Solid State Physics

An introduction to its theory

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Preface

This book is intended to be a realistic introduction to the theory of solid state physics. It is meant to fill the gap between the more empirical books such as Kittel's *Introduction to Solid State Physics* or Dekker's *Solid State Physics*, and the more advanced theoretical texts such as Kittel's *Quantum Theory of Solids*. No claim is made that the subject is covered comprehensively. This is clearly not possible within a book of this size. However, it is hoped that the included material will give a good basic background to the subject.

This text should be useful to research workers both in industry and university, and to final honours students. It should be especially appropriate to the several new M.Sc. courses in *Solid State Physics*. The reader is assumed to have taken a first course in Quantum Mechanics.

Problems are included at the end of each chapter and a few of these have been used to extend the theory slightly. M.K.S. (Sommerfeld) units are used throughout and the charge on the electron is taken as $-e = -1{\cdot}602 \times 10^{-19}$ C.

H. C.

Tynemouth, March 1968

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1

The One-electron Approximation

§ 1.1 The quantum mechanics

When it is noted that the interatomic distance in solids is of the order of a few angstrom units, it is not at all obvious how it is possible to separate the motion of the electrons in any sense. This monograph is primarily concerned with the results obtainable from the one-electron approximation and it is the purpose of the first chapter to indicate the relevant theoretical background. Initially it is necessary to explain how the motion of the electrons can be treated apart from the lattice of heavy ions and then to deal with the separation of the electrons themselves.

The results of the Schrödinger wave mechanics will be used freely throughout this book and perhaps it is as well to recount briefly the main results of quantum mechanics. For further information the reader is referred to any of the standard texts such as Schiff or Mandl.

In quantum theory, the state of any physical system is described as completely as possible by a wave function ψ which in general is complex and depends on the position co-ordinates of all the N particles and on the time. Strictly ψ depends upon the spin co-ordinates as well. This will be emphasized where appropriate.

The real quantity $\psi^*\psi d\tau$ is the probability that the co-ordinates q_i of the particles lie within the volume element

$$d\tau = dq_1 dq_2 \ldots dq_{3N}$$

at the time t.

To be physically meaningful, the wave functions must be single-valued and in general they are continuous and quadratically integrable. The latter property makes it possible to normalize the wave function to unity,

i.e.
$$\int \psi^* \psi d\tau = 1$$

The physical observables like energy and angular momentum which are present in classical theory in the form of dynamical variables are represented in quantum mechanics by operators which are both linear and Hermitian. A linear operator A has the property

$$A(a\psi_1 + b\psi_2) = aA\psi_1 + bA\psi_2 \qquad (1.1)$$

where ψ_1, ψ_2 are two state functions and a, b are constants. The Hermitian condition demands that

$$\int \psi_1^* A\psi_2 d\tau = \left(\int \psi_2^* A\psi_1 d\tau\right)^* \qquad (1.2)$$

There are some general rules to act as a guide in finding the form for these operators. In the Schrödinger representation they are:

(i) the operator representing one of the position co-ordinates q_i or the time t is simply q_i or t.

(ii) the operator representing one of the components of momentum p_i conjugate to q_i is $\frac{\hbar}{i}\frac{\partial}{\partial q_i}$.

The quantum operator representing a dynamical variable which is expressed in terms of the position co-ordinates, momentum and time is obtained by substitution using the above rules.

As an example consider the angular momentum of a point mass moving in some orbit. Classically the angular momentum

$\boldsymbol{L}$ of such a particle about an axis through the origin is given by the vector product

$$\boldsymbol{L} = \boldsymbol{r} \wedge \boldsymbol{p}$$

where $\boldsymbol{r}$ is the radius vector and $\boldsymbol{p}$ the momentum of the particle. For a particle moving in the x–y plane the angular momentum vector lies along the z-axis and

$$L_z = xp_y - yp_x$$

The quantum mechanical operator which represents the angular momentum is

$$\mathscr{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

If the state function ψ is an eigenfunction of the operator A corresponding to a classical variable,

i.e. $$\mathrm{A}\psi = a\psi \tag{1.3}$$

where a is some constant, then in this state the variable has precisely the value a. a is an eigenvalue. It can be shown that the eigenvalues of a Hermitian operator are real and that if ψ_i and ψ_j are eigenfunctions belonging to different eigenvalues then they are orthogonal,

i.e. $$\int \psi_i^* \psi_j \mathrm{d}\tau = 0 \quad i \neq j$$

Two operators A and B are said to commute if

$$(\mathrm{AB})\psi = (\mathrm{BA})\psi$$

when applied to an arbitrary wave function ψ. Quantum mechanical operators do not always possess this property. The operators representing the position co-ordinate x and the conjugate momentum p_x do not commute,

i.e. $$\frac{\hbar}{i}\left(\frac{\partial}{\partial x}x - x\frac{\partial}{\partial x}\right)\psi = \frac{\hbar}{i}\psi$$

When two operators commute it can be shown that there exists a set of functions which are simultaneously eigenfunctions for both operators. This result is important in the classification of states and is referred to again in Chapter 3.

In classical mechanics the Hamiltonian H defines the total energy for a conservative system. The time variation of the state is determined through Hamilton's equations. The most important quantum mechanical operator is the analogous Hamiltonian $\mathscr{H}$ obtained by substitution. The dependence of the state function ψ on the time is given by

$$\mathscr{H}\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t} \tag{1.4}$$

This is the time-dependent Schrödinger equation.

If ψ is an eigenfunction of the Hamiltonian operator, the eigenvalue gives the energy E of the state and the wave function merely changes its phase in time,

i.e.
$$\mathscr{H}\psi = E\psi \tag{1.5}$$
and
$$\psi_t(E) = \psi_0(E)e^{-iEt/\hbar} \tag{1.6}$$

Equation (1.5) is the time-independent Schrödinger equation. In an eigenstate of the energy, the average value of any observable A, defined by

$$\int \psi^* A\psi \mathrm{d}\tau$$

is a constant if A does not explicitly involve the time. The wave function is then said to define a stationary state.

For those readers completely new to solid state theory it is possible to omit the remainder of this chapter on a first reading.

§ 1.2 The Born–Oppenheimer approximation

The classical Hamiltonian for a collection of N particles of masses m_i and charges e_i respectively, is given by

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{\substack{i=1 \\ (i \neq j)}}^{N}\sum_{j=1}^{N} \frac{e_i e_j}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{1.7}$$

where $\boldsymbol{r}_i$ is the position vector of the ith particle. The first sum

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is taken over the 3N components of momenta and represents the kinetic energy of the system. The second term represents the electrostatic potential energy of the system and the sum is over all the possible pairs of particles. The corresponding quantum mechanical Hamiltonian is (omitting spin-dependent terms),

$$\mathscr{H} = \sum_i \left(\frac{-\hbar^2}{2m}\right)\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\sum_j \frac{e_i e_j}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{r}_j|} \qquad (1.8)$$

where ∇_i^2 operates on the spatial co-ordinates of the ith particle. The eigenfunctions of this operator must involve the 3N position co-ordinates of the system (4N if spin is included).

In a crystal there are two types of particles present, the nuclei and the electrons. For our purpose the structure of the nucleus may be ignored.

The Schrödinger equation for a stationary state of a crystal may be written

$$\mathscr{H}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)\, \Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = E_t\, \Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \qquad (1.9)$$

where the wave function Ψ and the Hamiltonian are functions of all the nucleus and electron co-ordinates $\boldsymbol{R}_i$ and $\boldsymbol{r}_i$ respectively. The number of variables is reduced if the atomic electrons are separated into core and valence electrons, although this division is somewhat arbitrary. The core electrons have atomic wave functions which do not overlap to any appreciable extent at the observed interatomic spacing in the crystal and consequently may be considered to be unaffected by combining the atoms to form a crystal. Conversely, the wave functions of the valence electrons overlap considerably, and are modified by the process of crystal formation.

The Hamiltonian of (1.9) then contains all the interactions of an assembly of ion cores and valence electrons and may be expressed as

$$\begin{aligned}\mathscr{H}(\boldsymbol{R}_1, \boldsymbol{R}_2 \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) &= \mathscr{H}_{\text{ion}}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots) + \mathscr{H}_{\text{electron}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \\ &\quad + \mathscr{H}_{\substack{\text{electron}\\ \text{-ion}}}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \qquad (1.10)\end{aligned}$$

where $$\mathscr{H}_{\text{ion}} = -\sum_i \frac{\hbar^2}{2M}\nabla_{R_i}^{\,2} + \frac{1}{2}\sum_{i \neq j}\sum W(\boldsymbol{R}_i - \boldsymbol{R}_j)$$

$$\mathscr{H}_{\text{electron}} = -\sum_i \frac{\hbar^2}{2m}\nabla_{r_i}^{\,2} + \frac{1}{2}\sum_{i \neq j}\sum \frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

and $$\mathscr{H}_{\substack{\text{electron}\\\text{-ion}}} = \sum_i\sum_j v\,(\boldsymbol{r}_i - \boldsymbol{R}_j)$$

The ionic Hamiltonian $\mathscr{H}_{\text{ion}}$ describes the motion of the set of like ions, each composed of a nucleus and a shell of core electrons, which interact through a potential $W(\boldsymbol{R}_i - \boldsymbol{R}_j)$. $\mathscr{H}_{\text{electron}}$ corresponds to the valence electrons which interact through a Coulomb potential. The electron-ion Hamiltonian takes account of the interaction between the ionic cores and valence electrons which are assumed to act through a potential $v(\boldsymbol{r}_i - \boldsymbol{R}_j)$.

The total crystal potential may be written

$$V_c = V_{\text{ion}} + V(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$

with

$$V_{\text{ion}} = \tfrac{1}{2}\sum_{i \neq j}\sum W(\boldsymbol{R}_i - \boldsymbol{R}_j)$$

$$V = \tfrac{1}{2}\sum_{i \neq j}\sum \frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_i\sum_j v(\boldsymbol{r}_i - \boldsymbol{R}_j)$$

where V_{ion} is the potential of interaction between the ion cores, and V is the potential of interaction of the electrons with the ion cores and with each other.

Because the electronic masses are much less than the ionic masses, the electrons move much more rapidly than the ions. In the 'Born–Oppenheimer' approximation (1927), the Schrödinger equation is solved for the N electrons in the field of all the ions in some fixed configuration. The electronic wave function $\psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$ depends on the variable positions of the electrons $\boldsymbol{r}_i$ and also on the nuclei-co-ordinates $\boldsymbol{R}_i$ regarded as parameters. The full crystal wave function is written

$$\Psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \Phi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)\,.\,\psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \quad (1.11)$$

where Φ is the lattice wave function describing the ionic motion and is a function of the co-ordinates $\boldsymbol{R}_i$ only.

ψ satisfies the equation,

$$\left[-\sum_i \frac{\hbar^2}{2m} \nabla_{ri}^2 + V(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)\right] \psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$
$$= E(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)\, \psi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \quad (1.12)$$

where m is the electron mass and ∇_{ri}^2 operates on the electron co-ordinates. The electron energy eigenvalue $E(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)$ depends upon the particular ionic configuration considered. This electron energy then appears as part of the effective potential for the nuclear motion.

$$\left\{-\sum_j \frac{\hbar^2}{2M} \nabla_{\boldsymbol{R}_j}^2 + [V_{\text{ion}}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots) + E(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)]\right\} \Phi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)$$
$$= E_L \Phi(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots) \quad (1.13)$$

The error produced by using the Born–Oppenheimer approximation is small when the characteristic frequencies of vibration of the ions are much smaller than the characteristic electronic frequencies. Generally this implies that the ionic mass may be much greater than the electronic mass which is, of course, correct. However, if the energy required to excite an electron to a higher level is small, implying a small electronic frequency, the approximation breaks down. This is the case for metals and then the ionic function Φ depends on the electron co-ordinates as well as the ionic co-ordinates.

Equation (1.12) describes the electronic motion in a static lattice. In practice it is solved assuming both the crystal symmetry and the lattice constant. This implies that the electronic potential is a function of the electron co-ordinates only, and so the electron energy cannot be used in (1.13) to determine the nuclear motion. The equation becomes

$$\left[-\sum_i \frac{\hbar^2}{2m}\nabla_{r_i}^2 + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)\right]\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = E\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) \quad (1.14)$$

the atomic co-ordinates being given their observed mean values. The potential includes all the interactions involving the valence electrons and can be written

$$V(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \sum_i V_L(\boldsymbol{r}_i) + V_e(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$

where $V_L(\boldsymbol{r}_i)$ represents the interaction between the *i*th electron and the ion cores and where V_e represents the total electron–electron interaction.

§ 1.3 One-electron approximation

It is extremely difficult to solve atomic or nuclear problems involving more than one electron. Even in the simplest cases complicated numerical procedures have proved necessary. The difficulty arises because the electron–electron potential contains terms of the form $e^2/4\pi\epsilon_0 \mid \boldsymbol{r}_i - \boldsymbol{r}_j \mid$ involving the spacial co-ordinates of two electrons. In the one-electron formulations approximate solutions which treat the electrons separately are considered. The Hartree method employs a simple product wave function of the form

$$\psi(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N) = \phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) \ldots \phi_N(\boldsymbol{r}_N) \quad (1.15)$$

It is important that the one-electron functions be normalizable and that there be as many as electrons present. For the ground state, the variational theorem of quantum mechanics requires that the expectation value of the energy be a minimum. Consequently, the best Hartree solution is that which minimizes the integral

$$\int \psi^*(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\mathscr{H}\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\mathrm{d}\tau \quad (1.16)$$

where $\mathscr{H}$ is the Hamiltonian of equation (1.14), subject to the restrictive conditions

$$\int \phi_i^*(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_1)\mathrm{d}\tau_1 = 1 \tag{1.17}$$

This procedure may be carried out by the method of Lagrange multipliers and the one-electron wave functions which minimize (1.16) and satisfy (1.17) are given by

$$\mathscr{H}_i\phi_i(\boldsymbol{r}_1) = E_i\phi_i(\boldsymbol{r}_1) \tag{1.18}$$

where $\mathscr{H}_i$ is the one-electron Hamiltonian.

$$\mathscr{H}_i = -\frac{\hbar^2}{2m}\nabla_1^2 + V_L(\boldsymbol{r}_1) + e^2\sum_j{}' \int \frac{\phi_j^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_2)}{4\pi\epsilon_0 |\boldsymbol{r}_1 - \boldsymbol{r}_2|}\mathrm{d}\tau_2 \tag{1.19}$$

The summation in the final term is over all the one-electron wave functions except the *i*th. Each term may be given a physical significance. The first term represents the kinetic energy of the first electron, the second term represents the interaction between the electron and the ion cores and the final term represents the average Coulomb energy of the electron in the field produced by all the other electrons.

The Hamiltonian is not identical for all electrons and the eigenfunctions are not orthogonal.

The simple Hartree method does not entirely neglect the influence of one electron upon another. Each electron moves in the average field of the remainder. However, there is a serious fault in the Hartree wave function. In quantum mechanics it is impossible to distinguish between identical particles. This means that if any two electrons are interchanged the initial and final states of the system must have identical physical properties. Consequently the wave function can only change by an unimportant phase factor. If the operator P_{ik} interchanges the co-ordinates (including spin) of the *i*th and *k*th electrons then

$$\mathrm{P}_{ik}\psi = e^{i\delta}\psi$$

By repeating this interchange the original wave function is restored. Hence it follows that $e^{i2\delta} = 1$ or $e^{i\delta} = \pm 1$,

i.e. $$P_{ik}\psi = \pm\psi$$

The wave function is either symmetric or antisymmetric with respect to permutations of the electron co-ordinates, when spin is included. Experimental evidence (Pauli principle) shows that electrons, and in fact all particles with half-integral spin, have antisymmetric wave functions. Such particles are called fermions.

The Hartree–Fock approach is to recognize that all electrons are identical and to start with a determinantal wave function satisfying the Pauli principle.

$$\psi = k \begin{vmatrix} \phi_1(\boldsymbol{r}_1, \sigma_1), \phi_1(\boldsymbol{r}_2, \sigma_2) \ldots \phi_1(\boldsymbol{r}_N, \sigma_N) \\ \cdot \\ \cdot \\ \cdot \\ \phi_N(\boldsymbol{r}_1, \sigma_1) \qquad\qquad \phi_N(\boldsymbol{r}_N, \sigma_N) \end{vmatrix} \tag{1.20}$$

$(\boldsymbol{r}, \sigma)$ denote the position and spin co-ordinates and k is a normalization constant ($k = 1/\sqrt{N}!$ if the ϕ's are orthonormal). It should be noted that if $\phi_i = \phi_j$, two rows are identical and the determinant vanishes. Only one electron may occupy a given spin-orbital. Similarly if $(\boldsymbol{r}_i, \sigma_i) = (\boldsymbol{r}_j, \sigma_j)$ two columns are identical and the determinant again vanishes. Two electrons with the same spin are never at the same position in space. The one-electron functions are again chosen to minimize the expectation value of the Hamiltonian (1.14) subject to the condition that each is normalized. It is necessary that the functions be linearly independent so that it is possible to form an orthogonal set from them (Adams, 1961).

The set of equations which the one-electron wave functions must satisfy can be written in the 'standard form'

$$\mathscr{H}_i\phi_i(\boldsymbol{r}_1) = E_i\phi_i(\boldsymbol{r}_1) \tag{1.21}$$

where the one-electron Hamiltonians are given by

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