Chapter 1

Introduction

First let's overview the topics to be discussed in the following chapters. An original textbook is *Electronic Theory of Solids*, Chapter 4 in *Fundamentals of Condensed Matter Physics II* written in Japanese by Toshinosuke Muto (Kyoritsu Shuppan, 1957). The book is now out of print.

We will see some fundamentals of the electron theory of solids in this book. Solid is one of the four states of matter: solid, liquid, gas, and plasma. It has a rigid structure in contrast to the other states, because atoms, ions or molecules bond together in a solid. Only a few grams of a solid consists of a huge number, about 10^{23}, of atoms. You may be able to calculate how many atoms are in a solid if its weight and atomic composition are given. We will focus on crystalline solids or *crystals* for simplicity. A basic building blocks made up of atoms or molecules are regularly repeated throughout a crystal. Owing to the repetition in structure, we do not have to deal with the whole atoms in a crystal, but it is enough to consider the atoms only within a single building block in many cases.

Each elemental solid, which consists of a single element, or solid compound has its intrinsic properties. They are used properly for a wide variety of purposes by taking account of their physical properties such as electrical conductivity, heat conductivity, magnetic property, optical properties, hardness and so on. Most physical properties are closely related to the behavior of so-called *valence electrons*.

Consider one of the valence electrons in a solid. We here distinguish the valence electrons from the rest of an atom or the *ion core*: nucleus and core electrons. The valence electron interacts with ion cores and the other valence electrons. Both ion cores and valence electrons in a solid run up to about 10^{23}. There are the electrostatic interaction described by Coulomb's

law, the magnetic interaction due to spin and orbital magnetic moments, and so on. Because the magnetic interaction is weak in general, though not always, we will consider only the electrostatic interaction. The state of the valence electrons is then governed by the Schrödinger equation for a many-body system consisting of the valence electrons and the ion cores with the electrostatic interaction. It is impossible to solve such an equation for an enormous number of interacting particles without any approximation.

(i) **Born-Oppenheimer approximation** to separate the motion of the valence electrons and the motion of the ion cores

If one assumes that *the motion of ion cores is much slower than the motion of valence electrons* and that *the interaction between the motion of ion cores and the motion of valence electrons is weak*, one can solve the electronic motion of equation with the ion cores fixed in a certain configuration. We will see this in Ch. 2. It is, however, still impossible to solve the Schrödinger equation for too many valence electrons.

(ii) **one electron approximation** to reduce the many-electron equation to a set of one-electron equations

Clamp the ion cores at the lattice points of the crystal and use an approximate potential energy that takes the average interaction of the electrons into account. Take the effect of the other electrons into account through the interaction field the valence electron experiences in the averaged charge density of all the other electrons.

Thus we then obtain *the one-electron potential* depending only on the coordinate of the electron of interest and it determines the one-electron wave function *orbital*. According to the Pauli's principle the resultant orbitals are used to construct the many-electron wave function, which is called as Slater determinant. Chapter 3 is devoted to the one-electron equation which governs the one-electron wave function and chapter 4 to validity of the independent electron approximation. Because the equation for a valence orbital includes all the other occupied valence orbitals, one should start from an appropriate set of wave functions and iterate until self consistency is achieved. [1].

Without such an elaborate task one can tell some properties of the one-electron state much easily with the aid of experimental data if one assumes that the one-electron potential has the same translational symmetry. The

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[1]This calculation can tell the valence electronic state without any resort to experiments. Thus it is called the empirical or first principle calculation.

one-electron wave function in a periodic potential is called as *the Bloch function*. The behavior of the Bloch function is treated by *the electronic band-structure theory*. The properties of the Bloch function will be seen in Ch. 5. Some simple band theories follows.

We note here that the above procedure is not always appropriate to all the crystal. The adiabatic approximation is valid for the ground state of the insulators whereas the assumption does not hold for metals or the excited states of a solid. In such cases one needs to consider the electron-phonon interaction.

The independent electron approximation also neglect *correlation* among the electrons; the probability of finding an electron at certain position in space depends on the positions of the other electrons. for example

- two electrons with parallel spins

  The two electrons tend to move away from one another according to the Pauli's principle. This is called as *exchange correlation* and plays an important role in evaluating the cohesive energy or in ferromagnetism The effect is approximately incorporated by using the *Slater determinant*.

- two electrons with anti-parallel spins

  The two electrons also tend to repel each other according to Coulomb's law, which also holds for the case (i). As is shown in Ch. 3, the Slater determinant gives a good approximation of many-electron wave function in the limit of weak interaction. Considering the electrostatic interaction between two electrons many-electron state is no longer expressed by a single Slater determinant and is a linear combination of Slater determinant for possible electronic configurations, so-called *configuration interaction*, CI. This is reminiscent of the perturbation theory in quantum mechanics, where the perturbation, Coulomb interaction between the two electrons in this case, results in a linear combination of the unperturbed wave functions, Slater determinants.

It depends on each material of interest how important is the effect of electron correlation. For example, many $3d$ transition-metal compounds and lanthanoide compounds are known as strongly correlated electron system. In Ch. 4 we consider the electron correlation from the beginning and show the validity of the one electron approximation without resorting to any spatial localization of a particular orbital.