9: Preface to Calculations

The beginning student of chemistry must have a knowledge of the theory which forms the basis for our understanding of chemistry and he must acquire this knowledge before he has the mathematical background required for a rigorous course of study in quantum mechanics. The present approach is designed to meet this need by stressing the physical or observable aspects of the theory through an extensive use of the electronic charge density.

The manner in which the negative charge of an atom or a molecule is arranged in three-dimensional space is determined by the electronic charge density distribution. Thus, it determines directly the sizes and shapes of molecules, their electrical moments and, indeed, all of their chemical and physical properties.

Since the charge density describes the distribution of negative charge in real space, it is a physically measurable quantity. Consequently, when used as a basis for the discussion of chemistry, the charge density allows for a direct physical picture and interpretation.

In particular, the forces exerted on a nucleus in a molecule by the other nuclei and by the electronic charge density may be rigorously calculated and interpreted in terms of classical electrostatics. Thus, given the molecular charge distribution, the stability of a chemical bond may be discussed in terms of the electrostatic requirement of achieving a zero force on the nuclei in the molecule. A chemical bond is the result of the accumulation of negative charge density in the region between any pair of nuclei to an extent sufficient to balance the forces of repulsion. This is true of any chemical bond, ionic or covalent, and even of the shallow minimum in the potential curves arising from van der Waals' forces.

In this treatment, the classifications of bonding, ionic or covalent, are retained, but they are given physical definitions in terms of the actual distribution of charge within the molecule. In covalent bonding the valence charge density is distributed over the whole molecule and the attractive forces responsible for binding the nuclei are exerted by the charge density equally shared between them in the internuclear region. In ionic bonding, the valence charge density is localized in the region of a single nucleus and in this extreme of binding the charge density localized on a single nucleus exerts the attractive force which binds both nuclei.

This web page begins with a discussion of the need for a new mechanics to describe the events at the atomic level. This is illustrated through a discussion of experiments with electrons and light, which are found to be inexplicable in terms of the mechanics of Newton. The basic concepts of the quantum description of a bound electron, such as quantization, degeneracy and its probabilistic aspect, are introduced by contrasting the quantum and classical results for similar one-dimensional systems. The atomic orbital description of the many-electron atom and the Pauli exclusion principle are considered in some detail, and the experimental consequences of their predictions regarding the energy, angular momentum and magnetic properties of atoms are illustrated. The alternative interpretation of the probability distribution (for a stationary state of an atom) as a representation of a static distribution of electronic charge in real space is stressed, in preparation for the discussion of the chemical bond.

Chemical binding is discussed in terms of the molecular charge distribution and the forces which it exerts on the nuclei, an approach which may be rigorously presented using electrostatic concepts. The discussion is enhanced through the extensive use of diagrams to illustrate both the molecular charge distributions and the changes in the atomic charge distributions accompanying the formation of a chemical bond.

The above topics are covered in the first seven sections of this web page. The final section is for the reader interested in the extension of the orbital concept to the molecular cases. An elementary account of the use of symmetry in predicting the electronic structure of molecules is given in this section.

Hamilton, 1970

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