

Chapter I

INTRODUCTION

In crystalline substances, whether metals or semiconductors, the constituent atoms are highly ordered in space, each atom being virtually fixed at the equilibrium site; therefore the arrangement of the atoms in crystals has only one configuration and has periodicity. An immediate consequence of this periodicity is the Bloch-Floquet theorem stating that the one-electron eigenfunctions are of the form

$$\Psi(\underline{r}) = \Psi_{n\mathbf{k}}(\underline{r}) = \exp(i\mathbf{k}\cdot\underline{r}) u_{n\mathbf{k}}(\underline{r}), \quad \text{-----}(1.1)$$

where the wave vector \mathbf{k} is in the first Brillouin zone, $u_{n\mathbf{k}}(\underline{r})$ has the periodicity of the crystal structure and $n = 1, 2, 3, \dots$ is the band index. Thus, all eigenfunctions (1.1) are extended: an electron described by (1.1) goes everywhere in the crystal with equal probability just as in the free electron case, and the periodicity also leads to the existence of gaps in the energy spectrum.

If metals are heated, or a large number of impurities are present in semiconductors, the lattice in which the electrons move will have several configurations and will no longer be periodic. The electron wave function can now no longer be described by Bloch waves. Such systems are called "Disordered Systems".

Disordered systems have recently attracted a great deal of attention on the part of theoretical physicists. Amorphous films of various materials and some kinds of glass are electronic semiconductors. In addition these amorphous materials are very useful in making switching devices. At the present time, conducting glass is the heart of switching

devices. The semiconductors used in transistors and most other electronic devices are crystalline. The theory of their behaviour has been developed in great details in the last 20 years and the agreement with experiment is good. The study of non-crystalline semiconductors is much newer and the mechanism by which they work is not fully understood, so the theory of their behaviour is of great interest. Today these devices cannot be produced in great quantities. Once the theory is known, it will be of great help in their production. And if disordered materials could replace crystalline semiconductors, this would be a successful step for the industrial world, because disordered materials can be used without purification or being made into crystals. The crystalline semiconductors, however, have to be pure crystals before they can be used, so they are harder to work with.

For a periodic structure, translational and point symmetry can themselves provide a significant amount of information about the wave functions and the spectrum. For disordered systems, Mott and Twose¹ were the first to suggest that the solutions for the electron states in a one-dimensional Kronig-Penney model were localized. A localized state in disordered systems is defined as follows. For such a state the solution of the Schrödinger equation, for a particular energy eigenvalue, will decay exponentially with distance from a particular point or region associated with the solution. In one dimension all solutions are known to be of this type and these are the most completely understood.

¹ N.F.Mott, and W.D. Twose, " The Theory of Impurity Conduction, " Advances in Physics, 10 (1961), 107.

There are obvious difficulties in carrying over the analysis to the more realistic three-dimensional case. Although exact conditions for the existence of such states have not been formulated, Mott² has made some general arguments about the conditions under which localized states may be expected to appear in a realistic disordered system. Mott's arguments are based upon consideration of the mean free path of the electron.

Owing to the difficulties in carrying over the analysis of the localized states, this thesis will not be concerned with the localized states, the main emphasis will be on the study of the density of states of disordered systems. Klauder³ has investigated the modification of electron energy levels of solids in the presence of a large number of randomly distributed impurities by using the diagrammatic perturbation methods familiar in field theory and many-body studies. Lifshitz⁴ has paid particular attention to the detailed study of the tail of the density of states of disordered systems. Mott² has given a very detailed discussion on disordered systems including both theory and experiment as well as new ideas in predicting the properties of disordered systems. His article is considered to be among the first in stimulating scientific study in this

² N.F. Mott, "Electrons in Disordered Structures," Advances in Physics, 16 (1967); 49.

³ J.R. Klauder, "The Modification of Electron Energy Levels by Impurity Atoms," Annals of Physics, 14(1961), 43.

⁴ I.M. Lifshitz, "The Spectrum of Disordered Systems," Advances in Physics, 13(1964), 483.

field. E.N. Economou⁵ and co-workers also give a good review on disordered systems.

In order to investigate the motion of electrons in a disordered system, it is reasonable to consider first the simplest model which retains the essentials of the disordered states. Until recently, the model was represented by independent electrons interacting with a disordered array of ions, and employed an effective medium approach which treated the system as translationally invariant. The electron wave functions can be obtained from the Schrödinger equation:

$$\left[i \hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 - \sum_{\alpha} U(\underline{r} - \underline{R}_{\alpha}) \right] \psi(\underline{r}, t) = 0, \quad \text{----- (1.2)}$$

where \underline{R}_{α} denote the atomic sites and $U(\underline{r} - \underline{R}_{\alpha})$ denote the interaction potential due to atoms at site \underline{R}_{α} . For a disordered system, \underline{R}_{α} are random variables, that is, they have a probability distribution. This distribution may take the form $P(\underline{R}_1, \dots, \underline{R}_N)$ which includes correlation between atomic sites. Even with this simplest model, the non-periodic distribution of \underline{R}_{α} brings in its train severe mathematical difficulties. No doubt eigenfunctions must exist, but they will be very complicated because they have to express the way in which an electron reacts to a highly irregular distribution of potential. Moreover, if we want to determine the density of states, we should in principle calculate the wave functions for a fixed configuration of ions and

⁵ E.N. Economou, and Others (comp.) Amorphous and Liquid Semiconductors. (J. Tauc, ed., Plenum Press 1974).

then average over the ensemble of all possible arrangements of ions. It is clearly impossible to do this in practice, but the Green function formalism allows us to calculate the ensemble averages of physical quantities without ever calculating wave functions for a specific ionic arrangement.

Edwards⁶ was the first to introduce the Green function, G , which satisfies the equation

$$\left[i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 - \sum_{\alpha} V(\underline{r} - \underline{R}_{\alpha}) \right] G(\underline{r}, \underline{r}'; t, t') = \delta(\underline{r} - \underline{r}') \delta(t - t')$$

to disordered systems. G is a function which gives the effect at (\underline{r}, t) of a disturbance $\Psi(\underline{r}', t')$ at another neighborhood and time. Thus

$$\Psi(\underline{r}, t) = \int G(\underline{r}, \underline{r}'; t, t') \Psi(\underline{r}', t') d\underline{r}'$$

This is the essence of Edwards' method in which the electron motion is studied by utilizing the property of G properly averaged over the distribution of atomic positions \underline{R}_{α} . Edwards has also shown that the averaged density of states can be now found from the averaged electron Green function $\langle G \rangle$. The problem of calculating the density of states then reduces to that of finding the averaged electron Green function. There are two important methods to obtain $\langle G \rangle$. One is to perform an expansion on $\langle G \rangle$ in terms of the free electron Green function, another is the method of path integrals which appears in Feynman and Hibbs⁷.

⁶ S.F. Edwards, "The Electronic Structure of Disordered Systems," Philosophical Magazine, 6 (1961), 617.

⁷ R.P. Feynman, and A.R. Hibbs, Quantum Mechanics and Path Integrals (New York: Mc Graw-Hill, 1965), P. 26.

The detailed procedure for the evaluation of the density of states in terms of the electron Green function and how it can be used will be shown in chapter II. The way to perform an expansion on $\langle G \rangle$ in a perturbation expansion of the free electron Green function will also be shown in chapter II, and a series of papers (Edwards^{8,6,9}, Beeby and Edwards¹⁰, Lukes¹¹ and Ballentine¹²) used this method in calculating the ensemble averaged Green function, hence the density of states will be only briefly mentioned.

By using a simple argument, Feynman can write the electron Green function in the form of path integrals. His argument will be discussed in chapter III and the mathematical formulation for deriving this expression directly from the Schrödinger equation will also be shown. An example of per-

⁸ S.F. Edwards, "A New Method for the Evaluation of Electric Conductivity in Metals," Philosophical Magazine, 3 (1958), 1020.

⁹ S.F. Edwards, "The Electronic Structure of Liquid Metals," Proceedings of the Royal Society A, 267 (1962), 518.

¹⁰ J.L. Beeby, and S.F. Edwards, "The Electronic Structure of Liquid Insulators," Proceedings of the Royal Society A, 274 (1963), 395.

¹¹ T. Lukes, "On the Electronic Structure of Disordered Systems," Philosophical Magazine, 12 (1965), 719.

¹² L.E. Ballentine, "Calculation of the Electronic Structure of Liquid Metals," Canadian Journal of Physics, 44 (1966), 2533.

forming direct path integrations is given in the case of a free electron. In addition, this chapter describes another method which was suggested in Feynman and Hibbs' book⁷ and example showing its application will be given for the case of a harmonic oscillator.

Edwards and Gulyaev¹³ have pointed out that the Feynman's path integral formalism helped to express the averaged electron Green function of disordered systems in the closed form but they did not give details. In chapter IV, the author tries to make a detailed derivation of this expression and will show that for a high density of scatterers, by keeping only the first two terms of the expansion of the exponent in this expression, the problem will become the same as that considered by Bezák^{14,15}. Bezák set about the problem by taking the auto-correlation function of the potential as Gaussian but keeping only the first two terms of the Gaussian expansion and using the method suggested in chapter III reduced the path integrals of $\langle G \rangle$ into the product of two functions, the exponential of the classical action and the path integrals of the deviation from the classical path. The classical action of disordered systems can

¹³ S.F. Edwards, and Y.B. Gulyaev, " The density of states of a highly impure semiconductor, " Proceedings of the Physical Society, 83 (1964), 495.

¹⁴ V. Bezák, " Path-integral theory of an electron gas in random potential, " Proceedings of the Royal Society of London A, 315 (1970), 339.

¹⁵ V. Bezák, " The partition sum of an ideal gas in a random potential, " Journal of Physics A: General Physics, 4(1971), 324.

be evaluated without too much difficulty by using the principle of least action, but the difficulty arises in carrying out the path integrals. Bezák used short-cut by trying to change the exponent in the path integrals to the integro-differential equation. In this way he was able to obtain the formula for the averaged Green function of disordered systems. Bezák's method will also be worked out from the beginning to the integro-differential equation in chapter IV.

In chapter V, we will use another method different from that of Bezák. Instead of trying to deduce an integro-differential equation, we will write the averaged Green function in terms of cumulant series introduced by Kubo¹⁶. The first two cumulants will be evaluated explicitly. The discussion will be given in chapter VI.



¹⁶ R. Kubo, "Generalized Cumulant Expansion Method," Journal of the Physical Society of Japan, 17 (1962), 1100.