THE ROLE OF THE SELF CONSISTENT FIELD
IN THE
BAND THEORY OF SOLIDS

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CONTENTS

ABSTRACT

This thesis is planned to give an account of the method known under the name "The Self Consisting Field" in the Band Theory Of Solids after the growing difficulties in the usual methods used in the theory. These difficulties become so huge that any reasonable advance in studying complicated solids become a laborious job.

This method received great attention as a sequence of the studies of the density-functional theories (Kohn and Sham, 1965) which gave a support for suggesting reasonable potentials of electrons in solids.

The method of self consisting field depends upon trying to build up a potential energy for the one-electron wave equation used for solution to give the band energies of electrons.

To make things clear it was important to give a short survey of the existing theory of the Band Structure of electrons and point out the huge difficulties appearing in three of the methods used. Although the use of the symmetry properties of the crystal under investigation played an important role in overcoming these difficulties.

We have chosen a recent model built up by Lawrence (1971) and worked out the corresponding energies and wave functions. The band

calculations are carried on using the method of phase shifts in close forms as functions of the atomic number Z and wave vector $\underline{k}$.

Relativistic corrections for the present model is provided. The present calculations depends upon the well known Foldy-Wouthuysen transformation of the Dirac Equation, which have been applied to other methods and for a large number of crystals. The first order correction proved to depend upon the 4th power of Z and hence is quite important for solids of large Z.

CHAPTER ONE

INTRODUCTION

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To study the electronic properties of solids, it is essential to solve or try to find an approximate solution for the wave equation of electrons in a solid. The problem is not simple as electrons are just one type of particles to be found in a solid. There, we may find ions of different types which are occupying vibrating sites in solids. These sites are characterized by certain symmetry properties forming thus a geometrical figure which is the lattice space of the solid structure.

Our electrons under investigation are necessarily originating from the outer shells of the atoms forming the solid and probably the impurity atoms present. These electrons are either fairly bound to its mother ions as in insulators or loosely bound to the impurity ions as in mother ions as in semiconductors and to the mother ions as in semimetals and metals. In all cases these electrons are interacting with the ions and with itself forming a complicated ensemble to study mathematically.

Many body problems has been proved to be always difficult problems to tackle , and the present one of electrons and ions,which attracted the attention of many theoretical physicists since the early days of the wave mechanics, is one of the most difficult problems in this field. The method of solution of the huge wave equation

$$H(\nabla^2, \underline{r}, \nabla^2, \underline{R})\, \Psi(\underline{r}, \underline{R}) = E\, \Psi(\underline{r}, \underline{R}) \qquad (1.1)$$

where $\underline{r}$, $\underline{R}$ are the collective position vectors of electrons and ions and where ∇^2, ∇^2 stands for the collective Laplacian operators for the assembly, depend upon a series of approximations which are related to the nature of the particles, one of which is the large difference in the masses of an electron and an ion, which is used to separate the electron wave equation. The result is a wave equation for electrons depending upon the collective wave vector $\underline{R}$ of ions, namely

$$H_e(\nabla^2, \underline{r}, \underline{R})\, \psi_e(\underline{r}, \underline{R}) = E_e\, \psi_e(\underline{r}, \underline{R}) \qquad (1.2)$$

with the Hamiltonian H_e (see chapter two for details)

$$H_e \equiv \sum_i \left\{ \frac{-\hbar^2}{2m} \nabla^2_i + \sum_{\underline{\ell}} \frac{-Z\, e^2}{|\underline{r}_i - \underline{R}_\ell|} + \sum_{j>i} \frac{e^2}{|\underline{r}_i - \underline{r}_j|} \right\} \qquad (1.3)$$

where i and j refers to electrons of position vectors $\underline{r}_i$ and $\underline{r}_j$ and where ℓ refers to ions of position vectors $\underline{R}_\ell$ which are *assumed to be at rest.* The potential energy is expressing the interaction of electrons with each other and with the ions. The wave function of ions is much more simplified but contains as a potential energy the interaction between ions and the electronic energy E which is a function of $\underline{R}$.

A further approximation is necessary in which equation (1.3) is separated into a set of Hamiltonians for the electrons producing what is established now as the *One Electron Wave Equation.* This is carried on through a Variational method (see chapter two section two). The result introduces an extra potential in the single electron Hamiltonian H_i which is simply written as

$$H_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{\ell}\frac{Z e^2}{|\underline{r}_i - \underline{R}_\ell|} + V_{coul} + V_{exch} \qquad (1.4)$$

where

$$V_{coul} = e^2 \sum_j \frac{|\psi_j(\underline{r}')|^2}{|\underline{r}_j - \underline{r}'|} d\underline{r}' \qquad (1.5)$$

$$V_{exch}\,\psi_i(\underline{r}) = -e^2 \sum_j \psi_j(\underline{r}) \int \frac{\psi^*(\underline{r}')\,\psi_i(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' \qquad (1.6)$$

$\psi_i(\underline{r})$ being the solution of

$$H_i\,\psi_i(\underline{r}) = E_e^{(i)}\,\psi_i(\underline{r}) \qquad (1.7)$$

resulting, thus, in an integro-differential equation which for further computations needs to be over simplified, i.e. replacing such potential terms by poor approximations. The result is that we are left with an oversimplified *non-reliable* wave equation for the One Electron representative.

An alternative method which may be adopted is the one-electron wave equation assumed in the simple form

$$\left[-\frac{h^2}{2m}\nabla^2 + V(\underline{r})\right]\psi(\underline{k},\underline{r}) = E(\underline{k})\,\psi(\underline{k},\underline{r}), \qquad (1.8)$$

in which the *potential energy $V(\underline{r})$ of the single electron is to be* assumed hoping that such a potential will produce accurate values for the electronic state. The only restriction to be imposed on $V(\underline{r})$ is that it must be invariant under the symmetry properties possessed by the crystal. Such potentials introduced in the wave equation are usually termed self-consistent potentials and are recently used (Moruzzi et.al., 1978; Janak et.al., 1975 and Gaspari and Gyorffy, 1972) successfully in electronic band approximations. In order to achieve a high degree of self-consistent procedure, more recent attempts are made by successively computing the crystal potential from the electronic wave functions. The so-obtained results were accurate enough to give meaningful results. It is quite important to notice that such self-consistent potentials are to be used only for band calculations and not to be applied to other physical quantities which depend upon the detailed structure of the potential energy.

In chapter two we give a brief account of the wave equation of the assembly of electrons and ions and outline the Born-Oppenheimer adiabatic approximation used to separate the variables, resulting in a wave equation for electrons depending upon the positions of the ions. The potential energy of the electrons is due to the interaction of electrons with themselves and with ions assumed to be at rest. The Hartree-Fock approximation is discussed in which a variational method is applied to a determinental form of one-electron-wave function leading to a One-Electron wave equation in which the electron-electron interaction term for potential is replaced by a Coulomb potential being the average value of the electronic interactions and an exchange potential in the form of an integral operator.

In section 2.1.3 we provide a short discussion of the Sommerfeld and Bloch theorems illustrating how the $\underline{k}$-vector is introduced in the Band theory. This $\underline{k}$-vector has proved to be important in all verses of this theorem.

Band calculations are briefly discussed in section 2.2 and we selected three methods out of the eleven methods known in Band approximations. These are the orthogonalized plane wave, cellular and augmented plane wave approximations. In these sample methods we discuss the difficulties arising when applying them to electronic energy calculations.

In section 2.2.4 we summarize the most recent and convenient method for estimating the band energy of solids. This method is used when the potential energy is built up and formulated. This method was originally constructed when impurity atoms are present and its presence destroys the periodicity of the lattice. Its analysis depends upon calculating the phase-shifts similar to what is performed in the theory of atomic scattering.

Chapter three is devoted to show how to build up a potential energy for the one-electron potential in a way to satisfy all the conditions and results of the Hartree-Fock theorem (see section 2.1.2). This method come as a sequence of the studies of the density-Functional theories (Kohn and Sham, 1965) whose results give a support for suggesting reasonable potentials. We considered a potential suggested by Lawrence (1971) and worked out its corresponding structure and wave functions in section 3.2. In section 3.3 we caried out the band calculations using the method of phase shifts which were obtained in closed forms as functions of the atomic number Z and the wave vector $\underset{\sim}{k}$.

In chapter four we considered the relativistic corrections to the band calculations. The method used depends upon the Foldy--Wouthuysen transformation which simplified Dirac equation. This procedure was applied in recent years to the energy states in a large number of crystals. In section 4.1 we give the equation and the method used while in section 4.2 we applied the results to our model using a perturbation method to solve the so-obtained wave equation. The first order correction is proved to depend upon the results show that this correction term depends upon the $4^{\underline{th}}$ power of Z and hence becomes more effectively as Z increases. Its effect is liable to be of great importance for $Z \gtrsim 30$ as was expected by many authors (see e.g. Moruzzi et.al., 1978).

CHAPTER TWO

METHODS USED IN THE BAND THEORY OF SOLIDS