{m}(\mathbf{r})$ is

$$\mathbf{m}(\mathbf{r}) = \frac{1}{2c}\,\mathbf{r}\times\mathbf{j}(\mathbf{r}) = \frac{1}{2c}\,\mathbf{r}\times\dot{\boldsymbol{\mu}}(\mathbf{r}) \quad . \tag{5}$$

In the absence of electric or magnetic fields $\mathbf{E}$ or $\mathbf{H}$, the charge distribution ρ_0 gives rise to the intrinsic or permanent dipole moment of the system and the current density $\mathbf{j}$ gives rise to the intrinsic magnetic moment.

In the presence of a finite uniform field, the additional terms contributing to the moment can be expanded in powers of the applied field. For example,

$$\boldsymbol{\mu} = \boldsymbol{\mu}^{(0)} + \boldsymbol{\mu}^{(1)} + \boldsymbol{\mu}^{(2)} + \cdots \tag{6}$$

$$= \int [\rho_0(\mathbf{r}) + \rho_1^E(\mathbf{r}) + \rho_2^E(\mathbf{r}) + \cdots]\,\mathbf{r}\,d\mathbf{r} \tag{7}$$

$$= \boldsymbol{\mu}^{(0)} + \boldsymbol{\alpha}\cdot\mathbf{E} + \tfrac{1}{2}\boldsymbol{\beta}:\mathbf{E}^2 + \cdots \quad . \tag{8}$$

The first-order correction to the charge distribution in the presence of the uniform electric field, $\rho_1^E(\mathbf{r})$, is related to the electric polarizability as follows:

$$\boldsymbol{\mu}^{(1)} = \boldsymbol{\alpha}\cdot\mathbf{E} = \int \rho_1^E(\mathbf{r})\,\mathbf{r}\,d\mathbf{r} \quad , \tag{9}$$

which for our purposes can be written as

$$= \int \boldsymbol{\alpha}(\mathbf{r})\cdot\mathbf{E}\,d\mathbf{r} \tag{10}$$

in which $\boldsymbol{\alpha}(\mathbf{r})\cdot\mathbf{E} = \rho_1^E(\mathbf{r})\,\mathbf{r}$ and

$$\boldsymbol{\alpha} = \int \boldsymbol{\alpha}(\mathbf{r})\,d\mathbf{r} \quad . \tag{11}$$

Thus, $\boldsymbol{\alpha}(\mathbf{r})$ can be termed an electric polarizability density. It yields the polarizability when integrated over the volume of the system. Note that for systems which have no permanent dipole moment, $\boldsymbol{\alpha}(\mathbf{r})\cdot\mathbf{E} = \rho_1^E(\mathbf{r})\,\mathbf{r}$ gives the electric dipole moment density in linear response. These definitions of electric polarizability density and electric dipole moment density were

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used by Theimer and Paul[2] to calculate anisotropic light scattering in a dense monatomic gas. They illustrated the polarizability density by a quantum-mechanical calculation of this function for the hydrogen atom.[2] The polarizability density has also been used by Oxtoby and Gelbart in their theory for the polarizability of a pair of interacting inert gas atoms.[3] Recent discussion of the limitations of the concept of polarizability density as applied to atoms and molecules has been given by Sipe and Van Kranendonk,[4] and by Clarke *et al.*[5]

Similarly, in a uniform magnetic field H, the magnetic moment **m** can be written as an expansion

$$\mathbf{m} = \mathbf{m}^{(0)} + \mathbf{m}^{(1)} + \mathbf{m}^{(2)} + \cdots \tag{12}$$

$$= \frac{1}{2c}\int \mathbf{r}\times[\mathbf{j}_0(\mathbf{r}) + \mathbf{j}_1^H(\mathbf{r}) + \mathbf{j}_2^H(\mathbf{r}) + \cdots]\,d\mathbf{r} \tag{13}$$

$$= \mathbf{m}^{(0)} + \boldsymbol{\chi}\cdot\mathbf{H} + \cdots , \tag{14}$$

in which $\mathbf{m}^{(0)}$ is the intrinsic magnetic moment and $\boldsymbol{\chi}\cdot\mathbf{H}$ is the field-induced magnetic moment. The first-order correction to the current density in the presence of a uniform magnetic field, $\mathbf{j}_1^H(\mathbf{r})$, is related to the magnetizability as follows:

$$\mathbf{m}^{(1)} = \boldsymbol{\chi}\cdot\mathbf{H} = \frac{1}{2c}\int \mathbf{r}\times\mathbf{j}_1^H(\mathbf{r})\,d\mathbf{r} \ . \tag{15}$$

Thus, magnetizability density $\boldsymbol{\chi}(\mathbf{r})$ can be defined by

$$\boldsymbol{\chi}(\mathbf{r})\cdot\mathbf{H} = \frac{1}{2c}\,\mathbf{r}\times\mathbf{j}_1^H(\mathbf{r}) \ . \tag{16}$$

We see that electric and magnetic property densities depend on the charge and current distributions of the system.

Origin dependence of property densities

We can see that the electric polarizability density function $\boldsymbol{\alpha}(\mathbf{r})$ is explicitly dependent on the choice of origin:

$$\boldsymbol{\alpha}(\mathbf{r})\cdot\mathbf{E} = \rho_1^E(\mathbf{r})\,\mathbf{r} \ . \tag{17}$$

Similarly, the magnetizability density function $\boldsymbol{\chi}(\mathbf{r})$ is origin dependent:

$$\boldsymbol{\chi}(\mathbf{r})\cdot\mathbf{H} = \frac{1}{2c}\,\mathbf{r}\times\mathbf{j}_1^H(\mathbf{r}) \ , \tag{18}$$

although the current density $\mathbf{j}(\mathbf{r})$ is itself origin independent.

An electronic property which is related to magnetizability is nuclear magnetic shielding σ^N. The energy of a diamagnetic system in a magnetic field is given by $-\frac{1}{2}\mathbf{H}\cdot\boldsymbol{\chi}\cdot\mathbf{H}$, where $\boldsymbol{\chi}\cdot\mathbf{H}$ is the induced magnetic dipole moment which interacts with the magnetic field. The energy of a nuclear moment in a molecule in a magnetic field is $-\boldsymbol{\mu}_N\cdot(\mathbf{1}-\boldsymbol{\sigma}^N)\cdot\mathbf{H}$. In terms of the current density, the shielding tensor $\boldsymbol{\sigma}^N$ is given by the following energy expression:

$$\boldsymbol{\mu}_N\cdot\boldsymbol{\sigma}^N\cdot\mathbf{H} = -\boldsymbol{\mu}_N\cdot\frac{1}{c}\int r_N^{-3}\,\mathbf{r}_N\times\mathbf{j}_1^H(\mathbf{r})\,d\mathbf{r} \ , \tag{19}$$

where $(1/c)\int r_N^{-3}\mathbf{r}_N\times\mathbf{j}_1^H(\mathbf{r})\,d\mathbf{r}$ is the shielding field at nucleus N. Thus, the nuclear magnetic shielding density $\boldsymbol{\sigma}^N(\mathbf{r})$ can be defined by

$$\boldsymbol{\sigma}^N(\mathbf{r})\cdot\mathbf{H} = -\mathbf{r}_N\times\mathbf{j}_1^H(\mathbf{r})/c r_N^3 \ . \tag{20}$$

Since the current density $\mathbf{j}(\mathbf{r})$ is origin-independent, the nuclear magnetic shielding density $\boldsymbol{\sigma}^N(\mathbf{r})$ is independent of the choice of origin, in principle. Thus, the nuclear magnetic shielding density function is a suitable choice for illustrating the characterization and applications of a typical property density function. The explicit origin dependence of the polarizability density and the magnetizability density functions necessitates a considered choice of origin except in cases (e.g., an atom) where a natural origin exists. For the polarizability density, there are some physical arguments which support the use of the midpoint of the line from the center of positive charge to the center of negative charge, as the most meaningful origin choice.[6] Previous polarizability density calculations[3-5] were not subject to origin-dependence ambiguity since they assumed atom-additive densities.

In the previous discussion we found that electric and magnetic property densities can be calculated from the charge and current density of the system. Let us consider our system to be a single molecule. In the Schrödinger formulation of the quantum theory, the expressions for the charge and current densities for a system with a single electron are taken to be, respectively,[7]

$$\rho(\mathbf{r}) = -e\Psi^*\Psi \tag{21}$$

and [neglecting the contribution of electron spin to $\mathbf{j}(\mathbf{r})$]

$$\mathbf{j}(\mathbf{r}) = \frac{-e\hbar}{2im}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - \frac{e^2}{mc}\mathbf{A}\Psi^*\Psi \ , \tag{22}$$

where $\mathbf{A}$ is the magnetic vector potential. Due to the field $\mathbf{H}$, $\mathbf{A} = \mathbf{A}_H$ in its simplest form is given by $\frac{1}{2}\mathbf{H}\times\mathbf{r}$. Ψ is a normalized solution of the generalized wave equation. Ψ can be expanded in powers of E or H:

$$\Psi = \Psi^{(0)} + E\Psi^{(1)} + E^2\Psi^{(2)} + \cdots \text{ or } \Psi = \Psi^{(0)} + H\Psi^{(1)} + H^2\Psi^{(2)} + \cdots . \tag{23}$$

Thus, the electric dipole moment density is given by

$$\boldsymbol{\mu}(\mathbf{r}) = -e\Psi^{(0)*}\mathbf{r}\Psi^{(0)} - e(\Psi^{(1)*}\mathbf{r}\Psi^{(0)} + \Psi^{(0)*}\mathbf{r}\Psi^{(1)})\cdot\mathbf{E} + \cdots , \tag{24}$$

which when integrated over $\mathbf{r}$ gives $\boldsymbol{\mu}^{(0)} + \boldsymbol{\alpha}\cdot\mathbf{E} + \cdots$. The current density can likewise be expanded as

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_0(\mathbf{r}) + \mathbf{j}_1^H(\mathbf{r}) + \mathbf{j}_2^H(\mathbf{r}) + \cdots , \tag{25}$$

in which

$\mathbf{j}_0(\mathbf{r}) = 0$ (in molecules which are symmetric under time-reversal $\Psi^{(0)}$ is real and the current density vanishes at all points in the absence of $\mathbf{H}$. In the presence of $\mathbf{H}$, $\Psi^{(1)}$ is imaginary.)

and

$$\mathbf{j}_1^H(\mathbf{r}) = -\frac{e\hbar H}{im}(\Psi^{(1)*}\nabla\Psi^{(0)} - \Psi^{(0)*}\nabla\Psi^{(1)}) - \frac{e^2}{mc}\mathbf{A}_H\Psi^{(0)*}\Psi^{(0)} \ , \tag{26}$$

and the magnetic dipole moment density is given by $(1/2c)(\mathbf{r}\times\mathbf{j}(\mathbf{r}))$.

From Eq. (24) we see that the electric polarizability density is given by

$$\boldsymbol{\alpha}(\mathbf{r}) = -e(\Psi^{(1)*}\mathbf{r}\Psi^{(0)} + \Psi^{(0)*}\mathbf{r}\Psi^{(1)}) \tag{27}$$

and from Eqs. (16) and (26) the magnetizability density is given by

$$\chi(\mathbf{r}) = -\frac{e\hbar}{2imc}(\Psi^{(1)*}\mathbf{r}\times\boldsymbol{\nabla}\Psi^{(0)} - \Psi^{(0)}\mathbf{r}\times\boldsymbol{\nabla}\Psi^{(1)*}) - \frac{e^2}{4mc^2}\Psi^{(0)}(\mathbf{r}\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r})\Psi^{(0)} \quad . \tag{28}$$

Similarly, using Eqs. (20) and (26), the nuclear magnetic shielding density can be defined as

$$\sigma^N(\mathbf{r}) = \frac{e\hbar}{imcr_N^3}(\Psi^{(1)*}\mathbf{r}_N\times\boldsymbol{\nabla}\Psi^{(0)} - \Psi^{(0)}\mathbf{r}_N\times\boldsymbol{\nabla}\Psi^{(1)*}) + \frac{e^2}{2mc^2r_N^3}\Psi^{(0)}(\mathbf{r}_N\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r}_N)\Psi^{(0)} \ . \tag{29}$$

$\Psi^{(1)}$ is the first-order correction to the wave function in the presence of an **E** or **H** field along the x, y, or z direction. In a one-electron system $\Psi(r)$ is a one-electron function and so are $\Psi^{(0)}$, $\Psi^{(1)}$, etc. In a multielectron system, in the context of the Born–Oppenheimer approximation, Ψ should be a multielectron function, such as the Kołos–Wolniewicz[8] function for H_2, with a parametric dependence on nuclear configuration. However, since such functions are not available for most molecules, we will consider the property densities in the context of the Hartree–Fock approximation using the density matrix formulation of McWeeny.[9,10]

We consider n occupied molecular spin orbitals ψ_1, ψ_2, $\cdots$ ψ_n, each of which is constructed from m orthonormal basis functions ϕ_1, ϕ_2, $\cdots$ ϕ_m:

$$\psi = \phi\mathbf{T} \ . \tag{30}$$

The spinless density matrix **P** is defined by

$$\mathbf{P} = 2\mathbf{R}, \tag{31}$$

$$\mathbf{R} = \mathbf{T}\mathbf{T}^{\dagger} \tag{32}$$

A sufficient condition for stationary energy is that the columns of **T** are eigenvectors of

$$\mathbf{hc} = \epsilon\mathbf{c} \quad . \tag{33}$$

The form of the Hamiltonian depends upon the electron distribution through the electron interactions, and hence upon the density matrix **R**:

$$\mathbf{h} = \mathbf{f} + \mathbf{G}(\mathbf{R}) \quad , \tag{34}$$

where **f** is a framework Hamiltonian including only the potential energy due to the nuclei, and the electron interaction matrix **G** is that defined by Roothaan.[11] Given a self-consistent solution for an unperturbed system with $\mathbf{R}^0$ and $\mathbf{f}^{(0)}$, the expansion

$$\mathbf{R} = \mathbf{R}^0 + \lambda\mathbf{R}^{(1)} + \lambda^2\mathbf{R}^{(2)} + \cdots \tag{35}$$

corresponds to the self-consistent solution for the perturbed system, with

$$\mathbf{f} = \mathbf{f}^{(0)} + \lambda\mathbf{f}^{(1)} + \lambda^2\mathbf{f}^{(2)} + \cdots \ . \tag{36}$$

The density matrix $\mathbf{R}^{(1)}$ resolves into its components[10] $\mathbf{R}_{11}^{(1)} = \mathbf{R}_{22}^{(1)} = 0$ and $\mathbf{R}_{21}^{(1)} = \mathbf{R}_{12}^{(1)\dagger}$. Thus,

$$\mathbf{R}^{(1)} = \mathbf{R}_{12}^{(1)} + \mathbf{R}_{12}^{(1)\dagger} = \mathbf{X} + \mathbf{X}^{\dagger} \tag{37}$$

and we need to determine only one component $\mathbf{R}_{12}^{(1)}$. $\mathbf{R}_{12}^{(1)}$ may be determined more conveniently in terms of the eigenvectors of h_0[10]:

$$h_0 = \sum_{i=1}^{m} \epsilon_i\mathbf{C}_i\mathbf{C}_i^{\dagger} \ , \tag{38}$$

which yields

$$\mathbf{X} = \mathbf{R}_{12}^{(1)} = \sum_{r}^{\text{occ}}\sum_{s}^{\text{unocc}} \frac{\Delta_{rs}^{(1)}}{\epsilon_r - \epsilon_s}\mathbf{C}_r\mathbf{C}_s^{\dagger} \ , \tag{39}$$

where

$$\Delta_{rs}^{(1)} = \mathbf{C}_r^{\dagger}(\mathbf{f}^{(1)} + \mathbf{G}(\mathbf{R}_{12}^{(1)}))\mathbf{C}_s \ . \tag{40}$$

In achieving self-consistency it is then only necessary to revise the coefficient of $\mathbf{C}_r\mathbf{C}_s^{\dagger}$ in Eq. (39) using an iterative procedure. Alternately, the coupled linear simultaneous equations (39) may be solved by standard numerical techniques.

Here, we may write[12]

$$\mathbf{f}^{(1)} = a\mathbf{f}^a + b\mathbf{f}^b + \cdots \ , \tag{41}$$

$$\mathbf{f}^{(2)} = a^2\mathbf{f}^{a^2} + b^2\mathbf{f}^{b^2} + ab\,\mathbf{f}^{ab} + \cdots \ , \tag{42}$$

where, for magnetic properties, in atomic units

$$a = c^{-2}\boldsymbol{\mu}_N, \qquad b = \mathrm{H} \ , \tag{43}$$

$$\mathbf{f}^a = \mathbf{M}_N/r_N^3 \ , \quad \mathbf{f}^b = \tfrac{1}{2}\mathbf{M}_H \ , \tag{44}$$

$$\mathbf{f}^{ab} = (\mathbf{r}_N\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r}_N)/2r_N^3 \ , \qquad \mathbf{f}^{b^2} = (\mathbf{r}\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r})/8 \tag{45}$$

M denotes the angular momentum operators $\mathbf{M}_H = i\,\mathbf{r}\times\boldsymbol{\nabla}$ and $\mathbf{M}_N = -i\,\mathbf{r}_N\times\boldsymbol{\nabla}$. This paper deals with magnetic property densities. Molecular electric property densities will be treated in a separate paper.[6] The energy term of interest in the case of nuclear magnetic shielding is[12]

$$\boldsymbol{\mu}_N\cdot\sigma^N\cdot\mathbf{H} = 2c^{-2}\,\mathrm{tr}[\mathbf{f}^{ab}\mathbf{R}^0 + \mathbf{f}^a\mathbf{R}^b] \ . \tag{46}$$

The components of the nuclear magnetic shielding tensor in atomic units (the H-atom shielding in a.u. is $c^{-2}/3 = 17.75$ ppm) are

$$\sigma_{\alpha\beta}^N = 2c^{-2}\,\mathrm{tr}\left[\frac{1}{2}\left(\frac{\mathbf{r}_N\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r}_N}{r_N^3}\right)_{\alpha\beta}\mathbf{R}^0 + \frac{(\mathbf{M}_N)_\alpha}{r_N^3}\mathbf{R}_\beta^{(1/2)M_H}\right] \tag{47}$$

for the α component of $\boldsymbol{\mu}_N$ and the β component of **H**. In the case of the magnetizability the energy term of interest is

$$-\tfrac{1}{2}\mathbf{H}\cdot\chi\cdot\mathbf{H} = 2\,\mathrm{tr}[\mathbf{f}^{b^2}\mathbf{R}^0 + \tfrac{1}{2}\mathbf{f}^b\mathbf{R}^b] \ . \tag{48}$$

The components of the magnetizability tensor are given by

$$\chi_{\alpha\beta} = -\,\mathrm{tr}[\tfrac{1}{2}(\mathbf{r}\cdot\mathbf{r}\,\mathbf{I} - \mathbf{r}\,\mathbf{r})_{\alpha\beta}\mathbf{R}^0 + (\mathbf{M}_H)_\alpha\mathbf{R}_\beta^{(1/2)M_H}] \ . \tag{49}$$

The elements of the density matrix in the basis of unperturbed molecular orbitals ψ_q^0, $q = 1, \ldots, m$ are obtained by solving the simultaneous equations

$$\mathbf{R}_{sq}^{(1)\beta}=\frac{1}{\epsilon_q-\epsilon_s}\left\{\frac{1}{2i}\,(\mathbf{r}\times\boldsymbol{\nabla})_{sq}^{\beta}\right.$$

$$\left.+\sum_{t=1}^{n}\sum_{u=n+1}^{m}\mathbf{R}_{ut}^{(1)\beta}[-(qt|us)+(qu|ts)]\right\}. \tag{50}$$

Thus, the components of the nuclear magnetic shielding and the magnetizability tensors are given by

$$\sigma_{\alpha\beta}^{N}=\sum_{t}^{n}\left(\frac{\mathbf{r}_N\cdot\mathbf{r}\mathbf{I}-\mathbf{r}\,\mathbf{r}_N}{c^2r_N^3}\right)_{tt}^{\alpha\beta}$$

$$+\sum_{s}\sum_{q}2\mathbf{R}_{sq}^{(1)\beta}\left(\frac{\mathbf{r}_N\times\boldsymbol{\nabla}}{ic^2r_N^3}\right)_{sq}^{\alpha} \tag{51}$$

and

$$\chi_{\alpha\beta}=-\frac{1}{2}\sum_{t}^{n}(\mathbf{r}\cdot\mathbf{r}\mathbf{I}-\mathbf{r}\,\mathbf{r})_{tt}^{\alpha\beta}$$

$$-\frac{1}{2}\sum_{s}\sum_{q}^{m}2\mathbf{R}_{sq}^{(1)\beta}\left(\frac{\mathbf{r}\times\boldsymbol{\nabla}}{i}\right)_{sq}^{\alpha}\quad. \tag{52}$$

In terms of the atomic orbital basis functions the nuclear magnetic shielding density function is

$$\sigma_{\alpha\beta}^{N}(\mathbf{r})=c^{-2}\sum_{\nu}\sum_{\lambda}\left[\tfrac{1}{2}P_{\nu\lambda}^{0}\phi_\nu((\mathbf{r}\cdot\mathbf{r}_N\,\delta_{\alpha\beta}-r_\alpha r_{N\beta})/r_N^3)\,\phi_\lambda\right.$$

$$\left.+P_{\nu\lambda}^{(1)\beta}\,\phi_\nu(\mathbf{r}_N\times\boldsymbol{\nabla}/ir_N^3)_\alpha\,\phi_\lambda\right] \tag{53}$$

and the magnetizability density function is:

$$\chi_{\alpha\beta}(\mathbf{r})=-\frac{1}{2}\sum_{\nu}\sum_{\lambda}\left[\tfrac{1}{2}P_{\nu\lambda}^{0}\phi_\nu(r^2\delta_{\alpha\beta}-r_\alpha r_\beta)\,\phi_\lambda\right.$$

$$\left.+P_{\nu\lambda}^{(1)\beta}\,\phi_\nu(\mathbf{r}\times\boldsymbol{\nabla}/i)_\alpha\,\phi_\lambda\right]\ , \tag{54}$$

where the elements of the density matrices in the atomic orbital basis are

$$P_{\nu\lambda}^{0}=\sum_{q=1}^{n}2\,a_{q\nu}^{0}a_{q\lambda}^{0} \tag{55}$$

and

$$P_{\nu\lambda}^{(1)\beta}=\sum_{q=1}^{n}\sum_{s=n+1}^{m}2\,\mathbf{R}_{sq}^{(1)}(a_{s\nu}^{0}a_{q\lambda}^{0}-a_{q\nu}^{0}a_{s\lambda}^{0})\quad. \tag{56}$$

Shielding density difference functions and maps

We can define density difference functions which may be useful in understanding (a) the chemical shielding in a molecule in its equilibrium configuration, and (b) the derivative of chemical shielding with respect to bond extension. The shielding density difference function due to molecular bond formation can be defined as[13]

$$\Delta\sigma^{N}(\mathbf{r})_M=\sigma^{N}(\mathbf{r})_{\text{molecule}}-\sigma^{N}(\mathbf{r})_{\text{atom}}\quad. \tag{57}$$

This density difference function illustrates the change in the atomic shielding densities resulting from the formation of the chemical bond. It provides a measure of the distortions present in the molecular shielding distribution relative to the original atom shielding density. Many chemical effects can be investigated using this difference function, e.g., effects of substitution of groups, changes in conformation, etc. Ideally, $\sigma(r)$ for both systems should be calculated using basis sets of the same quality, which may necessitate use of ghost orbitals on the smaller system.

The density difference function due to bond extension provides a physical interpretation of the derivative $(\partial\sigma/\partial\Delta R)$. For simplicity let us consider a diatomic molecule with the following equilibrium coordinates:

$$R^{\text{eq}}=X_N^{\text{eq}}-X_{N'}^{\text{eq}}\quad. \tag{58}$$

Let N be the nucleus of interest. The bond extension ΔR is

$$\Delta R=(X_N-X_N^{\text{eq}})-(X_{N'}-X_{N'}^{\text{eq}})\quad, \tag{59}$$

and

$$(\partial\boldsymbol{\sigma}^{N}/\partial\Delta R)_{\text{eq}}=(\partial\boldsymbol{\sigma}^{N}/\partial X_N)-(\partial\boldsymbol{\sigma}^{N}/\partial X_{N'})_{\text{eq}} \tag{60}$$

$$=\int[(\partial\boldsymbol{\sigma}^{N}(\mathbf{r})/\partial X_N)_{\text{eq}}-(\partial\boldsymbol{\sigma}^{N}(\mathbf{r})/\partial X_{N'}')_{\text{eq}}]\,d\mathbf{r}\,. \tag{61}$$

If an arbitrary space-fixed origin is chosen, about which $\boldsymbol{\sigma}^{N}(\mathbf{r})$ is expressed, and nucleus N is displaced, there will be large cancelling terms due to that part of $\boldsymbol{\sigma}^{N}(\mathbf{r})$ which "follows" nucleus N. The rest of the terms will be due to a "relaxation" of the shielding distribution during the displacement of nucleus N. This is analogous to the determination of force constants from charge density diagrams.[14] It is clear that insight into the nature and magnitude of $\partial\sigma/\partial\Delta R$ can be obtained by isolating the relaxation of the shielding distribution from its rigid following. This can be done by using a moving frame of reference.

Consider $\boldsymbol{\sigma}^{N}(\mathbf{r})$ expressed in terms of a coordinate system centered on nucleus N (the coordinate system therefore moves with N). This corresponds to the shielding distribution $\boldsymbol{\sigma}^{N}(\mathbf{r})$ being expressed as $\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)$, in which α are the parameters, e.g., linear coefficients in an orbital wave function, which are functions of nuclear position in the Born–Oppenheimer approximation. In the special case where all of $\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)$ rigidly follows N, α would be independent of X_N and there will be *no* contribution to $\partial\boldsymbol{\sigma}/\partial\Delta R$. Thus, the entire contribution to $\partial\sigma/\partial\Delta R$ is due to a relaxation of the shielding distribution during the displacement of nucleus N.

The recommended procedure (in a diatomic molecule) is to displace N, but fix N' so that the entire displacement is reflected in the change of X_N:

$$\partial\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)/\partial X_N$$

$$=\partial[\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)_{\substack{\text{rigid}\\ \text{following}}}+\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)_{\text{relaxed}}]/\partial X_N\,. \tag{62}$$

Since the derivative of the first term inside the brackets is zero,

$$(\partial\boldsymbol{\sigma}/\partial\Delta R)_{\text{eq}}=\int\partial[\boldsymbol{\sigma}^{N}(\alpha,\mathbf{r}_N)_{\text{relaxed}}]/\partial X_N\quad. \tag{63}$$

Note that the portion of the shielding density in the vicinity of N' will in general not follow the displacement of nucleus N, and hence, when expressed in coordinates centered on N, will appear to relax with respect to motion of N.

The density difference diagrams representing the relaxation with respect to displacement ΔR may be constructed by subtracting the equilibrium shielding distribution with nucleus N held fixed in space and N' displaced (in the moving frame of reference attached to N, N appears stationary), i.e., the density difference due to bond extension is

$$\Delta\boldsymbol{\sigma}^N(\mathbf{r}) = \boldsymbol{\sigma}^N(\mathbf{r}_N)_R - \boldsymbol{\sigma}^N(\mathbf{r}_N)_{R_e} \quad , \tag{64}$$

where R_e denotes the molecule at equilibrium and R that in which N is displaced. This difference function is obtained most easily if the grid of points for which $\boldsymbol{\sigma}^N(\mathbf{r})$ is calculated is always taken *with respect to center N*, whose shielding is being determined, as opposed to with respect to the molecular origin. The grid will be unchanged for the extended molecule and also will be unchanged for a different choice of gauge origin.

Practical gauge dependence of nuclear magnetic shielding and nuclear magnetic shielding densities

Although $\boldsymbol{\sigma}^N$ and $\boldsymbol{\sigma}^N(\mathbf{r})$ are gauge independent in principle, it is well known that, in practice, some fundamental properties of the true wave function do not hold for approximate wave functions, leading to different results for calculations using different gauge origins.[15] We will consider two origins and explore only the translational invariance of the shielding. For $\mathbf{r} = \mathbf{r}_N + \Delta\mathbf{r}$,

$$\boldsymbol{\sigma}^N_{\beta\alpha} = c^{-2}\sum \langle [r_N^2\,\delta_{\alpha\beta} + r_N \Delta r\,\delta_{\alpha\beta} - r_{N\alpha}(r_{N\beta} + \Delta r_\beta)]/r_N^3\rangle + c^{-2}\sum\sum P^{(1)'\alpha}\langle M_{\beta N}/r_N^3\rangle \quad , \tag{65}$$

$$\sigma^N_{\alpha\beta} = c^{-2}\sum \langle [r_N^2\,\delta_{\alpha\beta} + r_N\,\Delta r\;\delta_{\alpha\beta} - r_{N\beta}(r_{N\alpha} + \Delta r_\alpha)]/r_N^3\rangle + c^{-2}\sum\sum P^{(1)'\beta}\langle M_{\alpha N}/r_N^3\rangle \quad . \tag{66}$$

In principle, the difference between the shielding tensors calculated using two different origins separated by Δr is

$$c^{-2}\sum\langle [r_N\,\Delta r\,\delta_{\alpha\beta} - r_{N\alpha}\,\Delta r_\beta] r_N^3\rangle + c^{-2}\sum\sum(P^{(1)'\alpha} - P^{(1)\alpha})\langle M_{\beta N}/r_N^3\rangle = 0 \quad , \qquad \text{for } \sigma_{\beta\alpha} \tag{67}$$

and

$$c^{-2}\sum\langle [r_N\,\Delta r\,\delta_{\alpha\beta} - r_{N\beta}\,\Delta r_\alpha]/r_N^3\rangle + c^{-2}\sum\sum(P^{(1)'\beta} - P^{(1)\beta})\langle M_{\alpha N}/r_N^3\rangle = 0 \quad , \qquad \text{for } \sigma_{\alpha\beta} \quad . \tag{68}$$

However, since the second group of terms in Eq. (67) is not calculated with accuracy equal to that of the first sum of terms, in practice this difference is generally not zero. It also follows that in practice the difference between the shielding density functions $\boldsymbol{\sigma}^N(\mathbf{r})$ calculated using different gauge origins will not be zero.

The number of unique nonzero elements of the nuclear magnetic shielding tensor $\boldsymbol{\sigma}$ is determined by the symmetry of the site at which the nucleus of interest is located in relation to the molecule as a whole, the "nuclear site symmetry." The number of unique shielding components for various nuclear site symmetries has been determined by Buckingham and Malm.[16] In general, $\sigma_{\alpha\beta} \neq \sigma_{\beta\alpha}$ so that nine independent elements are required to specify fully the shielding tensor. However, in molecules possessing some symmetry, the nuclear site symmetry may be sufficiently high such that as few as one or two elements are unique and nonvanishing. Since symmetry is preserved in going from a full (infinite basis set) to a limited basis set, calculated $\sigma_{\alpha\beta}$ elements will still be zero or nonzero according to site symmetry. While the integrals $\sigma_{\alpha\beta}$ may be zero, the integrands, which are the densities $\sigma^N_{\alpha\beta}(\mathbf{r})$ in Eq. (67), will not vanish for any $\alpha\beta$. These density functions will present antisymmetrical features, as will be seen in densities for spherical systems such as the H atom and F^- ion.

The difference between Eq. (65) and (66) $(\sigma_{\beta\alpha} - \sigma_{\alpha\beta})$ should vanish whenever nuclear site symmetry dictates that these elements be equal. Since symmetry is preserved in going from a full to a limited basis set, the calculated $\sigma_{\beta\alpha} - \sigma_{\alpha\beta}$ will indeed vanish. On the other hand, the calculated density difference function $\sigma^N_{\beta\alpha}(\mathbf{r}) - \sigma^N_{\alpha\beta}(\mathbf{r})$ will not necessarily vanish. The terms

$$\sum\sum P^{(1)\alpha}_{\nu\lambda}\,\phi_\nu M_{\beta N}/r_N^3\phi_\lambda - P^{(1)\beta}_{\nu\lambda}\;\phi_\nu M_{\alpha N}/r_N^3\phi_\lambda$$

will generally not vanish unless α and β are related by symmetry because $P^{(1)\alpha}_{\nu\lambda}$ and $P^{(1)\beta}_{\nu\lambda}$ can not be calculated with absolute accuracy. This is another measure of the extent to which approximate wave functions do not satisfy the conditions for gauge invariance.

RESULTS

Since the nuclear magnetic shielding density function does not have an explicit origin dependence, it has been chosen to demonstrate the concept of the molecular property density function and to investigate its utility. Calculations of these functions were carried out for the following species: H atom, fluoride ion, and HF molecule. The species were chosen for the following reasons: The hydrogen atom shielding density can be expressed analytically and provides a known quantity with which approximate density functions can be compared.

The HF molecule is the smallest stable molecule containing both a proton and a nucleus which behaves as a typical "heavy" nucleus. It is well known that the shielding of ^{19}F and other heavy nuclei can be dominated by the paramagnetic term (as defined by the choice of gauge origin at the nucleus in question), and cannot be interpreted by extrapolation of insight gained from very accurate calculations of shielding in light nuclei such as ^{1}H and ^{3}He. The fluoride ion completes the set since the HF bond is highly ionic and comparison between the ^{19}F nucleus in the HF molecule and in the F$^-$ ion would be useful.

The display of the density function as a surface offers the best opportunity for visualization and comparisons. Nuclear magnetic shielding density maps were constructed using a grid of x_N, y_N, and z_N values for the points at which shielding densities are to be calculated. As discussed earlier, difference densities are obtained most easily if the grid of points is expressed with respect to the center N whose shielding is being determined, rather than with respect to a molecular or space-fixed origin. All figures shown here are maps of the shielding density for the $x_N = 0.0625$ a.u. plane, which presents essentially the same mapping as the $x_N = 0$ plane, without the attendant calculational difficulties due to singularities of the function. The molecular z axis is chosen along the F–H bond in the molecule. To display the features of the surfaces in figures of comparable size, the vertical axis is scaled as needed and truncated where necessary.

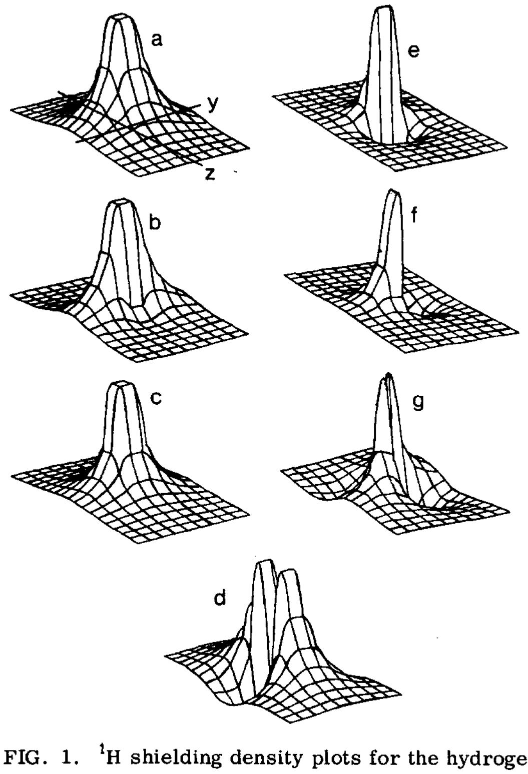

FIG. 1. ^{1}H shielding density plots for the hydrogen atom. The density plots shown are for the $x = 0.0625$ a.u. plane, for the components (a) σ_{xx}, (b) σ_{zz}, (c) $(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$, (d) $-[\sigma_{zz} - (1/2)\sigma_{xx} - (1/2)\sigma_{yy}]$, (e) σ_{xz}, (f) σ_{xy}, and (g) σ_{yz}.

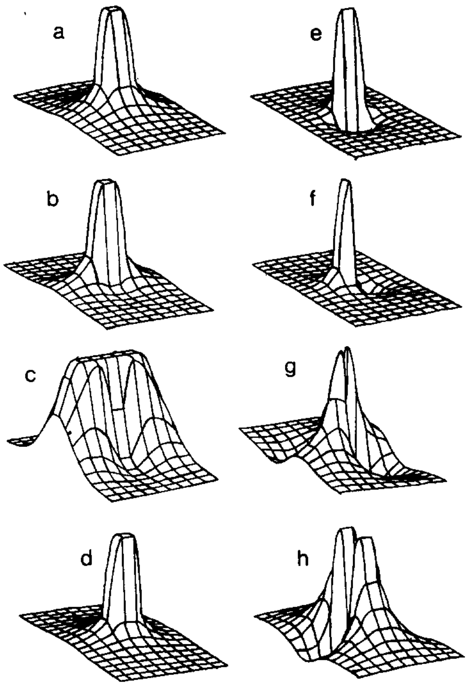

FIG. 2. ^{19}F shielding density plots for the F$^-$ ion. The density plots shown are for the $x = 0.0625$ a.u. plane, for the components (a) σ_{xx}, (b) σ_{zz}, (c) σ_{zz} truncated in order to show the features on an expanded density scale, (d) $(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$, (e) σ_{xz}, (f) σ_{xy}, (g) σ_{yz}, and (h) $-[\sigma_{zz} - (1/2)\sigma_{xx} - (1/2)\sigma_{yy}]$.

The density functions for ^{1}H shielding in the hydrogen atom, shown in Fig. 1, have a very simple mathematical form. For example, for the zz component,

$$\sigma_{zz}^{N}(\mathbf{r}) = \frac{1}{2\pi c^2}\,\frac{x^2+y^2}{r^3}\,\exp(-2r) \quad . \tag{69}$$

The density maps shown in Fig. 2 for various components of the ^{19}F shielding in fluoride ion show essentially the same features, although the density functions are not as conveniently written down in analytic form.

The density maps for the components of the ^{1}H shielding tensor and the trace of the ^{19}F shielding tensor in the HF molecule at its equilibrium configuration are shown in Figs. 3–5. The calculations for the HF molecule and fluoride ion were carried out using the Lie–Clementi basis which yields a near-Hartree–Fock energy for the ground state.[17] Figures 3 and 5(a) are the ^{1}H and ^{19}F shielding density maps for $\mathbf{r}$ and $\mathbf{M}_\mathrm{H}$ defined with the origin at the **F** nucleus, whereas Figs. 4 and 5(b) are with the origin at the H nucleus. The shielding density maps are different for different gauge origins, as are the integrated values which had previously been reported by Day and Buckingham.[15] In principle, neither the nuclear magnetic shielding nor its density function are gauge dependent. However, in practice, the limitations of the basis set used, as well as the deficiencies of the coupled Hartree–Fock method, give rise to some gauge dependence since the conditions for gauge invariance are not satisfied. This gauge dependence will be discussed further. Figures 3 and 4 show that there are sizeable contributions to the ^{1}H shielding in the HF molecule from the region around the fluorine nucleus. The ^{19}F shield-

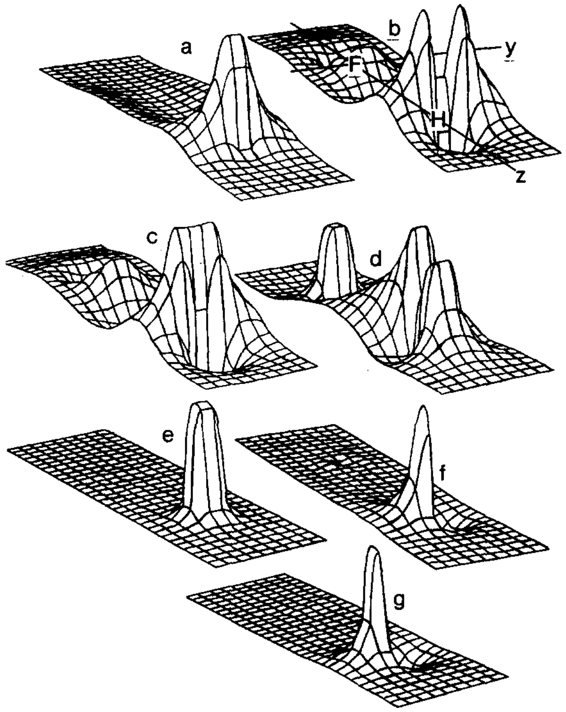

FIG. 3. ^{1}H shielding density plots for the HF molecule, with gauge origin at F. The density plots shown are for the $x=0.0625$ a.u. plane, for the components (a) σ_{zz}, (b) σ_{xx}, (c) $(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$, (d) $(\sigma_{\parallel}-\sigma_{\perp})$, (e) $-\sigma_{xz}$, (f) σ_{yx}, and (g) σ_{yz}.

ing density plots in HF are not nearly as interesting since they have features very similar to that of the fluoride ion, with small contributions from the vicinity of the **H** nucleus. Thus, only the trace is shown in Fig. 5,

We have calculated the (HF molecule - H atom) shielding density difference maps for the ^{1}H nucleus. One is shown in Fig. 6, in which we see a rather pronounced difference in densities between these two systems. The density difference map clearly shows the substantial contributions from the region near the F nucleus to the ^{1}H shielding upon molecule formation. We have also calculated the (HF molecule - F ion) shielding density difference maps for the ^{19}F nucleus. Two of these are shown in Fig. 7. Since the HF molecule has a fairly high ionic character, the fluoride ion rather than the fluorine atom is used for comparison with the molecule. The fluoride ion calculation was carried out using the same basis set as for the HF molecule, i.e., including ghost orbitals, to ensure that this comparison is not invalidated by a difference in basis set size. In contrast to the ^{1}H shielding, the ^{19}F shielding difference map shows very little contribution from the region around the other nucleus. It also shows the asymmetry in the ^{19}F shielding density which arises as the presence of the proton distorts the charge distribution of the fluoride ion.

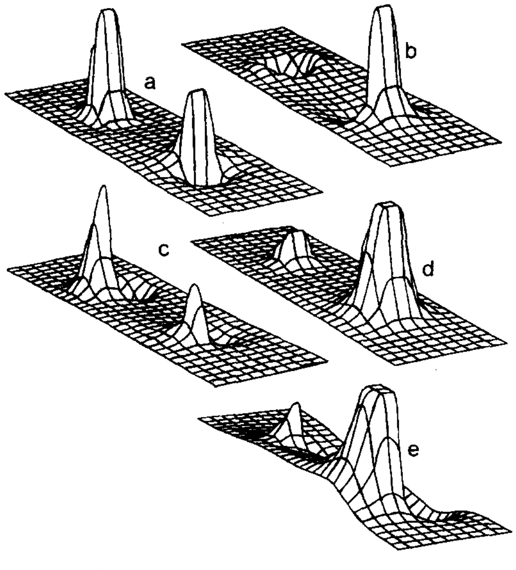

FIG. 4. ^{1}H shielding density plots for the HF molecule, with gauge origin at H. The density plots shown are for the $x=0.0625$ a.u. plane, for the components (a) $\sigma_{\parallel}-\sigma_{\perp}$, (b) σ_{xx}, (c) σ_{yx}, (d) σ_{xz}, and (e) $-\sigma_{yz}$.

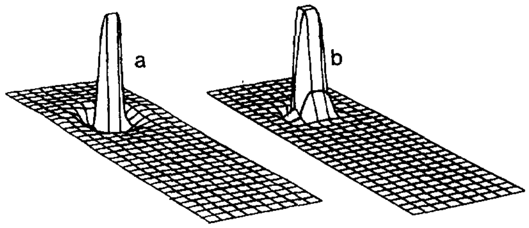

FIG. 5. ^{19}F shielding density plot for the HF molecule (a) with gauge origin at F, (b) with gauge origin at H. The function plotted is the isotropic average $(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$ for the $x=0.0625$ a.u. plane.

Figure 8 shows the $(\mathrm{HF}_{\mathrm{ext}}-\mathrm{HF}_{\mathrm{eq}})$ difference map, where the $\mathrm{HF}_{\mathrm{ext}}$ denotes an HF molecule in which the bond is extended by 0.1 a.u. beyond the equilibrium configuration. As discussed earlier, this difference map provides a physical interpretation of the derivative $(\partial\sigma/\partial\Delta R)$. From these maps we can see that the portion of the shielding density in the vicinity of the H nucleus contributes very little to $\partial\sigma^{\mathrm{F}}/\partial\Delta R$. This is not surprising in view of the observation that the shielding density function $\boldsymbol{\sigma}^{\mathrm{F}}(\mathbf{r})$ in the HF molecule shows very little contribution from the region of the H nucleus (see Fig. 5). While it is perhaps too soon to generalize

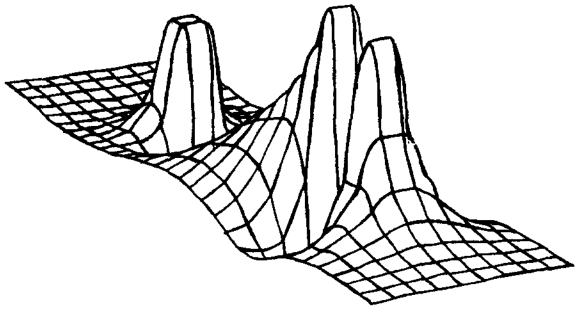

FIG. 6. ^{1}H shielding density difference map for the HF molecule minus H atom. The difference map of the isotropic average $-\Delta(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$ is shown.

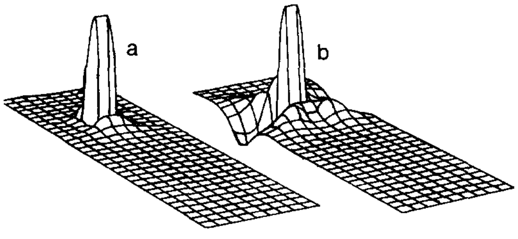

FIG. 7. ^{19}F shielding density difference maps for the HF molecule minus fluoride ion. The components shown are (a) $-\Delta\sigma_{yy}$ and (b) $-\Delta\sigma_{zz}$.

our finding to other fluorides, our results are at least consistent with the observation that empirical values of $\partial\sigma^{F}/\partial\Delta R$ have the same sign and nearly the same magnitudes for different molecules (e.g., SiF_4, CF_4, and BF_3).[18] On the other hand, Fig. 8 shows that there is a sizeable contribution to $\partial\sigma^{H}/\partial\Delta R$ from the region near the F nucleus. This too is consistent with experiment. While there is relatively little empirical information about $\partial\sigma^{H}/\partial\Delta R$ in various molecules, what is available does indicate that this derivative is negative in H_2, HCl, and HBr and has a magnitude which varies by as much as a factor of 20.[19,20]

Figure 9 illustrates the gauge dependence of the nuclear magnetic shielding density in practice. The density difference for ^{19}F or ^{1}H shielding using two different gauge origins should in principle be zero everywhere. The density difference shown in Fig. 9 integrates to a very small number in the case of ^{19}F shielding, since the + and − parts of the surface nearly cancel. This illustrates one of the effects of moving the gauge origin from a favorable (according to the criteria stated by Moccia, for example[21]) to a less favorable center, which is to generate large cancelling + and − terms. In the case of ^{1}H shielding the contributions centered at F are less accurately calculated when the gauge origin is at the H center. The integrated values have been calculated by Day and Buckingham (27.266 and 35.777 ppm for origins at F and H, respectively).[15] Figure 9 clearly shows that the contributions from the vicinity of the F nucleus are the ones which lead to a larger ^{1}H shielding parameter when the gauge origin is chosen at the H rather than the F center. The origin dependence observed here assesses the degree of accuracy of the wave function in those regions of space where circulation of charges is induced by magnetic fields.

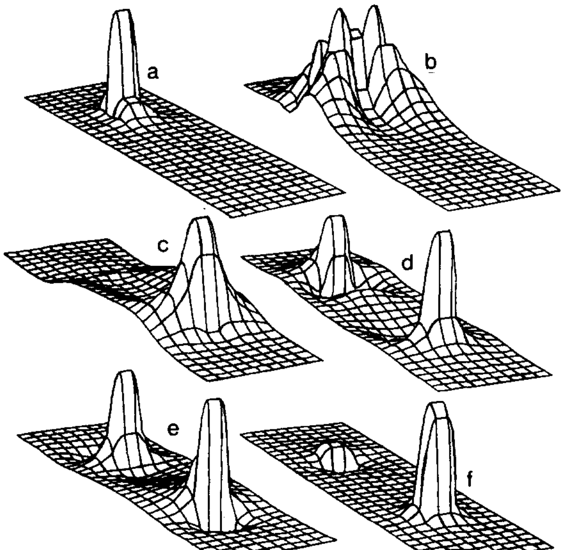

FIG. 8. Shielding density difference maps for the HF molecule upon bond extension, HF at $R_e + 0.1$ a.u. minus HF at the equilibrium distance. (a) and (b) show the ^{15}F shielding density differences $-\Delta\sigma_{yy}$ and $-\Delta\sigma_{zz}$, respectively. The rest of the density difference maps are for ^{1}H shielding: (c) $-\Delta\sigma_{zz}$, (d) $-\Delta\sigma_{xx}$, (e) $-\Delta(\sigma_{\parallel} - \sigma_{\perp})$, (f) $\Delta\sigma_{xz}$, (g) $\Delta\sigma_{yz}$, and (h) $-\Delta\sigma_{xy}$.

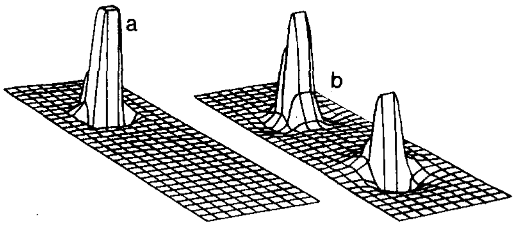

FIG. 9. Shielding density difference maps for the HF molecule, indicating the difference between calculations with gauge origin at F and gauge origin at H. In the absence of any practical gauge dependence, these maps should be zero everywhere. (a) shows the difference for the *xx* component of ^{19}F shielding and (b) shows the difference for the *xx* component of ^{1}H shielding.

Figures 1 and 2 show the antisymmetry of the density functions $\sigma^{N}_{\alpha\beta}(\mathbf{r})$ $(\alpha \neq \beta)$ for the H atom and F^- ion, respectively. For these spherical systems α, $\beta = x$, y, and z are all related by symmetry so these densities integrate to zero as expected. For the sites of both the ^{1}H and ^{19}F nuclei in the HF molecule (with the z axis along the bond), x and y are related by symmetry. Figure 10 shows that the difference function

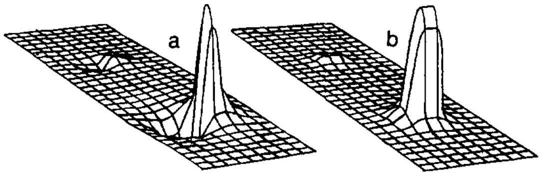

FIG. 10. Shielding density difference maps for the HF molecule, indicating the difference between the off-diagonal tensor components of the ^{1}H shielding densities: (a) shows the density difference $\sigma_{yz} - \sigma_{zy}$ and (b) shows the difference $\sigma_{xz} - \sigma_{zx}$. Note that σ_{yz} is the shielding tensor element corresponding to the y component of μ_N and the z component of the applied magnetic field, whereas σ_{zy} is the shielding tensor element corresponding to the z component of μ_N and the y component of the applied field. For the nuclear site symmetry of H in HF, these elements should be equal. Any difference observed must be a manifestation of the practical gauge invariance of the shielding calculation.

$\sigma^N_{yz}(\mathbf{r}) - \sigma^N_{zy}(\mathbf{r})$ does not vanish as it should in principle, indicating the inadequacy of the $P^{(1)\alpha}_{\nu\lambda}$ and $P^{(1)\beta}_{\nu\lambda}$ calculations. Similarly, $\sigma^N_{xz}(\mathbf{r}) - \sigma^N_{zx}(\mathbf{r})$ is nonvanishing. On the other hand, the function $\sigma^N_{xy}(\mathbf{r}) - \sigma^N_{yx}(\mathbf{r})$ (not shown) is zero everywhere because of symmetry.

CONCLUSIONS

We have discussed the general concept of a density function for a molecular electronic property. We have considered the origin dependence, in principle as well as in practice, of some electric and magnetic property densities. We explored the use of property density maps and density difference maps for the interpretation of changes in an electronic property upon molecule formation and upon bond extension. The utility of this concept appears promising.[22] We foresee an important application in providing a physical basis for or against qualitative interpretations of chemical effects on NMR shifts or other electronic properties. Any arguments based on constructs such as inductive effect and the like can be tested against density difference maps which do show where the contributions to the shifts are coming from. For example, a density difference map for ^{1}H shielding (hydrogen-bonded dimer minus isolated monomer) would be a good starting point for the discussion of hydrogen bonding shifts. This would be an improvement over a discussion of hydrogen bonding shifts based entirely on two calculated numbers, the calculated shielding parameters themselves, i.e., the integrated values. Property density difference maps for two or more related properties may be compared with one another and may also be compared with charge density difference maps. Such comparisons will elicit the changes in a given electronic property which accompany the polarizations and charge shifts shown by the charge density difference maps. They will also indicate the similarities and differences of two related properties and to what extent they assess different parts of the wave function or are measures of the same phenomenon. The variety of possible applications of property density maps appears to be virtually unlimited.

ACKNOWLEDGMENTS

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