

Visualization of Shapes of Molecular Anions *

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A recently formulated strict definition of the boundary surface of molecular anions has been employed for the visualization of some simple systems. The examples included are CN^- , N_3^- , NO_3^- , ClO_4^- , ClO_3^- , and BrO_3^- ions. A discussion on the anisotropy of electrostatic interaction of these anions is also presented.

Key words: Anions; Molecular electrostatic potential.

One could expect to find a simple yet rigorous treatment of anisotropies of polyatomic ions in treatises on structural and inorganic chemistry. However, despite many discussions [1–4] of sizes, shapes and anisotropies of interactions, a unified approach to these anisotropies is, to the authors' knowledge, conspicuous by its absence from the chemical literature. In fact, desirability of such an approach is apparent from many diverse areas in chemistry. The classic book due to Wells [2] depicts the 'pictures' of CN^- and OH^- anions in the crystals of NaCN and Ca(OH)_2 . Marcus [3] has discussed the size and shape of a planar nitrate anion and inferred (from neutron diffraction studies) that the axial and equatorial 'radii' of NO_3^- are 1.26 and 2.01 Å, respectively. The subject of anisotropy in gas-phase ionic interactions [4] is receiving considerable attention in experimental thermochemistry. Thus, the need of a simple practical visualization of polyatomic ions can hardly be overemphasised and this is what is attempted in this note.

Recent investigations due to Gadre et al. [5] provide a clue to such three-dimensional visualization of polyatomic anions. They showed that the Molecular Electrostatic Potential (MESP) of a negative ion, X^{q-} (owing to its asymptotic decay as $-q/r$) must exhibit a negative-valued (V) minimum along any arbitrary ray starting from the nuclear skeleton. They also demonstrated the existence of a surface Ω obeying

$\nabla V \cdot d\mathbf{S} = 0$ ($d\mathbf{S}$ being the outward normal) for linear anions [5c, 5d]. This ensures, via the Gauss' theorem, that Ω encloses a net zero charge, i.e. all the negative charge, $-q$, is resident outside Ω , and hence justifies the use of Ω for visualizing the shape, size and anisotropies of V along it. These works, which are generalizations of atomic results [6] due to Sen and Politzer, provide us with an algorithm for colour-graphics visualization of sizes, shapes and anisotropies of molecular anions.

- (i) Take an arbitrary ray in a direction (θ, φ) (starting with (0, 0)) emanating outward from a fixed point, say the centre of mass of the nuclear framework.
- (ii) Compute the MESP at points along this ray.
- (iii) Locate the most negative-valued MESP points, store its co-ordinates and the corresponding V .
- (iv) Repeat steps (i) through (iii) for a large mesh of θ and φ (typically 2500 points).
- (v) Develop the anionic "minimal" surface Ω for visualization with the help of these data.

The graphics work presented here has been developed for an HP 835 Turbo SRX, HP 98752A graphics terminal and HP point-jet XL colour plotter. The MESP values for CN^- , ClO_3^- , BrO_3^- , ClO_4^- , N_3^- and NO_3^- ions were generated from the fully geometry-optimized HF-SCF wavefunctions*. The package TURBOMOLE [7] by Ahlrichs et al. was employed for this purpose with basis-sets of tzp (triple-zeta + polarization) or better quality [8]. Only a mar-

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* The resulting bond-lengths and bond-angles are 1.162 Å (CN^-), 1.503 Å, 108.22° (ClO_3^-), 1.600 Å, 107.10° (BrO_3^-), 1.459 Å (ClO_4^-), 1.164 Å (N_3^-) and 1.221 Å (NO_3^-), respectively.

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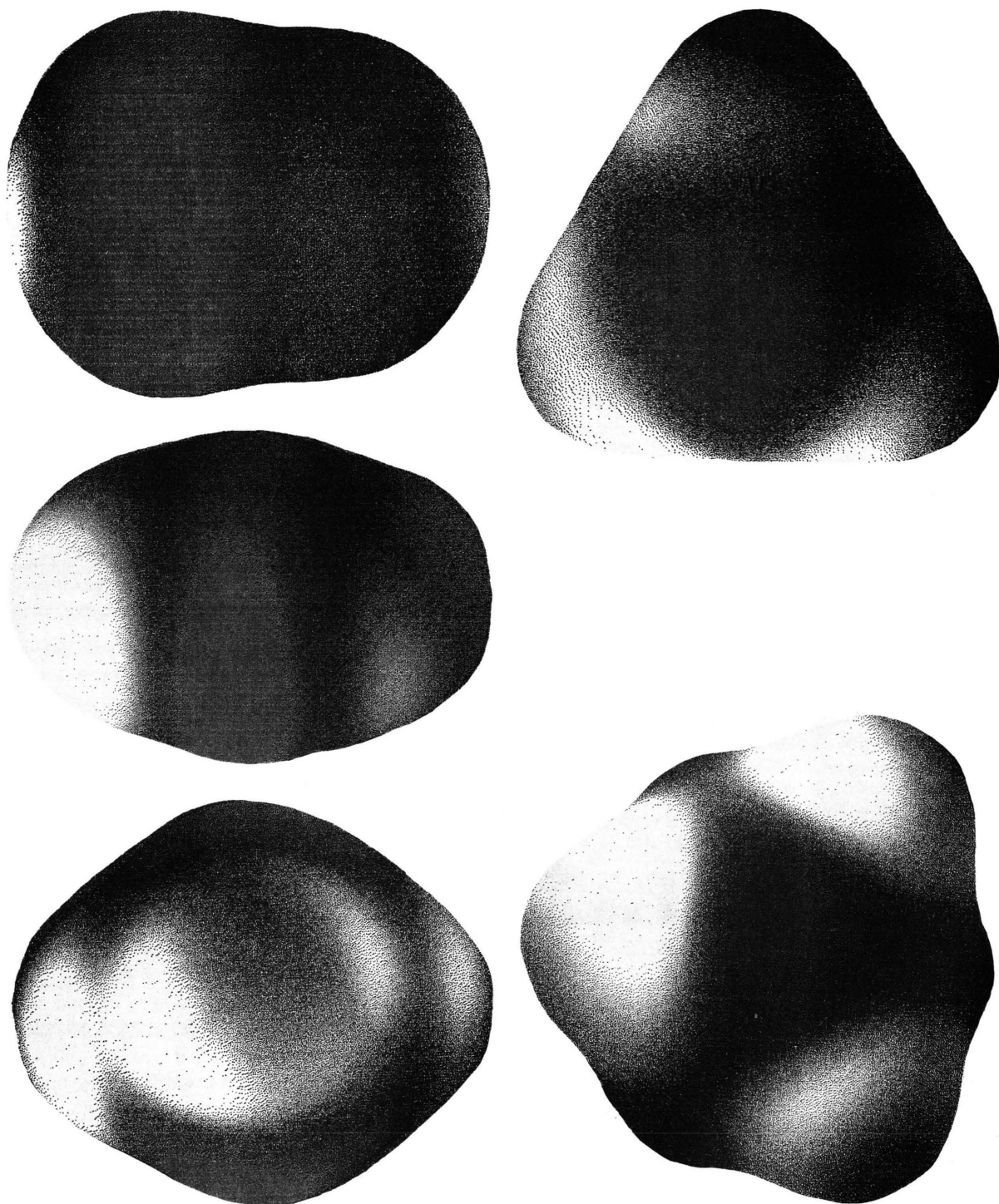


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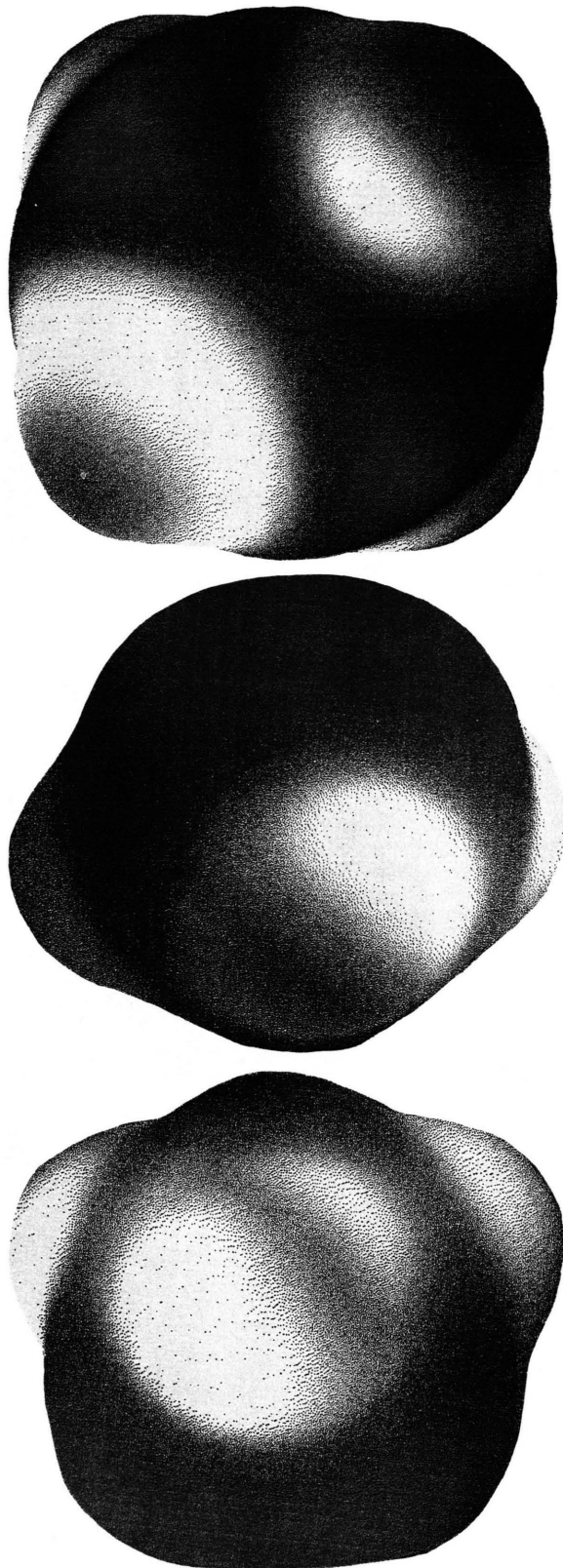
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Figs. 1–8. The “minimal” MESP surface for some molecular anions. The original colouring of these computer graphs (red for the most (M) and blue for the least (L) negative MESP values with linearly interpolated mixed colours for intermediate values; illumination from the lower left) is reproduced by its grey-values. – Fig. 1: CN^- (upper left; from left to right: red tip, blue belt, violet belt, reddish tip), Fig. 2: N_3^- (left centre; red cap, blue belt, red cap), Fig. 3: NO_3^- , equatorial view (lower left) and Fig. 4: NO_3^- , polar view (centre top; blue pole caps, red equatorial bulges), Fig. 5: ClO_4^- view in the direction of a C_3 -axis (centre bottom) and Fig. 6: ClO_4^- , view in the direction of an S_4 -axis (upper right; red bulges with violet tips on a blue body), Fig. 7: ClO_3^- (right centre; three red bulges on a blue body), Fig. 8: BrO_3^- (lower right; as ClO_3^-). The corresponding M and L values for these species are (in a.u.): CN^- (–0.32, –0.26); N_3^- (–0.28, –0.21); NO_3^- (–0.28, –0.18); ClO_4^- (–0.23, –0.17); ClO_3^- (–0.28, –0.14); BrO_3^- (–0.27, –0.12).



ginal dependence of the MESP topography, including the location of critical points, was noticed with further enhancement of the basis-set quality. The “minimal” surfaces (Ω) thus generated do not exactly satisfy $\nabla V \cdot dS = 0$, but were verified to lie close to such a surface (deviations less than 1 pm) by suitable translation of the origin. Figures 1–8 display these surfaces for CN^- , N_3^- , NO_3^- (2 views), ClO_4^- (2 views), ClO_3^- and BrO_3^- , respectively. Red colour denotes the most (M) negative MESP values and the blue one stands for the least (L) negative ones: linear interpolation is employed for the intermediate MESP values. It may be pointed out that these pictures provide, for the first time in the chemical literature, a simple, yet rigorous means for the visualization of anisotropies in molecular anions. Of course, our treatment does not incorporate solvent- or crystal-effects. However, it offers a practical and consistent view of anionic anisotropies.

Interesting qualitative information, comparable to that obtainable from MESP maps of molecules, can be brought out directly from these pictures. The CN^- ion (Fig. 1) exhibits highly negative MSP values at both the ends, and so do the terminal atoms in N_3^- (Figure 2). The NO_3^- ion appears rather flattened along the C_3 -axis (Figs. 3 and 4) in accordance with the neutron diffraction data [3] cited above. For instance, the ClO_4^- ion (Figs. 5 and 6) appears to be rather spherical, as chemical intuition predicts, with the maximally negative MESP region around the oxygen lone-pairs. On the other hand, ClO_3^- and BrO_3^- (Figs. 7 and 8) appear rather aspherical, with marked anisotropies in the heavy-atom lone-pair regions.

More quantitative information can be extracted by inspecting the values of the potential V or the radius r (from the centre of mass) along the surface Ω . For instance, the smallest and largest r -values for the NO_3^- ion are 1.75 and 2.47 Å, respectively. This leads to a difference in the smallest and largest radii as 0.72 Å, which could be compared with the difference of 0.76 Å ($r_{\text{equatorial}} - r_{\text{axial}}$) obtained from neutron data [4]. Our values of r range from 2.1 to 2.73 Å for ClO_4^- in reasonably good agreement with the neutron data values of 2.13 to 2.51 Å. We have, however, no indication that BrO_3^- is smaller than ClO_3^- as predicted by thermochemical radii [1, 3]. Our spherically averaged values for these systems turn out to be 2.24 Å and 2.09 Å, respectively.

One may obtain a measure of ‘deviation from sphericity’ [5d] (for the electrostatic interactions with the surrounding) via a dimensionless parameter $\Delta V/\bar{V}$.

Here, ΔV is the r.m.s. deviation of V along Ω , viz. $\Delta V = \sqrt{\sum (V_i - \bar{V})^2 / N}$, and \bar{V} the corresponding average value. Exactly spherical systems would have $\Delta V / \bar{V} = 0$ with higher values of this parameter showing increasing deviations from sphericity for long-range electrostatic interactions. The values of this parameter turn out to be 0.05, 0.07, 0.12, 0.15, 0.24 and 0.27 for CN^- , ClO_4^- , N_3^- , NO_3^- , ClO_3^- and BrO_3^- , respectively. Our prediction of near-sphericity of CN^- is vindicated by the conclusions [4] based on gas-phase clustering experiments mentioned above. Yet another independent evidence is furnished by the flatness of the potential energy surface for the interaction between CN^- and a Li^+ cation noticed by Schleyer *et al.* [9].

In summary, the MESP maps, which have been successfully exploited [10] for making simple qualitative chemical predictions of reactivities, also provide a practical yet rigorous topographical means of probing anionic anisotropies and offering their visualization.

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