Graphics visualization of molecular surfaces

S. R. Gadre and A. Taspa

Department of Chemistry, University of Poona, India

An algorithm for generation and visualization of a variety of molecular surfaces is described. The algorithm employs center-of-mass or nuclei-centered spherical polar coordinate systems. In the present work, surfaces based on two fundamental molecular scalar fields, viz., the molecular electron density (MED) and the molecular electrostatic potential (MESP), are considered. Four such surfaces are presented: a constant MED surface with $\rho = 0.002$ au; a minimal MESP anionic surface defined recently by Gadre et al.;[5] a molecular covalency surface with a constant MESP value χ (χ being the Mulliken electronegativity value); and the van der Waals (vdW) surface. The MESP is superposed as a "texture" on the first and last surfaces.

The color graphics visualization of these surfaces is implemented on a Silicon Graphics IRIS 4D/20 workstation. Several illustrative examples are presented.

Keywords: molecular graphics, molecular surfaces

INTRODUCTION

Powerful methods for theoretical and computational investigations of molecular electronic structure[1] have become available with the advent of more powerful computers during the last two decades or so. One can thereby generate molecular electronic wavefunctions and properties in a routine way for small- and medium-sized molecules. On the other hand, workstation-based graphics tools enable the attractive visualization of these properties. Certainly, to a practicing chemist it is more valuable to get a three-dimensional representation of the molecular property under consideration, rather than to read and try to interpret "numbers gushing from a computer."[2]

Three-dimensional information for molecules can be extracted in terms of a variety of scalar fields. Molecular electron densities (MEDs) in position and momentum spaces, molecular electrostatic potentials (MESPs), as well as bare nuclear potentials (BNPs), are some of the scalar

fields utilized in the literature for visualization purposes. In particular, the pioneering works due to Bader[3] have popularized the use of the MED, as well as its Laplacian, in chemical literature. Hehre et al., as well as Bader et al.,[3] advocate the use of a constant electron density (MED = 0.002 au) for the visualization of molecular shapes and sizes. This surface encloses approximately 98% of the electronic charge of neutral molecules.[3] This surface, with a superposed property of MESP has been utilized by Politzer et al.[4] for predicting the sites of nucleophilic attack. The logic here is that there are no nonnuclear maxima within the MESP. Hence, one has to devise a surface property for modeling nucleophilic substitutions. The van der Waals surface (vdW) is also routinely employed in the literature for predicting reactivity patterns of molecules.

Recent works due to Gadre and coworkers[5–8] have offered definitions of some novel MESP-based molecular surfaces. An example of such a surface is the so-called minimal MESP surfaces for anions.[5] The construction of this surface is based on the theorem proved by Pathak and Gadre:[6] along every ray in any outward direction starting from a nucleus in a molecule, the MESP V must attain at least one negative-valued minimum. Such a surface encompasses all outward lying negative MESP-valued critical points, and satisfies the equation $\vec{\nabla}V \cdot d\vec{s} = 0$, where $d\vec{s}$ is the outward normal to the surface. The authors further proved[6] that the net charge residing outside this surface *equals* the formal charge carried by the anion. This construction was later utilized by Gadre et al.[7] for three-dimensional visualization of anionic surfaces.

More recently, Gadre[8] has defined a *covalency surface* for molecules as an isopotential surface with $V = (I + A)/2$. Here, I and A are, respectively, the ionization potential and electron affinity of the molecule under consideration. This definition follows the earlier works due to Politzer et al.[9] for the case of atomic systems. More recently, Harbola et al.[9] conjectured that "the corresponding formula should also work for molecules. However, this has not yet been tested." The work due to Gadre[8] provides this generalization. However, for graphical visualization purposes, the covalency surface offers an illustration of a constant MESP surface.

The vdW surfaces have been employed widely in the literature for several decades. In particular, they are widely used for obtaining potential-derived atomic charges.[10] In this method, the atom-centered charges are obtained by effective least-squares fits to the MESP on the Connoly envelopes (based on scaled vdW spheres).

GENERATION OF THE SURFACES

In this section, we present the algorithm for generating various surfaces described in the present work. The main algorithm is discussed with reference to the simple MED $\rho = 0.002$ surface. For a complicated molecule this algorithm may not generate the proper surface. In such a case, the main algorithm is extended to generate polygons for the complicated surface, and is discussed in a later section. The simple molecules are those (e.g., ClO_3^- or NO_2^-) which lack complicating features such as a large ring, or bent structures (e.g., the zeolite cluster or crown ether). Another potential candidate for a complex surface is the C_{60}^- anion, which has recently been studied.[11] The construction of other surfaces, like the covalency surface, the minimal MESP surface, etc., can be made with very little modification to the main algorithm.

The algorithms for generating the surfaces discussed here are based on spherical polar coordinate systems. The main objective of the algorithm is to find a point (x,y,z) lying on the surface on a ray along the direction (θ,φ) emerging from a reference point—for example, a nucleus or the center-of-mass of the molecule.

It is easier to construct surfaces when the points are uniformly distributed. The (θ,φ) mesh is found to be very useful in this respect. The construction of the polygons can then be done by simply connecting the points on the neighboring rays corresponding to (θ,φ), $(\theta,\varphi + \Delta\varphi)$, $(\theta + \Delta\theta, \varphi + \Delta\varphi)$, and $(\theta + \Delta\theta,\varphi)$ for all θ and φ in the mesh. The basic algorithm given below illustrates the generation of the MED $\rho = 0.002$ surface for simple molecules. One can generate other property-based surfaces (isosurfaces) by substituting the property evaluation routine in place of the MED evaluation routine, and searching for the required value instead of 0.002 au. The surface generation part of the algorithm is implemented using FORTRAN on PARAM and a Silicon Graphics IRIS 4D/20. The visualization part is written in C with the GL library on a SG IRIS 4D/20 workstation.

Algorithm for generating simple surfaces (MED $\rho = 0.002$)

Step 1. Select a ray emanating outwards from the center-of-mass in a direction (θ,φ) (starting with $\theta = 0.0$ and $\varphi = 0.0$, say). The program will evaluate the density values along this ray to find the required point.

Step 2. Find the interval on this ray which brackets the required density value of 0.002 au. To find this interval, take some initial trial radius r on the given ray and consider the interval $[r - \delta r, r]$ as the "near" interval and the interval $[r, r + \delta r]$ as the "far" interval.

Step 3. Evaluate ρ at the endpoints of the near and far intervals and check whether the 0.002 value lies in between.

Step 4. If the value does not lie in this interval, then shift the near interval closer by some δr and the far interval outwards by δr. That is, the next near interval will be $[r - 2\delta r, r - \delta r]$ and the next far interval will be $[r + \delta r, r + 2\delta r]$. After forming these new intervals repeat Step 3.

Step 5. Once the interval which brackets the required value is found, then by applying a quadratic interpolation and bisection method within that interval, find the coordi-

nate on the ray which satisfies the condition $\rho = 0.002$, to a prescribed numerical accuracy.

Step 6. Repeat Steps 2 to 5 for the complete mesh of θ and φ, θ varying from $0°$ to $180°$, and φ varying from $0°$ to $360°$ with some delta (typically, 7200 points, with $\Delta\theta$ and $\Delta\varphi$ equal to $3°$).

Step 7. For visualization, generate quadrilaterals by joining the coordinates of the rays corresponding to (θ,φ), $(\theta, \varphi + \Delta\varphi)$, $(\theta + \Delta\theta, \varphi + \Delta\varphi)$, and $(\theta + \Delta\theta, \varphi)$ for all (θ,φ), and construct the surface.

Step 8. Use may be made of additional features, such as shading of the quadrilaterals, hidden-line removal, texture of some other properties, etc., to improve the visualization.

Modifications for generation of anionic minimal surfaces

For generating simple minimal surfaces for anions, the only modifications to the preceding algorithm will be in the searching process on the given ray. Here we search for a *directional negative-valued minimum* in the MESP function along the ray (θ,φ).

For minimal surfaces, checking the interval entails determining whether the MESP function value of the middle point on the interval is smaller than the lower and upper bound points. That is, whether $V(r - \delta r) > V(r_m) < V(r)$, where r_m is the middle point on the interval under consideration.

It is known that finding a minimum of a function can be done by checking if the first derivative of the function is zero at a point. This property can be used for calculation purposes. Once the relevant interval is found, then using Lagrange interpolation, a quadratic curve is fitted in the interval, and its derivative is equated to zero. By solving the quadratic equation, the point where the function value is minimum can be obtained. The condition that $|\vec{\nabla} V \cdot \vec{ds}| < \epsilon$ could be checked before actually plotting the surface.

Only these modifications need to be done; the remaining steps are identical to those discussed in the preceding section.

Extensions for generating complex surfaces

Since most of the simple molecular surfaces are closed surfaces, the basic algorithm can be used. However, some molecular surfaces may be complicated in shape, and in general, can contain "holes" if the molecule is a ring structure, as in crown ether, the C_{60}^- anion,[11] zeolite, etc. Else, they may possess long bent chain structures, such as the one exhibited by the trilaurin molecule.[10] The basic algorithm may not generate a proper surface for these kinds of cases. Hence, some improvements to the main algorithm are required, as discussed below.

Instead of taking the center-of-mass of the molecular frame as the origin of the polar coordinate system, each nuclear (atomic) coordinate of the molecule can be considered to be the origin, and for each such origin, the surface can be generated. It may be noted that, for a given molecule, there may be multiple surfaces. These surfaces are later merged to form a single surface by eliminating the overlapping points. The modifications required in the main algo-

rithm for the generation of complex (multicentered) surfaces are described in the following steps:

- For each nuclear coordinate in the molecule, generate the surface using the basic algorithm (i.e., find the required surface value for all the given rays of θ and φ per atomic coordinate).
- Consider such an atom-based surface S_1. For all polygon points in S_1, find the nearest surface center point (by using the distance formula). Classify the polygons of the surface according to the following criteria:
  - All four points of the polygon are nearer to its own surface center coordinate (i.e., S_1)
  - All four points of the polygon are closer to some other surface's center coordinate (say, S_m)
  - Some points of the polygon are closer to its surface center (i.e., S_1) and some are closer to another surface center (S_m).
- For all the surfaces (from S_1 to S_n), classify the polygons according to these criteria.
- For visualization, consider all the polygons which satisfy the first criterion and ignore all the polygons which satisfy the second criterion.
- The polygons which satisfy the third criterion are the polygons at the boundaries of the intersections of two or more surfaces. If we ignore these polygons, then there appears a gap at these boundaries. But if we consider these polygons, then some polygons which are very large do not show the real surface, though all the four points lie on the surface. If one takes $\Delta\theta$ and $\Delta\varphi$ very small, then there do not appear any gaps at these boundaries; otherwise small gaps may be seen. Hence, some technique must be developed to fill in these gaps. In one such technique, the points of the polygon which are nearer to some other surface (S_m) are replaced by that particular surface's center coordinate. By doing this, the polygons which are at the boundaries will be rotated, and will enter the other surface, which is joined to the center coordinate of surface S_m. Hence, some portion of these polygons will fill in the gaps. Another way would be to interpolate the lines of the polygon (consider that the points P_1, P_3 are closer to S_1 and that the points P_2, P_4 are closer to S_2), say P_1P_2 and P_3P_4 till the points $P'_3P'_4$ are found close to the center of S_1.

Generation of van der Waals' surfaces with MESP texture

For the vdW surface representation, the points are generated on the spheres of vdW radii centered at nuclear positions.
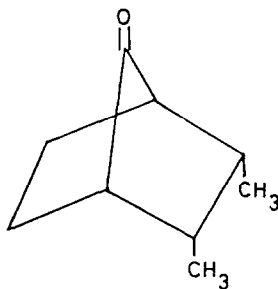

Figure 1. 2,3 Dimethyl norbornyl 1-one.

(Note that here the searching process is *not* involved.) For each point in the (θ,φ) direction on this surface, the MESP (or any other property to be textured) can be calculated for superposition. The construction of the surface is done as discussed in the basic algorithm. But while constructing the surface, one can ignore the quadrilaterals which are inside other spheres. For superposition, the colors for each quadrilateral are assigned based on the MESP (or other property evaluated at that point).

ILLUSTRATIVE EXAMPLES

All the calculations (at the restricted Hartree-Fock level) for the generation of the surfaces were performed employing a parallel package INDMOL.[12] Information regarding the basis set used is specified below.

MED = 0.002 surfaces

Color Plate 1 shows the $\rho = 0.002$ surface of the $B_5H_5^{2-}$ ion.[13] This surface was generated (employing the DZp basis set) using the basic algorithm, with $\Delta\theta = 5°$ and $\Delta\varphi = 5°$.

Color Plate 2 shows the MED $\rho = 0.002$ surface of the 2,3 dimethyl Norbornyl 1-one molecule (cf. Figure 1)[14] with two end methyl groups. For the Hartree-Fock calculation, a 6-31G basis was employed. On this surface, the MESP is textured according to its values. The deepest red color indicates the most negative MESP value, and the deepest blue color indicates the most positive MESP value, around the carbonyl O atom. Intermediate colors are mixed and assigned for a range of MESP values. From the figure, it is observed that the nucleophilic attack is from the syn end, as it has recently been observed experimentally.[13]

Minimal MESP surfaces

Color Plates 3 and 4 show, respectively, the minimal surfaces of chlorate (ClO_3^-) and phenolate ($C_6H_5O^-$) anions. The corresponding basis sets are TZp and DZ. It has been verified numerically that the polygons generated with the single-centered algorithm satisfy $|\nabla V \cdot d\vec{s}| < \sim 10^{-3}$ or less. On this surface, the texture of the directional minimum MESP values for corresponding rays is superposed. Ranges are made out of these MESP values, and the corresponding colors are varied from red to blue. Red represents the most negative MESP value, and blue refers to the least negative MESP value. Linear interpolation is done for the intermediate color mixtures.

Covalency surfaces

Color Plates 5 and 6 depict, respectively,[8] the covalency surfaces of boron trifluoride (BF_3), employing the DZ2p basis set, and trans butadine (C_4H_6), using the 6-31G basis, respectively. These pictures are constructed by using the multicenter algorithm. One may further superpose electron density as a texture on these surfaces.

Van der Waals surfaces

Color Plates 7 and 8 show the vdW surfaces, with MESP texturing, of the ethane (C_2H_6) molecule (4-31G basis) and

the ZSM-5 (STO-3G) zeolite cluster. The MESP value ranges and its corresponding assigned color representations are also shown. Here, the basicity patterns of the various oxygens are clearly brought out from the figures.

CONCLUSIONS

In summary, an algorithm to generate and visualize a variety of molecular surfaces is described in the present work. The construction of these surfaces is made on the basis of two fundamental chemical properties, viz., the molecular electron density and the molecular electrostatic potential. One can texture a surface, such as MED = 0.002 or a van der Waals surface, with the MESP values. This clearly brings out the reactive sites in the molecule. On the other hand, the minimal MESP surface for anions can be utilized to predict potential sites of electrophilic attacks. The multicenter algorithm discussed here for the complex molecules is not expected to pose any problems. However, in the case of anions which are doughnut-shaped, such as C_{60}^-, only the "outer" MESP minimal surface can be obtained with this algorithm. If implemented on the Silicon Graphics IRIS 4D/20, the surface plotting typically take less than 10% of the time required for its quantum chemical generation. The programs described here are available for distribution through the Center for Development of Advanced Computing (C-DAC) at a nominal cost. Queries for this may be addressed to one of the authors (Gadre). These surfaces are constructed by the use of one-electron properties, and are not expected to show much variation with basis set (beyond DZ-quality), or correlation. It is thus hoped that these MED- and MESP-based surfaces can be meaningfully employed for molecular structure and reactivity studies.

ACKNOWLEDGMENTS

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