PART I

ELECTRON STATES IN CRYSTALLINE SOLIDS

CHAPTER 1

THE ONE ELECTRON THEORY OF SOLIDS
1.1 Introduction

The solution of the Schrödinger equation for a crystalline solid is essentially a many-body problem containing a large number of interacting particles. For, even if we restrict our investigations to the case of a perfect crystal, and neglect effects that arise from the motion of the atomic nuclei, we are still left with a many-electron problem which cannot be solved explicitly, and thus requires an approximate method for its solution. One of the most fruitful methods devised for the solution of many-electron problems is the one-electron formulation, in which the total wave function for the system of electrons is chosen to be a combination of functions, each of which involves the coordinates of only one electron.

Two types of wave functions for this interacting system of electrons are in use. In the Hartree method, the trial function is taken to be a simple product of single particle orbitals, and a variational calculation is performed by varying each orbital in an arbitrary fashion. Here, however, each electron moves in the average field of the fixed charges and \((N-1)\) other electrons, so that while calculating the wave function of one electron, the others are distributed throughout the wave function according to the statistical probability that they will be found at any one coordinate. Hence, though the electrons tend to avoid regions of high average potential energy, they do not tend to avoid one another because of their Coulomb repulsion, so that no account is taken of the correlated motion of the electrons. Further, the use of a simple product does
not satisfy the Pauli exclusion principle, for it is not anti-symmetric in the exchange of electrons. These two shortcomings of the Hartree method can best be overcome by choosing the wave function of the system to be a Slater determinant (Slater, 1929) of one-electron functions:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(r_1) & \phi_1(r_2) & \cdots & \phi_1(r_N) \\
\phi_2(r_1) & \phi_2(r_2) & \cdots & \phi_2(r_N) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_N(r_1) & \phi_N(r_2) & \cdots & \phi_N(r_N)
\end{vmatrix}$$

where \((N!)^{-\frac{1}{2}}\) is the normalising constant in the case when the \(\phi_i\)'s are orthonormal to each other. This condition may be assumed, as it simplifies the handling of the problem, but does not place any important restriction on the \(\phi_i\)'s. Here, the antisymmetric nature is automatically ensured, and a certain amount of correlation between electrons of the same spin is introduced as well.

Before incorporating the condition (1.1) in the case of solids, we divide the electrons into two classes: (1) the inner electrons which belong to closed shells, and (2) the outer electrons whose wave functions are appreciably affected by changes in the inter-atomic distances, and which, therefore contribute to the binding energy of the solid. Thus each nucleus and its rigidly attached unit of electrons produces an ion core potential for the rest of the system. The whole assembly of electrons is now reduced to an assembly of \(N\) outer electrons interacting with each other and with
a group of 'M' fixed rigid ion cores. The Hamiltonian of the system is given by:

\[ H = \sum_{i}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i + V_i \right) + \frac{1}{2} \sum_{i,j}^{'} \frac{e^2}{\text{r}_{ij}^2} \]

\[ = \sum_{i} H_i + \frac{1}{2} \sum_{i,j}^{'} \frac{e^2}{\text{r}_{ij}^2} \quad (1.2), \]

'\( V_i \)' being the potential of the \( i \)th electron in the field of all the 'M' ion cores. By applying the Variational Principle (Reitz, 1955), one obtains with the help of equations (1.1) and (1.2):

\[ H_i \phi_i(\text{r}_i) + e^2 \sum_{j} \left[ \int \phi_j(\text{r}_j) \left( \frac{e^2}{\text{r}_{ij}} \right)^2 \right] \phi_i(\text{r}_i) \]

\[- e^2 \sum_{j} \left[ \frac{\int \phi_j^*(\text{r}_j) \phi_i^*(\text{r}_i) \phi_i(\text{r}_j) \phi_j(\text{r}_i) \text{d} \tau_2 / \text{r}_{ij}^2}{\phi_i^*(\text{r}_i) \phi_i(\text{r}_i)} \right] \phi_i(\text{r}_i) \]

\[- E_i \phi_i(\text{r}_i) = 0 \quad (1.3). \]

This is the celebrated Fock's equation, in which the second term represents the Coulomb potential energy, acting on the electron at position \( \text{r}_i \), of all the electronic charge, including that of the \( i \)th wave function. The third term is the famous exchange term which arises from the antisymmetric nature of the wave function (1.1), and which may be interpreted as the exchange potential energy, at the position \( \text{r}_i \), produced by the exchange charge density (Slater, 1951),

\[- e \sum_{j} \frac{\phi_j^*(\text{r}_j) \phi_i^*(\text{r}_i) \phi_i(\text{r}_j) \phi_j(\text{r}_i)}{\phi_i^*(\text{r}_i) \phi_i(\text{r}_i)} \quad (1.4), \]

located at the position \( \text{r}_2 \) of the second electron. Detailed
considerations show that the principal effect of exchange interaction is to remove one electron from the immediate vicinity of $\vec{r}_1$, where the wave function of the electron is being calculated, i.e., it is as if the electron carries around with it a hole, sometimes called the Fermi or exchange hole (Slater, 1951; Wigner and Seitz, 1933), so that the probability that a second electron of the same spin may be found in its immediate neighbourhood is practically zero. This correlation is an accidental one, arising from the Pauli principle and not from the repulsive Coulomb interaction. Nevertheless, the Pauli principle is effective in accounting for some correlation between electrons of the same spin and thereby reducing the average potential energy of the system.

Finally, it is necessary to mention two important features of $\phi_i(\vec{r}_i)$: first, the solutions of Fock's equations are orthogonal to each other, as is directly evident from the set of equations (1.3). Secondly, the solution of Hartree's or Fock's equation requires a self-consistent field calculation, i.e., an initial potential is constructed by an intelligent guess for the wave functions and the usual method of iteration is followed until the final wave functions determine a potential which is self-consistent to a high order of accuracy.

1.2 Localised Solutions and Crystal Orbitals

The solution of the Hartree's or Fock's equation may be obtained once the boundary conditions are given. Those conditions determine the nature of the solution. Two independent types of
solution of equation (1.3) may be shown to exist for solids:
(1) localised wave functions (Heitler and London, 1927), each of
which is large in the vicinity of one ion core in the crystal and
(2) crystal orbitals (Hund, 1928; Mulliken, 1928; Bloch, 1928),
which extend throughout the entire crystal lattice. These two types
of solutions provide different approaches to the crystal problem
which are more or less complementary. Because of its simplicity,
the crystal orbital method is more widely used.

It must be pointed out that the use of localised orbitals
introduces some correlation, in the sense that the electrons are
kept apart by being forced to be on different atoms. Although,
this is clearly an advantage of the above scheme, it is balanced
by the fact that crystal orbitals, particularly those of low energy,
are smoother than atomic-type wave functions and thus produce a
lower mean kinetic energy.