

MOBILE ELECTRONS IN MOLECULES: THE ANISOTROPY OF THE CURRENT-INDUCED DENSITY (ACID) [1]

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ABSTRACT

We have shown that the anisotropy of the induced current density (ACID) can be interpreted as the density of the delocalized electrons in molecules. The ACID scalar field, which can be plotted as an isosurface, is a powerful and generally applicable method for investigating and visualizing delocalization and conjugative effects, e.g. stereoelectronic effects in reactions, the anomeric effect, aromaticity, homoaromaticity *etc.*

INTRODUCTION

The problem of localized versus delocalized bonding is almost as old as chemical structure theory itself. The first localized structures were probably drawn by A. S. Couper in 1859 in *Ann. Chim.* [1] and by Kekulé in 1860 in his famous “*Lehrbuch der Organischen Chemie*”. [3] The latter formulae are known as “Wurstformel” (sausage formula).

Only a few years later Kekulé realized that ascribing fixed bonds to carbon does not explain the properties of benzene [4] and he suggested that the six carbon atoms are somehow combined in a common nucleus. In today’s terminology we would

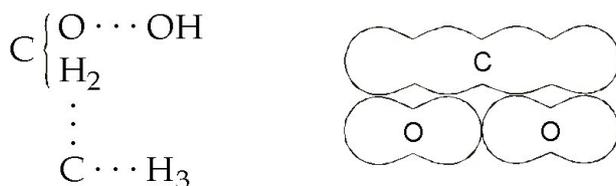


Figure 1: Historical localized bonding concepts of Couper ($\text{CH}_3\text{CH}_2\text{OH}$, left) and Kekulé (CO_2 , right).

say that he realized that the localized bonding concept fails in the case of benzene. His rather fuzzy description was criticized by contemporary colleagues, who tried to preserve the fixed bonding concept by proposing localized structures (Claus, [5] Städeler, [6] Kolbe, [7] Ladenburg, [8] Wichelhaus [9] and Meyer [10]). Driven either by his genius or simply by the need to save his six-ring structure, Kekulé proposed a mechanical collision or vibration of the six carbon atoms exchanging double and single bonds. Even though this view might seem quite close to our understanding today, Kekulé did not have a real chance to provide an answer on a sound physical basis.

Delocalization is a phenomenon that can only be explained by quantum theory. Thus the community had to wait for quantum mechanics to enter the field of chemistry. Erich Hückel published the decisive papers on delocalization in 1931 [11] and 1932. [12] He not only explained aromaticity, but also other forms of π -conjugation.

Today we use two different concepts to explain delocalization: VB- and MO-theory. In its simplest and most approximate application, valence bond theory describes delocalization by drawing mesomeric structures (mixing VB configurations). MO theory inherently considers delocalization by a linear combination of atomic orbitals to a set of molecular orbitals that extend over the whole molecule. Both methods, however, exhibit the drawback that they are “*unanschaulich*” (not easily interpretable). In larger, and particularly in non-planar systems, the situation becomes complicated and conjugative effects are difficult to “extract” from a number of other phenomena.

Our main goal, therefore, was to develop a method to visualize delocalized (mobile) electrons in molecules. Moreover, the method should also provide a simple means to quantify conjugation. Since delocalization is a quantum theoretical property, (even though it is not an observable) we searched for a suitable interpretation of a quantum chemical observable that avoids empirical parameters.

MAGNETIC PROPERTIES OF MOLECULES, THE ACID METHOD

There are a number of criteria derived from the observables energy and geometry to describe delocalization and conjugation. Conjugation usually leads to changes in energy and geometry with respect to a reference system without conjugation. The choice of the reference system is ambiguous and so are the numbers representing the strength of conjugation. Moreover, the numbers calculated by energy and geometry considerations are not suitable for visualization.

Magnetic properties of molecules have been used to describe aromaticity, which is a special type of cyclic delocalization. The magnetic susceptibility,

the anisotropy of the magnetic susceptibility and the NICS method (based on the magnetic shielding) provide numbers that must be compared with reference systems to quantify aromaticity.

Even though these methods provide valuable information, they are restricted to aromaticity and are difficult to visualize as a molecular property with spatial resolution. Closest to a visualization concept are the so-called current density plots. The current density is a vector field obtained by calculating the current induced by an external magnetic field at each point in space. Remember from high school physics that a magnetic field induces a current that follows the “left hand rule” (if the thumb points parallel to the magnetic field **B** the remaining fingers indicate the direction of the induced current **J** e.g. in a solenoid).

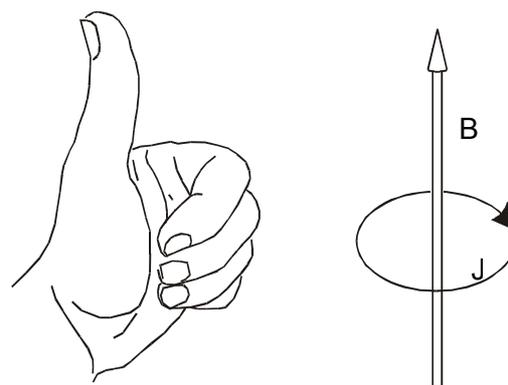


Figure 2: The “left hand rule” for determining the direction of an induced current.

In quantum mechanics, the situation is more complicated. The quantum theoretical equation for the calculation of the induced current density $\vec{J}^{(1)}$ is obtained by a first order perturbation treatment and can be expressed in vectorial form as follows: [13,14]

$$\vec{J}^{(1)} = -i \left(\frac{eh}{2m_e} \right) \sum_{n=1}^N (a_n - a_n^*) (\Psi_n \nabla \Psi_0 - \Psi_0 \nabla \Psi_n) - \frac{e^2}{m_e} \vec{A} \rho \quad (1)$$

The summation includes all solutions of the

Schrödinger equation for the unperturbed system. Ψ_n are the corresponding wavefunctions and $\rho = \Psi_0^2$ is the electron density in the unperturbed system. \mathbf{A} is the vector field. The coefficients a_n are obtained by applying perturbation theory using the magnetic field as the perturbation. Since a vector field is difficult to visualize (a vector is assigned to each point in space), a reference plane in which the current vectors are projected is usually selected (see Figure 3):

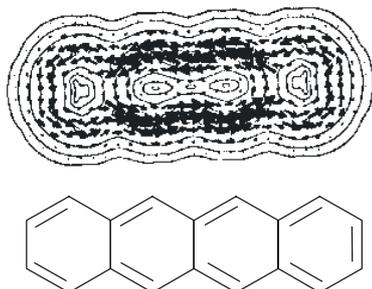


Figure 3: π -current density of tetracene, calculated in a plane parallel to and at a distance of one a_0 from the plane of the molecule (Steiner, E.; Fowler, P. W. *Int. J. Quant. Chem.* **1996**, 60, 609)

The arrows in Figure 3. represent the “interatomic currents” (a notation introduced by London), [15] which are interpreted as mobile or delocalized electrons. Currents that follow the left hand rule are called diatropic and are characteristic of aromatic systems. Those flowing in the reverse direction are paratropic and are observed in antiaromatic systems. The analysis of induced currents is a powerful tool for investigating aromaticity and NMR shielding effects.

However, there are three major drawbacks:

1. Since a graphical 3-D representation of a vector field is impossible (a vector is assigned to each point in space) the method is restricted to planar systems or arbitrary chosen sectional planes.
2. The current density is a function of the overall electron density (see last term in Eq. (1)). Hence, the largest currents are

induced close to the nuclei, where the electron density is highest. Since these local currents are much larger than the interatomic currents, they often obscure delocalization effects.

3. Current density maps in terms of delocalization are only interpretable in case of cyclic conjugation (aromaticity and antiaromaticity).

To avoid these problems we must satisfy the following conditions:

1. The parameter representing delocalization should be a scalar field to allow plotting as an isosurface.
2. The scalar field should be independent of the relative orientation of the molecule and the magnetic field (the current density is not).
3. The scalar field should not be a function of the electron density (the isosurface should represent the density of delocalized electrons and not the density as a whole).
4. The method should be generally applicable, not only for aromatic systems but also for any kind of conjugation (through bond, through space, ...) in any kind of system (ground state, excited state, transition state, ...)

The anisotropy of the induced current density $\Delta T_S^{(1)}$ is such a parameter. It can be computed from the current density tensor according to the following equation: [1, 16]

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

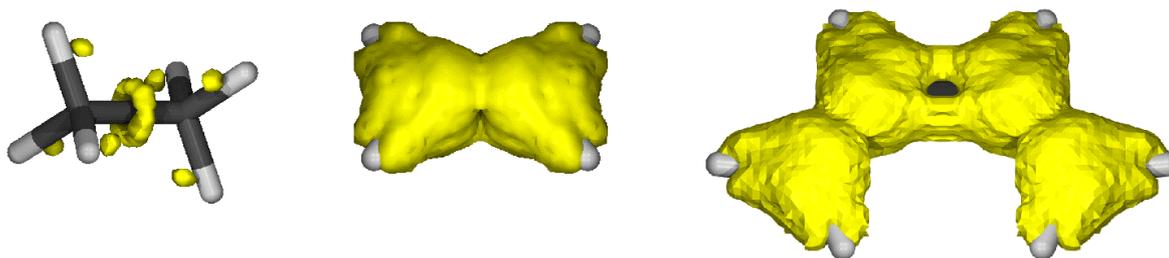


Figure 4: ACID surfaces of ethane, ethylene and *s-cis*-butadiene.

VISUALIZATION

We compute the current density tensor field using the continuous set of gauge transformation (CSGT) method, developed by Keith and Bader [17, 18] implemented in the Gaussian suite of programs. [19] Link 1002 was changed in such a way that the current density vector field was written to a file. The data was transformed to the scalar field of the anisotropy of the induced current density (ACID) according to the above equation and written in the in the cub file format. Isosurfaces were plotted using Povray. For 3D animations we used the Chime plugin, which is able to read cub files.

To provide additional information on the magnitude and direction of currents (e.g. diatropic or paratropic), current density vectors can be plotted onto the isosurface of ACID.

The only parameter that can be chosen in ACID is the isosurface value. This provides control over the sensitivity of the method and a way to quantify conjugative effects (small conjugative effects can be visualized using small isosurface values). We define the isosurface value at which the topology of the ACID boundary surface changes (e.g. breaks in two independent enveloping surfaces) as the critical isosurface value (CIV). The smaller the CIV between two atoms or groups the weaker is the conjugation.

EXAMPLES

We have tested our method extensively. In the first test stage we investigated small and well-known systems to prove consistency with current knowledge. Further emphasis was put on the fact that a broad range of conjugative effects should be covered to prove general applicability. The examples include different types of conjugation such as linear π -, cyclic π - (aromatic), through-bond- and through-space-conjugation. The systems investigated are ground states, excited states, and transition states.

In agreement with the general view of delocalization, alkanes such as methane, butane and cyclohexane do not exhibit delocalized bonds. This is represented by small ACID values around the nuclei and bonds. At isosurface values of 0.05 a.u. (the standard value used in most examples) only small areas of toroidal topology between two bonded nuclei (C-C and C-H) are visible, whereas double bonds exhibit ACID values at least two orders of magnitude larger. Interpreted in traditional terms, this means that the two electrons in a double bond are delocalized over both *p*-orbitals of the sp^2 carbons. In linearly π -conjugated molecules such as butadiene, delocalization is represented by a continuous boundary surface including all conjugated sp^2 carbons. However,

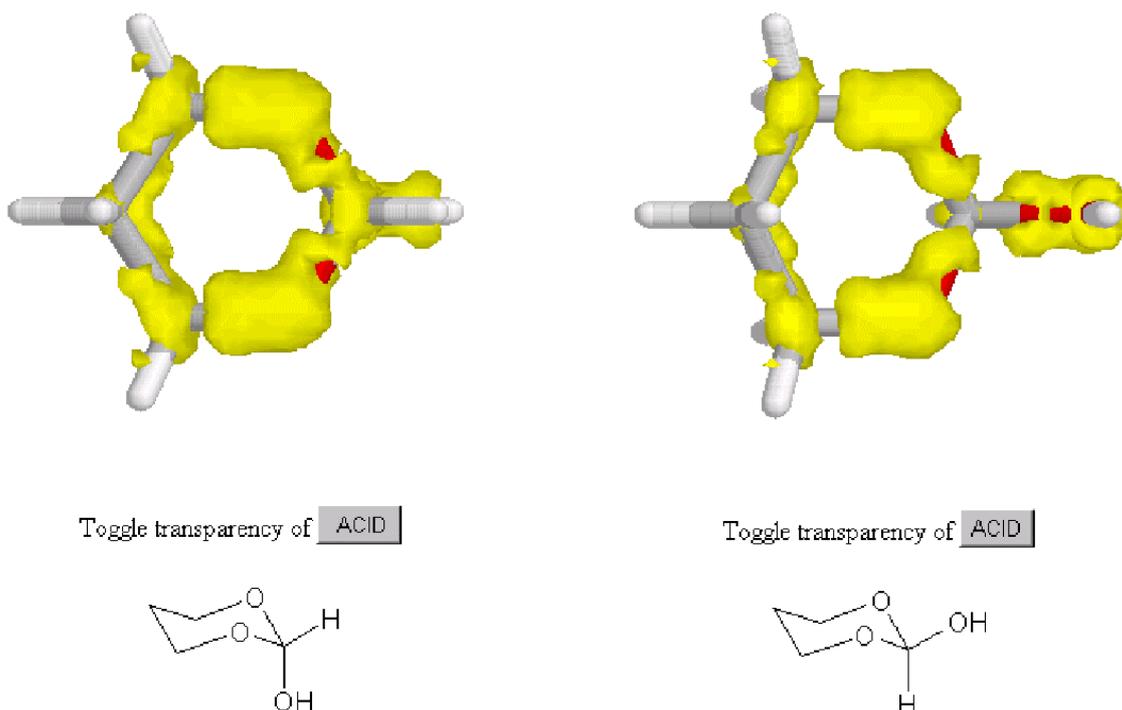


Figure 5: The anomeric effect in 2-hydroxy-1,3-dioxane.

again in agreement with the intuitive view, conjugation is less pronounced between the double bonds than within each double bond. The above defined critical isosurface value (CIV) is lower for the single bond between two double bonds than for the double bond itself. Thus, visualization of molecules using the ACID method is complementary to the information retained from the structural formulae, which only represent localized bonds. ACID plots for ethane, ethylene and *s-cis*-butadiene are shown in Figure 4.

More difficult to represent by traditional methods, and more interesting to investigate, are through-bond and through-space interactions. Figure 5 shows the anomeric effect in 2-hydroxy-1,3-dioxane as an example. For steric reasons (1,3-interactions) substituents in cyclohexane, tetrahydropyran, 1,3-dioxane and other six-membered rings with chair conformations usually prefer the equatorial over the axial position. Exceptions are heteroatom substituents in the α -position to a heteroatom in the ring. This is due

to the conjugation of the σ^* bond of the exocyclic C-heteroatom bond with the lone pair of the heteroatom in the ring. This conjugation is more favorable in the axial than in the equatorial position. What is difficult to explain within MO theory is instantly visible in the ACID plot.

There is a continuous isosurface from the lone pair of the endocyclic O to the exocyclic O-atom in the axial conformation and there is a discontinuity between the two O's in the equatorial conformation. Hence, the conjugation in the axial conformation is more pronounced, making it more stable. Note that there is also hyperconjugation between the ring O-atom and the neighboring CH_2 -group. This is another example of a well-known effect that is difficult to explain in terms of MO-theory but instantly visible in our ACID plot.

IMPLEMENTATION IN A GRAPHIC

ENVIRONMENT

Delocalization and conjugation are among the most important concepts in chemistry. These principles

are taught separately in organic, inorganic and physical chemistry from different points of view. The ACID method allows for the first time an integrated approach to teaching delocalization. To this end, we have implemented the ACID plots described above with additional 30 examples in a graphical environment for teaching purposes. We consider the following features to be important for didactical reasons:

1. Figures should replace text wherever possible.
2. Learning information should be divided into modules that fill one screen page (scrolling should be avoided).
3. One module (screen) should present only one main message.
4. The screen pages should present the information in such a way that the message becomes clear just by reading the titles and taking a close look at the pictures (self-explanatory as far as possible).
5. 3D-objects such as molecules and isosurface plots should be represented as 3D objects that can be translated, rotated and zoomed by the user. Additional information not necessary for understanding the main message should only be available in pull down menus.
6. Information containing dynamic data, such as conformational movements or reactions should be represented as dynamic objects (movie). Unlike videos that can be interrupted by pushing a (virtual) button, the movies should advance stepwise by interaction of the user (absolute control of the speed by the user, self-paced learning).
7. Important stages in a movie should be directly addressable by buttons.
8. If a movie contains 3D objects (e.g. molecules on a reaction coordinate) it should be possible to manipulate (translate, rotate, zoom) the 3D-objects in each frame of the movie by user

interaction.

9. Interactive features should be used whenever possible (explorative learning), e.g. different isosurface values for representation of the ACID should be offered in a menu so that the user can determine the critical isosurface value by trial and error.

Our learning module so far includes 25 molecules as 3D objects, and 6 reactions as movies. The graphic interface (learning environment) will be further refined in an iterative process by testing the system with students.

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