

Electrostatics in Chemistry

3. Molecular Electrostatic Potential: Visualization and Topography

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Topographical features of the electrostatic potential of molecules (MESP) are discussed. Three-dimensional visualization of the MESP of some small molecules is presented. The details are correlated with the reactivity of molecules.

Introduction

In the first two parts¹ of this series, we have given an introduction to atomic and molecular electrostatic potentials (ESP). The relationship with some other molecular properties such as the electronic energy, electron density, ionic radius, etc., was also discussed. It was pointed out that the molecular electrostatic potential (MESP) is used extensively on qualitative and semi-quantitative levels as a probe for locating the reactive sites in a molecule. For example, by employing MESP contour maps, one can 'see' the spatial regions in which the MESP is negative and to which an electrophile would initially be attracted. For instance, as seen in Part 2 of this series, the contour maps of N_2 and HF show that the MESP at the N and H ends are negative and positive, respectively. A simple qualitative reasoning would yield a structure of a weakly bonded complex $N_2 \cdots HF$ with the H pointing towards the most negative region near the N atom, as revealed by the MESP maps.

While the above analysis is simple, the information provided by the contour maps is not sufficient to quantify the process of intermolecular interactions. For this purpose, a knowledge of the exact position of the MESP minimum and the MESP value at that point would be needed. As we shall see in the next section, a minimum is one of the possible critical points (CPs) of the MESP. Usually, there are many minima. It has been noted that

¹ 1. Basic Principles, *Resonance*, Vol.4, No.2, 11–19, 1999.

2. Electrostatic Potentials of Atoms, Ions and Molecules, *Resonance*, Vol.4, No.5, 40–51, 1999.

an electrophile prefers to be near the most negative valued MESP minimum. Similarly, the strength of attraction (interaction energy) is governed by the distribution of MESP around such a critical point. In effect, the CPs provide more concise information regarding such weak interactions and therefore they can be used along with the contour maps for locating the exact sites of the attack. In this article, we present an introduction to topography and visualization of MESP with some specific examples.

Introduction to Topography

A topographical (*topos* = place; *graphia* = mapping) map of a geographical region usually describes the features of the region such as equal altitude points, hill tops etc., and is familiar to us since high school days. *Figure 1* brings out with the help of contours, equal height points of a hill and a valley. The two peaks (maximum) of the hill are shown by the green dots. The two contours with the same value (40m) and each of them surrounding one of the peaks, indicate that the points between these contours are below 40m. The depth (denoted by negative numbers) of the

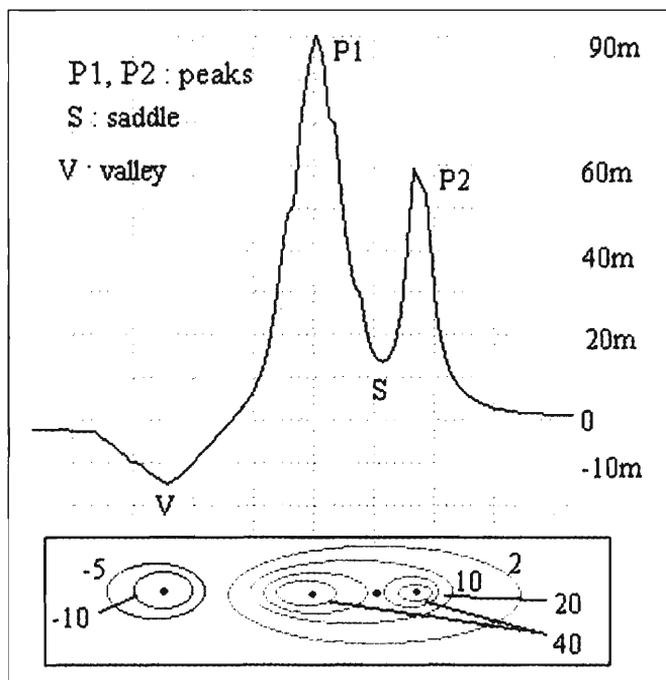


Figure 1. A planar side view of a hill and a valley (above). The numbers to the right indicate height at different levels. The corresponding contour maps are shown in the rectangle below. The red and green coloured contours show height below and above the zero level surface respectively. The green dots indicate peak points (maxima), red dot shows the maximum depth point (minima) and the brown dot shows the saddle point.

valley at various levels is shown by red contours. The red dot shows the deepest point. This contour map thus offers pictorial information of height at various places. The main advantage of topography is that it provides essential information such as location and values of the function at the minimum, maximum and iso-valued points rather succinctly.

The topographical parameters, such as minima, maxima etc., of a function can be searched by invoking the well-known conditions involving the first and second derivatives. Let us illustrate these with the help of a simple function of one variable, $y = \sin(x) + \cos(x)$. Here, the angle x is restricted to assume values between 0 and 2π radians. The plot of the function y is shown in *Figure 2*. The plot shows that the value of y is maximum and minimum at $\pi/4$ and $5\pi/4$ respectively. It can be verified by applying the following conditions of minimum and maximum at these x values.

$$(i) \quad y' = \frac{dy}{dx} = \cos(x) - \sin(x) \Big|_{x=\pi/4, 5\pi/4} = 0$$

$$(ii) \quad y'' = \frac{d^2y}{dx^2} = -\sin(x) - \cos(x) \Big|_{x=5\pi/4} > 0$$

for a minimum, and

$$(iib) \quad y'' = \frac{d^2y}{dx^2} = -\sin(x) - \cos(x) \Big|_{x=\pi/4} < 0$$

for a maximum.

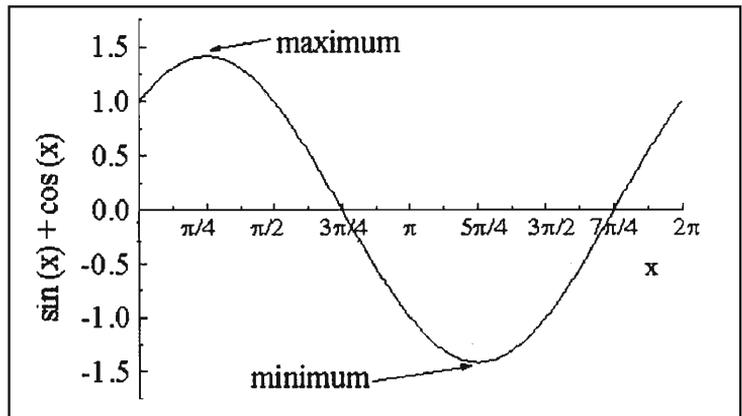


Figure 2. $y = \sin(x) + \cos(x)$ for plot of the function in $0 \leq x \leq 2\pi$.

These points are termed as critical points (CP). The condition (ii) yields, $y'' = -(\sin(x) + \cos(x))$, the value of which is -1.41421 and $+1.41421$ at $\pi/4$ and $5\pi/4$ respectively.

A generalization of the above treatment is needed for a function $f(x_1, x_2, \dots, x_n)$ of several variables. Here, the entire first order partial derivatives must vanish at the CP. Further, the signs of the second order partial derivatives can be used for describing the nature of the CP. Inspecting the signs of the eigenvalues of the respective Hessian matrix does this. The elements of the Hessian matrix are given by

$$H_{ij} = \left[\frac{\partial^2 f}{\partial x_i \partial x_j} \right]_P \tag{1}$$

These are evaluated at the critical point, P . The CPs are then classified according to the nature of the eigenvalues of the corresponding Hessian matrix. The eigenvalues can be calculated by using the equation, $\det(\lambda I_n - H) = 0$, where λ is the eigenvalue and I_n is the unit matrix of rank n .

If one or more eigenvalues is/are zero, then the corresponding CP is termed as a degenerate one. Otherwise, it is said to be of non-degenerate type. The nature of CP can be denoted as (rank, signature). Here, rank is the number of non-zero eigenvalues of the Hessian matrix and the signature is defined as the algebraic sum of the signs of these eigenvalues. Consider now a function of three variables, $f(x, y, z)$, say. Here the rank of the Hessian matrix is 3, and each of the three non-zero eigenvalues can assume either a + or a - sign. The algebraic sum of these three signs can take only four values: +3, +1, -1 or -3. Therefore, four types of CPs are possible for rank 3. The (3, +3) is referred to as a local minimum. The (3, +1) and (3, -1) are termed as saddle points and a CP (3, -3) represents a local maximum. For a function of two variables, only one type of saddle of nature (2, 0) is possible. Let us illustrate it using a function, $f(x, y) = x^2 + y^2 - 3xy$.



Box 1. Poincaré–Hopf Relationship

For a continuous, non-negative and three dimensional scalar field, such as the molecular electron density, the number of critical points of various types is connected by the Poincaré–Hopf relationship, viz.

$$n_{-3} - n_{-1} + n_{+1} - n_{+3} = 1.$$

Here n_{-3} , n_{-1} , n_{+1} and n_{+3} denote the number of (3, -3), (3, -1), (3, +1) and (3, +3) type CPs respectively.

The Hessian matrix for this function is

$$H = \begin{bmatrix} 2 & -3 \\ -3 & 2 \end{bmatrix}.$$

The eigenvalue equation is

$$\begin{vmatrix} \lambda-2 & 3 \\ 3 & \lambda-2 \end{vmatrix} = 0$$

and the roots of this equation are: $\lambda = +5$ and -1 . This analysis shows that the point (0, 0) is a saddle of type (2, 0).

Let us now consider another simple function of three variables, viz., $f(x, y, z) = 2x^2 + 4y^2 - 7z^2$. The first order partial derivatives of $f(x, y, z)$ are: $\partial f/\partial x = +4x$, $\partial f/\partial y = +8y$ and $\partial f/\partial z = -14z$. These derivatives are zero at $x = 0$, $y = 0$ and $z = 0$ and hence (0, 0, 0) is a critical point. The nature of this CP can be understood by examining the signs of the second order partial derivatives of the function or the diagonal elements of Hessian matrix (1) as given below. The other partial derivatives i.e. H_{xy} , H_{xz} , etc. are zero. The arrangement of partial derivatives in the matrix form yields a diagonal Hessian matrix at (0, 0, 0), with the diagonal elements 4, 8, -14. The rank of this square matrix is 3 and the algebraic sum of the signs of the diagonal elements is +1. Therefore, the nature of the function at the CP is (3, +1) i.e. a saddle point. Let us take yet another example, viz., $f(x, y, z) = (y^2 - x^2)/2 + 2(x + y)z$. The first order partial derivatives of f vanish at a point (0, 0, 0) and thus it is a critical point. The corresponding Hessian matrix is:

$$H = \begin{bmatrix} -1 & 0 & 2 \\ 0 & 1 & 2 \\ 2 & 2 & 0 \end{bmatrix}$$

The eigenvalues of this matrix turn out to be: 0, 3, -3. Here one eigenvalue is zero and therefore, the CP at (0, 0, 0) is a degenerate one.

Topography is found to be a very useful tool for analysis of physicochemical quantities, which are dependent on many variables. For instance, topography is widely employed for investigating potential energy surfaces, which are useful in the studies of reaction dynamics. Further, topographical approach employing values of the electronic energy, the partial derivatives and Hessian matrix is found useful for locating transition states. As noted earlier, electron density and MESP contour maps of molecules provide useful pictorial information regarding the charge distribution of molecular systems. However, a detailed topographical characterization is found to be more valuable.

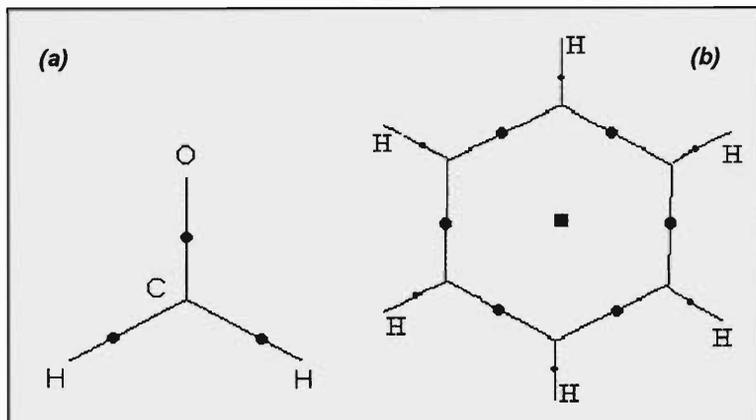
Topography of the Molecular Electron Density

Molecular electron density (MED) is one of the fundamental scalar functions, which describes the probabilistic charge distribution of the molecule. Richard Bader has pioneered the topographical investigation of MED since the 1960s. He developed a method (named by him as *atoms in molecule* approach) based on topographical concepts. The MED attains a maximum at the nuclear positions and shows a saddle point generally along the path that joins two nuclei. We illustrate here the MED topographical features of two molecules in their ground states. The (3, -1) MED CPs of formaldehyde and benzene molecules are displayed in *Figure 3*. The maxima in MED that appear at the nuclear positions are not shown in the figure. An additional (3, +1) CP appears at the center of the benzene ring. In particular, Bader has also correlated the parameters of the MED topography with the fundamental chemical concepts such as bond order, bond ellipticity etc. For instance, the bond order b can be estimated from the relation $b = \exp[A(\rho_b - B)]$, where ρ_b is the MED at (3, -1) CP which always appears in between the two bonded atoms, A and B are the appropriately defined parameters. Similarly, the bond ellipticity can be determined as $\varepsilon = [\lambda_1/\lambda_2 - 1]$, where λ_1 and λ_2 are the eigenvalues corresponding to the so-called soft curvatures.

The MED topography has been widely used for understanding



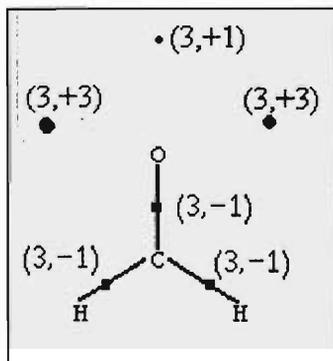
Figure 3. MED critical points of the formaldehyde (HCHO) and benzene (C_6H_6) molecules. Filled circles denote (3, -1) saddle points and filled square denotes (3, +1) CP. See text for details.



the nature and properties of the chemical bond in a molecule. In particular, it has been mainly used for the analysis of the electronic rearrangements that accompany the interactions of atoms to form molecules. However, the MED topography does not directly reveal the location of lone pairs, features of π bond, molecular reactivity, etc.. These features can be studied by exploring the topography of molecular electrostatic potential (MESP). As seen in Part 2 of this series, the MESP explicitly reflects the entire molecular charge distribution, including nuclei and electrons and hence is more suitable for investigating chemical bonding and reactivity patterns.

Topography of the Molecular Electrostatic Potential (MESP)

Figure 4. Nature and location of MESP CPs of the formaldehyde (HCHO) molecule (See text for details).



As discussed in Part 2 of this series, the MESP possesses rich topographical features. The topographical analysis includes characterization of critical points (CP) such as location of CP and the nature (minima, maxima etc.) of MESP at the CP.

Figure 4 shows schematically the locations of MESP CPs of the formaldehyde (HCHO) molecule. These positions have been determined using indigenously developed computer programs UNIMOL and UNIPROP. Three types of CPs are encountered in the MESP of HCHO molecule. Similar to the MED, a saddle point of type (3, -1) is observed between each pair of bonded nuclei, corresponding to a minimum along the internuclear axis.

It is a positive valued bond CP, indicating that the internuclear region (C=O, C-H) is mostly dominated by the nuclear potential. A unit charge placed at bond CP feels no electrostatic force from either direction along the bond. Thus the position of bond CP defines a physical border point between two atoms. This point has been related to the covalent radii of the bonded atoms. The MESP at $(3, -1)_{\text{CO}}$ and $(3, -1)_{\text{CH}}$ CPs are 3829.6 kJ/mol and 2308.2 kJ/mol respectively. The two identical $(3, +3)$ CPs, appearing on each side of the C=O bond, are the most negative valued MESP minima (-204.6 kJ/mol). The negative valued $(3, +1)$ saddle CP joining these two minima occurs along the C_2 axis with the MESP value of -178.9 kJ/mol.

It is indeed instructive to explore the topographical as well as MESP features of polyatomic molecules in their full three-dimensional glory! The CPs and MESP isosurfaces of some more molecules are depicted in *Figure 5*. *Figure 5(a)* shows the isopotential surfaces and negative valued CPs for the water (H_2O) molecule. Two symmetrical minima $(3, +3)$ occur in a plane perpendicular to the molecule indicating the existence of lone pairs: the 'rabbit ears' as described by chemists. A $(3, +1)$ type saddle appears on the molecular axis. The MESP values at minima and saddle point are -246.6 kJ/mol and -243.9 kJ/mol respectively. The numerically large MESP values at CPs suggest the strong interaction of an electrophile near the oxygen. *Figure 5(b)* shows the isopotential surfaces and CP for the ammonia (NH_3) molecule. The appearance of CP on nitrogen, away from the hydrogen atoms and the very large MESP (-327.9 kJ/mol) value at this point predicts a large donor interaction energy with an electrophile at this site. A degenerate ring CP (*Figure 5(c)*) occurs in the MESP of the acetylene (C_2H_2) molecule. The MESP value at the CP is -86.6 kJ/mol. It suggests that an electrophile may approach this molecule close to the ring CP.

The CPs of cyclopropane (C_3H_6) appear in the molecular plane as can be seen from *Figure 5(d)*. Thus, the most likely positions for electrophilic attack are in the molecular plane, along a line perpendicular to C-C bond. This is also in agreement with the

Box 2. Topography of Molecular Electron Density

R F W Bader of McMaster University, Canada, has pioneered these studies. A pair of bonded nuclei always displays a $(3, -1)$ - type saddle between them. This has been termed by him as bond-saddle. A ring (e.g. in cyclopropane or benzene molecules) has a signature of a $(3, +1)$ saddle. A cage structure (such as in cubane) shows up as a $(3, +3)$ minimum. The MED is always maximum at the nuclear positions (but very rarely at some non-nuclear sites as well).

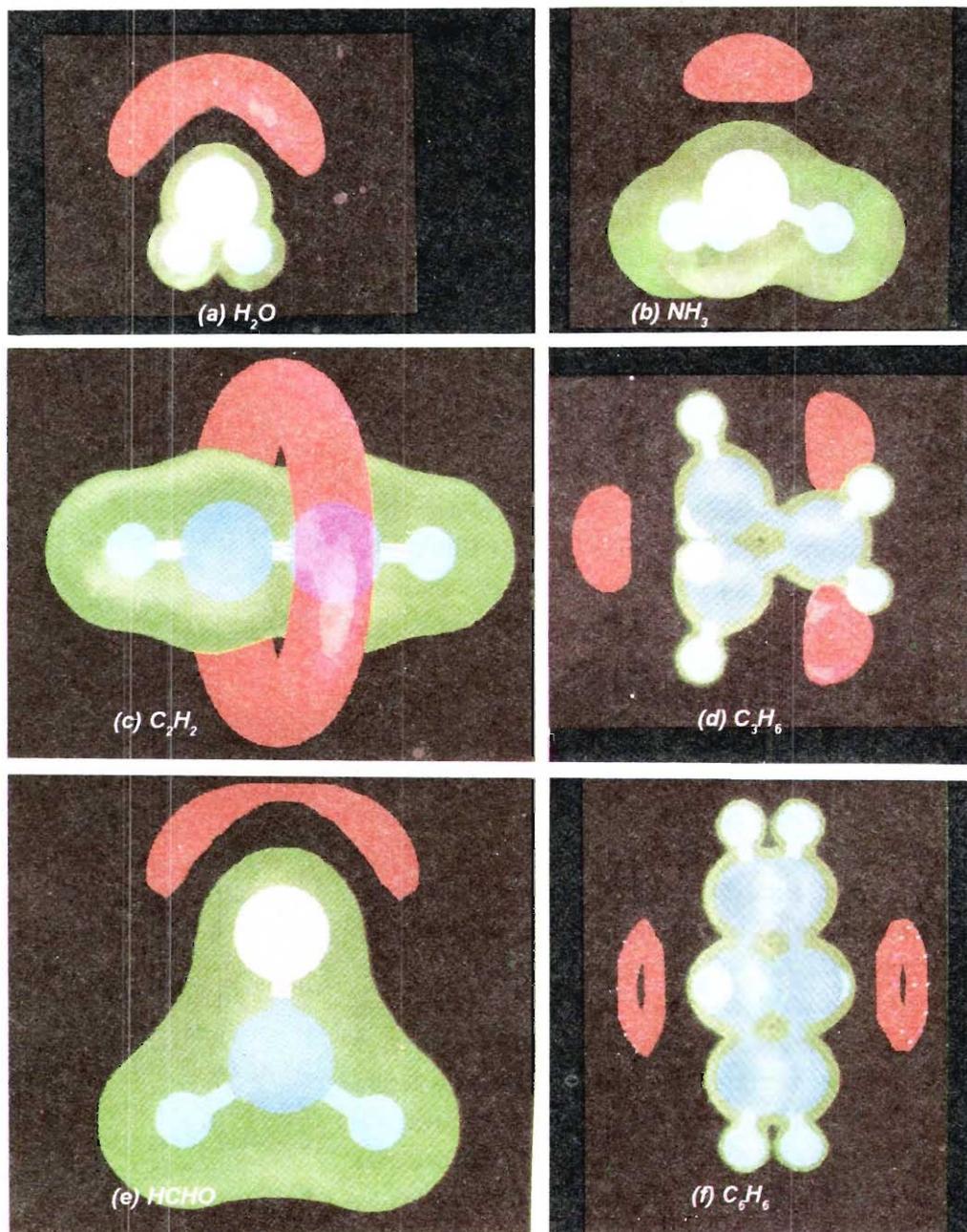


Figure 5. Isopotential surfaces of H_2O , NH_3 , C_2H_2 , C_3H_6 , HCHO and C_6H_6 molecules. Green and red coloured surfaces show positive and negative potentials respectively. The small black dots in the red surface indicate the negative MESP-valued critical points (values in kJ/mol). See text for details. The green (G), and red (R) surface values are : (a) H_2O : G(263); R(-210); (b) NH_3 : G(263); R(-263); (c) C_2H_2 : G(263); R(-79) (d) C_3H_6 : G(1843); R(-252); (e) HCHO : G(263); R(-176); (f) C_6H_6 : G(1843); R(-84).

'banana bond' model for this molecule. The CPs of formaldehyde (HCHO) (*Figure 5(e)*) appear in the molecular plane, as seen earlier. The MESP value at the minima (-204.6 kJ/mol) is found to be numerically very large as compared to that of the lone pair of oxygen of water molecule. The MESP at the minima suggests a strong interaction along a line at an angle of ca 120° with the C=O bond.

The topography of benzene (C_6H_6) molecule is very interesting. As seen from the *Figure 5(f)*, six minima and the intervening six saddles arranged in a ring structure appear on both sides of the molecular plane of C_6H_6 . A saddle (3, -1) CP appears along the C_6 axis at the center of the ring. Thus, an electrophile is expected to approach this molecule either from the top or bottom of the ring plane.

To summarize, the topographical features of MESP and the pictorial representation of MESP in the form of contours and isosurfaces are very useful for exploring the structure and reactivity of the molecule. By considering the usefulness of the MESP, various electrostatic based models have been developed for the investigation of intermolecular interactions.

Accurate investigation of intermolecular interactions can be carried out theoretically using *ab initio* calculations. These methods give quantitative results but they are not always suitable for large molecular systems. To perform the study on such systems, simpler models have been developed. These models use electrostatic potentials, electrostatics driven charges, some calibration constants, etc.. Some of the recent models and their applications to weak intermolecular interactions will be discussed in Part 4 of this series.

Suggested Reading

- [1] See I Stewart, *Sci. Amer.*, 264, 123 (1991), for a lucid, semi-popular introduction to topographical concepts written in the style of Gulliver's travels.
- [2] See for a summary of the applications of MESP topography, SR Gadre, PK Bhadane, S S Pundlik and S S Pingale, in *Molecular Electrostatic Potentials: Concepts and Applications*, 219-255, Ed. J S Murray and K D Sen, Elsevier, Amsterdam, 1996.
- [3] R F W Bader, *Atoms in Molecules: A Quantum Theory*, Oxford, 1990.

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All the results of nature are only mathematical results of a small number of immutable laws.

Laplace