1.1: Introduction

The understanding and prediction of the properties of matter at the atomic level represents one of the great achievements of twentieth-century science. The theory developed to describe the behavior of electrons, atoms and molecules differs radically from familiar Newtonian physics, the physics governing the motions of macroscopic bodies and the physical events of our everyday experiences. The discovery and formulation of the fundamental concepts of atomic physics in the period 1901 to 1926 by such men as Planck, Einstein, de Broglie and Heisenberg caused what can only be described as a revolution in the then-accepted basic concepts of physics.

The new theory is called quantum theory or quantum mechanics. As far as we now know this theory is able to account for all observable behaviour of matter and, with suitable extensions, for the interaction of matter with light. The proper formulation of quantum mechanics and its application to a specific problem requires a rather elaborate mathematical framework, as do proper statements and applications of Newtonian physics. We may, however, in this introductory account acquaint ourselves with the critical experiments which led to the formulation of quantum mechanics and apply the basic concepts of this new mechanics to the study of electrons.

Specifically the problem we set ourselves is to discover the physical laws governing the behaviour of electrons and then apply these laws to determine how the electrons are arranged when bound to nuclei to form atoms and molecules. This arrangement of electrons is termed the electronic structure of the atom or molecule. Furthermore, we shall discuss the relationship between the electronic structure of an atom and its physical properties, and how the electronic structure is changed during a chemical reaction.

Rutherford's nuclear model for the atom set the stage for the understanding of the structure of atoms and the forces holding them together.

From Rutherford's alpha-scattering experiments it was clear that the atom consisted of a positively-charged nucleus with negatively-charged electrons arranged in some fashion around it, the electrons occupying a volume of space many times larger than that occupied by the nucleus. (The diameters of nuclei fall in the range of l ´ 10-12 ® 1 ´ 10-13 cm, while the diameter of an atom is typically of the order of magnitude of 1 ´ 10-8 cm.) The forces responsible for binding the atom, and in fact all matter (aside from the nuclei themselves), are electrostatic in origin: the positively-charged nucleus attracts the negatively-charged electrons. There are attendant magnetic forces which arise from the motions of the charged particles. These magnetic forces give rise to many important physical phenomena, but they are smaller in magnitude than are the electrostatic forces and they are not responsible for the binding found in matter.

During a chemical reaction only the number and arrangement of the electrons are changed, the nucleus remaining unaltered. The unchanging charge of the atomic nucleus is responsible for retaining the atom's chemical identity through any chemical reaction. Thus for the purpose of understanding the chemical properties and behaviour of atoms, the nucleus may be regarded as simply a point charge of constant magnitude for a given element, giving rise to a central field of force which binds the electrons to the atom.

Rutherford proposed his nuclear model of the atom in 1911, some fifteen years before the formulation of quantum mechanics. Consequently his model, when first proposed, posed a dilemma for classical physics. The nuclear model, based as it was on experimental observations, had to be essentially correct, yet all attempts to account for the stability of such a system using Newtonian mechanics ended in failure.

According to Newtonian mechanics we should be able to obtain a complete solution to the problem of the electronic structure of atoms once the nature of the force between the nucleus and the electron is known. The electrostatic force operative in the atom is well understood and is described by Coulomb's law, which states that the force between two particles with charges e_1 and e_2 separated by a distance R is given by:

$$F \propto \frac{e_1 e_2}{R^2}$$

There is a theorem of electrostatics which states that no stationary arrangement of charged particles can ever be in electrostatic equilibrium, i.e., be stable to any further change in their position. This means that all the particles in a collection of positively and negatively charged species will always have resultant forces of attraction or repulsion acting on them no matter how they are arranged in space. Thus no model of the atom which invokes some stationary arrangement of the electrons around the nucleus is possible. The electrons must be in motion if electrostatic stability is to be preserved. However, an electron moving in the field of a nucleus experiences a force and, according to Newton's second law of motion, would be accelerated. The laws of electrodynamics state that an accelerated charged particle should emit light and thus continuously lose energy. In this dynamical model of the atom, all of the electrons would spiral into the nucleus with the emission of light and all matter would collapse to a much smaller volume, the volume occupied by the nuclei.

No one was able to devise a theoretical model based on Newtonian, or what is now called classical mechanics, which would explain the electrostatic stability of atoms. The inescapable conclusion was that the classical equations of motion did not apply to the electron. Indeed, by the early 1900's a number of physical phenomena dealing with light and with events on the atomic level were found to be inexplicable in terms of classical mechanics. It became increasingly clear that Newtonian mechanics, while predicting with precision the motions of masses ranging in size from stars to microscopic particles, could not predict the behavior of particles of the extremely small masses encountered in the atomic domain. The need for a new set of laws was indicated.
