On the graphical display of molecular electrostatic force-fields and gradients of the electron density

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Gradients of the electrostatic potential and electron density of methyl fluoride are displayed as coloured regions on isopotential surfaces. Shading is used to achieve 3D perception and also to encode the direction of the gradient. Colouring the density by the magnitude of the gradient is demonstrated to provide an intrinsic mechanism for colouring the molecular density, so that the underlying atomic structure is vividly displayed in hues commonly used in molecular ball and stick models. The algorithm for contouring a 4D object and drawing coloured, shaded isopotential surfaces is described.

Keywords: methylfluoride, electrostatic potential, electron density, density colouring

The properties and chemistry of a molecule are determined by its structure. Differences between structures of molecules can be used to correlate, explain and predict differences in observed properties and reactions. Although rarely acknowledged explicitly, the concept of 'structure', as used by chemists, embodies both the static structural framework and the responses of the frame to perturbations. Thus, chemists speak not only of chemical bonds, but strong and weak bonds, as well as hard and soft vibrational modes. It is the 'flexible' interpretation of structure that perpetuates structural models.

The following sections describe the use of computer generated graphics for displaying information about molecular responses to structural perturbations and the 'hardness' or 'softness' of molecules in the vicinity of the molecular surface. Some years ago, Wilson[1] built a computer controlled tactile feedback system (called a 'touchy-feely machine) which allowed direct interaction of the chemist with a molecular dynamics simulation. Thus the user had direct interaction with molecular forces which are the gradients of the molecular energy. This paper focuses on the graphical display of changes in the molecular electron density and electrostatic potential, rather than the tactile display of the gradients of the molecular energy.

All reported densities and electrostatic potential are generated using the INDO/S model[2]. The molecular geometries are determined using the optimization methods developed by Zerner and Head with the standard INDO parameterization[3]. The use of semiempirical models is strictly a matter of convenience, and all algorithms, results and procedures are directly applicable to *ab initio* models as well.

GRADIENTS OF THE ELECTROSTATIC POTENTIAL AND DENSITY

The molecular energy, $E(R)$, is a scalar field defined over R, the coordinates of the nuclei in the molecule. On the other hand, the electrostatic potential, $V(r;R)$, and the molecular electron density, $\rho(r;R)$, are both scalar fields defined over all space, r, and all nuclear arrangements, R. Thus, the electrostatic potential and the density can have gradients with respect to two different classes of coordinates. The first is the gradient with respect to r, $\nabla V(r)$ and $\nabla \rho(r)$. The second is the gradient with respect to internuclear displacements R, $\nabla V(R)$ and $\nabla \rho(R)$. Both gradients provide information about the molecular structure and its response to perturbations.

In the case of the electrostatic potential, $-\nabla V(r)$ is the force on a unit test charge at position r. The electrostatic force, or electric field, can be used to describe long-range dipole–molecule interactions. Recently, Lavery and Pullman[4] have emphasized the importance of electric fields for the interpretation of biological activity. They projected shadows of molecular van der Waals surfaces and coloured the shadows to indicate electrostatic potentials and fields.

For the density, $\nabla \rho(r)$ represents the neighbouring anisotropy of the density. The shortest path between two bonded nuclei that passes through the saddlepoint of the electronic density in the internuclear region and follows the density gradient from the saddle point to each nucleus is the bond path, defined by Bader[5]. Concepts such as 'partitioning surfaces' and 'atoms in a molecule' are also derived from $\nabla \rho(r)$. For both V and ρ, the gradient with respect to r can be useful in generating effective graphical displays.

GRAPHICAL REPRESENTATION OF V AND ρ

The surfaces of 3D objects (balls, cones, etc.) are described as parametric functions of two variables and thus form scalar fields over two variables. Similarly, scalar fields over three variables can be visualized as surfaces of 4D objects. While the display of 3D objects has been a textbook exercise for ten years[6] and the holographic display of space-filling molecular models was demonstrated in 1977[7], the display of 4D objects requires the translation of four dimensions into three, or fewer, spatial dimensions and the use of colour, or motion, for representation of higher dimensions. Pictorial representations of molecular densities have been classified[8] by dimensionality (2, 3 or 4) and by type (graphs, contour, etc.). The best possible display must preserve the three-dimensionality of the molecular structure while giving 'complete' information on the potential or density. Thus an ideal depiction of V and ρ requires a 4D display.

A commonly used method for displaying molecular orbitals and densities (see Colour Plate 1) was developed by Jorgensen[9,10] who displayed constant amplitude molecular orbital surfaces as wire frames with different constant amplitude surfaces 'coloured' according to value of the contour. More recently, Houte, Pietro and Hehre[11] have developed a ray-tracing algorithm for displaying constant amplitude orbital surfaces as shaded coloured surfaces. The ray-tracing method starts from the viewing plane and traces toward the molecule, evaluating the orbital amplitude as the trace proceeds. The trace terminates when it encounters the sought-for orbital surface, and the surface element is drawn. The ray-tracing method achieves efficiency by directly constructing the *viewable* surface (see Colour Plate 2) and avoiding the search for hidden lines required by Jorgensen's method. It also eliminates the problems which Jorgensen's method can encounter if the surface is not closed.

Both approaches give information about orbital amplitudes and the direction of its gradient (which is always perpendicular to the direction of the constant amplitude surface). In the wire frame model, the direction of the gradient is coded in the curvature of the wires. In the shaded surface model, the intensity of the reflected light is proportional to the gradient along the direction from the light source.

Fuller and Dos Santos[12] have developed a method for displaying *both* the magnitude and direction of the gradient using a vector field display of 3D arrows. This traditional display is not very suitable for lower resolution raster devices more commonly used in many laboratories.

Usually, constant-value representations of functions, like the density or electrostatic potential, are restricted to two, or three, values of the function to keep the picture clear. However, even with the restriction to a few constant value surfaces, constant surface pictures can be made more informative by colouring portions of the surfaces.

Colour Plate 3 is an isopotential picture of the electrostatic potential of methyl fluoride in which the magnitude of the gradient on the surface has been colour-coded. The surfaces in Figure 3 give complete information about the isopotentials in methyl fluoride

and the magnitude and direction of the gradient. The red and yellow mushroom cap above the fluorine atom is the -0.03 Hartree (-19 kcal) isopotential surface. The blue and white isopotential enclosing CH_3F is the $+0.03$ Hartree ($+19$ kcal) isopotential surface. Each surface has its own four-colour code for the magnitude of the gradient. The negative (positive) surface uses the colours violet, red, yellow and white (green, cyan, blue, and white) to indicate the change from nearly zero to large positive magnitudes. Several points about this surface should be noted. First, nucleii are always contained within positive isopotential surfaces. Second, proper choices of the positive isopotential contour level yield isopotentials similar to molecular van der Waals surfaces. Third, the mushroom cap over F describes the potential from the F lone pairs and remains further away from F than would be anticipated from more usual representation by partial charges drawn on molecular skeletons. Finally, the colour changes from red to white (blue to white) occur as the top of the F atom is approached and the positive and negative surfaces come closer together. This is as expected, since the forces between a positive point charge and a negative point charge are greatest along the line joining the points.

Colour Plate (4a) shows a monochromatic 0.01 isodensity surface of CH_3*. The surface is remarkably uninteresting. If it were not for the atom labels, it would be extremely difficult to distinguish the F atom from a C or H atom. Colour Plate 4(b) shows the same 0.01 isodensity surface coloured by the magnitude of the gradient. The colour code is as follows:

Colour	Gradient value	
Yellow	0.0000–0.0156	
Violet	0.0156–0.0313	
White	0.0313–0.0468	Carbon, Hydrogen
Blue	0.0468–0.0625	Nitrogen
Red	0.0625–0.0781	Oxygen
Green	0.0781–0.0938	Fluorine
Cyan	0.0938–0.1094	
Yellow	0.1094–∞	

The colour code was derived by computing 0.01 isodensity surfaces for CH_4, NH_3, H_2O and HF. The average of the gradient on the parts of the surface within 1.5 times the atomic covalent radius was computed for each atom. Within the INDO/S approximation, on the 0.01 isodensity surface, the following average magnitudes of the gradient are found: H (0.043), C (0.042), N (0.052), O (0.062), F (0.076). By comparison, in CH_3F, F has an average gradient of 0.073 and C an average gradient of 0.046. The values of the gradient as a function of atomic nuclear charge approximately fit a straight line with a slope of about $1/100$. The colour code is chosen so that values of the gradient near the characteristic gradient of a particular atom are coloured according to generally recognizable atomic model colours. Hydrogen is white, nitrogen is blue, and oxygen is red. Since black is difficult to shade with a limited intensity range and since the gradients for carbon and hydrogen are essentially equal, carbon is assigned white. Fluorine is treated like chlorine and assigned green. Because atomic densities vary systematically, similar characteristic colour assignments can be made for any

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*The term '0.01 isodensity' means the orbital density on this surface has a value of 0.01. Since there are two electrons per orbital in CH_3F, the electron density on the 0.01 isodensity surface is 0.02.
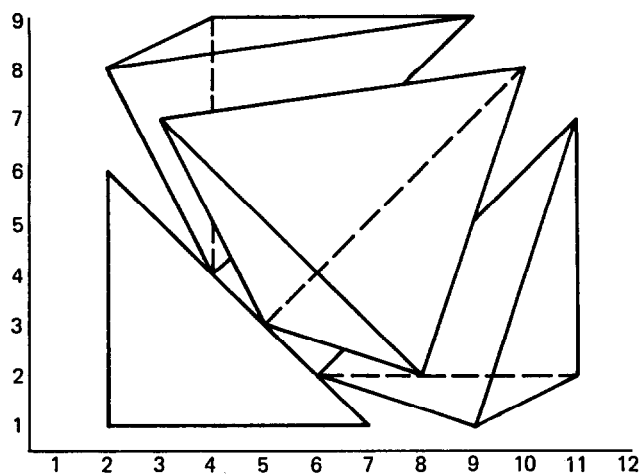
Figure 1. The five tetrahedra partitioning of grid cells for contour generation. To simplify the picture, the front upper right-hand tetrahedron is not displayed. Note that this is a left-handed partitioning because the diagonal cut on the front face starts in the upper left-hand corner

isodensity value.

As anticipated,[5] the region near the fluorine atom has the largest gradient (green), while the C and H regions have the lowest gradient (white). Similarly, the red and blue bands around the C–F bond are expected. By the same token, the solid colour surrounding each atom is no accident and the colour change between two atoms occurs near the atomic surface boundary[†]. This Colour Plate shows that for a given value of the density, atoms can be distinguished (coloured) by the gradient. In this sense, atoms in molecules have intrinsic colours.

METHOD FOR DISPLAY GENERATION

The method used for the generation of Colour Plates 3 and 4 deserves some comment because it is different from the methods used in References 2 and 3 (Colour Plates 1 and 2 respectively), it is faster for the concurrent generation of many views, and because it can handle open surfaces without problem. Colour Plates 3 and 4 are generated from a list of function values and gradients calculated on a 3D grid. The grid divides the potential into adjacent cells, or boxes. Colours are assigned to each box corner according to the magnitude of the gradient. Isovalued surfaces are found by partitioning each box containing a section of the isopotential into five tetrahedra (see Figure 1). Four tetrahedra result from cutting off the corners of the box. The fifth comes from the middle of the box. The function values at the corners of each tetrahedron are checked and any intersections of the contour with edges of the tetrahedron are calculated by linear interpolation. The coordinates of the edge intersections form the corners of one, or more, triangles which are pushed onto a data stack defining the surface. In addition, the interpolated components of the gradient vector and the interpolated value of the colour at each triangle corner are pushed onto the stack.

Next, the stack containing the surface information is passed to a display procedure which (1) aligns the surface to the viewing angle, (2) converts coordinates, gradients

†Note that the algorithm described later could be easily augmented to search for gradient extrema on the isodensity surface and more rigorously assign colour regions based on atomic surface boundaries.

and colours to integer format* and (3) draws a filled triangular patch with full interpolation of colour *and* shade by using an incremental DDA (digital differential analyser) algorithm[6]. Surfaces are hidden by storing new colour values for a given pixel (display dot) if the new z value is smaller than the current z value for that pixel; that is, the pixel is coloured if it is closer to the observer than the pixel currently stored in the display. The shading technique is a simplification of that of Phong[13]. The significance of the smooth shading is illustrated by Colour Plate 5 in which shading is done according to the magnitude of the normal vector to the triangle and is not interpolated (flat shading). The light model is a diffuse reflection model in which light is reflected from the surface according to Lambert's law and the light source is placed far behind the observer. Thus the light reflected from a surface section towards the observer is proportional to the component of the normal (gradient) of the isovalue surface in the direction of the observer. In the observer's frame, this is the z-component of the normal (gradient).

Currently, the display procedure is well-developed with some graphics display manufacturers implementing either Phong or Gourad shading with z-buffering on specialized graphics processors. Thus this algorithm is appropriate for evolving graphics hardware.

The present implementation generates the entire picture on a DEC VAX 11/780 and downloads it to a DEC PRO 350 microcomputer for display. Approximately 300 CPU seconds are used to generate five views of a function defined on a $51 \times 51 \times 51$ grid. The microcomputer display is a standard PRO 350 bit map video controller with the standard extended bit map module and colour monitor. Normally, the controller operates in eight colour (3-bit plane) mode with a resolution of 1024×256 pixels. However, the display can be programmed to trade-off resolution for increased colour[14]. For this work the colour graphics display was set to a resolution of 256×256 pixels with 12 colour bit-planes (4096 colour mode).

Photographs of the RGB monitor screen are taken on Kodacolour VR film (ASA 100) and Kodak Ektachrome 100 at 0.5 s using a 50mm lens with 2 × macro-focusing teleconverter at f-stop 5.6. For the photographs, the video display controller operates in interlaced mode.

Subdivision of the grid boxes into tetrahedra and linear interpolation along the edges evolved from the 2D contouring algorithms used by McIntosh[15], who implemented contour searching by splitting a rectangular grid into triangles and interpolating between corners of the triangles. Using tetrahedra, such as triangles, minimizes the number of intersections which arise from contours passing through the solid and therefore simplifies program logic.

To ensure that the surface is continuous, lines along one face of a cube must match lines along the opposing face of the adjacent cube. Matching is accomplished by restricting linear interpolation across a face to

*Conversion to integer format is certainly not necessary and could be eliminated if graphics hardware optimized for floating point arithmetic is used to draw the triangle stack and/or align it. On the other hand, if the triangles are to be drawn using most minicomputer or microcomputer processors, then the use of integer format and the incremental DDA can speed the drawing process.

function values defined on the face, and by alternating left- and right-handed tetrahedral divisions of the cubes (see Colour Plate 5).

The reduction of constant value surfaces to lists of triangular patches can be important if hidden surface algorithms other than z-buffering are used since a triangular patch is flat and therefore, the surface is entirely composed of flat faces[16]. Furthermore, the use of triangles insures that concave polygons are shaded, an important consideration for some display processors which implement hardware assisted shading.

After considerable experimentation, the magnitude of the gradient is coded in cartographic fashion like a political map. Although it seems logical to colour adjacent patches denoting different magnitudes of the gradient with similar colour hues, adjacent similar hues are confusing. The limited grey scale (16 intensity level) and limited colour range causes adjacent similar hues to be interpreted as changes in shading, not as changes in hue. In part, this is due to the use of a limited number of intensity levels for shading. Thus as the intensity levels of a colour composed of red, green and blue components are scaled down to simulate shading, the ratio of red, green and blue intensity can change slightly resulting in a slight change of hue. The hue shift with intensity change could be eliminated by using pure red, green, blue or equal mixtures of red, green and blue. However, pure colours are perceived with different luminous intensities, with green perceived as being brighter than red or blue[17]. Thus 'white' has been added to the red and blue to increase their perceived intensities. Consequently, shading causes hue shifts.

GRADIENTS WITH RESPECT TO NUCLEAR MOTION

The change in a scalar function $\varphi(r;R)$ with a change in molecular geometry, δR, at point r_0 is $\varphi(r_0;R) - \varphi(r_0;R + \delta R)$. The gradient with respect to the motion of nucleus N is the vector field defined by the vector

$$\nabla \varphi = \frac{\partial \varphi}{\partial X_N} i + \frac{\partial \varphi}{\partial Y_N} j + \frac{\partial \varphi}{\partial Z_N} k$$

The response of the electrostatic potential to changes in the location of nucleii may be displayed using the algorithm described in the previous section. Differences in the electrostatic potential of two different geometries can be displayed as coloured areas on an isopotential surface for one of the geometries. Colour Plate 6 is a difference plot of the electrostatic potentials of the CH_3F molecule at the equilibrium geometry and the CH_3F molecule with the C–F bond lengthened by 0.03 Å. The difference is displayed on the isopotential surface of the equilibrium geometry.

Colour Plate 6 can be interpreted by considering changes in the net atomic charges derived from a Mulliken population analysis. As the C—F bond is lengthened the net charge on the F atom becomes more negative (CH_3F separates to F— and CH_3+). Within a point-charge model of the electrostatic potential, the increase in negative charge leads to a larger 0.03 isopotential surface. In this case, the larger surface completely encloses the 0.03 isopotential surface in the equilibrium geometry CH_3F. Thus, as Colour Plate 6 shows, only one colour around the F atom is expected on the differ-

ence plot. The C atom charge also increases in magnitude and is expected to be predominantly white. A blue colour for the hydrogren atoms is expected since the H atom charge decreases as the C–F bond distance increases.

Colour Plate 7 shows the 0.01 isodensity surface of CH_3F with the C–F bond stretched 0.2 Å by moving the F atom along the z axis. This is the kind of geometry change which produces elements of the gradient tensor in cartesian coordinates. The colour coding method of Colour Plate 4(b) is used on the surface. With the 'atoms in molecules' colour coding scheme used, there is little visible difference between Colour Plates 7 and 4(b). Colour Plate 8 shows the 0.03 isodensity surface of equilibrium geometry of CH_3F with the difference between it and the 0.03 isodensity surface of CH_3F stretched 0.2 Å colour coded on the surface. From Colour Plate 8, it is clear that the charge has been increased to the left of F and decreased to the right of it. The explanation is simple. When F is moved, and the positions of C and H are kept constant, the high density centre of the F atom approaches the leftmost side of the isodensity causing an obvious build-up of density there, depleting it from the righthand side. More interesting is the extent of the density change between the C and H atoms which are not moved. Here the density on the 0.03 isodensity surface is decreased to the back of the H atoms and increased in front of the carbon. Colour Plate 8 shows that a localized bond stretch significantly affects density values in other parts of the molecule and the coupling to local bond motion is significant.

CONCLUSIONS

Constant-valued surfaces of electrostatic potentials and molecular electron densities are economically generated from tabulated values of the full function and displayed as solid, shaded isopotential surfaces. The shading facilitates 3D perception and encodes the direction of the gradient. Colouring the isovalue surface by the magnitude of the gradient increases the information content of the diagram and provides the possibility of new insights into molecular structure. With the advent higher performance of microcomputer displays, such as the one used here, routine use of solid, shaded models will be available to a much wider group of users.
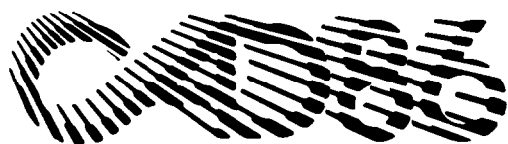
ACKNOWLEDGEMENTS

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