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Delocalization of Electrons in Molecules[†]

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We report a general method for the investigation and quantification of delocalization in molecules. The method is based on the anisotropy of the current-induced density (ACID). Compared to the current density, which has been frequently used to investigate delocalization, the ACID approach has several advantages: it is a scalar field which is invariant with respect to the relative orientation of the magnetic field and the molecule, it is not a simple function of the overall electron density, it has the same symmetry as the wave function, and it can be plotted as an isosurface. Several selected examples demonstrate the predictive power and the general applicability of this method.

I. Introduction

Delocalization and conjugation[1−3] are among the most important concepts in chemistry. Chemists use them as a tool in their every day work for the interpretation of chemical phenomena and physical properties of molecules. Magnetic criteria, such as the magnetic susceptibility, anisotropy or exaltation of the magnetic susceptibility,[4] and nucleus-independent shifts[5,6] have been widely used to quantify the "degree" of aromaticity[7] of various chemical systems. These methods, however, are restricted to cyclic systems or only provide a single number, which does not give information on contributions located at different points in space.[8] Current density maps, therefore, have been applied to investigate magnetic properties with spatial resolution in detail.[9−18] There are, however, several disadvantages to this approach. (1) The current density is a vector field which graphically can only be represented in an arbitrary chosen sectional plane. (2) The vector field depends on the relative orientation of the molecule and the magnetic field. An unambiguous choice of the plane and the magnetic field is only possible in planar systems for which this method has been almost exclusively used. (3) The most severe drawback for the analysis of delocalization effects, however, is the fact that the diamagnetic part of the current density simply maps the electron density. The ultimately localized chemical system, a single atom, exhibits strong ring currents in an external magnetic field.

The anisotropy of the induced current density has been used to prove the aromaticity in the transition state of an electrocyclic reaction by Wallenborn et al.[19] The authors propose a definition of the anisotropy that avoids the ambiguous choice of a reference plane in nonplanar cyclic systems. We now investigate the method in detail[20] and propose the use of the anisotropy of the current-induced density (ACID) as a general method that is applicable to any molecular system (not only cyclic systems). The ACID can be interpreted as a representation of delocalized electrons. It provides a simple way for the quantification of conjugative effects and can be used for any type of conjugation (not only aromaticity).

The ACID method is a useful tool in the hands of experimental chemists to explain stereoelectronic effects in structures (e.g., anomeric effect), the stereochemistry of reactions (e.g., regio- and stereochemistry in pericyclic reactions), and a number of other properties of chemical systems.

II. Theoretical Method

A. Induced Current Density. The induced current density $\vec{\mathbf{J}}^{(1)}$ is given by

$$\mathbf{T}: \qquad \mathbf{T}_{\nu\mu} = \frac{\partial \mathrm{J}_\nu}{\partial \mathrm{B}_\mu} \qquad (\text{at } B = 0) \qquad \vec{\mathbf{J}}^{(1)} = \mathbf{T}\cdot\vec{\mathbf{B}} \tag{1.1}$$

It can be computed by standard perturbation theory. The resulting equation for $\vec{\mathbf{J}}^{(1)}$ can be split in two terms, a diamagnetic $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ and a paramagnetic term $\vec{\mathbf{J}}_\mathrm{p}^{(1)}$:

$$\vec{\mathbf{J}}_\mathrm{d}^{(1)} = -\frac{e^2}{m_\mathrm{e}}\vec{\mathbf{A}}\Psi_0{}^2 \tag{1.2}$$

$$\vec{\mathbf{J}}_\mathrm{p}^{(1)} = -\mathrm{i}\left(\frac{e\hbar}{2m_e}\right)\sum_{n=1}^{N}(a_n - a_n^*)(\Psi_n\nabla\Psi_0 - \Psi_0\nabla\Psi_n) \tag{1.3}$$

Whereas $\vec{\mathbf{J}}^{(1)}$ is independent of the gauge origin if a full basis set is provided, the two separate terms $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ and $\vec{\mathbf{J}}_\mathrm{p}^{(1)}$ are not and therefore do not have a physical significance except, however, if one of the two terms vanishes.

B. Anisotropy of the Current (Induced) Density (ACID). The anisotropy σ is defined as the standard deviation of the eigenvalues e_i of a matrix:

$$\sigma^2 = \sum_i (e_i - \bar{e})^2 \tag{2.1}$$

With $\bar{e} = {}^1/_n\sum_i e_i$ and $\sum_i e_i = \mathrm{tr}\ \mathbf{T}$ we obtain

$$\sigma^2 = \sum_i e_i{}^2 - \frac{1}{n}(\sum_i e_i)^2 \tag{2.2}$$

$$= \mathrm{tr}\ (\mathbf{T}^2) - \frac{1}{n}(\mathrm{tr}\ \mathbf{T})^2 \tag{2.3}$$

[†] Dedicated to Prof. Henning Hopf on the accasion of his 60th birthday.

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For a three-dimensional case ($n = 3$) the anisotropy of the induced current density is calculated as

$$\Delta\mathbf{T}^{(1)^2} = t_{xx}{}^2 + t_{yy}{}^2 + t_{zz}{}^2 + 2t_{xy}t_{yx} + 2t_{xz}t_{zx} + 2t_{yz}t_{zy} - \frac{1}{3}(t_{xx} + t_{yy} + t_{zz})^2$$

$$= \frac{1}{3}[(t_{xx} - t_{yy})^2 + (t_{yy} - t_{zz})^2 + (t_{zz} - t_{xx})^2] + 2(t_{xy}t_{yx} + t_{xz}t_{zx} + t_{yz}t_{zy}) \quad (2.4)$$

A real matrix **T** can be decomposed into a symmetric and antisymmetric part $\mathbf{T} = \mathbf{T}_\mathrm{S} + \mathbf{T}_\mathrm{A}$. This yields for the anisotropy of **T**:

$$\Delta\mathbf{T}^{(1)^2} = \Delta\mathbf{T}_\mathrm{S}^{(1)^2} + \mathrm{tr}\Delta\mathbf{T}_\mathrm{A}^{(1)}\,\Delta\mathbf{T}_\mathrm{A}^{(1)^+} \quad (2.5)$$

The anisotropy of the antisymmetric part does not have physical significance and can be neglected. Thus, the second term of eq 2.4 can be factorized and we obtain

$$\Delta\mathbf{T}_S^{(1)^2} = \frac{1}{3}[(t_{xx} - t_{yy})^2 + (t_{yy} - t_{zz})^2 + (t_{zz} - t_{xx})^2] + \frac{1}{2}[(t_{xy} + t_{yx})^2 + (t_{xz} + t_{zx})^2 + (t_{yz} + t_{zy})^2] \quad (2.6)$$

This definition of the anisotropy of the induced current density ($\Delta\mathbf{T}_\mathrm{S}^{(1)}$) other than conventional methods[21] includes the off diagonal elements of the current density tensor ($t_{\mathrm{n}k}, n \neq k$). The definition is identical with a formula that has been used by Wallenborn et al.[19,20] In asymmetric tops or especially systems of $D_{\infty h}$ or $C_{\infty v}$ symmetry, two of the principal values of t are identical:

$$\begin{aligned} t_{xx} &= t_{yy} \\ t_{xy} + t_{yx} = 0 &\rightarrow t_{xy} = -t_{yx} \\ t_{yz} + t_{zy} = 0 &\Rightarrow t_{yz} = -t_{zy} \\ t_{zx} + t_{xz} = 0 &\Rightarrow t_{zx} = -t_{xz} \end{aligned} \quad (2.7)$$

Accordingly, the anisotropy function simplifies to

$$\Delta\mathbf{T}^{(1)}{}_{\mathrm{asymm.top}} = t_{zz} - t_{xx} \quad (2.8)$$

which is frequently used as an anisotropy definition.

C. Symmetry Properties of the Induced Current Density. On the basis of eqs 1.2, 1.3, and 2.6 the symmetry of (a) the vector field of the current density and (b) of the scalar field of the anisotropy of the current density can be derived. To achieve this, the diamagnetic and the paramagnetic parts of the current density must be treated separately.

Symmetry of $\vec{J}_d^{(1)}$**.** Provided that exact wave functions (complete basis sets) are used, a free choice of the gauge origin is possible. For the sake of simplicity the origin of the coordinate system will serve as the gauge origin.

Except for the vector potential $\vec{\mathbf{A}}$, there are only scalar parameters in the diamagnetic part of the current density (eq 1.2). All scalar parameters are constant except for the electron density. The electron density $\Psi_0{}^2$ always forms the basis of the totally symmetrical irreducible representation of the point group of the ground-state wave function Ψ_0. Therefore, the symmetry of $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ is only determined by the function of the vector potential $\vec{\mathbf{A}}_q$. A magnetic field oriented in the z direction defines the vector potential $\vec{\mathbf{A}}_z$ with the gauge origin $\vec{\mathbf{R}} = \vec{\mathbf{0}}$ ($\vec{\imath}$, $\vec{\jmath}$, and $\vec{\mathbf{k}}$ are the unit vectors in the x, y, z directions):

$$\vec{\mathbf{A}}_z = -y\vec{\imath} + x\vec{\jmath} \quad (3.1)$$

The vector potentials $\vec{\mathbf{A}}_x$ and $\vec{\mathbf{A}}_y$ are obtained by cyclic exchange:

$$\vec{\mathbf{A}}_x = -z\vec{\jmath} + y\vec{\mathbf{k}} \quad (3.2)$$

$$\vec{\mathbf{A}}_y = -x\vec{\mathbf{k}} + z\vec{\imath} \quad (3.3)$$

The vector functions $\vec{\mathbf{A}}_q$, $q \in \{x,y,z\}$ are characterized by the fact that they define vectors which are tangential with respect to concentric circles around the coordinate axis q ("curl" function). The symmetry of such a function is identical with the symmetry of the rotation R_q with respect to the coordinate axis q. Since $\vec{\mathbf{A}}_q$ is always orthogonal to $\vec{\mathbf{B}}$ and because $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ differs from $\mathbf{A}_q$ only by a factor, both assertions are also true for $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$. Both the rotational symmetry of $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ and orthogonality of $\vec{\mathbf{J}}_\mathrm{d}^{(1)}$ and $\vec{\mathbf{B}}$ are equivalent to the classical concept of induced currents.

Symmetry of $\Delta T_d^{(1)}$. The first column of the tensor $\mathbf{T}_\mathrm{d}^{(1)}$ corresponds to the vectorial current density induced by a magnetic field in the x direction ($t_{xx}\vec{\imath} + t_{xy}\vec{\jmath} + t_{xz}\vec{\mathbf{k}}$), and the second and third columns represent the corresponding vectors in the y and z directions. Hence the elements of the current density tensor can be easily calculated using eqs 1.2, 3.1, 3.2, and 3.3.

$$\mathbf{T}_\mathrm{d}^{(1)} = \frac{e^2}{m_\mathrm{e}}\Psi_0{}^2\begin{pmatrix} a_{xx} & a_{yx} & \mathrm{a}_{\mathrm{zx}} \\ \mathrm{a}_{\mathrm{xy}} & \mathrm{a}_{\mathrm{yy}} & \mathrm{a}_{\mathrm{zy}} \\ \mathrm{a}_{\mathrm{xz}} & \mathrm{a}_{\mathrm{yz}} & a_{zz} \end{pmatrix} = -\frac{e^2}{m_e}\Psi_0{}^2\begin{pmatrix} 0 & z & -y \\ -z & 0 & x \\ \mathrm{y} & -x & 0 \end{pmatrix} \quad (3.4)$$

Using eq 2.6, one can write

$$\Delta\mathbf{T}_\mathrm{d}^{(1)} = -\frac{e^2}{2m_\mathrm{e}}\Psi_0{}^2\left[\frac{1}{3}[(0-0)^2 + (0-0)^2 + (0-0)^2] + \frac{1}{2}[(-z+z)^2 + (-x+x)^2 + (-y+y)^2]\right]^{0.5} = 0 \quad (3.5)$$

$\Delta\mathbf{T}_\mathrm{d}^{(1)}$ vanishes at all points in space. Therefore, the anisotropy of the total current density can be written as the sum of the anisotropies of dia- and paramagnetic currents (which is normally not the case). In other words: *the diamagnetic current density does not contribute to the anisotropy!*

$$\Delta\mathbf{T}^{(1)} = \Delta\mathbf{T}_\mathrm{d}^{(1)} + \Delta\mathbf{T}_\mathrm{p}^{(1)} = \Delta\mathbf{T}_\mathrm{p}^{(1)} \quad (3.6)$$

The diamagnetic current density mainly represents the electron density (eq 1.2). By forming the anisotropy of the current density, we remove this unwanted information since we only want to map the delocalized electrons. The remaining paramagnetic current density tensor $\Delta\mathbf{T}_\mathrm{p}^{(1)}$ is a function of the first-order correction of the wave function $\Psi^{(1)}$. Expressed in anthropomorphic terms: the anisotropy of the induced current density represents the "answer" of the wave function to the perturbation by the magnetic field.

Symmetry of $\vec{J}_p^{(1)}$. The following considerations are based on the condition that Ψ_0 is totally symmetric in one of the Abelian point groups. If this is the case, the coefficients a_n in the linear combination $\Psi^{(1)}$ are only different from zero if the wave functions Ψ_n are of a certain symmetry because the integral in eq 3.7:

$$\Psi^{(1)} = \sum_{n=1}^{N} a_n \Psi_n = \sum_{n=1}^{N} \frac{\langle \Psi_n | \hat{H}^{(1)} | \Psi_0 \rangle}{E_0 - E_n} \Psi_n \qquad (3.7)$$

is only different from zero if the integrand is totally symmetric. Since Ψ_0 is totally symmetric, Ψ_n must be of the same symmetry as $\hat{H}^{(1)}$. The symmetry of $\hat{H}^{(1)}$ depends on the magnetic field and corresponds to the symmetry of a rotation R_q with repect to an axis q, which is parallel to the magnetic field because $\hat{H}^{(1)}$ includes the angular momentum operator (see section 1).

Now it is possible to determine the position dependent part of the summands of $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$, which is

$$(\Psi_n \nabla \Psi_0 - \Psi_0 \Delta \Psi_n) \qquad (3.8)$$

The symmetry of the summands is identical because the same functions and operators appear and because the direct products commute in abelian point groups. Since Ψ_0 also is totally symmetric, the symmetry is only determined by the wave function Ψ_n and the operator ∇. As demonstrated above, the rotations R_q can be used instead of Ψ_n. The symmetry of a differentiation to q ($q \in \{x,y,z\}$) is identical to the symmetry of the function $f = q$ (the notation $\Gamma(a) = \Gamma(b)$ in the following means that a and b form the basis of the same irreducible representation):

$$\Psi_n \nabla = \Psi_n \left(\frac{\partial}{\partial x} \cdot \vec{\imath} + \frac{\partial}{\partial y} \vec{\jmath} + \frac{\partial}{\partial z} \vec{\mathbf{k}} \right)$$

$$\Gamma(\Psi_n \nabla) = \Gamma(R_q(x \cdot \vec{\imath} + y \cdot \vec{\jmath} + z \cdot \vec{\mathbf{k}})) \qquad (3.9)$$

In symmetry determinations of vector functions, one has to consider that the transformation of the coordinate system does not only effect the parameter of the function but also the functional values. Therefore, the vector function

$$f(x,y,z) = x \cdot \vec{\imath} + y \cdot \vec{\jmath} + z \cdot \vec{\mathbf{k}}$$

forms the basis of the totally symmetric point group in each abelian point group because

$$f(x'y'z') = \mathbf{D}\, f(x,y,z)$$

or

$$f(x'y'z') = -\mathbf{D} f(x,y,z)$$

with

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \mathbf{D} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

is true for any symmetry operation $\mathbf{D}$ to which f is symmetrical or antisymmetrical. In our case eq 3.9 simplifies:

$$\begin{aligned} \Gamma(\Psi_n \nabla) &= \Gamma(R_q(x \cdot \vec{\imath} + y \cdot \vec{\jmath} + z \cdot \vec{\mathbf{k}})) \\ &= \Gamma(R_q) \times \Gamma(x \cdot \vec{\imath} + y \cdot \vec{\jmath} + z \cdot \vec{\mathbf{k}}) \\ &= \Gamma(R_q) \\ \Rightarrow \Gamma \vec{\mathbf{J}}_{\mathrm{p}}^{(1)} &= \Gamma(R_q) \end{aligned} \qquad (3.10)$$

In contrast to the diamagnetic part $\vec{\mathbf{J}}_{\mathrm{d}}^{(1)}$, *the paramagnetic current density* $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ *does not necessarily have to be orthogonal to the magnetic field* because the vectorial part of $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ does not exhibit this restriction. Both terms $\vec{\mathbf{J}}_{\mathrm{d}}^{(1)}$ and $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ are symmetrical to a C_n axis parallel to the magnetic field if the point group of the wave function Ψ_0 contains a corresponding operation. In other words, the paramagnetic term of the induced current density forms the basis of the same irreducible representation as the rotation around the Cartesian axis which is parallel to the magnetic field.

Symmetry of $\Delta T_p^{(1)}$. To determine the symmetry of $\Delta \mathbf{T}_{\mathrm{p}}^{(1)}$, we set up the current density tensor and a corresponding symmetry equivalent tensor and used the results of eq 3.9. For a magnetic field oriented in the x direction, we can write

$$\vec{\mathbf{J}}_{\mathrm{p}}^{(1)} = t_{xx} \vec{\imath} + t_{xy} \vec{\jmath} = t_{xz} \vec{\mathbf{k}}$$

$$\Gamma(\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}) = \Gamma(\Psi_n \nabla) = \Gamma(R_x \cdot \mathrm{x} \cdot \vec{\imath} + R_x \cdot y \cdot \vec{\jmath} + R_x \cdot z \cdot \vec{\mathbf{k}}) \qquad (3.11)$$

The first (second, third) column of the tensor $\mathbf{T}_{\mathrm{p}}^{(1)}$ corresponds to $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ if a magnetic field is applied in the x (y, z) directions. From eq 3.9 and $q \in \{x,y,z\}$ it can be concluded:

$$\Gamma(\mathbf{T}_{\mathrm{p}}^{(1)}) = \Gamma \begin{pmatrix} R_x \cdot x & R_y \cdot x & R_z \cdot x \\ R_x \cdot y & R_y \cdot y & R_z \cdot y \\ R_x \cdot z & R_y \cdot z & R_z \cdot z \end{pmatrix} \qquad (3.12)$$

For R_q the following symmetry relationships are true

$$\Gamma(R_x) = \Gamma(y \cdot z) \qquad (3.13)$$

$$\Gamma(R_y) = \Gamma(x \cdot z) \qquad (3.14)$$

$$\Gamma(R_z) = \Gamma(x \cdot y) \qquad (3.15)$$

Consequently, the tensor has the following form:

$$\Gamma(\mathbf{T}_{\mathrm{p}}^{(1)}) = \Gamma \begin{pmatrix} xyz & x^2z & x^2y \\ y^2z & xyz & xy^2 \\ yz^2 & xz^2 & xyz \end{pmatrix} \qquad (3.16)$$

Since the squares of the coordinate axes are always totally symmetric, we can write

$$\Gamma(\mathbf{T}_{\mathrm{p}}^{(1)}) = \Gamma \begin{pmatrix} xyz & \mathrm{z} & \mathrm{y} \\ \mathrm{z} & \mathrm{xyz} & \mathrm{x} \\ \mathrm{y} & \mathrm{x} & xyz \end{pmatrix} \qquad (3.17)$$

It is easy to show that the summands of the six sums in the anisotropy eq 2.6 have the same symmetry, so they can be treated as a set. Furthermore, all six sums are squared and therefore the sum of the squares is totally symmetric. Consequently, $\Delta \mathbf{T}_{\mathrm{p}}^{(1)}$ is also totally symmetric within the point group of the wave function Ψ_0. The same is true for $\Delta \mathbf{T}^{(1)}$ if the gauge origin is selcted as $\vec{\mathbf{R}} = \vec{\mathbf{0}}$ because, as shown above, the diamagnetic term $\Delta \mathbf{T}_{\mathrm{d}}^{(1)}$ vanishes. Equation 3.18 summarizes the derivation:

$$\Delta \mathbf{T}^{(1)} = \Delta \mathbf{T}_{\mathrm{p}}^{(1)}$$

$$\begin{aligned} \Gamma(\Delta \mathbf{T}^{(1)}) &= \Gamma \left[\left[\frac{1}{3} [(xyz)^2 + (xyz)^2 + (xyz)^2] + \frac{1}{2} [z^2 + x^2 + y^2] \right]^{0.5} \right] \\ &= \Gamma(\Psi_0) \end{aligned} \qquad (3.18)$$

For closed shell molecules in the ground state this means that the ACID isosurface has the same symmetry as the molecule. This is different from the current density itself which is of the same symmetry as the rotation of one of the Cartesian axes depending on the orientation of the magnetic field. The symmetry properties are another advantage of using the anisotropy of the current density over the current density for the visualization of delocalization.

III. Applications

A. Computational Details. Approximations have to be used to calculate the induced current density in molecules. We applied the continuous set of gauge transformation (CSGT) method of Bader et al.,[10,11,22] which is implemented in the GAUSSIAN98 program[23] to calculate the current densities. Link 1002 was modified to write the current density, which was transformed into a rectangular grid (cube-file) and visualized with Gaussview or the Persistance of Vision Raytracing-Software. All molecules were optimized at the B3LYP/6-31G* level of theory and verified as stationary points using normal coordinate analysis. The CSGT calculations were performed at the same level of theory.

B. Model Systems. In the following we investigate simple model systems to reveal how the anisotropy of the current density (ACID) can characterize delocalized systems.

Atomic Orbitals. Occupied atomic orbitals are model cases of perfectly localized electrons. The calculation of the ACID in these systems therefore is an important test for a method describing and visualizing delocalized electrons.

In one-atomic systems, one can select a "natural" gauge origin that gives rise to a vanishing paramagnetic part $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ of the induced current density.[24] The natural gauge is the position of the nucleus and the origin of the coordinate system. Because $\Delta\mathbf{T}_{\mathrm{d}}^{(1)}$ vanishes (eq 3.6) the ACID in all atomic systems at all points in space is zero. In other words: Magnetic fields with different orientations but of the same magnitude at the same position induce currents of the same magnitude that are perpendicular to the magnetic field.

Molecular Orbitals: σ Orbitals. The most simple model of a σ bond is two interacting s orbitals at two different atoms, which happens to be the case in the ground state of the hydrogen molecule.

Group theoretical considerations indicate that the ACID in H_2 should be different from zero. As in the previous chapter we select the gauge origin $\vec{\mathbf{R}} = \vec{\mathbf{0}}$, which leads to a vanishing $\Delta\mathbf{T}_{\mathrm{d}}^{(1)}$. To calculate $\Delta\mathbf{T}_{\mathrm{p}}^{(1)}$, the integral

$$an = \frac{\langle\Psi_n|\hat{H}^{(1)}|\Psi_0\rangle}{E_0 - E_n}$$

(see eq 3.7) has to be evaluated. This term is only different from zero if $\Psi_n\hat{H}^{(1)}\Psi_0$ is totally symmetric. Ψ_0 is totally symmetric and the operators $\hat{H}_x^{(1)}$, $\hat{H}_y^{(1)}$ and $\hat{H}_z^{(1)}$ each have the symmetry of the rotation around the coordinate axis that is parallel to the magnetic field. Within the $D_{\infty h}$ point group, we obtain the following symmetry relationships:

$$\Gamma(\Psi_n\hat{H}_x^{(1)}\Psi_0) = \Gamma(\Psi_n) \times \Pi_{\mathrm{g}} \times \Sigma_{\mathrm{g}}^{+} = \Gamma(\Psi_n) \times \Pi_{\mathrm{g}} \tag{4.1}$$

$$\Gamma(\Psi_n\hat{H}_y^{(1)}\Psi_0) = \Gamma(\Psi_n) \times \Pi_{\mathrm{g}} \times \Sigma_{\mathrm{g}}^{+} = \Gamma(\Psi_n) \times \Pi_{\mathrm{g}} \tag{4.2}$$

$$\Gamma(\Psi_n\hat{H}_z^{(1)}\Psi_0) = \Gamma(\Psi_n) \times \Sigma_{\mathrm{g}}^{-} \times \Sigma_{\mathrm{g}}^{+} = \Gamma(\Psi_n) \times \Sigma_{\mathrm{g}}^{-} \tag{4.3}$$

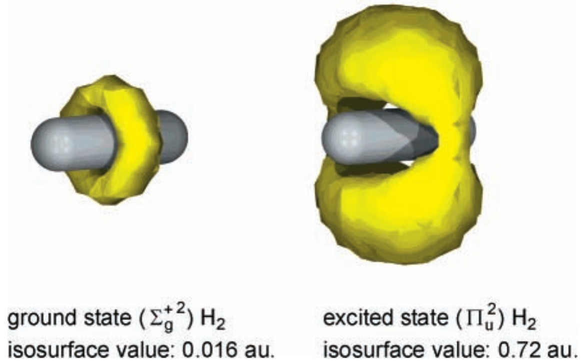

Figure 1. ACID of a prototype σ and π bond.

$\Gamma(\Psi_n)$ denotates the symmetry of the Ψ_n wave function. The terms are only totally symmetric if $\Gamma(\Psi_n)$ has Π_{g} symmetry in (4.1) and (4.2) and Σ_{g}^{-} in (4.3). Whereas the first condition can be met, there is no wave function of Σ_{g}^{-} symmetry.[25] $\vec{\mathbf{J}}_{\mathrm{p}}^{(1)}$ therefore vanishes if a magnetic field is applied in the *z* direction. $\Delta\mathbf{T}_{\mathrm{p}}^{(1)}$ adopts the following form if one assumes that the remaining elements of the tensor are not accidentally zero.

$$\mathbf{T}_{\mathrm{p}}^{(1)} = \begin{pmatrix} t_{xx} & t_{yx} & 0 \\ t_{xy} & \mathrm{t}_{\mathrm{yy}} & 0 \\ t_{xz} & \mathrm{t}_{\mathrm{yz}} & 0 \end{pmatrix} \qquad t_{rs} \neq 0, \quad r,s \in \{x,y,z\} \tag{4.4}$$

The anisotropy has also to be different from zero because of the terms $(t_{xx} - t_{zz})^2$, $(t_{yy} - t_{zz})^2$, $(t_{xz} + t_{zx})^2$, and $(t_{yz} + t_{zy})^2$ (see eq 2.6). This is generally true for molecules of $D_{\infty h}$ symmetry. Figure 1 shows the calculated ACID isosurface of the hydrogen molecule. The ACID is largest in the plane σ_h, which is perpendicular to the line connecting both nuclei. The isosurface has the shape of a torus. The toroidal topology of the ACID of σ bonds is also found in larger molecules like methane or cyclohexane. However, the ACID values of σ bonds normally are extremely small.

p Orbitals. The Π_{u}^2 excited state of the hydrogen molecule represents the simplest case of a bonding π orbital (Figure 1). Compared to the σ orbital, the ACID of the π orbital is almost 2 orders of magnitude larger (note that for graphical reasons the ACID's in Figure 1 are plotted at very different isosurface values). The topology of the isosurface is also toroidal but it does not exhibit axial ($D_{\infty h}$) but planar (D_{2h}) symmetry. The much larger ACID of the π compared to the σ bond is due to the fact that Ψ_n, with symmetries other than Π_{g}, can lead to nonvanishing coefficients a_n. Since Ψ_0 now has Π_{g} symmetry, Ψ_n has to be of Σ_{g}^{+} (magnetic fields in *x* and *y* directions) or Π_{g} symmetrical (magnetic fields in the *z* direction) to give rise to a nonzero contribution to the ACID.

C. Molecules. For illustration, the isosurface of the ACID of cyclohexane, cyclohexene, cyclohexadiene, and benzene is given in Figure 1. In agreement with the generally accepted concept of delocalization, cyclohexane exhibits only a very small anisotropy (toroidal areas around C−H and C−C bonds). In cyclohexene the double bond is represented by a boundary surface that encloses both sp^2 carbon atoms. Consequently, cyclohexadiene exhibits two boundary surfaces for both double bonds that are connected, indicating conjugation between the two double bonds. The ACID isosurface of benzene has the topology of a torus and the current density vectors plotted on top of the isosurface indicate a strong diamagnetic ring current.

Particularly advantageous compared to other approaches is the ACID method in treating noncyclic and nonplanar conjugation. Figure 2 compares butadiene and vinylcyclopropane. Cyclopropanes are known to exhibit partial double bond

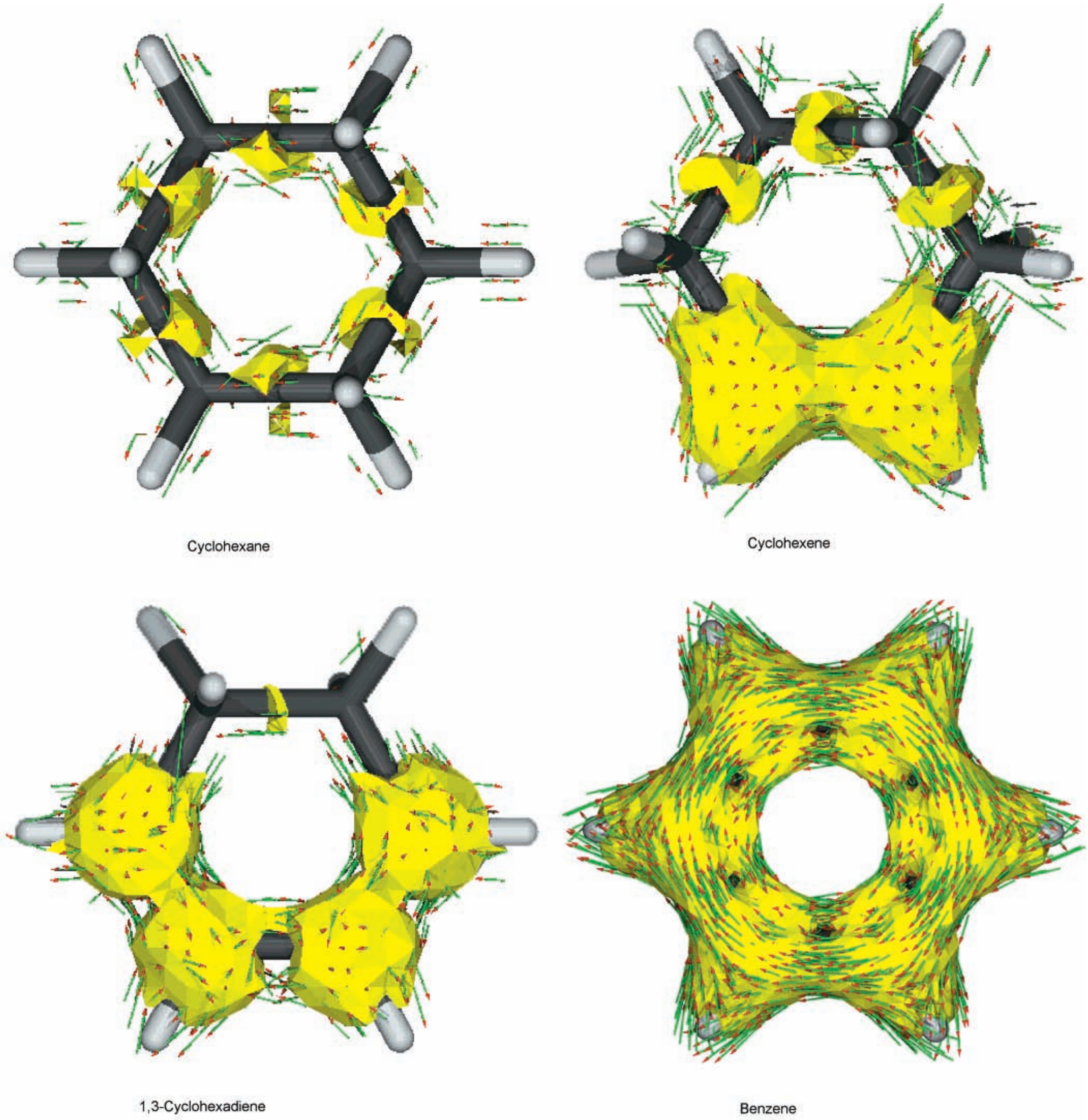

Figure 2. Isosurfaces of the anisotropy of the induced current density (ACID) of cyclohexane, cyclohexene, 1.3-cyclohexadiene, and benzene at an isosurface value of 0.05. Current density vectors are plotted onto the isosurface. The vector of the magnetic field is perpendicular to the ring plane (in the case of cyclohexane C1, C2 and the midpoint of the C4−C5 bond and in cyclohexene C2, C3 and the midpoint of the C5−C6 bond define an approximate ring plane).

character.[26] Like double bonds but less pronounced, the Walsh orbitals of cyclopropane undergo conjugation with neighboring π systems. The extent of conjugation can be quantified by giving the "critical" isosurface value at which the topology of the ACID boundary surface (delocalized system) changes. The continuous boundary surface enclosing the conjugating carbon atoms between the two double bonds in *cis*-butadiene breaks at an isosurface value of 0.0684 and the double bond and the cyclopropane ring in *cis*-vinylcyclopropane are separated at 0.0519, indicating a weaker conjugation in the latter system. Note that the cyclopropane ring exhibits a weak cyclic σ-type conjugation,[27,28] which is in agreement with earlier findings.

Even more subtle interactions like the anomeric effect can be investigated (Figure 3). Conjugation between the lone pair of the ring oxygen and the exocyclic C−O σ* orbital, which is more favorable in the axial than in the equatorial conformation is accounted for the preference of the former conformation in 2-hydroxy -and 2-methoxytetrahydropyranes.[29] The different extent of conjugation is indeed clearly visible in the ACID plot of axial and equatorial 2-hydroxytetrahydropyran. The boundary surface of the conjugating O−C−O part of the structure is continuous in the axial conformation (critical isosurface value: 0.0579) and clearly separated between the lone pair oxygen and the exocyclic C−O bond in the equatorial conformation (critical isosurface value: 0.0469).

Homoaromaticity is another important type of conjugative

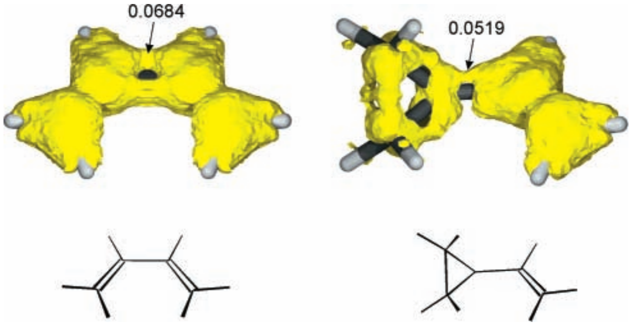

Figure 3. ACID isosurfaces of (*Z*)-butadiene (C_{2v}) and (*Z*)-vinylcyclopropane at an isosurface value of 0.05. The critical isosurface values of 0.0684 and 0.0519 indicate that conjugation is more pronounced between two double bonds than between a double bond and a three membered ring.

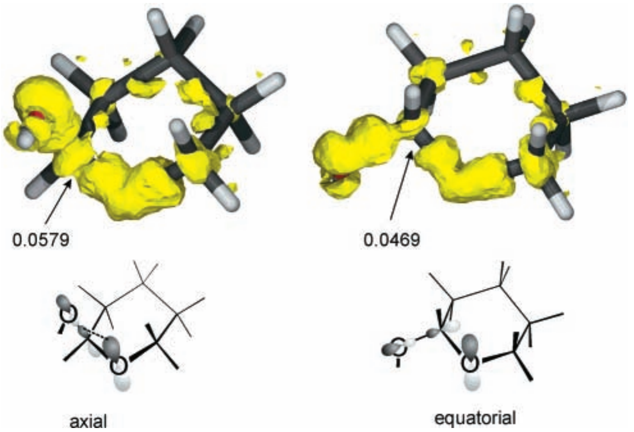

Figure 4. ACID isosurface of 2-hydroxytetrahydropyran (isosurface value 0.05). Conjugation is more pronounced in the axial than in the equatorial conformation (anomeric effect). Note that there is also a weak hyperconjugation between the lone pair of the ring oxygen and the neighboring CH_2 group on the right.

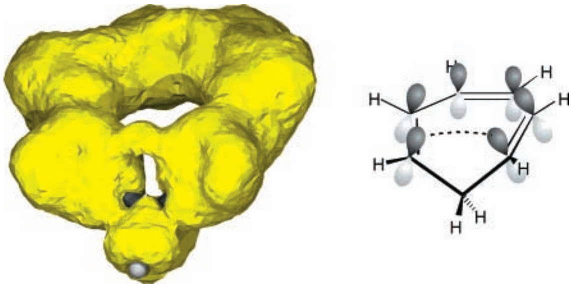

Figure 5. Through space interaction in cycloheptatriene. ACID isosurface at 0.027.

interaction.[30] In a number of cases it had been the subject of controversial discussions.[31] Homoconjugation has been invoked to explain thermodynamic[32] and NMR data of cycloheptatriene.[33] The ACID plot at an isosurface value of 0.027 clearly confirms the through space interaction bridging the CH_2 group (Figures 4and 5).

D. Basis Set Dependence. Calculations of magnetic properties of molecules suffer from a limitation known as the gauge problem. Since the magnetic perturbation is not invariant with respect to translations, values of magnetic properties depend on the choice of origin for the calculation, if approximate wave functions are used. To overcome the gauge problem, either very large basis sets are needed or gauge invariant procedures have to be used. A number of different approaches have been developed.[34,35] Even though the CSGT method achieves gauge invariance by calculating the induced current density by performing a gauge transformation for each point in space, basis set convergence for absolute shielding constants is only observed at large basis sets.[35] To assess the basis set dependence of the ACID method, we calculated the critical isosurface value at which the two double bonds in *trans*-butadiene form separate ACID isosurfaces (Table 1). Up to the 6-311+G(2df,3p) basis there is no clear basis set convergence, but a 6-31G* basis is obviously a good compromise between accuracy and computational cost in molecules of closed shell character.

TABLE 1: Critical Isosurface Values at Which the Continuous ACID Isosurface of (*E*)-Butadiene Breaks into Two Parts Each Enveloping the Corresponding Double Bond[a]

	method	
basis set	RHF	B3LYP
STO-3G	0.046	0.045
3-21G	0.052	0.050
6-31G*	0.054	0.058
6-31G**	0.062	0.064
6-311G**	0.054	0.060
6-311+G**	0.054	0.058
6-311+G(2df,3p)		0.076

[a] Geometries are optimized at the B3LYP/6-31G* level of density functional theory. Current densities were calculated using the CSGT method implemented in Gaussian 98.

IV. Conclusion

The ACID is an intuitive and generally applicable method for the investigation and visualization of delocalization and conjugation. It is directly derived from a quantum theoretical quantity and does not include empirical parameters that have to be fitted (or could be manipulated to achieve agreement between theory and experiment). It does not represent the charge distribution (the ACID value can be zero at points where the electron density is large) but only electrons that are not localized at the nuclei. As a tool for the investigation of molecular properties, the ACID is complementary to the electrostatic surface and the electron density, which provides information about charge and steric interactions.

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