Electrostatics in Chemistry

2. Electrostatic Potentials of Atoms, Ions and Molecules

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Electrostatic Potential (ESP) generated by a chemical species is widely used as a tool for exploring its properties and locating potential sites for interaction with other moieties. In this article, the features of ESPs of atoms, ions and molecules are discussed.

Introduction

In Part 1[1] of this series, an introduction to elementary electrostatics has been provided. The present article deals with the electrostatic features of atoms, ions and molecules.

Molecular systems are made up of atoms. The structure and properties of atoms in a molecule are significantly altered due to interatomic interactions. However, as a starting point, it is advisable to perform the study of isolated atoms. This can be done by applying methods of theoretical chemistry. The exact or approximate solution of time-independent Schrödinger equation can yield the wave function of an isolated atom or molecule. This wave function is then employed for obtaining the corresponding electronic properties such as electron density, electrostatic potential, electric field, etc. These properties are useful for obtaining a qualitative 'understanding' of the interactions of that species. The electrostatics of the hydrogen atom was presented in Part 1 of this series. In this part, the characteristics and applications of the electrostatic potential of many-electron atoms, ions and molecules are discussed.

Electrostatic Potential of Atoms and Singly Charged Monoatomic Ions

As seen in Part 1 of this series, the electrostatic potential (ESP) of a free atom with the nuclear charge Z and electron density $\rho(r)$

is given [in atomic units (a.u.), which are used throughout this article, unless specified otherwise] by

$$V(r) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3\mathbf{r'} \qquad (1)$$

The first term on the right hand side of the equation is the potential due to the nuclear charge and the second term gives the potential generated by the continuous electronic charge distribution described by $\rho(\mathbf{r})$. It will be assumed here that the electron density (and hence the ESP) for an atom is spherically symmetric. The electronic energy of an atom is related closely to the corresponding electrostatic potential at the nucleus. This was recognised quite early, in 1927, within the historical Thomas–Fermi theory. The energy of an atom within this theory turns out to be $E = (3/7) Z V(0)$, where $V(0)$ is the ESP at the nucleus.

The ESP can be directly measured from X-ray scattering experiments, and a comparison with its theoretical counterpart is possible. The electrostatic potential of a neutral atom or an atomic ion can be theoretically calculated by using (1). We have seen in Part 1 that the electron density of the hydrogen atom can be calculated from the exact wave function obtained by solving the Schrödinger equation. However, for the atoms containing more than one electron, it is not possible to find the exact solution of the Schrödinger equation due to the interelectronic repulsion. The wave function for such atoms can be obtained by using some approximate methods. As noted above, these wave

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Box 1. The Thomas and Fermi Theory

Thomas and Fermi independently proposed a statistical atomic model, based on semiclassical considerations, in 1927. In this theory, the electron density, $\rho(r)$, is regarded as a basic variable and bears a simple relation with the corresponding electrostatic potential value, $V(r)$, viz. $\rho(r) = 2^{3/2} V^{3/2}/(3\pi^2)$. The total atomic energy within this theory is related to the ESP value at the nucleus. This theory as well as its numerous variants (including the Thomas–Fermi–Dirac and Thomas–Fermi–Dirac–Weizsäcker theories) may be considered as the precursors of the density functional theory which was put on a firm footing by Kohn and co-workers in 1964 and 1965.

functions are used for extracting the corresponding electron density, $\rho(r)$. The $\rho(r)$ thus obtained is subsequently used for the ESP evaluation.

The ESP thus calculated for some atoms and ions is shown in *Figure* 1. *Figures* 1(a) and (b) show the ESP of two closed-shell atoms, *viz.* Mg and Zn. It may be noticed that the ESP assumes arbitrarily large values near the nucleus. It decreases monotonically and drops out to very small (e.g. < 0.01 a.u.) values beyond a distance of ~1Å (~2 a.u.) and is almost negligible beyond the distance of 2 Å. *Figures* 1(c) and (d) display the ESP of two monopositive cations Li^+ and Na^+. The trend of the cationic ESP's is similar to that of neutral atoms, although the magnitude of ESP is larger than that of atoms.

However, anions behave quite differently in this respect. The ESP plots for singly charged atomic anions F^- and Cl^- are depicted in *Figures* 1(e) and (f) respectively. Here too the ESP near the nucleus is very large and positive, since Coulomb's law dictates that the ESP of a singly charged anion must decay asymptotically as $-1/r$, and is a smooth function. Hence, it has to cross zero at $r = r_z$, say. It has been suggested by Politzer and co-workers that the value of r_z may be related to the covalent radius of the corresponding atom. Further, for $r > r_z$ the ESP becomes negative and attains a negative valued minimum at $r = r_m$. After this, it reaches zero $\sim -1/r$ as r tends to ∞. Recently, Sen and Politzer have proposed the use of r_m as a measure of ionic radius of a negative ion. According to them, integrated electronic charge in a sphere of radius r_m centered at nucleus equals the nuclear charge (see next section). They have reported r_m values for the anions of the main group elements which show a good agreement with the corresponding literature values. For example, r_m values reported by them for F^- and Cl^- are 1.08 and 1.63Å respectively, which are found to be very close to the crystallo-graphically determined ionic radii (F^- 1.17, Cl^- 1.67Å). Ionic radii for some monatomic ions are tabulated in *Table* 1.

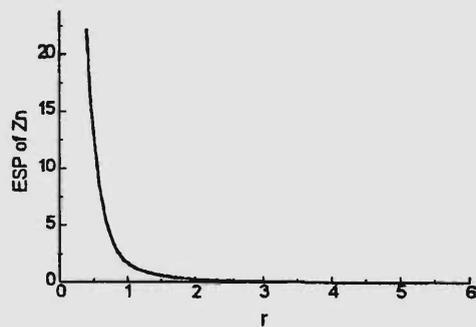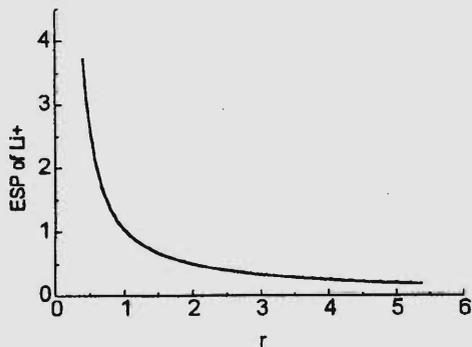In fact, the atomic and molecular ESPs exhibit rather interesting

Table 1. Radii of some monatomic ions.

Ion	radius in Å
Li^+	0.90
Be^{+2}	0.59
B^{+3}	0.41
O^{-2}	1.26
F^-	1.19
Na^+	1.16
Mg^{+2}	0.86
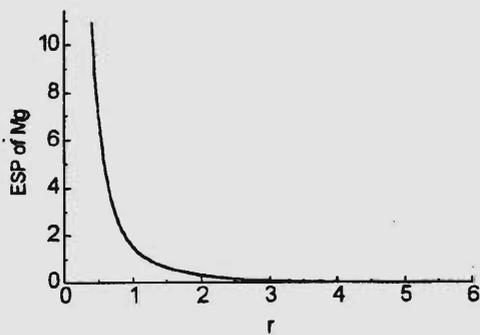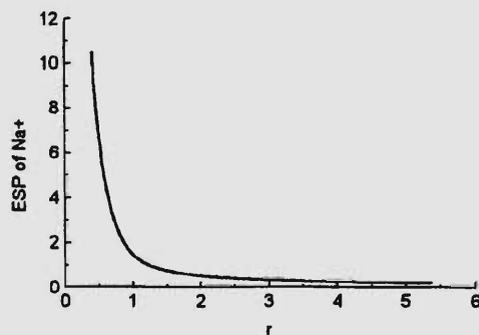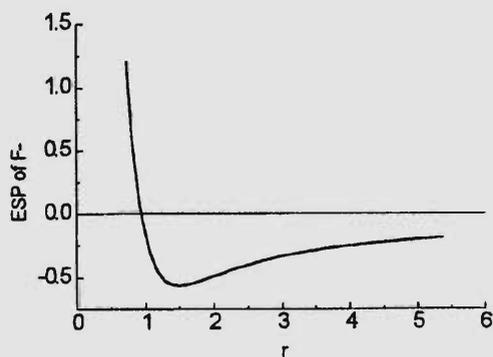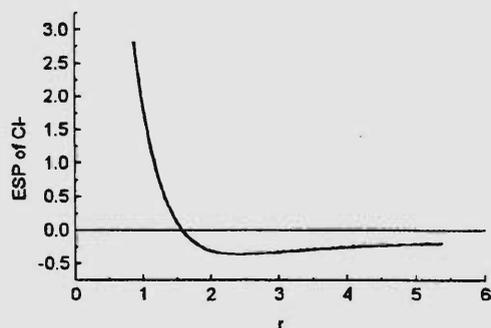
Figure 1. Electrostatic potentials (ESP) of some atoms [(a) Mg, (b) Zn], and monopositive [(c) Li⁺, (d) Na⁺] and mononegative [(e) F⁻ , (f) Cl⁻] ions. The values of r and ESP are in a.u.

and general maximal and minimal characteristics. These are summarized along with graphics visualization of MESPs in the following sections.

Maximal and Minimal Characteristics of ESPs.

As seen in the previous article, the ESP at a non-nuclear site satisfies the Poisson equation (written in atomic units) viz.

$$\nabla^2 V(r) = 4\pi\rho(r). \tag{2}$$

The atomic ESP is, in general, a function of r, θ, ϕ. For a spherically symmetric system, since $V(r)$ does not depend upon the angular variables θ and ϕ, the expression for $\nabla^2 V$ simplifies to

$$\nabla^2 V(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV(r)}{dr}\right) \tag{3}$$

This, on further simplification, yields

$$\frac{d^2V}{dr^2} + \frac{2}{r}\frac{dV}{dr} = 4\pi\rho(r) \tag{4}$$

The electron density on the right side of the above equation is a non-negative quantity at all the points in space. This second order differential equation may be used to arrive at minimal and maximal characteristics of the atomic ESP. It was shown by Weinstein and others that the atomic ESP cannot show a maximum. The condition for a maximum of a function is that the first derivative vanishes and the second one is negative. Now, assume that the potential V is maximum at point $r = R$.

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Box 2. Simeon Denis Poisson (1781–1840)

Poisson was a very productive mathematician as seen from the frequency of occurrence of his name in textbooks. The Poisson equation, viz. $\nabla^2 V = \rho/\varepsilon_0$, where V and ρ denote respectively the electrostatic potential and the corresponding charge density, is his most noted contribution in potential theory. The Poisson equation (1812) was a result of his discovery that the Laplace equation for the gravitational case holds only at the points where no mass is located.

Then at the point R, the first derivative of V is zero and the second derivative is negative. However, note that the right hand side of (4) is non-negative, leading to a contradiction. This proves that the electrostatic potential *cannot* have a non-nuclear maximum. This feature has already been observed in the *Figure* 1, for neutral atoms as well as anionic and cationic systems.

However, for a monatomic anion, the possibility of a *minimum* in $V(r)$ *does exist*. As seen earlier, this is due to the fact that as r approaches 0, $V(r) \to \infty$. It decays to zero asymptotically as $-1/r$. Thus, considering the smoothness properties, it must show a minimum at some finite radius. Sen and Politzer simplified (1) as,

$$V(r) = \frac{Z}{r} - \frac{4\pi}{r} \int_0^r r'^2 \, \rho(r')dr' - 4\pi \int_r^\infty r' \, \rho(r')dr' \qquad (5)$$

The first order derivative of $V(r)$ is, hence,

$$\frac{dV}{dr} = -\frac{Z}{r^2} + \frac{4\pi}{r^2} \int_0^r r'^2 \, \rho(r')dr'$$

Suppose that a minimum occurs at distance r_m. Then at $r = r_m$ the derivative is zero and a substitution in (5) yields

$$Z = 4\pi \int_0^{r_m} r'^2 \, \rho(r')dr' \qquad (6)$$

The right hand side of (6) is the total electronic charge enclosed within the sphere of radius r_m. In other words, the excess electronic charge (–1 for monatomic anions) is located beyond the radial distance r_m, and therefore r_m can be viewed as the radius of the ion. In the same spirit, $V(r_m)$ should be a measure of the strength of the ion's interaction energy with positive ions, and thus it can be related to the lattice energy. These propositions were checked out by Sen and Politzer.

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Molecular Electrostatic Potential (MESP)

As seen in Part 1 of this series, the MESP generated by a molecule containing N atoms with nuclear charges $\{Z_A\}$ placed at $\{R_A\}$ and the quantum mechanically calculated charge distribution of electrons represented by $\rho(\mathbf{r})$ is given by

$$V(\mathbf{r}) = \sum_{A=1}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} d^3\mathbf{r}' \tag{7}$$

Here $|\mathbf{r}-\mathbf{R}_A|$ represents the distance from the nucleus A to the reference point $\mathbf{r}$.

The above equation shows that the electrostatic potential is certainly specific to a given molecular geometry, and the value of $V(\mathbf{r})$ in any particular region depends on whether the effect of nuclei or electrons is dominant there. Thus, MESP is positive in the region close to nuclei and negative in the electron-rich region. Due to this nature, MESP is capable of exhibiting rich topographical features which will be examined in the next part of this series. In this light, it may be noted that the negative valued MESP points in the vicinity of the molecule provide information about possible sites of the electrophilic attack.

How do the MESP maps look? *Figure* 2 presents the MESP planar contour maps of some small diatomic molecules. Contour in a plane is a curve that joins the points bearing constant value. For example, a circle is a (positive-valued) contour of the function $f(x, y) = x^2 + y^2$. The green, blue and red colors show the positive, zero and negative potential contours respectively. *Figures* 2(a) and (b) show the contour maps of H_2 and N_2 molecules respectively. The MESP near the nuclei of these molecules is positive, although its value for N_2 is found to be more than the H_2 one. The MESP at the ends of the N_2 molecule is negative, suggesting that an electrophile may approach the molecule along its axis. For the H_2 molecule, the magnitude of negative MESP is very small as compared to the positive one. This implies small but finite possibility of binding with electrophile

The MESP at the
ends of the N_2
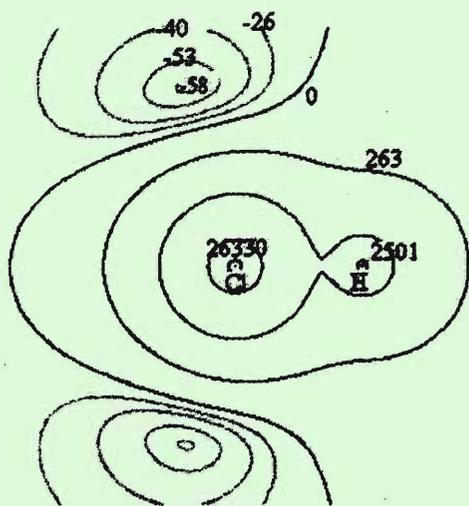molecule is
negative,
suggesting that an
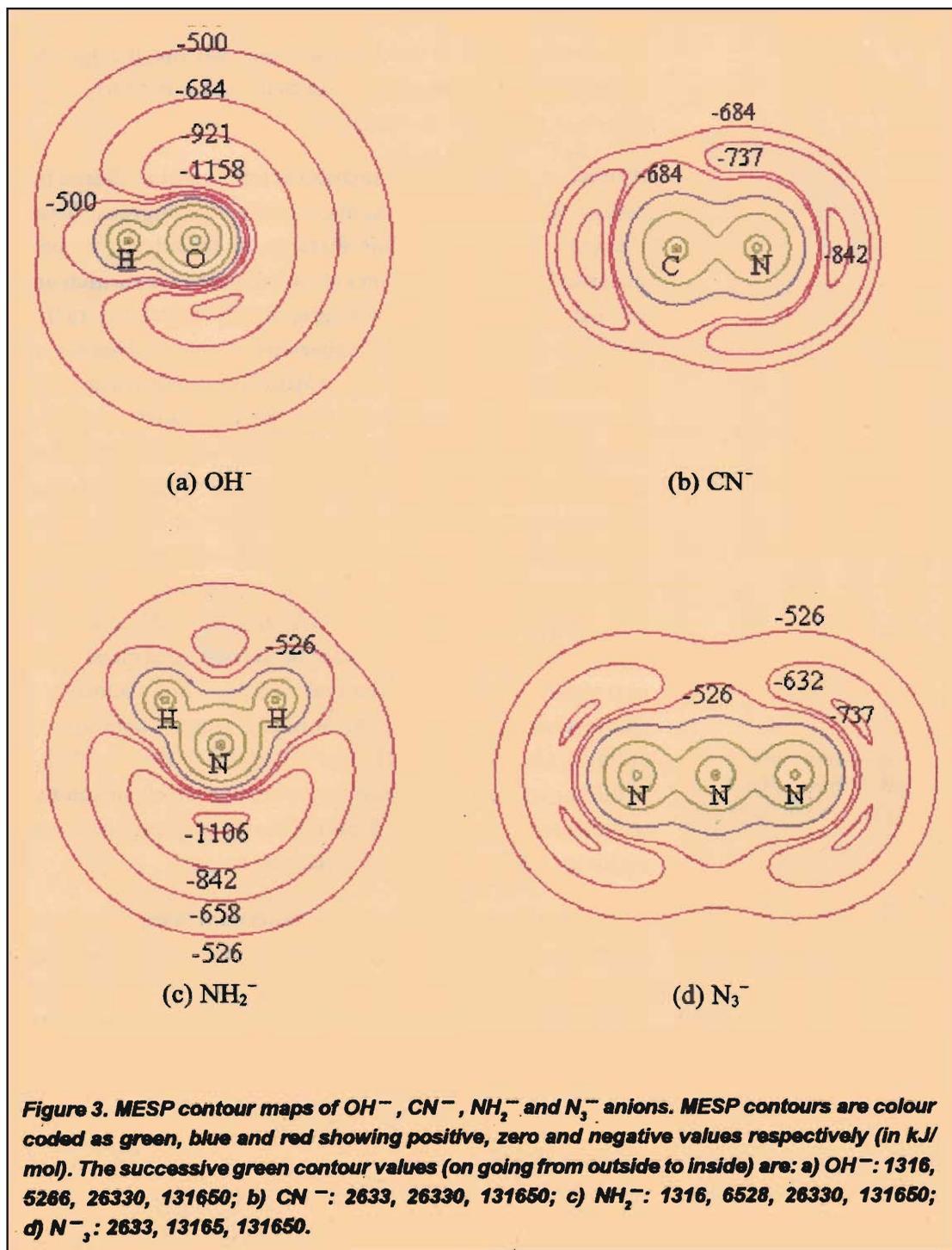electrophile may
approach the
molecule along its
axis.
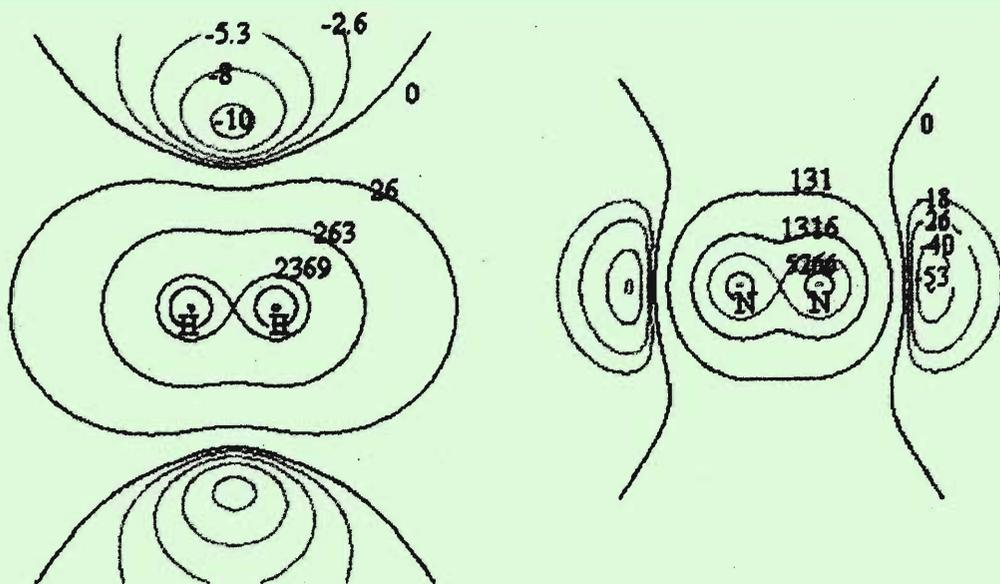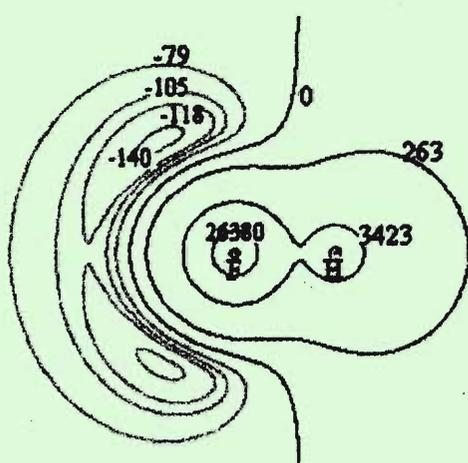
Figure 2. MESP contour maps of H₂, N₂, HF and HCl molecules. MESP contours are color coded
as green, blue and red denoting positive, zero and negative values respectively (in kJ/mol).

and that too along a direction perpendicular to the H-H bond. *Figures* 2(c) and (d) depict the contour maps of HF and HCl, respectively. The MESP near the F or Cl atoms is found to be negative, whereas it is positive near the H end, in tune with chemical intuition. The F end in HF is found to be more negative as compared to the Cl end in HCl as dictated by the electronegativity arguments. Further, the no (non-nuclear) maximum theorem for atomic ESP's seen earlier is also valid for the molecular case as well (see Suggested Reading). The proof, first given by Gadre and Pathak, is again based on the Poisson relation (2).

As seen earlier, the MESP plot of a monatomic anion furnishes useful information about its covalent and ionic radius. To check its applicability for the polyatomic anions, ESP's of some small molecular anions (OH– , CN– , NH_2– and N_3–) have been presented in *Figure* 3. Again here, the green, blue and red colors depict the positive, zero and negative MESP respectively. The MESP in the vicinity of nuclei of the anions is found to be positive, although its magnitude is less than that in the neutral molecule. This is due to the excess electronic charge that reduces the magnitude of scalar potential in the nuclear region. *Figure* 3 shows that each anion is surrounded by the zero MESP contour. It indicates that a unit charge placed at any point on this contour will not experience the existence of an anion. Further, the figure shows that each anion is also surrounded by two negative valued contours bearing the same MESP value. The most negative MESP contours are seen to lie in between these two same valued contours suggesting that there exist minimum MESP valued points between these contours. Generalizing the results of Sen and Politzer, Gadre and others (see Suggested Reading) have shown that, for any molecular anion, along a ray going out from a nucleus in any arbitrary direction, at least one negative valued MESP minimum occurs. If all these minima are joined, a surface is formed. This surface is termed as the minimal surface (minimum potential surface). They have also shown that at any point r on the minimal surface

> The MESP in the vicinity of nuclei of the anions is found to be positive, although its magnitude is less than that in the neutral molecule.

Figure 3. MESP contour maps of OH^-, CN^-, NH_2^- and N_3^- anions. MESP contours are colour coded as green, blue and red showing positive, zero and negative values respectively (in kJ/mol). The successive green contour values (on going from outside to inside) are: a) OH^-: 1316, 5266, 26330, 131650; b) CN^-: 2633, 26330, 131650; c) NH_2^-: 1316, 6528, 26330, 131650; d) N_3^-: 2633, 13165, 131650.

S, $\nabla V(\mathbf{r})$. $d\mathbf{S} = 0$, where $d\mathbf{S}$ is an infinitesimal vector perpendicular to S at $\mathbf{r}$. It has been noticed that the average radius value computed from such a minimal surface is nearly equal to the ionic radius of the anion.

A practical way for the estimation of ionic radii is offered by X-ray crystallography, from the distance of closest approach between the ions. In crystals, this distance is considered to be the distance between the centers of two adjacent ions which are in mutual contact. The crystallographically calculated radii are based on the assumption of sphericity of anions. However, the physical boundary defined by the MESP minimal surface suggests that the anions can also possess specific shapes. A detailed investigation on the shapes and sizes of some anions has been carried out using MESP minimal surface. It has been shown that the shape of anions such as OH^-, CN^-, NH_2^-, N_3^- is non-spherical. The calculated radii of these anions along the long and short axes of the ellipsoid turn out to be: OH^- (1.58, 0.93 Å), CN^- (1.72, 1.41Å), NH_2^- (1.9, 1.1Å) and N_3^- (1.55, 2.32Å). The average of these values is found to be in good agreement with the corresponding thermochemical radius. For example, the thermochemical radii for the anions discussed here are: OH^- (1.33 Å), CN^- (1.91 Å), NH_2^- (1.73 Å) and N_3^- (1.95 Å). Thus the MESP provides a framework for describing the shapes and sizes of polyatomic anions, and permit us to go beyond the non-realistic spherical shapes of molecular anions.

A comment on representation of molecular charge densities by point charges is in order here. Consider the Laplace equation at a site occupied by no such point charge, viz. $\nabla^2 V = 0$. It can be readily shown that such a V (produced by point charges) *cannot* exhibit maxima or minima. The point charge representation of molecules, so often used in the literature, thus suffers from a fundamental limitation that it cannot faithfully reproduce the MESP minima.

To summarize, the atomic and molecular ESPs provide valuable information on ionic radii and reactivity. The pictorial represen-

Box 3. Pierre Simon Laplace (1749–1827)

Laplace was the son of a farmer, eventually took up several academic and administrative positions. The theory of probabilities and celestial mechanics are considered as his most noteworthy contributions. His chief contribution to potential theory is the so-called Laplace equation, viz. $\nabla^2 V = 0$.

tation of MESP in the form of contours and isosurfaces is a valuable tool for exploring the interaction of molecules with the interacting moieties. In the present article, the features of ESP s of atoms, ions and molecules have been explored by the corresponding maps in two dimensions. It is indeed instructive to inspect these maps in their full three-dimensional glory! This visualization and topography mapping of molecular ESPs will be taken up in the following part of this series.

Suggested Reading

[1] P Politzer and D G Truhlar, ed. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, Plenum, New York, 1981.

[2] J S Murray and K D Sen ed., *Molecular Electrostatic Potentials: Concepts and Applications*, Elsevier, Amsterdam, 1996.

Some of the significant original research articles related to the present articles are:

[3] H Weinstein, P Politzer and S Srebrenik, *Theor. Chim. Acta*. Berl., 38, 159, 1975.

[4] K D Sen and P Politzer, *J.Chem. Phys.* 90, 4370, 1980; 91, 5123, 1989.

[5] S R Gadre and R K Pathak, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 102, 189, 1990.

[6] R K Pathak and S R Gadre, *J. Chem. Phys.*, 93, 1770, 1990.

[7] S R Gadre, S A Kulkarni and I H Shrivastava, *J. Chem. Phys.*, 96, 5253, 1992.

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Drawings and specifications of the newly completed Statue of Liberty appear in *Scientific American*, which closely monitors all phases of installation.

In the same year, the publication reports that new paper negatives can substitute for fragile glass versions in photography. The savings in weight and expense allow amateur and professional photographers to take their cameras beyond their studios with ease.

Scientific American, September 1995