PART
1

INTRODUCTION

1.1 ELECTRONIC STRUCTURE PROBLEM

Felix Bloch first discussed the eigen functions of the Schrödinger equation for an electron in a crystal. The theorems proved at that time (1928) are the foundation of all subsequent work on the quantum theory of solids. The properties of matter under normal conditions are, at microscopic level, governed by the behavior of the electrons as these light particles in their motion almost immediately follow the heavier nuclei. A precise knowledge of the electronic band structures is thus the first step towards understanding the physical properties of matter. Historically, one may distinguish a phase, during which various methods cellular, orthogonalized plane wave (OPW), augmented plane wave (APW), Green's function, etc. were invented but gave only limited results because of the enormous labour involved in implementing these schemes on band calculators.

The next phase began in the 50's with the advent of electronic computers. Very elaborate programs were constructed and set going, for various materials, but the outcome was often disappointing. Generally speaking, the different methods appeared to converge satisfactorily to match the same numerical results, but these were often a long way from the experimental information that was coming from Fermi surface and optical studies. The recognition of the sensitivity of the one-electron energie $E(\vec{k})$ to the form of potential $V(\bar{r})$ generated a new philosophy: the determination of band structure came to be regarded as an art, where one tried to build up a model of the energy surface represented by some parameters but consistent both with experimental and with some rough algebraic approximation to the solution of Schrödinger equation. The success of this procedure has revolutionized the whole theory of metals. To make further progress, however, it was essential to combine technique art with science. So we have learned to treat this problem as one where algebraic analysis, numerical computation, and physical intention all have their part.

The band structure problem is a many-body problem corresponding to the motion of enormous number of electrons and of nuclear particles in the crystal. With the aid of density functional theory (DFT), the many-electron problem can be reduced to a problem with one-electron moving in an effective crystal potential. Once the effective one electron crystal potential $V(\bar{r})$ is constructed with the aid of certain approximations, e.g., one-electron approximation [1] and Born-Oppenheimer approximation [2], the problem remains of solving the Schrödinger equation

$$\left[-\nabla^2+V(\bar{r})\right]\ \Psi_{jk}(\bar{r})=E_{jk}\,\Psi_{jk}(\bar{r}). \tag{1.1}$$

The energy band structure calculations are often done in a self-consistent manner. To achieve this one solves the Schrödinger equation and the electronic charge density is constructed as;

$$\rho(\bar{r})=\sum_{jk}^{occ.}\left|\ \Psi_{jk}(\bar{r})\ \right|^2 \tag{1.2}$$

and then a new field is constructed by solving Poisson's equation;

$$\nabla^2 u(\bar{r})=-8\pi\rho(\bar{r}) \tag{1.3}$$