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.
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

\[ F_{2,1} = \frac{q_2 q_1 (r_1 - r_2)}{4\pi\varepsilon_0 |r_1 - r_2|^3} \]  

Here \( F_{2,1} \) is the force acting upon \( q_1 \), \( r_1 \) and \( r_2 \) 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 \( F_{2,1} \) (Equation 1) is unchanged when extra point charges are included. Such forces are pair-wise additive and the total force \( F_1 \) on the point charge \( q_1 \) due to point charges \( q_2, q_3, \ldots q_n \) is given by

\[ F_1 = \sum_{i=2}^{n} F_{i,1} = \frac{q_1}{4\pi\varepsilon_0} \sum_{i=2}^{n} \frac{q_i(r_i - r_1)}{|r_1 - r_i|^3} \]  

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.

Figure 1. A schematic representation of the force \( F_{2,1} \) exerted by \( q_2 \) on \( q_1 \). The charges, \( q_1 \) and \( q_2 \) are located at \( r_1 \) and \( r_2 \) respectively.