
Electrostatics in Chemistry

1. Basic Principles

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Electrostatics plays an important role in weak intermolecular interactions. The present series is aimed at understanding these electrostatic aspects. This article presents the fundamental concepts of electrostatics as applied to atoms and molecules. The electric field and potential due to a set of discrete as well as continuous charge distributions are discussed along with their graphic visualization. Fundamental theorems in electrostatics are also summarized.

Introduction

A chemist regards atoms and molecules as the operational building blocks of matter. The electrostatic interaction energy between the positively charged nucleus and negatively charged electrons is a dominant contribution to the total energy of an atom. Atoms come together and form molecules. Molecular chemistry, the chemistry of the covalent bond, deals with the structures, properties and reactions of these molecules. A new branch of chemistry developed in recent years, viz., *supramolecular chemistry*, which is defined as the chemistry beyond the molecule [1], deals with the complexes of two or more molecular subunits. This fundamental subject of molecular recognition has found widespread applications in many branches of chemical sciences such as analytical chemistry; bioinorganic and bioorganic chemistry; catalysis, including the chemistry of enzymes, etc. It is generally recognized that electrostatics plays an important role in these recognition processes. Therefore, a proper background in supramolecular science must include an understanding of electrostatics. In this series of articles, basic molecular electrostatics and its applications to weak intermolecular interactions will be discussed.

For an excellent summary of the field of supramolecular chemistry, readers are referred to the article by J-M Lehn in *Resonance*, Vol.1, No.3, p.39, 1996.

Electrical Charges and Coulomb's law

The development of electrostatics is based on the idea of an electric charge. The experimental facts about electric charges are:

i) Two kinds of electric charges exist in nature. These are called the positive and negative charges (the present labels of positive and negative to charges of proton and electron, respectively, are indeed a historical accident).

ii) The force between two point charges is directly proportional to their product and inversely proportional to the square of the distance between them and acts along the line joining them.

The above experimental results are combined together in *Coulomb's law*

$$\mathbf{F}_{2,1} = \frac{q_2 q_1 (\mathbf{r}_1 - \mathbf{r}_2)}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|^3} \quad (1)$$

Here $\mathbf{F}_{2,1}$ is the force acting upon q_1 , \mathbf{r}_1 and \mathbf{r}_2 are the position vectors of q_1 and q_2 respectively, with respect to an arbitrary origin O as shown in *Figure 1*.

The electrostatic forces between a pair of point charges are not affected by the inclusion of other point charges. Thus the force $\mathbf{F}_{2,1}$ (Equation 1) is unchanged when extra point charges are included. Such forces are pair-wise additive and the total force \mathbf{F}_1 on the point charge q_1 due to point charges q_2, q_3, \dots, q_n is given by

$$\mathbf{F}_1 = \sum_{i=2}^n \mathbf{F}_{i,1} = \frac{q_1}{4\pi\epsilon_0} \sum_{i=2}^n \frac{q_i (\mathbf{r}_1 - \mathbf{r}_i)}{|\mathbf{r}_1 - \mathbf{r}_i|^3} \quad (2)$$

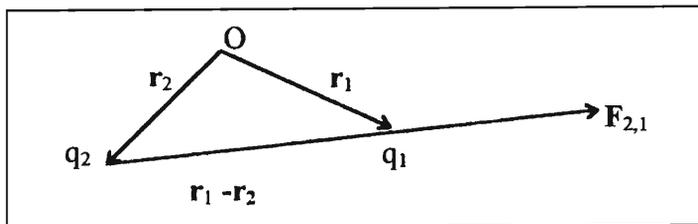


Figure 1. A schematic representation of the force $\mathbf{F}_{2,1}$ exerted by q_2 on q_1 . The charges, q_1 and q_2 are located at \mathbf{r}_1 and \mathbf{r}_2 respectively.

Box 1

Charles Augustin de Coulomb (1736–1806) was a French physicist who investigated the well-known law later named after him, for describing the relationship between two electrostatic charges. He developed a very sensitive instrument for the measurement of the electrostatic force. He also served later as an engineer in the French armed forces located in West Indies.

Box 2. How Close to 2 is the Exponent in Coulomb's Law?

Assuming the distance dependence in Coulomb's law [cf. eq. (1)] to be r^{-m} , it is interesting to know how much is the deviation of m from 2. Various experiments have been designed for this purpose essentially based on measurement of the electric field inside a hollow charged sphere, since $m=2$ implies that field must vanish exactly. Cavendish carried out his classic experiments and showed that the intensity is very close to zero. Later Maxwell, in 1870, with a similar experiment concluded that the value of m cannot differ from 2 by more than $1/21,600$. Plimpton and Lawton in 1936 using more sophisticated apparatus showed that this deviation is not more than 2×10^{-9} . Williams, Faller and Philips have improved this number to $\sim 10^{-16}$ in 1971.

This additive property of electrostatic forces is known as the superposition principle.

Electrostatic Potential and Field

The force experienced by a unit charge placed at a reference point is called the electric field at that point. The force experienced by the point charge q_1 in the presence of point charges q_2, q_3, \dots, q_n is given by

$$\mathbf{F}_1 = q_1 \mathbf{E}, \tag{3}$$

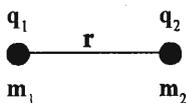
where \mathbf{E} is the electrostatic field produced by q_2, q_3, \dots, q_n . A comparison of (2) and (3) shows that the electrostatic field at the position of q_1 is

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=2}^n \frac{q_i(\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3}. \tag{4}$$

Now consider a test positive charge q that is to be moved from point A to B in the electric field \mathbf{E} . The electric field exerts a force $q\mathbf{E}$ on the charge. The work done by an external agent in moving the charge through distance $d\mathbf{l}$ is $-q\mathbf{E} \cdot d\mathbf{l}$, where the negative sign indicates that the work is done against the field. For moving the charge from point A to B , the work done is obtained by a suitable integration, viz.

$$W_{AB} = -q \int_A^B \mathbf{E} \cdot d\mathbf{l}$$

Box 3. Why is the Gravitational Force Ignored in Comparison to the Electrostatic One Acting Between the Subatomic Particles?



The above figure shows two charged particles of masses m_1 and m_2 and carrying charges q_1 and q_2 of the same sign respectively, separated by a distance r . The electrostatic and gravitational forces (in Newtons N) acting between the particles are:

$$|F_{\text{coul}}| \cong 9 \times 10^9 (q_1 q_2 / r^2) \text{ N and } |F_{\text{grav}}| \cong 6.67 \times 10^{-11} (m_1 m_2 / r^2) \text{ N}$$

If both the particles are taken to be electrons, then by substituting the values of mass and charge of electron in the above equations yields

$$|F_{\text{coul}}| \cong (9.0 \times 10^9 \times (1.6 \times 10^{-19})^2) / r^2 \text{ N; } |F_{\text{grav}}| \cong (6.7 \times 10^{-11} \times (9.1 \times 10^{-31})^2) / r^2 \text{ N}$$

$$|F_{\text{coul}}| / |F_{\text{grav}}| \cong 4.2 \times 10^{42}$$

This analysis shows that the attraction between two electrons due to the gravitational force is negligible as compared to the electrostatic attraction or repulsion between them and thus can be ignored when the latter are present.

The work done in moving an electric charge from point A to point B in an electrostatic field is independent of the path taken between A and B . This observation indicates that the electrostatic field, which is a vector field, can be defined by a scalar electrostatic potential. The work done on a unit charge, while moving it from point A to B is called the potential difference, $V_B - V_A$, which is independent of the path, and for a closed loop it is zero. If point B is pulled out to infinity, then this is called the potential V at point A . The potential at a reference point r located at distance r from a point charge q is given as

$$V(r) = \frac{q}{4\pi\epsilon_0 r}$$

Invoking the superposition theorem, the potential at point r due to n number of discrete point charges turns out to be the sum of the individual potentials. i.e.

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^n \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|} \quad (5)$$

Electrostatic Potential and Field due to a Collection of Point Charges

Equation (5) can be used for evaluating the electrostatic potential produced at a point \mathbf{r} by a set of point charges q_i located at \mathbf{r}_i . The corresponding electric field can be calculated by taking (the negative) gradient of (5) viz $\mathbf{E} = -\nabla V$. To illustrate the interesting characteristics of the potentials and fields generated by a set of point charges, a few combinations of charges are selected. For simplicity, we use the so-called atomic units (au) wherein $|e| = m_e = 4\pi\epsilon_0 \hbar^2 = 1$. The potential and field magnitudes are also reported in au.

It is certainly interesting to explore the three-dimensional features of these two entities with the three-dimensional visualization tools offered by computers. Surfaces on which the function value is constant, as visualized in three dimensions, are termed as isosurfaces. Light effects are used to vividly bring out the three-dimensional features. The corresponding curves in two dimensions are called as contours. Electric field being a vector quantity is depicted by an arrow pointing in an appropriate direction with the field magnitude colour-coded on it.

Two Positive Charges

Let us consider two unit positive charges that are separated by a unit distance. *Figure 2* shows the isopotential surfaces with values of 1.0 (inner) and 0.5 (outer). The potential reaches infinity on approaching the sites of the charges. It reaches a directional minimum at the midpoint of the charges. Further, it decreases asymptotically to zero as $2/r$. *Figure 3* shows the isopotential contours on which the electric field vectors are superposed. The potential and field values decrease as one traverses outward from the charges. The contours tend to

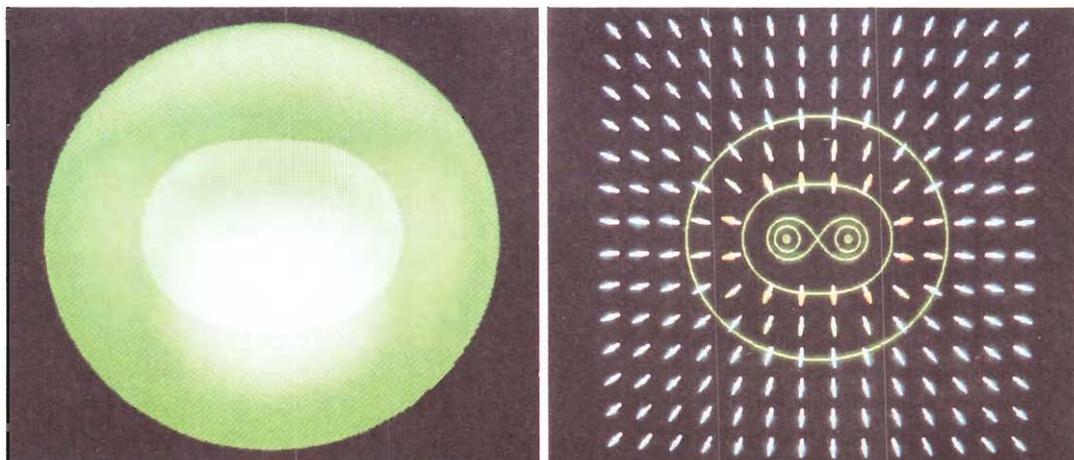


Figure 2(left). Isopotential surfaces of two unit positive charges separated by a unit distance. The potential values are 1 and 0.5 for inner and outer surfaces respectively (all values in au). See text for details.

Figure 3(right). Electrostatic potential contours and electric field vectors produced by two unit positive charges separated by a unit distance. The contour values are 3.0, 2.0, 1.0 and 0.5. The magnitude of electric field is colour coded as follows, blue: 0 to 0.2, green: 0.2 to 0.4; yellow: 0.4 and beyond.

become spherical in the immediate vicinity of the point charges.

Dipole

A dipole consists of two charges with magnitudes $+q$ and $-q$ separated by some distance. *Figure 4* depicts isopotential surfaces of a dipole constituted by two unit charges kept at a unit distance with green and red colours depicting positive and negative potentials respectively. The potential value is maximum near to the charges and it is zero at the midpoint of two charges. *Figure 5* shows the corresponding isopotential contours and field vectors. Some molecules possess permanent dipole moments in their ground states. A few of these are listed in *Table 1*.

Quadrupole

Figure 6 displays the isopotential surfaces of a quadrupole (with point charges $+1, -1, +1$ and -1 placed consecutively at the corners of a square of unit length). The magnitude of the electrostatic potential increases in the inward direction. *Figure 7* shows

Table 1. Dipole moments for some selected molecules. (Cm=Coulomb meter)

| Molecule | Dipole moment 10^{-30} Cm |
|----------------------------------|--------------------------------|
| CO | 0.37 |
| H ₂ O | 6.2 |
| SO ₂ | 5.4 |
| CH ₃ F | 6.2 |
| CH ₃ Cl | 5.9 |
| CHCl ₃ | 3.5 |
| C ₆ H ₅ Cl | 5.7 |

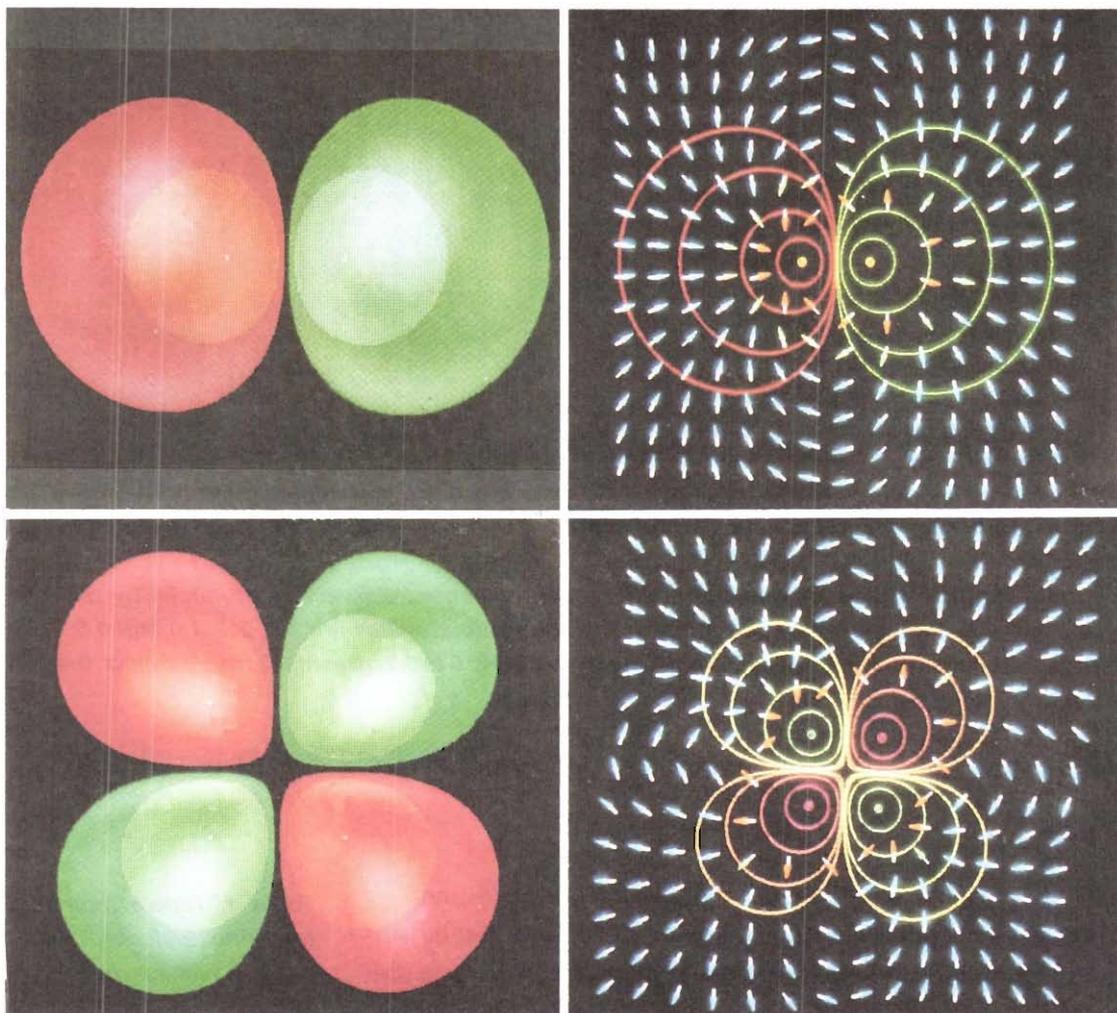


Figure 4(left-top). Isopotential surfaces due to two equal and opposite unit charges separated by unit distance. The green and red coloured surfaces show positive and negative potentials respectively. The magnitude of potential is 0.4 (inner) and 0.1 (outer).

Figure 5(right-top). Electrostatic potential vectors produced by a unit dipole. The potential and field decreases in outward direction. The green and red coloured contours show positive and negative potentials respectively. The magnitude of contour values is 1.0, 0.3, 0.1 and 0.05 (all values in au). The electric field values are coded as: blue: 0 to 0.1; green 0.1 to 0.3; orange: 0.3 and higher.

Figure 6(bottom-left). Isopotential surfaces of a quadrupole (two parallel inverted dipoles). The green and red coloured surfaces show positive and negative potentials respectively. The magnitude of potential is 0.4 (inner) and 0.1 (outer). See text for details.

Figure 7 (bottom-right). Electrostatic potential contours and electric field vectors produced by a unit quadrupole. The green and red coloured contours show positive and negative potentials respectively. The magnitudes of contour values are 1.0, 0.3, 0.1 and 0.05. The electric field is colour coded as blue: 0 to 0.1; green: 0.1 to 0.3; orange: 0.3 and beyond.

respective isopotential contours and the field vectors.

Continuous Charge Distribution

Equations 4 and 5 describe the potential and electric field at a point due to a set of point charges. The charge distribution within atoms and molecules is not as simple as that of point charges. This is because of the smeared, probabilistic electronic charge distribution. For a continuous charge distribution the summation in (5) must clearly be replaced with an integral. For this case, (5) assumes the form

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}') d^3r'}{|\mathbf{r} - \mathbf{r}'|} \tag{6}$$

where $\rho(\mathbf{r}')$ is charge density of the continuous charge distribution and d^3r' is an infinitesimally small volume element.

Examples of Electrostatic Potentials from Continuous Charge Distributions

Potential Due to s Type Gaussian Function

A general Gaussian function centered at A can be expressed in Cartesian coordinates as

$$\eta(\mathbf{r}) = N x_A^l y_A^m z_A^n \exp(-\alpha r_A^2) \tag{7}$$

where N represents the normalization constant and $r_A = (x_A^2 + y_A^2 + z_A^2)^{1/2}$. In the above expression, l, m, n are integers. For the simplest case of an s type Gaussian they are zero, and (7) becomes

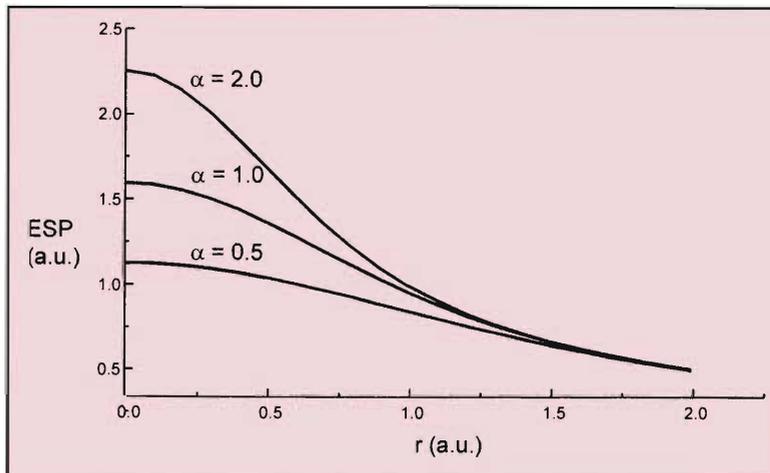
$$\eta(\mathbf{r}) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2).$$

The potential due to s type gaussian turns out to be

$$V(\mathbf{r}) = 2^{3/2} \sqrt{\frac{\alpha}{\pi}} F_0(-2\alpha r^2),$$

where F_0 is a special function, defined as

Figure 8. Plot of electrostatic potential due to an *s* type Gaussian function for different values of exponent α vs distance r . See text for details.



$$F_0(t) = \int_0^1 \exp(-tu^2) du.$$

Figure 8 displays the plot of electrostatic potential due to *s* type Gaussian for different values of α . It shows that the potential around the origin decreases as α decreases, and at larger values of r , the potential decays quite rapidly irrespective of the value of α . It also shows that at $r = 0$ the potential value is finite and rather flat in nature. Despite these drawbacks, Gaussians are often used as approximate descriptions of atomic orbitals in quantum chemical calculations, since their use facilitates quick computation of molecular energies and properties.

The Hydrogen Atom

The hydrogen atom is the simplest of all chemical elements and consists of one proton and one electron. The exact solution of the Schrödinger equation for the hydrogen atom gives the following ground state wave function and the corresponding electron density:

$$\Psi(r) = (1/\pi)^{1/2} \exp(-r); \rho(r) = |\Psi(r)|^2 = (1/\pi) \exp(-2r).$$

By substituting this expression for $\rho(r)$ in (6) and carrying out the integration, the electrostatic potential due to hydrogen atom



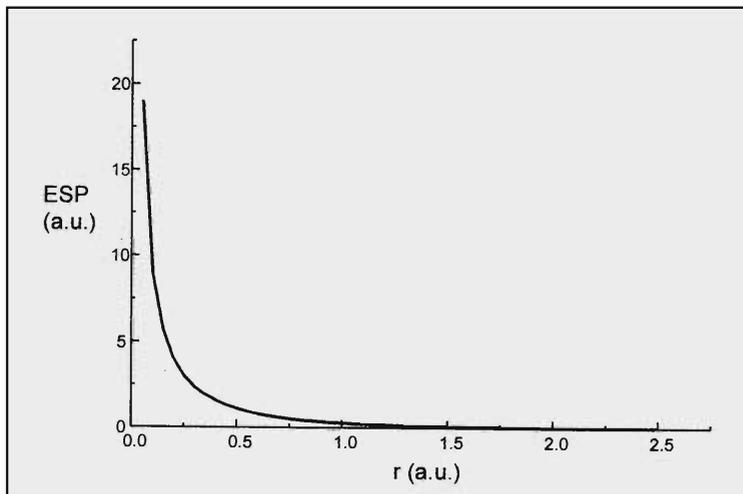


Figure 9. Plot of the electrostatic potential generated by the hydrogen atom vs radial distance, r .

including the proton comes out to be:

$$V(r) = (1 + 1/r) \exp(-2r) \tag{8}$$

Figure 9 depicts the plot of electrostatic potential for the hydrogen atom. It shows that the potential is always positive and decreases monotonically exhibiting no maxima or minima. The potential attains arbitrarily large values as r tends to zero. Further, it decays rapidly for large values of r .

Gauss' Theorem, Poisson's and Laplace's Equations

As seen earlier, the electric field due to a point charge q at a distance r from it is given by¹,

$$\mathbf{E} = (q / 4\pi\epsilon_0 r^2) \hat{r}$$

¹ \hat{r} is a unit vector along \mathbf{r} .

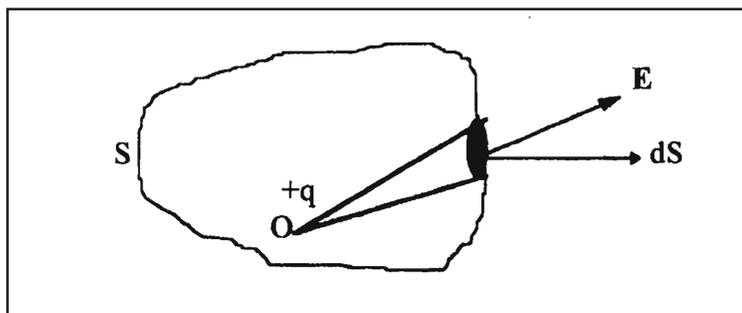


Figure 10. Illustration of Gauss' theorem. Here S is an arbitrary surface; dS a small surface element, $+q$ is the charge placed at point O and E , the intensity of electric field.

Carl Friedrich Gauss (1777–1855) was born in the German city of Brunswick, as a son of a day labourer. The duke of Brunswick recognised this infant prodigy and took charge of his education. His *Allgemeine Lehrsätze* dealt with theory of forces of inverse-square type. This marked the formal beginning of the subject of *potential theory*. His other noted contributions include the prediction of the position of an asteroid named Ceres, construction of a 17-sided polygon with a compass and a ruler alone, proof of the fundamental theorem of algebra and the construction of telegraph.

For a more detailed account of his life and contributions, see the article by D Surya Ramana in *Resonance*, Vol.2, No.6, p.60, 1997.

The electric flux passing through a sphere of radius r centered at the point charge is defined as

$$\begin{aligned} \text{Flux} &= \text{Surface area} \times \text{component of } \mathbf{E} \text{ perpendicular to surface} \\ &= 4\pi r^2 (\bar{\mathbf{E}} \cdot \hat{\mathbf{r}}) = q / \epsilon_0 \end{aligned} \tag{9}$$

In a general case, (*Figure 10*) where an arbitrary surface S encloses an arbitrary charge distribution, the direction of \mathbf{E} and its magnitude will be different at different points on S and (9) needs to be generalized. In *Figure 10*, an illustration of this is provided for an arbitrary surface S , where dS denotes a small surface element. The total flux can be calculated by adding the effects of all such elements by moving the element dS on the entire surface. It can be shown that the total flux through any closed surface S enclosing charge q is q/ϵ_0 , i.e.

$$\oint \mathbf{E} \cdot d\mathbf{S} = q / \epsilon_0 \tag{10}$$

This result is the celebrated Gauss' theorem. The divergence theorem can be used to convert (10) in the integral form into a differential equation relating the electric field $\mathbf{E}(\mathbf{r})$ at point \mathbf{r} to the corresponding local charge density $\rho(\mathbf{r})$.

$$\nabla \cdot \mathbf{E} = \rho(\mathbf{r}) / \epsilon_0 \tag{11}$$

In view of the usefulness of the scalar potential, it is often necessary to express (11) in terms of V rather than \mathbf{E} . Since $\mathbf{E} = -\nabla V$, (11) becomes

$$-\nabla^2 V = \rho(\mathbf{r}) / \epsilon_0 \tag{12}$$

The equation (12) is referred to as Poisson's equation. If the region under consideration contains no charge density, (12) becomes

$$\nabla^2 V = 0 \tag{13}$$

This equation is known as Laplace's equation, and such a differential equation is encountered in many branches of science and engineering.



Conclusions

It is now widely acknowledged that electrostatics plays an important role in molecular recognition processes. The electrostatic potential is found to be a useful tool for describing molecular structure and reactivity. The study of electrostatic potentials and fields due to discrete as well as continuous charge distributions presented in this article may be taken as a first step in understanding this subject.

In the next part, we shall examine some interesting consequences of the principles presented in this article. In particular, we shall consider the characteristics of atomic and molecular electrostatic potentials.

Suggested Reading

- [1] J-M Lehn. *Nobel Lectures in Chemistry 1981-1990*, Ed. Bo G Malström. World Scientific. Singapore, 1992.
- [2] S R Gadre, P K Bhadane, S S Pundlik and S S Pingale. *Molecular Electrostatic Potentials, Concepts and Applications*. Ed. JS Murray and K D Sen. Elsevier. Amsterdam. 1996.
- [3] M Purcell. *Electricity and Magnetism*. McGraw Hill. Singapore, 1981.

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Never lose sight of the role your particular subject has within the great performance of the tragicomedy of human life; keep in touch with life – not so much with practical life as with the ideal background of life, which is ever so much more important; and, *Keep life in touch with you*. If you cannot – in the long run – tell everyone what you have been doing, your doing has been worthless.

Erwin Schrödinger