

RhoScope: A highly portable computer program for visualization of the zero-flux atomic surfaces

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Atomic boundaries are defined within the topological theory of atoms in molecules as zero-flux surfaces in the gradient of electron density. The so-defined atomic surfaces often have quite complicated shapes that reflect the local characteristics of the electron distribution. A highly portable computer visualization program, called RhoScope, that displays the zero-flux atomic surfaces is described in this article. Examples of atomic surfaces in the C_{60} cluster and the C_2H_2LiCl carbenoid, rendered with the help of RhoScope, are presented.

Keywords: atoms in molecules, zero-flux atomic surfaces, electron density

INTRODUCTION

Among many concepts often taken for granted by chemists is that of atoms in molecules. Although deceptively simple from the conceptual point of view, a theoretically rigorous definition of atoms in molecules can be obtained only with the help of quantum mechanics. As the electronic wavefunction of any chemical system contains all the information about its electronic structure, a universally applicable definition of atoms in molecules has to take the relevant characteristics of the electronic wavefunction into account.

A quantum mechanically consistent theory of atoms in molecules has been proposed by Bader¹ and has found numerous applications in the rigorous description of electronic structures of chemical systems.¹⁻⁸ In this theory, the knowledge of the electron density, $\rho(\vec{r})$, is sufficient to define both the atoms and the bonding pattern in any molecule. In order to accomplish this, a complete set of critical (extremal or stationary) points, $\{\vec{r}_{crit}\}$, at which the gradient of $\rho(\vec{r})$ vanishes,

$$\vec{\nabla}\rho(\vec{r}_{crit}) = 0 \quad (1)$$

Color Plates for this article are on page 35.

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is first determined. The set of position vectors, $\{\vec{r}_{crit}\}$, is then used as a starting point for construction of the so-called zero-flux surfaces, $\{S_A\}$. These surfaces, which constitute atomic boundaries, have the following property:

$$\forall_{\vec{r} \in \{S_A\}} \vec{n}(\vec{r}) \cdot \vec{\nabla}\rho(\vec{r}) = 0 \quad (2)$$

In other words, the normal to the surface, $\vec{n}(\vec{r})$, is orthogonal to the density gradient, $\vec{\nabla}\rho(\vec{r})$, at any point \vec{r} that lies on the atomic surface, S_A , of any atom, A. Determination of atomic surfaces involves either solving the respective differential equations² or tracing the boundaries of attractor basins.⁹ In either case, the resulting atomic zero-flux surface, S_A , is represented by a finite grid of points. These points are given by the intersections of rays extending from the nucleus, A, in the directions given by two spherical angles (θ, ϕ) with the corresponding atomic surfaces. Thus, each grid point, k, is assigned a five-component vector $(\theta_k, \phi_k, w_k, R_k, R'_k)$, where R_k is either zero or the distance of the second intersection from the nucleus, R'_k is the distance of either the first or the third intersection and w_k is the corresponding weight of numerical quadrature that is used in evaluation of atomic properties (see the following). If there are no intersections in the direction (θ_k, ϕ_k) (i.e., the atom is open in this direction), R'_k is set to a large number R_{max} (usually equal to 10 au, 1 au = 52.9 pm).

The atomic surfaces are often determined for the purpose of calculating one-electron properties of atoms in molecules. Let Ω_A (the atomic basin of A) be the portion of Cartesian space that is demarcated by the atomic surface, S_A . The atomic contribution to the one-electron property associated with operator \hat{O} is given by^{1,2}

$$\langle \hat{O} \rangle_A = \sum_j n_j \int_{\Omega_A} \psi_j^*(\vec{r}) [\hat{O}\psi_j](\vec{r}) d\vec{r} \quad (3)$$

where $\psi_j(\vec{r})$ is the jth natural orbital of the chemical system in question and n_j is its occupancy. In practice, the integrals entering Equation 3 are obtained by means of a mixed numerical-analytical quadrature,¹⁰

$$\begin{aligned} \langle \psi_j | \hat{O} | \psi_j \rangle_A &= \int_{\Omega_A} \psi_j^*(\vec{r}) [\hat{O}\psi_j](\vec{r}) d\vec{r} \\ &= \sum_k w_k \int_{R_k}^{R'_k} \psi_j^*(\vec{r}) [\hat{O}\psi_j](\vec{r}) r^2 dr \quad (4) \end{aligned}$$

where the point \vec{r} lies on the ray (θ_k, ϕ_k) at the distance, r , from the nucleus, A . The definition (Equation 3), when used in conjunction with the quadrature (Equation 4), affords rigorously defined atomic properties such as charges, kinetic energies and multipole moments with little computational effort.

Applications of atomic surfaces are not limited to the determination of atomic properties. As has been recently demonstrated,^{11,12} atoms (especially functional groups) are often highly transferable between similar molecules. Large molecules, such as polypeptides,¹¹ can be assembled from atoms and functional groups by anchoring them at the respective zero-flux surfaces. The electronic properties of molecules obtained by summing up the contributions from the assembled atoms are in good agreement with their exact counterparts.

In light of these considerations, visualization of the zero-flux atomic surfaces is of great importance to many aspects of electronic structure calculations. Such visualization can facilitate understanding of the topology of the electron density, which is often quite complicated.¹³ It can also aid researchers in studies of transferability of atoms and functional groups, and detection of possible errors and inaccuracies in the computed atomic surfaces. It should be emphasized here that the zero-flux surfaces have to be displayed without any smoothing in order to make such detection feasible. At the same time, the computed open surfaces usually have very rough boundaries that must be smoothed before displaying. For this reason, none of the commonly used plotting packages, such as AVS or Iris Explorer, can be used for our purpose and customized software has to be written. It is obvious that an atomic surface visualization program should be highly portable, easy to use and should readily interface with the presently used atomic surface determination software.^{9,14} In this report, we describe such a program, which is called RhoScope.

PROGRAM RHOSCOPE

The program RhoScope is written in C and currently runs on the IBM RS6000 and Silicon Graphics workstations. Because it uses only very basic graphics routines of the GL library¹⁵ that can be easily replaced by analogous routines from other packages, porting it to other machines is expected to pose no difficulties. RhoScope reads the atomic surface data from the output files of atomic surface determination programs such as VECSURF (which is a stripped down version of VECAIM)¹⁴ and PROSURF (which is derived from the program PROMEGA).⁹ These files are also used in efficient calculations of atomic properties with the program ATOMICI.¹⁰ The surface determination programs are interfaced with widely used quantum-chemical software such as GAUSSIAN 90¹⁶ and TURBOMOLE.¹⁷

RhoScope has several features that facilitate manipulation of the visualized atomic surfaces. The atomic surfaces can be translated in three directions X , Y and Z , and rotated with three Euler angles, THETA, PHI and ALPHA. Two modes of rotation are available, namely rotation around the nucleus in question (suitable for global explorations of the surface) and rotation around the current viewpoint, affording a detailed, local view. The current viewpoint itself can be

changed through translating or descending, with the latter involving motion along the current view ray.

The viewing direction can be reversed with the BACKWARD/FORWARD switch and the visual angle can be adjusted with the ZOOM option. The atomic surfaces can be displayed either as shaded objects (option OPALESCENT) or as wire frames (option TRANSPARENT). In the wire frame mode, the hidden lines of the surface are removed, whereas in the shaded objects mode, surfaces can be illuminated with either point (option POINT) or diffuse (option SURFACE) light. With the HUE option on, the surfaces displayed in the shaded objects mode acquire hues dependent on the distance from the nucleus.

All of the previously described options are entered either through sliders or push buttons, making the use of RhoScope transparent even to an inexperienced user. The UNSTICKY/STICKY option causes each click of the mouse button to be interpreted as either a single event or a sustained action, making simple animations possible.

The rendering of atomic surfaces carried out by RhoScope commences with construction of the surface grid from the input data (which is done by considering the nearest neighbors of each point) and triangulation of the entire surface. A direct display of the resulting triangles is not recommended, as it produces very rough sawtoothlike boundaries for open surfaces. To alleviate this possible problem, the boundaries of open surfaces are smoothed. The smoothing algorithm proceeds as follows. First, it finds all pairs of triangle edges that belong to the same boundary and share a common vertex. Second, if the two remaining free vertices in the pair of edges are not currently connected and the angle between the edges lies between critical values (equal to ca. 11° and 169° in our program), then the possibility of creating a new edge by connecting the free vertices is considered. Third, the new edge (and the resulting new triangle) is accepted if it does not pass through any of the existing triangles and the angle between the normals to the triangles that incorporate the two existing edges is less than a critical value (currently ca. 35°). These three steps of the smoothing algorithm are iterated until no new triangles are created.

Finally, the triangles are displayed on the screen. In the shaded objects mode, the triangles are drawn as filled polygons with the color intensity determined according to the illumination mode. In the point illumination mode, the intensity is proportional to the cosine squared of the angle between the normal to the triangle and the position vector of the triangle center with respect to the viewpoint. In the surface illumination mode, however, the intensity is calculated according to the same formula, but using the angle between the normal to the triangle and the direction of the z -axis instead. On the other hand, in the wire frame mode, the triangles are drawn as three separate lines and the hidden lines are eliminated by a software-imposed z -buffering. In either case, the surfaces are not smoothed. As already mentioned in the Introduction, this is done deliberately in order to facilitate visual detection of potential inaccuracies, errors or local defects in the computed zero-flux surfaces.

EXAMPLES AND DISCUSSION

The control panel of RhoScope is displayed in Color Plate 1. The nine sliders that occupy the lower portion of the window

control three coordinates of the viewpoint, three view angles and the values of DESCENT, ZOOM and HUE. The current values of these parameters, which can also be changed by clicking on the appropriate + and - fields, are displayed in the windows positioned below the respective sliders. The remaining options are switched on and off by six push buttons. Clicking on the seventh push button exits the program.

The atomic surface displayed in Color Plate 2 is that of the carbon atom in the C_{60} cluster, calculated at the HF/4-31G level of theory. Thanks to its high icosahedral symmetry, the cluster is composed of 60 identical atoms. Each of these atoms is shaped in the form of a sharp triangular pyramid that extends from the cluster center and is open to the outside. The three walls of the pyramid correspond to three bonds that connect each carbon atom with its neighbors. At the view angle displayed, the nucleus of the carbon atom is hidden from view. One should note the readily discernible corrugations on the walls, which are due to the less-than-perfect performance of the surface determination program.

Our two other examples employ atoms in the $H_2C=C\cdot LiCl$ carbenoid that have quite interesting surfaces. In this molecule, the formally divalent carbon atom of the $H_2C=C\cdot$ moiety is bonded to the $LiCl$ molecule in a linear fashion. Its atomic surface, calculated from the MP2/6-311G** electron density, is displayed in Color Plate 3. The carbon atom (with the position of its nucleus denoted by a blue dot) has a bipartite zero-flux surface. The upper part of the surface corresponds to the $C-Li$ bond and the lower part demarcates the two carbon atoms of the carbenoid. The indentation in the upper part, which originates from the small lithium atom, is clearly visible. In contrast, the carbon-carbon atomic boundary is almost flat.

The lithium atom also leaves its mark on the atomic surface of chlorine in the same carbenoid. The surface, which is shown in Color Plate 4, is almost open, with the chlorine atom occupying the right portion of the plate (note the Cl nucleus). By comparing this surface with the previous one (after rotating it clockwise by 90°), one immediately concludes that the lithium atom, in this case, has a shape resembling a flying saucer.

These examples illustrate some of the many morphologies possessed by atoms in molecules. With the use of RhoScope, the complicated shapes of the zero-flux atomic surfaces can be examined, explored from both outside and inside, and checked for possible imperfections or errors. With its high portability, RhoScope can be run on most of the currently available Unix workstations and even on high-end personal computers after only minimal adjustments to the code.

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REFERENCES

- 1 Bader, R.F.W. *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990
- 2 Biegler-König, F.W., Bader, R.F.W. and Tang, T.H. Calculation of the average properties of atoms in molecules II. *J. Comput. Chem.* 1992, **3**, 317-328
- 3 For a recent review on rigorous analysis of electronic wavefunctions, see Cioslowski, J. and Surjan, P.R. An observable-based interpretation of electronic wavefunctions: application to "hypervalent" molecules. *J. Mol. Struct. (THEOCHEM)* 1992, **255**, 9-33
- 4 Cioslowski, J. Isopycnic orbital transformations and localization of natural orbitals. *Int. J. Quantum Chem.* 1990, **S24**, 15-28
- 5 Cioslowski, J. Partitioning of the orbital overlap matrix and the localization criteria. *J. Math. Chem.* 1991, **8**, 169-178
- 6 Cioslowski, J. and Mixon, S.T. Covalent bond orders in the topological theory of atoms in molecules. *J. Am. Chem. Soc.* 1991, **113**, 4142-4145
- 7 Cioslowski, J. and Mixon, S.T. Topological properties of electron density in search of steric interactions in molecules: electronic structure calculations on ortho-substituted biphenyls. *J. Am. Chem. Soc.* 1992, **114**, 4382-4387
- 8 Cioslowski, J. and Mixon, S.T. Electronegativities *in situ*, bond hardnesses, and charge-transfer components of bond energies from the topological theory of atoms in molecules. *J. Am. Chem. Soc.* 1993, **115**, 1084-1088
- 9 Keith, T.A. *Molecules in Magnetic Fields*. PhD thesis, McMaster University, 1993
- 10 Cioslowski, J., Nanayakkara, A. and Challacombe, M. Rapid evaluation of atomic properties with mixed analytical/numerical integration. *Chem. Phys. Lett.* 1993, **203**, 137-142
- 11 Chang, C. and Bader, R.F.W. Theoretical construction of a polypeptide. *J. Phys. Chem.* 1992, **96**, 1654-1662
- 12 Bader, R.F.W., Popelier, P.L.A. and Keith, T.A. Theoretical definition of a functional group and the molecular orbital paradigm. *Angew. Chem. Int. Ed.*, in press
- 13 Cioslowski, J., Mixon, S.T. and Edwards, W.D. Weak bonds in the topological theory of atoms in molecules. *J. Am. Chem. Soc.* 1991, **113**, 1083-1085
- 14 Cioslowski, J. An efficient evaluation of atomic properties using a vectorized numerical integration with dynamical thresholding. *Chem. Phys. Lett.* 1992, **194**, 73-78
- 15 McLendon, P. *Graphics Library Programming Guide*, Silicon Graphics Inc., Mountain View, California, 1992
- 16 Frisch, M.J., Head-Gordon, M., Trucks, G.W., Foresman, J.B., Schlegel, H.B., Raghavachari, K., Robb, M., Binkley, J.S., Gonzalez, C., Defrees, D.J., Fox, D.J., Whiteside, R.A., Seeger, R., Melius, C.F., Baker, J., Martin, R.L., Kahn, L.R., Stewart, J.J.P., Topiol, S. and Pople, J.A. GAUSSIAN 90, Revision F. GAUSSIAN, Inc., Pittsburgh, Pennsylvania, 1990
- 17 Ahlrichs, R., Bär, M., Häser, M., Horn, H. and Kölmel, C. Electronic structure calculations on workstation computers: the program system TURBOMOLE. *Chem. Phys. Lett.* 1989, **162**, 165-169