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Properties of atoms in molecules: Magnetic susceptibilities

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The molecular magnetic susceptibility tensor χ is expressible as a sum of atomic or group contributions. An atomic contribution consists of a basin and a surface component; the former is given by the integral of a magnetization density over the basin of the atom, and the latter, by the integral of the flux in the position weighted current density through the interatomic surfaces that the atom shares with its bonded neighbors. The surface component is obtained as a consequence of the atomic hypervirial theorem defining the average of the velocity operator. Magnetic properties are determined by the observable electron current density, and the atomic behavior of this field has been correlated with corresponding behavior of the electron density. Thus the importance of the magnetization within an atomic basin relative to the flux in current through its interatomic surfaces parallels the extent to which the electron density is localized within the individual atomic basins. For example, 77% of the pronounced anisotropy in benzene arises from the flux in current through the interatomic surfaces of the ring atoms induced by a field applied perpendicular to the ring surface. The methyl and methylene group contributions to $\bar{\chi}$ are found to be transferable in the homologous series of hydrocarbons and to equal Pascal's group increments within experimental error.

INTRODUCTION

The magnetic susceptibility χ was among the earliest of properties to indicate that a molecular property could be equated to a sum of atomic or group contributions. This was first demonstrated by Henrichsen in 1888[1] who found an apparent, nearly constant contribution from the methylene group to the total magnetic susceptibility for a homologous series of hydrocarbons. The only way of experimentally demonstrating the existence of atomic additivity for a given property is to show that one can assign an atomic value, with an uncertainty less than the experimental error, that is applicable to that atom in all the members of a given series of molecules. Thus the experimental demonstration of atomic additivity demands satisfaction of two requirements—that each atom or group Ω makes a separate, *additive* contribution $M(\Omega)$ to the average value of a given property M, as expressed in Eq. (1),

$$\langle M \rangle = \sum_{\Omega} M(\Omega) \tag{1}$$

and that the value of this atomic contribution be *transferable* from one molecule to another throughout a given series. When both conditions are satisfied, one obtains so-called atomic or group additivity schemes for various properties. The existence of such schemes was demonstrated early on for the molar volumes,[2] molar refractions,[3] polarizabilities,[4] heats of formation,[5] and magnetic susceptibilities[6,7] for the normal hydrocarbons when expressed in terms of contributions from the methyl and methylene groups.

All additivity schemes exhibit discrepancies when the range of systems is extended beyond simple homologous or structurally related series of molecules. In Pascal's scheme,[7] e.g., the mean magnetic susceptibility $\bar{\chi}$, equal to one-third the trace of the tensor χ, is expressed as a sum of

atomic contributions, supplemented with a set of constitutive corrections, the constitutive corrections being assigned on the basis of the nature of the bonded interactions for the atom in question. This has led to the development of additivity schemes based on both atomic and/or bond increments for $\bar{\chi}$,[8,9] and to discussions of whether the atom or the bond is the fundamental quantity in determining the additive contributions for a given property. A general consensus of opinion arose that there was no theoretical justification for the atomic additivity expressed in Eq. (1), i.e., that a given property is determined by the sum of separate well-defined contributions from each atom in the system.

Attempts to obtain theoretical models for the additivity of the magnetic susceptibility using orbital theories have led to the same conclusions. Pople[10] developed a model of Pascal's scheme based on the linear-combination-of-atomic-orbitals (LCAO) expansion of molecular orbitals expressed in terms of GIAOs with the neglect of overlap-type integrals. This scheme was criticized by Haberditzl[9] and by Hameka,[11] the latter author having proposed a model based on the concept of a bond susceptibility, as expressed in terms of localized bond orbitals.[12] More recently, Zanasi and Lazzeretti[13] have proposed a partitioning of $\bar{\chi}$ into atomic contributions, using the Mulliken[14] partitioning of the total density to determine the diamagnetic contributions. All three orbital approaches calculate separate paramagnetic and diamagnetic contributions to $\bar{\chi}$, thereby introducing an unnecessary gauge dependence into the results.

The theory of atoms in molecules establishes the quantum mechanical basis for the atomic additivity expressed in Eq. (1) for all properties.[15] It also determines the condition which must be met for an atomic value to be transferable from one system to another to give an additivity scheme. This theory has been shown to recover the experimentally observed additivity schemes for the molar vol-

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umes,[16] heats of formation,[17] and polarizabilities[18] of the normal hydrocarbons, as well as predicting the measured strain energies of cyclic hydrocarbons,[17] energies which are defined relative to the energy of the transferable methylene group of the acyclic series. The present paper demonstrates that the theory of atoms in molecules recovers Pascal's methyl and methylene group contributions to $\bar{\chi}$. The demonstration that the group incremental values for a given property predicted by theory equal those measured in the laboratory for a series of molecules is the basis for the identification of the atoms of theory with those of experiment.

While additivity schemes provide a touchstone with the experimental evidence for atoms in molecules, the principal purpose of this paper is to provide a physical basis for the interpretation and prediction of the molecular magnetic susceptibility by relating it to the atomic behavior of the observable current density.

The theory of atoms in molecules is based on an extension of the principle of stationary action to a subsystem bounded by a surface of zero flux in the gradient vector field of the electron density [Eq. (6) of the preceding paper[19]]. The operative statement is given in terms of a variational statement of the Heisenberg equation of motion for an observable $\hat{G}$,[15]

$$\delta\mathscr{L}(\Psi,\Omega,A) = (1/2)[(i/\hbar)\langle[\hat{H},\hat{G}]\rangle_\Omega + cc], \qquad (2)$$

where the functional dependence of the Lagrangian integral $\mathscr{L}$ on the vector potential $\mathbf{A(r)}$ indicates that the variational principle applies to a system in the presence of a magnetic field.[20]

It is known that gauge invariance in the presence of such a field ensures the equation of continuity, or conservation of the current in a stationary state.[21] These results are obtainable from Eq. (2), when Ω refers to the total system by setting the generator $\hat{G}$ equal to an operator describing families of gauge transformations for the vector potential $\mathbf{A(r)}$. The corresponding atomic statements of these results are also obtained directly from Eq. (2) by considering the gauge transformations given by $\mathbf{A'}=\mathbf{B}\times(\mathbf{r}+\mathbf{d})/2$, where $\mathbf{r}$ is the electronic position vector and $\mathbf{d}$ is its displacement. The commutator $(i/\hbar)[\hat{H}(\mathbf{A}),\mathbf{r}]$ equals the velocity operator $\hat{r}(\mathbf{r})/m$ defined in Eq. (4) of the previous paper.[19] It is the appropriate averaging of this operator that yields the velocity or current density $\mathbf{J(r)}$ [Eq. (5) of the previous paper[19]]. Thus the atomic average of the commutator, the right-hand side of Eq. (2), for $\hat{G}=\hat{r}$ yields $\mathbf{J}(\Omega)$, the atomic average of the electron velocity

$$\mathbf{J}(\Omega) = \int_\Omega \mathbf{J(r)}dr. \qquad (3)$$

For a stationary state, the variation in the atomic Lagrangian induced by the action of the generator $\mathbf{r}$, the left-hand side of Eq. (2), equals the position weighted flux of $\mathbf{J(r)}$ through the atomic surface, and thus the atomic statement of the hypervirial theorem for a shift in gauge origin is given by[22]

$$\mathbf{J}(\Omega) = \oint dS\, \mathbf{J(r)r\cdot n(r)}. \qquad (4)$$

This result can also be obtained through the use of the identity given in Eq. (5)[15]

$$\mathbf{\nabla\cdot[J(r)r]} = \mathbf{J(r)} + \mathbf{r\nabla\cdot J(r)} \qquad (5)$$

and the requirement given in Eq. (6) that the current be conserved in a stationary state

$$\mathbf{\nabla\cdot J(r)} = 0. \qquad (6)$$

Hence Eq. (4) implies conservation of the current over each atomic basin.

DEFINITION OF ATOMIC CONTRIBUTIONS TO THE MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility can be expressed as

$$\chi\cdot\mathbf{B} = (1/2c)\int \mathbf{r}\times\mathbf{J}^{(1)}(\mathbf{r})dr \qquad (7)$$

as shown in Eq. (15) of the preceding paper.[19] Following Jameson and Buckingham,[23] one defines a magnetizability density $\chi(\mathbf{r})$ as

$$\mathbf{m}^{(1)}(\mathbf{r}) = \chi(\mathbf{r})\cdot\mathbf{B} = (1/2c)\mathbf{r}\times\mathbf{J}^{(1)}(\mathbf{r}). \qquad (8)$$

The component of the magnetization density in the direction i resulting from the current induced by a unit field applied in the direction k, $\mathbf{J}^{k(1)}$, is given by

$$\chi_{ik}(\mathbf{r}) = (1/2Bc)[\mathbf{r}\times\mathbf{J}^{k(1)}(\mathbf{r})]_i. \qquad (9)$$

Its integration over all space yields the corresponding component of the symmetrical magnetic susceptibility tensor χ. The magnetization density as written is origin dependent. The definition of an atomic contribution must be origin independent if theory is to recover the experimental observation of transferable group contributions to the mean susceptibility $\bar{\chi}$.

The theory of atoms in molecules has shown that the extent of transferability of any atomic property, including one induced by an external field, is determined by the corresponding extent of transferability of the atom's electron density. If an atom has the same form in two systems, it contributes the same amounts to all properties in both systems, paralleling in the limit, the behavior observed for two identical isolated systems.[24] Thus it should be possible to state the definition of an atomic contribution to χ and hence to $\bar{\chi}$ entirely in terms of contributions determined by the current within the basin of the atom and by its flux through the atomic surface. This is accomplished by making the substitution $\mathbf{r}=\mathbf{r}_\Omega+\mathbf{X}_\Omega$, where $\mathbf{r}_\Omega$ is the electronic position vector measured from nucleus Ω with position vector $\mathbf{X}_\Omega$. This yields

$$\chi_{ik}(\mathbf{r}) = (1/2Bc)[(\mathbf{r}_\Omega+\mathbf{X}_\Omega)\times\mathbf{J}^{k(1)}(\mathbf{r})]_i. \qquad (10)$$

Integration of this density over each atom in the system, using Eq. (3) for the definition of $\mathbf{J}^{(1)}(\Omega)$, yields (to simplify notation, the remaining discussion is given in terms of the vector quantity $\mathbf{D}$ χ)

$$\mathbf{B} \cdot \int \chi(\mathbf{r}) d\mathbf{r} = \sum_{\Omega} [\mathbf{B} \cdot \chi_b(\Omega) + (1/2c)\mathbf{X}_{\Omega} \times \mathbf{J}^{(1)}(\Omega)], \tag{11}$$

where $\chi_b(\Omega)$ is the contribution to χ arising from the magnetization of the density in the basin of atom Ω,

$$\mathbf{B} \cdot \chi_b(\Omega) = (1/2c) \int_{\Omega} \mathbf{r}_{\Omega} \times \mathbf{J}^{(1)}(\mathbf{r}) d\mathbf{r} \tag{12}$$

and the origin dependence is relegated to the terms involving the nuclear coordinates. These terms, when properly grouped together, describe the contribution to the atomic magnetization resulting from the flux in the position weighted current through the surface of the atom, as obtained using the atomic hypervirial theorem for $\hat{G} = \mathbf{r}$ [Eq. (4)]. Thus the atomic expression for χ is given by a basin and a surface term

$$\mathbf{B} \cdot \chi(\Omega) = \mathbf{B} \cdot \chi_b(\Omega) + \mathbf{B} \cdot \chi_f(\Omega), \tag{13}$$

where $\chi_b(\Omega)$ is defined in Eq. (12) and the surface contribution $\chi_f(\Omega)$, which is proportional to the flux in $\mathbf{J}^{(1)}(\mathbf{r})\mathbf{r}$ across the atomic surface, is given by

$$\mathbf{B} \cdot \chi_f(\Omega) = (1/2c) \sum_{\Omega'} [\mathbf{X}^c(\Omega|\Omega') - \mathbf{X}_{\Omega}]$$

$$\times \oint dS(\Omega|\Omega',\mathbf{r}) \mathbf{J}^{(1)}(\mathbf{r})\mathbf{r} \cdot \mathbf{n}'(\mathbf{r}), \tag{14}$$

where $\Omega' \neq \Omega$. The sum runs over every atom or group Ω' linked to atom Ω by a bond path and sharing with it an interatomic surface denoted by $S(\Omega|\Omega',\mathbf{r})$. An interatomic surface is defined by the trajectories of $\nabla\rho$ which terminate at the position of the corresponding bond critical point, denoted by the vector $\mathbf{X}^c(\Omega|\Omega') = \mathbf{X}^c(\Omega'|\Omega)$ (Fig. 1). The unit vector $\mathbf{n}'(\mathbf{r})$ is outwardly directed from the basin of Ω'. The surface terms vanish if the current flow is totally contained within the basin of the atom and thus $\chi_f(\Omega)$ is a measure of the extent to which the current trajectories are contiguous over the basins of adjoining atoms, resulting in a flow of current across the interatomic surfaces.

The surface integral is origin independent, as is clear from Eq. (4), and through the use of this equation, one can show that the sum of $\chi(\Omega)$ over all of the atoms in a molecule yields the molecular value for χ. The flux in $\mathbf{J}^{(1)}(\mathbf{r})\mathbf{r}$ through the surface $S(\Omega|\Omega')$ can be replaced by the integral of the current over the group Ω' [Eq. (4)]

$$\mathbf{J}^{(1)}(\Omega') = \oint dS(\Omega|\Omega',\mathbf{r}) \mathbf{J}^{(1)}(\mathbf{r})\mathbf{r} \cdot \mathbf{n}'(\mathbf{r}). \tag{15}$$

With this substitution, the atomic summation of Eq. (14) yields

$$\sum_{\Omega} \sum_{\Omega'} [\mathbf{X}^c(\Omega|\Omega') - \mathbf{X}_{\Omega}] \times \mathbf{J}^{(1)}(\Omega')$$

$$= \sum_{\Omega} \sum_{\Omega'} \mathbf{X}^c(\Omega|\Omega') \mathbf{J}^{(1)}(\Omega')$$

$$+ \sum_{\Omega} \mathbf{X}_{\Omega} \times \mathbf{J}^{(1)}(\Omega) = \sum_{\Omega} \mathbf{X}_{\Omega} \times \mathbf{J}^{(1)}(\Omega). \tag{16}$$
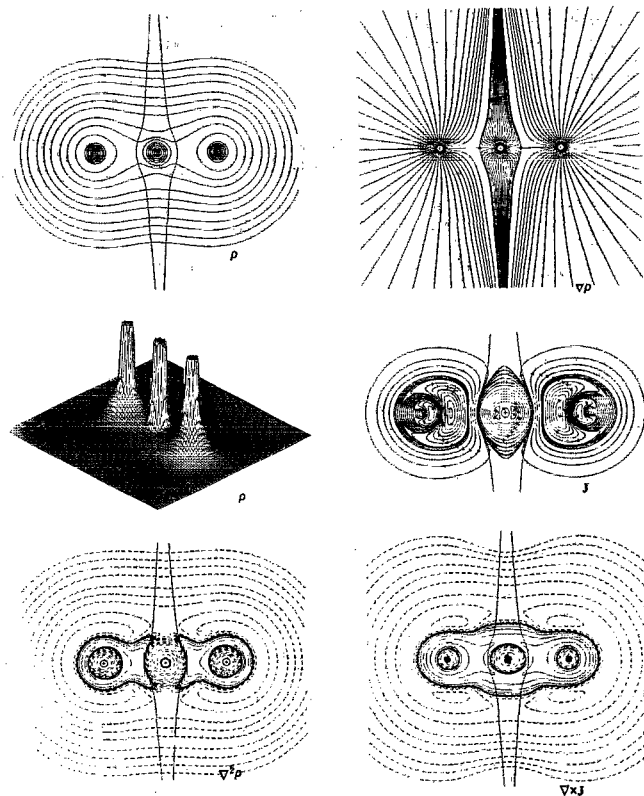

FIG. 1. Displays of scalar and vector fields for carbon dioxide for a plane containing the nuclei. Contour and relief maps are shown for the electron density ρ and a contour map for the Laplacian $\nabla^2\rho$. Solid (dashed) contours in the latter map denote regions of charge concentration (depletion). The atomic basins and surfaces are defined in terms of the trajectories of $\nabla\rho$. The bond critical points are denoted by dots. They serve as the termini for the trajectories defining the interatomic surfaces whose intersection with this plane are indicated in all the planar displays. The displays of the current and its curl are for an applied field directed out of and perpendicular to the plane of the diagram. Solid (dashed) contours in the curl map denote an inwardly (outwardly) directed flux of the vorticity lines. Note the similarity in the shell structure exhibited by the $\nabla^2\rho$ and $\nabla \times J$ fields.

Since $\Sigma_{\Omega'}\mathbf{X}^c(\Omega|\Omega') \times \mathbf{J}^{(1)}(\Omega') = -\mathbf{X}^c(\Omega'|\Omega) \times \mathbf{J}^{(1)}(\Omega)$, the first term on the right-hand side vanishes. This result and the final term are obtained using the identity $\Sigma_{\Omega'}\mathbf{J}^{(1)}(\Omega') = -\mathbf{J}^{(1)}(\Omega)$, which follows from the atomic summation of Eq. (4)

$$\sum_{\Omega} \mathbf{J}^{(1)}(\Omega) = \int \mathbf{J}^{(1)}(\mathbf{r}) d\mathbf{r} = 0, \tag{17}$$

or from Eq. (5) by its integration over all space. Thus the atomic summation of the basin and surface terms is equivalent to the integration of the magnetization density over all space [Eq. (11)].

Corresponding basin and surface terms arise in the definition of the atomic contribution to the dipole moment or to the change in this moment induced by an external field, the polarizability. For these properties, the substitution $\mathbf{r} = \mathbf{r}_{\Omega} + \mathbf{X}_{\Omega}$ yields a basin term corresponding to the static dipolar polarization of the atomic charge distribution $\mathbf{M}(\Omega)$, or the corresponding field induced quantity $\alpha_b(\Omega)$. The origin dependent terms are of the form $\mathbf{X}_{\Omega}q(\Omega)$ [cf.

Eq. (11)], where $q(\Omega)$ is the static or induced atomic charge, i.e., the terms resulting from the interatomic transfer of charge, static or field induced. Here, as in the magnetic susceptibility, the origin dependence is removed by making use of the fact that the atomic property involved in these terms vanishes when summed over all the atoms in the molecule, i.e., cf. Eq. (17)

$$\sum_\Omega q(\Omega) = 0. \qquad (18)$$

Thus the atomic contribution to the polarizability can be expressed as

$$\alpha(\Omega) = \alpha_p(\Omega) + \alpha_c(\Omega)$$

$$= \int_\Omega \mathbf{r}_\Omega \rho^{(1)}(\mathbf{r}) d\mathbf{r} + \sum_{\Omega'} [\mathbf{X}^c(\Omega|\Omega') - \mathbf{X}_\Omega] q^{(1)}(\Omega'), \qquad (19)$$

where the contribution to α arising from the polarization of the density over the basin of the atom $\alpha_p(\Omega)$ is defined in analogy with Eq. (12). The second term arises from the transfer of charge between the atoms. Its apparent dependence on net charges of atoms or groups bonded to Ω can be removed using Poisson's equation, which replaces each $q^{(1)}(\Omega)$ with the surface integral of the associated flux in the electric field[25]

$$\alpha_c(\Omega) = (-1/4\pi) \sum_{\Omega'} [\mathbf{X}^c(\Omega|\Omega') - \mathbf{X}_\Omega]$$

$$\times \oint dS(\Omega|\Omega',\mathbf{r}) \mathbf{E}^{(1)}(\mathbf{r}) \cdot \mathbf{n}'(\mathbf{r}), \qquad (20)$$

where $\mathbf{E}(\mathbf{r})^{(1)}$ is the electric field defined by the electrostatic potential. Thus the atomic contribution to the polarizability [or to the molecular dipole moment with $\rho^{(1)}(\mathbf{r})$ replaced by $\rho(\mathbf{r})$] can be expressed as a sum of a basin and a surface term where the surface term is determined by the flux in the electric field, arising from the interatomic charge transfer, through the interatomic surfaces $S(\Omega|\Omega')$ bounding atom Ω. Previous accounts of the atomic contributions to the polarizability[18] employed Eq. (19) for α_c, rather than Eq. (20) as given here. Of course, both equations yield identical results.

The only proof that these definitions of field induced atomic properties have physical relevance is to demonstrate that they recover the measured additive contributions to $\bar\alpha$ and $\bar\chi$ in a homologous series of molecules. This has already been demonstrated for the mean polarizability of the methyl and methylene groups for the normal hydrocarbons[18] and, as demonstrated here, Pascal's values for the mean magnetic susceptibility of these same groups are also faithfully reproduced by the theory of atoms in molecules.

While an electric field results in a first-order change in the charge density and causes measurable shifts in the interatomic surfaces,[26] the first-order correction to $\rho(\mathbf{r})$ vanishes for an applied magnetic field, since $\psi^{(1)}$ is pure imaginary. Magnetic fields of strengths used experimentally cause no calculated change to $\rho(\mathbf{r})$ or to its dependent

properties such as the interatomic surfaces and associated critical points.

It is important to note that $\chi(\Omega)$, like all atomic properties, is completely determined by the electronic charge or current distribution of just atom Ω. The atomic statement of Ehrenfest's theorem, the atomic force theorem,[15] shows that the properties of the atom are totally determined by the mechanical and magnetic pressures acting on each element of area in its atomic surface $S(\Omega,\mathbf{r})$. An atom and its properties are transferable between systems to the extent that its atomic surface remains unchanged by the transfer.[20] It will be demonstrated that the vector current generated by an external magnetic field within an atomic basin and its position weighted flux through the atomic surface exhibit the same degree of transferability as does the atom's distribution of charge.

All of the current distributions and calculated values of χ and $\bar\chi$ reported here are determined using either the individual gauges for atoms in molecules (IGAIM) method or the method of continuous gauge transformations.[27] These methods yield values for $\bar\chi$ which, in general, are in agreement with experiment. The coupled-perturbed Hartree–Fock procedure is used for the calculation of $\mathbf{J}^{(1)}(\mathbf{r})$, as coded in CADPAC.[28] All calculations use the $6\text{-}311++G(2d,2p)$ set of basis functions[29] with the exception of those for pentane for which the diffuse function on H was omitted due to disk size limitations. Values for χ are reported in units of 1×10^{-6} cgs emu, abbreviated in the text to "u."

ATOMIC CONTRIBUTIONS TO χ

CO_2—a polar charge distribution

In ionic and polar molecules, both the contours of the electron density and the trajectories of the current density exhibit atomic-like behavior. This is exemplified by molecular currents displayed in the previous paper[19] and in Fig. 1 of this paper which shows the atomic-like nature of the physically important fields ρ, $\nabla\rho$, $\nabla^2\rho$, $\mathbf{J}^{(1)}$, and $\nabla\times\mathbf{J}^{(1)}$ for the carbon dioxide molecule. The presence of paramagnetic currents in the basin of the electropositive atom is a general feature of systems with significant interatomic charge transfer for a field applied perpendicular to the direction of charge transfer. In such systems, the interatomic surfaces are placed so as to almost totally contain the associated current loops. A comparison of the maps for $\mathbf{J}^{(1)}$ and $\nabla\times\mathbf{J}^{(1)}$ show that the center points for the paramagnetic flows in the C and O basins occur within the shell of outward flux in the curl of J, i.e., in the direction of the applied field as required by Stoke's theorem. Note the similarities in the shell structures exhibited by the Laplacian of $\rho(\mathbf{r})$ and the curl of $\mathbf{J}^{(1)}(\mathbf{r})$.

The circular diamagnetic current flow about the internuclear axis induced by a field parallel ($\parallel$) to this axis makes the largest single atomic contribution to $\bar\chi$ for carbon dioxide (Table I) for which the experimental value is -21.0 u.[19] There is no net flux in this current through the interatomic surfaces and thus there are no surface contributions to $\chi_\parallel$. Since the current flows for a perpendicular

TABLE I. Atomic contributions to magnetic susceptibility in CO_2. Units are cgs ppm.

Atom Ω	$\chi_b^\perp (\Omega)$	$\chi_b^\parallel (\Omega)$	$\bar{\chi}_b(\Omega)$	$\chi_f^\perp (\Omega)$	$\chi_f^\parallel (\Omega)$	$\bar{\chi}_f(\Omega)$	$\chi_\perp$	$\chi_\parallel$	$\bar{\chi}$
C	+0.96	−2.16	−0.08	−0.91	0.00	−0.61	+0.05	−2.16	−0.69
O	−8.98	−11.92	−9.96	−0.86	0.00	−0.58	−9.85	−11.92	−10.54
CO_2	−17.00	−26.00	−20.01	−2.65	0.00	−1.77	−19.66	−26.00	−21.78

field ($\perp$) are atomic-like in this polar system, the surface contributions to $\chi_\perp$ are relatively small in magnitude, the flux in the position weighted current through the interatomic surfaces contributing only 9% to the total susceptibility. The carbon basin contribution to $\chi_\perp$ is positive, as a consequence of the dominance of the paramagentic flow within the basin of this atom, while the corresponding contributions for the larger oxygen basins, which are dominated by diamagnetic currents, are negative and large in magnitude. The atomic contributions to $\bar{\chi}$ and hence the value of $\bar{\chi}$ itself are understandable in terms of the atomic properties of the current density and the atomic-like shell structure exhibited by the curl of $J^{(1)}$.

Benzene—a delocalized charge distribution

The atomic-like form of the current in CO_2 is to be contrasted with the situation in benzene for a field applied parallel to the principal symmetry axis [Fig. 2(a)]. In this molecule, the fluxes in the current through the carbon–carbon interatomic surfaces account for 60% of the parallel component of the magnetic susceptibility (Table II). The current maps are calculated using the continuous origin method, while the data in Table II are obtained using IGAIM. Lazzeretti et al.[30,31] and Augspurger and Dykstra[32] have also reported calculations of the magnetic properties of benzene using a single gauge origin at the charge centroid. Lazzeretti et al.[31] use basis sets of increasing size, up to one consisting of 474 primitives, contracted to 396 basis functions, the latter yielding values for $\bar{\chi}$ and its anisotropy $\Delta\chi = \chi_\parallel - \chi_\perp$ of −62.7 and −68.2 u, respectively. Augspurger and Dykstra use a basis set comparable to the one employed here and obtain values for $\bar{\chi}$ and $\Delta\chi$ of −89.62 and −48.59 u, respectively. Both sets of results are in poorer agreement with the experimental values of −54.8 u for $\bar{\chi}$ (Ref. 33) and −59.7 u for $\Delta\chi$ (Ref. 34) than are the results obtained here.

A set of diamagnetic current loops and its contained center point is found in each of the C–C and C–H bonded regions, with the center points for the former lying in the C–C interatomic surfaces [Fig. 2(a)]. Bonded sets of current loops are characteristic of a *shared* atomic interaction,[15] one for which the Laplacian of ρ exhibits a corresponding shared charge concentration in the bonded region [Fig. 2(d)]. The curl of the $J^{(1)}$ map [Fig. 2(c)] mimics not only the shell structure of $\nabla^2\rho$, but also its bonded features, the flux antiparallel to B in the valence shell of $\nabla \times J^{(1)}$ for a carbon atom forming three shared regions with its bonded neighbors. There are two more center points in the basin of each carbon atom. One is slightly displaced off the nucleus and serves as a center for a dia-

magnetic flow. The other is found in the core shell where the flux in the curl of J is parallel to B and thus serves as the center for a paramagnetic flow.

The outermost valence shell in $\nabla \times J$ for the carbon atoms overlap one another in the ring's interior. Since the flux in this shell is parallel to B, the (2,0) center point at the ring center and its associated stagnation path serve as the axis for a set of paramagnetic current loops. Thus the shell structure of the curl of J provides a simple explanation of the origin of the central paramagnetic current in benzene. This behavior could be predicted on the basis of the analogous shell structure exhibited by $\nabla^2\rho$, which is positive in the ring interior, as a result of the overlap of the corresponding valence shells of charge depletion of the atoms forming the ring.

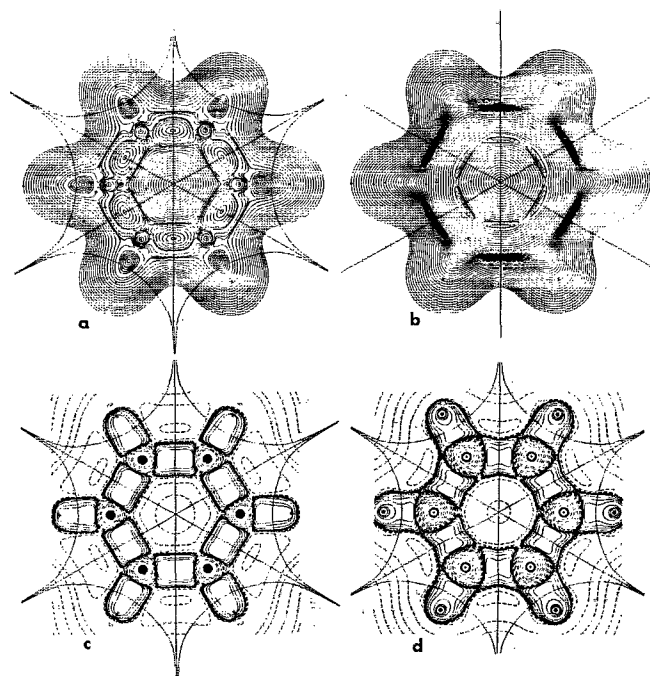Outer current loops of relatively small magnitude encompass the entire molecule in the plane of the nuclei.

FIG. 2. Displays of the current density, its curl, and the Laplacian of ρ for the benzene molecule in the plane containing the nuclei. The maps for $J^{(1)}$ and its curl are for a field directed out of and perpendicular to the plane. In (a) the current density is shown in the symmetry plane. (b) is a projection onto a plane 0.8 a.u. above the symmetry plane of the trajectories which intersect it. In addition to the outer diamagnetic and inner paramagnetic flows, there is a vestige of each bonded set of diamagnetic current flows present. The shell structure and regions of charge concentration/depletion defined by $\nabla^2\rho$ in (d) are similar to the shell structure and regions of outwardly/inwardly directed flux in the $\nabla \times J^{(1)}$ field in (c).

TABLE II. Atomic contributions to magnetic susceptibility in benzene. Units are cgs ppm.

Atom Ω	$\chi_b^\perp(\Omega)^a$	$\chi_b^\parallel(\Omega)^b$	$\bar{\chi}_b(\Omega)$	$\chi_f^\perp(\Omega)^a$	$\chi_f^\parallel(\Omega)^b$	$\bar{\chi}_f(\Omega)$	$\chi_\perp{}^a$	$\chi_\parallel{}^b$	$\bar{\chi}$
C	−2.23	−3.56	−2.67	−0.56$^{H\ c}$ −1.79$^{R\ d}$ −2.35$^{T\ e}$	−1.35$^{H\ c}$ −10.48$^{R\ d}$ −11.83$^{T\ e}$	−0.82$^{H\ c}$ −4.68$^{R\ d}$ −5.51$^{T\ e}$	−4.57	−15.39	−8.18
H	−1.29	−1.29	−1.29	−0.33	−0.79	−0.48	−1.62	−2.08	−1.77
C$_6$H$_6$	−21.10	−29.11	−23.77	−16.08	−75.72	−35.96	−37.18	−104.83	−59.73

$\Delta\chi = -67.65$	$6\Delta\chi(C) = -64.92$	$6\Delta\chi(H) = -2.76$
$\Delta\chi_f = -59.64$	$6\Delta\chi_f(C) = -56.88$	$6\Delta\chi_f(H) = -2.76$
$\Delta\chi_b = -8.01$	$6\Delta\chi_b(C) = -7.98$	$6\Delta\chi_b(H) = 0.00$

[a]The symbol $\perp$ refers to axes perpendicular to the principal rotation axis and corresponding atomic values are averaged over both $\perp$ field directions.
[b]The symbol $\parallel$ refers to the principal rotation axis.
[c]H refers to current flux through C|H surface.
[d]R refers to current flux through C|C surfaces in a ring.
[e]T refers to total current flux contribution.

However, for planes sufficiently displaced from the symmetry plane, only the central stagnation line remains for a diamagnetic current flow encompassing the entire molecule. For a plane displaced by 0.8 a.u. [Fig. 2(b)] the current map exhibits an outer diamagnetic flow bounding an inner paramagnetic flow. The diamagnetic current flow about the ring contributes substantially to the position weighted flux of $\mathbf{J}^{(1)}$ through the interatomic surfaces of the atoms forming the ring. Figure 3 displays the current induced by a field applied in the plane of the ring. The distribution is more atomic-like in this case, exhibiting a separate center point and an associated set of current loops in the basin of each hydrogen atom.

The carbon basin contributions to χ exhibit a relatively small anisotropy. Its origin is made clear in terms of the current density map for a $\perp$ field shown in Fig. 3, which shows the presence of a substantial paramagnetic current localized in the basin of a carbon atom. The surface terms are three times the magnitude of the basin term for a $\parallel$ field. The largest of the surface terms arise from the flux in the current induced by a parallel field through the inter-atomic surfaces separating the atomic basins in the ring of bonded carbon atoms. These C|C surface terms exhibit a large anisotropy, equal to -8.7 for a single carbon atom. This is the origin of the large anisotropy in χ observed for benzene and it is a direct result of the delocalized nature of the current induced by a parallel field shown in Fig. 2(a) compared to its atomic-like nature when induced by a perpendicular field shown in Fig. 3. The contributions to $\bar{\chi}$ from current fluxes through the C–H interatomic surface are relatively small for both C and H and the basin contributions to χ(H) exhibit no anisotropy. Ninety-six percent of the value of $\Delta\chi$ calculated for the gas phase comes from the carbon atom contributions, 77% having its origin in a current flowing from the basin of one carbon atom into that of its neighbor. The current plot in Fig. 2(b) and the relative values of the basin to surface contributions to $\bar{\chi}$ (C) confirm the existence of a significant diamagnetic current encompassing the ring of the benzene molecule.

PREDICTION OF PASCAL'S ATOMIC SUSCEPTIBILITIES FOR HYDROCARBONS

Table III lists the calculated values of $\bar{\chi}$ and the diagonal elements $\chi_\parallel$ and $\chi_\perp$ of the tensor χ for the normal hydrocarbons together with the experimental values for $\bar{\chi}$. The symbols $\parallel$ and $\perp$ denote the longitudinal and perpendicular components, respectively, with the latter pair differentiated with subscripts i and o to denote the contributions directed *in* and *out* of the plane containing the carbon nuclei and two of the terminal protons (see Fig. 4). The magnetic susceptibilities of these molecules, unlike their polarizabilties,[18] do not exhibit large anisotropies. The value of $\Delta\chi$ decreases slightly from ethane to pentane, while the corresponding anisotropies in the polarizability increase nearly fivefold. The nonlinear increase in $\alpha_\parallel$ with chain length results from a field induced transfer of charge over the length of the molecule.

Table IV lists the contributions from the methyl and methylene groups to $\bar{\chi}$, together with the separate contributions $\bar{\chi}_b$ and $\bar{\chi}_f$. The group contributions to $\bar{\chi}$ exhibit the same pattern of transferability as do the corresponding group contributions to the volume, energy, first moment,
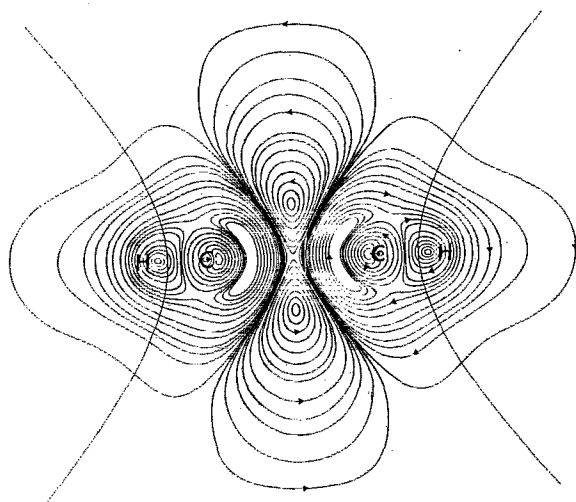

FIG. 3. A map of the current density in benzene in a plane perpendicular to the plane of the nuclei and containing a C_2 axis passing through the nuclei of two C–H groups.

TABLE III. Calculated magnetic susceptibility tensor χ in hydrocarbons. Units are cgs ppm.

Molecule	$\chi_{\perp i}$	$\chi_{\perp 0}$	$\chi_{\parallel}$	$\bar{\chi}$	Increment	$\bar{\chi}$(Expt.)[a]
CH_4	-18.20	-18.20	-18.20	-18.20		$(-18.7, -17.4)$
C_2H_6	-26.94	-26.94	-31.63	-28.50	-10.30	$(-27.4, -26.8)$
C_3H_8	-40.08	-38.79	-42.35	-40.41	-11.91	$(-40.5, -38.6)$
C_4H_{10}	-51.00	-50.41	-55.19	-52.20	-11.79	(-50.0)
C_5H_{12}	-62.93	-61.75	-65.95	-63.54	-11.34	(-63.1)

[a]Experimental values are from Ref. 35.

and mean polarizability. Reference 18 provides a full discussion of this point. Briefly, a methyl group in molecules following ethane in the series is bonded to a methylene group from which it withdraws a small fixed amount of charge $-0.018e$, an amount independent of chain length. The decrease in energy of the methyl group resulting from this charge transfer is equal to the increase in energy of the methylene group and, consequently, energy as well as charge is conserved. The value of $\bar{\chi}(CH_3)$ in ethane is therefore somewhat less than its value for the methyl groups in the remaining molecules, for which it remains essentially constant. The value of $\bar{\chi}(CH_2)$ for the methylene group in propane, since it contributes charge and energy to two methyl groups, is slightly less than the value of $\bar{\chi}(CH_2)$ for the other molecules wherein two methylene groups are each bonded to but a single methyl.

The transfer of charge and energy from CH_2 to CH_3 is damped by a single group and thus the central methylene group in pentane should exhibit a zero net charge and possess the energy of the repeating transferable methylene group labeled CH_2^0. The difference in $\bar{\chi}(CH_2)$ for this methylene group and those bonded to a single methyl is so small for the magnetic susceptibility that the value $\bar{\chi}(CH_2^0)$ for the central group in pentane falls within the average value of those obtained for the methylene groups bonded to a single methyl.

The value of $\bar{\chi}(CH_3)$ for the transferable methyl group is -14.50 u with a mean deviation equal to 0.02 u, which is smaller than the experimentally measured variations in the value of $\bar{\chi}$ for the normal hydrorcarbons. The same degree of transferability is found for the methylene groups, with $\bar{\chi}(CH_2)$ equal to -11.54 u. The value assigned to the

central methylene group in pentane is equal to the incremental difference in the values of $\bar{\chi}$ for the butane and pentane molecules to within 2%. Thus, theory defines the transferable methyl and methylene groups in this series of molecules. The transferable nature of the current for these groups is illustrated by the displays of the magnitude and the curl of J for the butane and pentane molecules (Fig. 4).

The central transferable methylene group may be represented symbolically by $|CH_2^0|$, with the vertical bars denoting the two interatomic surfaces linking the group to the remainder of the molecule, and graphically through a display of the two interatomic surfaces and their intersection with the 0.001 a.u. envelope of the electronic charge density (Fig. 5). This envelope determines the van der Waals shape of the group and replaces those portions of the atomic surfaces which occur infinitely far from the nuclei. This distribution of charge in real space, up to and including the interatomic surfaces, is transferable without detectable change from pentane on, in the succeeding members of the homologous series. Thus, as demanded by the atomic force theorem, it contributes a constant amount to the average value of each property in every molecule in which it occurs. These properties include those induced by externally applied fields and it is therefore an observation that *if the charge density of an atom is transferable between systems, then so is the field induced current density and its derived properties.*

The theoretical group values are close to the corresponding contributions quoted by Pascal and Pacault,[7] equal to 14.2 u for methyl and 11.4 u for methylene, values obtained by fitting experimental values of $\bar{\chi}$ for a wide range of molecules. Taking into account the spread displayed by the experimentally determined group values which can be as large as 1 u, it is clear that the methyl and methylene groups of theory recover the experimentally observed additivity of the magnetic susceptibility for the hydrocarbon molecules. They do in fact predict a greater degree of transferability than has so far been experimentally observed with present techniques.

The same pattern in transferable values is exhibited by the basin and surface flux contributions to the group values. The surface flux contributions to $\bar{\chi}$ are comparable to those from the atomic basins, a reflection of the shared nature of the valence electron density and current in these molecules, as illustrated by the maps of the current density shown for ethane in Fig. 6. There are internal flux contributions from the C–H surfaces and another from the ex-
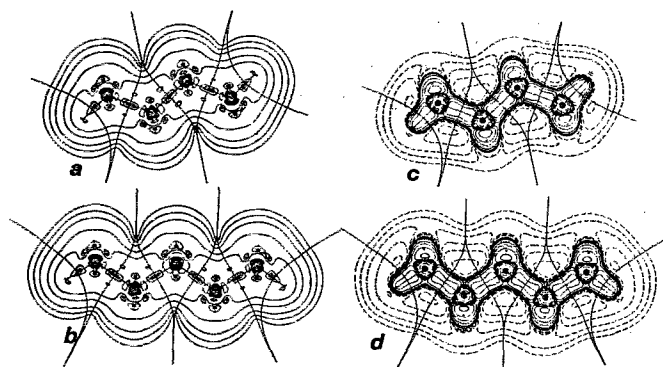

FIG. 4. Maps of the magnitude and curl of the current density for butane and pentane in a plane containing the carbon nuclei.

TABLE IV. Group contributions to magnetic susceptibility tensor in hydrocarbons. Units are cgs ppm.

Molecule	Methyl group			Methylene group		
	$\bar{\chi}_b(\Omega)$	$\bar{\chi}_f(\Omega)$	$\bar{\chi}(\Omega)$	$\bar{\chi}_b(\Omega)$	$\bar{\chi}_f(\Omega)$	$\bar{\chi}(\Omega)$
CH_4	−9.81	−6.22	−16.03			
C_2H_6	−8.45	−5.80	−14.25			
C_3H_8	−8.37	−6.11	−14.48	−6.06	−5.39	−11.45
C_4H_{10}	−8.38	−6.15	−14.53	−5.96	−5.61	−11.57
C_5H_{12}	−8.37	−6.12	−14.49	−5.96	−5.55	−11.51
C_5H_{12}	(Unique methylene)			−5.83	−5.71	−11.54

ternal C–C surface, which total -1.27 ± 0.01 u for a transferable methyl group. A methylene group has two external C|C interatomic surfaces and two such contributions per group (Fig. 5). The corresponding contribution to $\bar{\chi}_f(CH_2)$ for the flux through each C|C surface is -1.31 ± 0.04 u, close to the corresponding value for the methyl group. The individual atomic contributions to the group values exhibit the same degree of constancy as found for the complete group, the value of $\bar{\chi}_b(H)$ for one of the two equivalent hydrogens of methyl, e.g., exhibiting a variation of ± 0.01 u about a mean value of -1.47 u. Because of the constancy in the charge distributions of the methyl and methylene groups in this series, all properties are similarly preserved. Thus the sum of the atomic averages of r_Ω^2, a quantity assumed to be proportional to the diamagnetic contribution in the modeling of $\bar{\chi}$, has the value 13.83 a.u. for methyl and 11.74 a.u. for methylene.

It is possible to observe an almost constant transferable contribution to $\bar{\chi}$ even from a very electronegative group such as |OH or |F in a homologous series if the group is buffered by one or more methylene groups. This is illustrated by the data in Table V which lists a number of properties for the OH and F groups in H|OH and H|F along with the values of ρ and $\nabla^2\rho$ at the bond critical point. Succeeding entries in Table V give the changes in the values of the properties, relative to the values for the preceding compound, for the addition of each CH_2 group. The values of all properties change considerably when a methylene group is interspersed between H and the electronegative group X to transform HX into the methyl derivative.

The addition of a second methylene group causes only small changes, changes which become smaller still for the addition of the third methylene group to give the propyl derivative. Even with three methylene groups interspersed between the original point of substitution, there are small but significant perturbations transmitted to the surface and
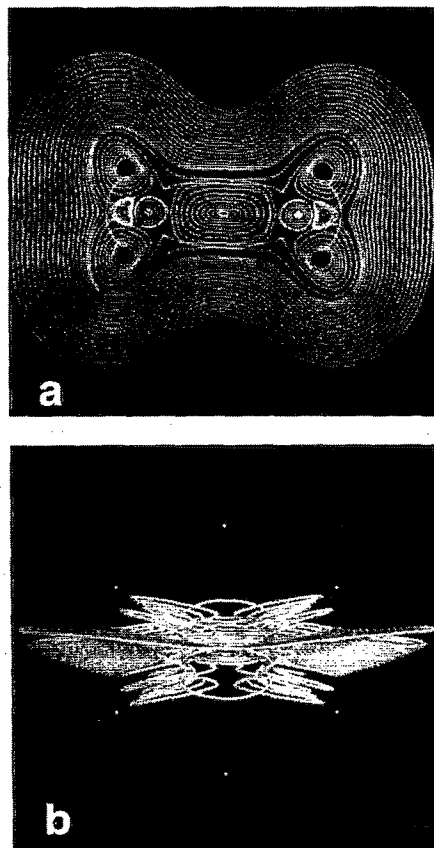
FIG. 6. (a) Current density in the ethane molecule in a plane perpendicular to a σ_d symmetry plane which is parallel to the applied field. This is not a symmetry plane and the current density is nonplanar. The critical point at the center lies in the σ_d symmetry plane and it is a (2,0) center point. Each carbon basin contains two center points and two saddle points on the C–C axis. There are also surface points and spirals associated with the protons. Their out-of-plane behavior is made evident in (b), which shows the same induced current viewed along the C–C axis. This current distribution in ethane is similar to that induced in the ethene molecule by a field applied perpendicular to the σ_h plane [cf. Fig. 8 of the preceding paper (Ref. 19)] and this accounts for the nearly identical values for the corresponding components of the carbon shielding tensor.
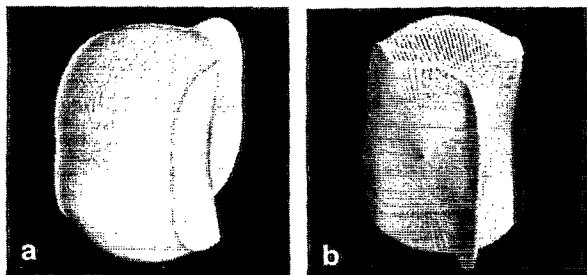

FIG. 5. A view of the transferable methylene group of the normal hydrocarbons with the van der Waals surface of two hydrogen atoms in the foreground in (a) and with the two C|C interatomic surfaces in the foreground in (b). The bond critical point is denoted by a dot in one such surface.

TABLE V. Incremental changes in properties[a] for group X.

Property	H|X	HCH$_2$|X	HCH$_2$CH$_2$|X	HCH$_2$CH$_2$CH$_2$|X
X=OH				
$\bar{\chi}$	−13.11	+1.63	−0.10	+0.04
$\bar{\chi}_b$	−11.73	+1.69	+0.12	+0.02
$\bar{\chi}_f$	−1.39	−0.06	−0.22	+0.03
q	−0.627	−0.016	−0.007	−0.004
E	−75.7147	−0.0888	−0.004	+0.003
v^b	168.80	−13.69	−0.69	+0.65
ρ_b	0.3964	−0.1309	−0.0031	+0.0001
$\nabla^2\rho_b$	−3.1057	+2.7639	+0.0116	+0.0074
X=F				
$\bar{\chi}$	−10.03	+0.92	+0.02	+0.02
$\bar{\chi}_b$	−9.63	+1.16	+0.16	+0.02
$\bar{\chi}_f$	−0.40	−0.24	−0.14	0.00
q	−0.779	0.044	−0.006	−0.001
E	−99.8149	−0.0220	+0.0082	+0.0061
v^b	130.44	−22.84	−2.91	+3.26
ρ_b	0.4042	−0.1632	−0.0051	+0.0002
$\nabla^2\rho_b$	−4.0047	+4.3951	−0.0150	+0.0102

[a]All quantities in atomic units except for $\bar{\chi}$, which is in cgs ppm.
[b]Volume of X out to 0.001 a.u. density envelope.

basin of the X group, perturbations which, as described in a companion study, are responsible for substituent effects on nuclear magnetic resonance (NMR) chemical shifts. Experimentally, the X group would appear to contribute an essentially fixed amount to the magnetic susceptibility of the normal alcohols and flourides following the ethyl derivative. The other properties exhibit a similar degree of transferability for the OH group, where even the energy changes by less than 2 kcal/mol. The energy and volume of the more electronegative F atom are somewhat less transferable. Contributions from a given group to a system's properties can assume essentially constant, additive values when the group is sufficiently isolated from the point of substitution, a single methylene group acting as a sufficient buffer for the magnetic susceptibility in the hydrocarbons.

MAGNETIC SUSCEPTIBILITIES OF THREE-CARBON RINGS

The observed value of $\bar{\chi}$ for cyclohexane 68.7 u (Ref. 35) is in acceptable agreement with the value of 69.2 u calculated using six times the value of $\bar{\chi}$ (CH$_2$) for the transferable methylene group. This method cannot, however, be used to predict the susceptibility of cyclopropane. Subjecting the standard methylene group CH$_2^0$ to the geometrical constraints imposed by a three-membered ring perturbs the group. Specifically, a small amount of electronic charge −0.048e is transferred from the hydrogens to carbon causing the energy of the group to increase by 9.1 kcal/mol, exactly one-third of the so-called strain energy.[17] Other properties, including the polarizability, undergo corresponding changes.[18] The effects of ring strain and delocalization of charge on the magnetic susceptibility are investigated through a study of the properties of cyclopropane C$_3$H$_6$ and cyclopropenyl cation C$_3$H$_3^+$.

The current maps for these molecules (Fig. 7) exhibit a paramagnetic circulation in the interior of the ring, such
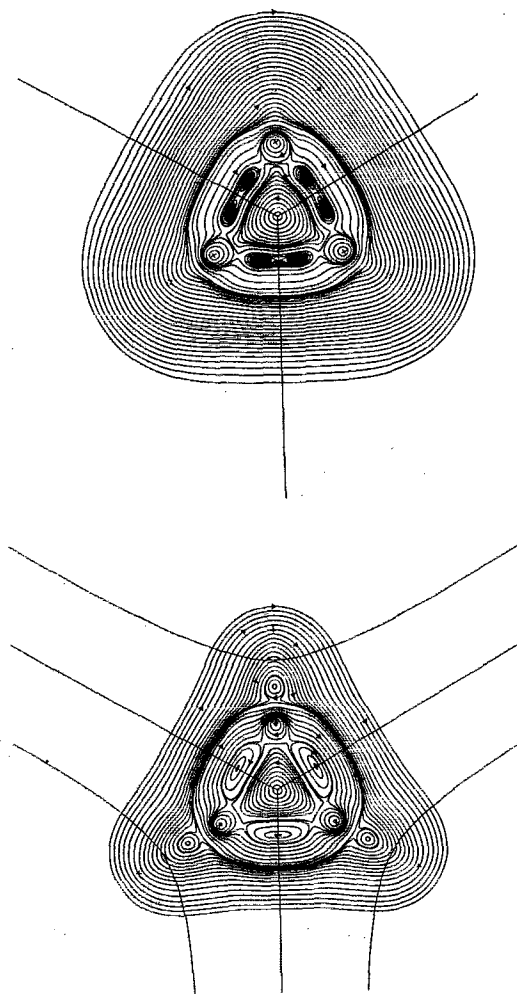

FIG. 7. Displays of the current density in (a) cyclopropane and (b) cyclopropenium cations in the plane containing the carbon nuclei for a field directed out of and perpendicular to the plane of the diagrams.

as that found in benzene. This is anticipated on the basis of the properties of the curl of **J** for a carbon atom as discussed above in the case of benzene. The current map for cyclopropenium ion is overall similar to that for benzene. However, in cyclopropane, the bonded set of diamagnetic current loops shared by the carbons is replaced by a linked pair of spirals, the center point being replaced by a saddle point. The magnitudes of the diamagnetic currents are largest in the plane of the ring nuclei and are most pronounced in cyclopropane, where only the carbon nuclei are found in the ring surface. The contributions to $\chi_\parallel$ (C) resulting from the current fluxes across the C|C interatomic surfaces of the ring atoms induced by a parallel field are −16.6 u for cyclopropane and −14.2 for cyclopropenium ion and there is a collective or ring current contribution to $\bar{\chi}$ in a three-membered ring.

Cyclopropane

The calculated value of $\bar{\chi}$ for cyclopropane (Table VI) is more negative by 6.91 u than that predicted on the basis of the value for the transferable methyl group, with $\bar{\chi}$(CH$_2^0$) = −11.54 u. The molecule also exhibits a sizeable anisotropy $\Delta\chi$ = −10.66 u, with the preferred axis of mag-

TABLE VI. Atomic contributions to magnetic susceptibility tensor (χ) in cyclopropane. Units are cgs-ppm.

Atom Ω	$\chi_b^{\perp}(\Omega)$[a]	$\chi_b^{\parallel}(\Omega)$[b]	$\bar{\chi}_b(\Omega)$	$\chi_f^{\perp}(\Omega)$[a]	$\chi_f^{\parallel}(\Omega)$[b]	$\bar{\chi}_f(\Omega)$	$\chi_{\perp}$[a]	$\chi_{\parallel}$[b]	$\bar{\chi}$
C	-4.31	-5.96	-4.86	-2.45^{2H} [c]	-1.07^{2H} [c]	-1.99^{2H} [c]	-8.45	-12.57	-9.82
				-1.69^{R} [d]	-5.53^{R} [d]	-2.97^{R} [d]			
				-4.14^{T} [e]	-6.60^{T} [e]	-4.96^{T} [e]			
H	-1.38	-1.51	-1.42	-0.73	-0.33	-0.59	-2.11	-1.83	-2.02
C_3H_6	-21.22	-26.93	-23.13	-16.75	-21.69	-18.40	-37.97	-48.63	-41.53

$\Delta\chi = -10.66$ $3\Delta\chi(C) = -12.36$ $6\Delta\chi(H) = 1.67$
$\Delta\chi_f = -4.94$ $3\Delta\chi_f(C) = -7.38$ $6\Delta\chi_f(H) = 2.40$
$\Delta\chi_b = -5.71$ $3\Delta\chi_b(C) = -4.95$ $6\Delta\chi_b(H) = -0.78$

[a]The symbol $\perp$ refers to axes perpendicular to the principal rotation axis and corresponding atomic values are averaged over both $\perp$ field directions.
[b]The symbol $\parallel$ refers to the principal rotation axis.
[c]H refers to current flux through the C|H surface.
[d]R refers to current flux through C|C surfaces in a ring.
[e]T refers to total current flux contribution.

netization parallel to the symmetry axis, compared to the near isotropic behavior of CH_2^0 for which $\Delta\chi = -0.40$ u. Nearly all of the anisotropy originates within the carbon atoms, whose contribution is -12.4 u. Of this amount, -11.5 u arises from the flux of current through the C|C interatomic surfaces of the ring induced by the parallel field. The net contribution to $\Delta\chi$ resulting from the surface terms is reduced to -4.9 u because of the countering behavior of the current fluxes through the C|H interatomic surfaces. The remaining anisotropy stems directly from the basins of the carbon atoms. Forming a three-membered ring causes a considerable change in the magnetic properties of the carbon atoms of the methylene groups and induces a behavior in these atoms with similarities to that found in benzene, but to a much reduced degree. In benzene, 77% of the anisotropy originates in the flow of current across the interatomic surfaces of the atoms of the ring with only a relatively small contribution from the atomic basins.

The transfer of charge from H to C occurring when CH_2^0 is transferred to a three-membered ring causes only very small reductions in the magnitudes of the basin and surface contributions to $\bar{\chi}(H)$, but relatively large changes to $\bar{\chi}(C)$. The magnitude of $\bar{\chi}_b(C)$ increases by 1.8 u and

its anisotropy by a factor of 2, and overall, the basin and surface contributions to $\bar{\chi}(CH_2)$ change from -5.9 and -5.7 u in the standard group to -7.7 and -6.1 u, respectively, in cyclopropane. Thus the increased magnetizability and and its anisotropy in the cyclic compound have their origin in the changed behavior of the carbon atoms with respect to both their basin contributions and the substantial increase in the current flow across the C|C interatomic surfaces caused by a parallel field.

Cyclopropenium cation

This molecule possesses two π electrons and is the simplest of the Hückel aromatic systems. Its magnetic properties have been previously studied by Lazzeretti and Zanasi[36] and it is calculated to exhibit a magnetic anisotropy equal to almost half that for benzene (Table VII). The value of $\bar{\chi}$ for the ion is, however, less than one-third of the value for benzene, primarily because of a reduction in the value of $\bar{\chi}(C)$. The contributions from the hydrogen atoms, which bear most of the positive charge $q(H) = +0.235$ are also reduced for both field directions, and the value of $\bar{\chi}(CH)$ changes from -10.0 u in benzene to -6.2 u in cyclopropenium ion. The relatively small

TABLE VII. Atomic contributions to magnetic susceptibility tensor (χ) in a cyclopropenyl cation. Units are cgs ppm.

Atom Ω	$\chi_b^{\perp}(\Omega)$[a]	$\chi_b^{\parallel}(\Omega)$[b]	$\bar{\chi}_b(\Omega)$	$\chi_f^{\perp}(\Omega)$[a]	$\chi_f^{\parallel}(\Omega)$[b]	$\bar{\chi}_f(\Omega)$	$\chi_{\perp}$[a]	$\chi_{\parallel}$[b]	$\bar{\chi}$
C	-0.42	-4.97	-1.94	-0.28^{H} [c]	-1.44^{H} [c]	-0.66^{H} [c]	-2.01	-11.13	-5.05
				-1.30^{R} [d]	-4.73^{R} [d]	-2.45^{R} [d]			
				-1.59^{T} [e]	-6.17^{T} [e]	-3.11^{T} [e]			
H	-0.78	-0.99	-0.85	-0.14	-0.69	-0.32	-0.92	-1.68	-1.17
$C_3H_3^+$	-3.61	-17.87	-8.36	-5.17	-20.56	-10.30	-8.77	-38.44	-18.66

$\Delta\chi = -29.64$ $3\Delta\chi(C) = -27.36$ $3\Delta\chi(H) = -2.28$
$\Delta\chi_f = -15.39$ $3\Delta\chi_f(C) = -13.74$ $3\Delta\chi_f(H) = -1.65$
$\Delta\chi_b = -14.28$ $3\Delta\chi_b(C) = -13.65$ $3\Delta\chi_b(H) = -0.63$

[a]The symbol $\perp$ refers to axes perpendicular to the principal rotation axis and corresponding atomic values are averaged over both $\perp$ field directions.
[b]The symbol $\parallel$ refers to the principal rotation axis.
[c]H refers to current flux through the C|H surface.
[d]R refers to current flux through C|C surfaces in ring.
[e]T refers to total current flux contribution.

value of $\bar{\chi}(C)$ is a result of a great reduction in the magnitude of the basin contribution for a perpendicular field, from -2.2 to -0.4 u, with a smaller reduction in the associated surface flux term. Thus unlike benzene, where 77% of the anisotropy arises from the fluxes in currents through the C|C interatomic surfaces, nearly one-half of the anisotropy in cyclopropenium ion has its origin in the differing magnetizations of the basins of the carbon atoms and only -10.3 u or one-third of the anisotropy arises from the fluxes in current through the C|C interatomic surfaces of the ring. The contribution to $\chi_f(C)$ from the C|C fluxes for a parallel field is -4.7 u in the ion compared to -10.5 u in benzene. Clearly, the basis for the magnetizability of the cyclopropenium ion is different from that found for benzene in that the dominant contribution does not arise from a current flowing from the basin of one ring atom into that of a neighbor.

CONCLUSIONS

Every atom makes an additive contribution to the magnetic properties of the system of which it is a part. Like atomic contributions to other properties, the extent to which the atomic magnetization is transferable from one system to another parallels the corresponding transferablity of the atom's charge distribution, the properties of an atom changing in direct response to the change in its form in real space. Examples have been given of group susceptibilities that are predicted to be transferable without change to within experimental error. It has also been demonstrated that a single methylene group is a sufficient buffer to ensure that a given group contributes essentially constant, additive values to many properties. The magnetic properties are determined by the observable electron current density and the atomic behavior of this field has been correlated with corresponding behavior of the electron density. Thus the importance of the magnetization within an atomic basin relative to the fluxes in currents through the interatomic surfaces parallels the extent to which the electron density is localized within the individual atomic basins. Also of importance is the demonstrated presence of paramagnetic currents in the basins of electropositive atoms for a field applied perpendicular to the direction of charge transfer. This effect explains, e.g., the presence of a pronounced anisotropy in the carbon shielding in methyl fluoride, while that for flourine is nearly isotropic.

This paper demonstrates that the fields $\rho(\mathbf{r})$ and $\mathbf{J}^{(1)}(\mathbf{r})$, together with their derived fields $\nabla\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, and $\nabla\times\mathbf{J}^{(1)}(\mathbf{r})$, provide a basis for a unified theory of the properties of matter at the atomic level.

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