

FoP3B Part I Lecture 1: Free and nearly-free electron solids

Electronic structure is fundamental to solid state physics. From the energies and distribution of electrons in solids it is possible to predict many physical properties, such as electrical, thermal conductivity, elastic stiffness, magnetism etc. Calculating the electronic structure for even a simple solid is however a formidable task, due to interactions between the many electrons and nuclei in the solid. It has taken well over a century for the theory to mature to the current state-of-the-art. A hierarchical grouping of the different theories is given below. The first three theories are based on the *independent electron approximation*, where interactions between electrons in the solid are ignored (this can be partly justified using the Pauli Exclusion principle).

(i) Free electron theory: first proposed by Paul Drude in 1900 and based on the kinetic theory of gases. The electrons obey the classical Maxwell-Boltzmann distribution. Drude's theory successfully explained many experimental observations at the time, but there were also failures, notably the specific heat of electrons. In 1927 Arnold Sommerfeld used the newly developed quantum mechanics to replace the Maxwell-Boltzmann distribution with the Fermi-Dirac distribution, and obtained more accurate results. Apart from electron-electron interactions, the free electron theory also ignores interactions of the electrons with nuclei.

(ii) Nearly-free electron theory: here the electron-nuclear interaction is introduced using quantum mechanical perturbation techniques. Electron-nuclear interaction is crucial for explaining the electron behaviour close to the 'Brillouin zone boundaries'¹. Because perturbation methods are used the theory is only valid for light atoms, where the electron-nuclear interaction is weak.

(iii) Bloch wave theory: developed by Felix Bloch this theory is valid for any electron-nuclear interaction regardless of its strength. The periodic property of crystals is exploited to analyse electronic structure.

(iv) Hartree Theory: developed by Douglas Hartree this theory was the first to include electron-electron interactions. It is the starting point for more advanced theories of electronic structure, such as density functional theory.

In this course we will only be covering the first three theories. Although not complete, it is still sufficiently advanced to enable a deep understanding of electrons in solids.

Free Electron Theory

It is important to first define what we mean by 'free electrons'. Figure 1a shows the structure of a free electron solid (e.g. a metal). The **ion cores** consist of positively charged nuclei and *bound* electrons that shield the positive charge from the rest of the solid. In between the ion cores are the **free electrons**, which are delocalised and can move throughout the solid. The material properties are largely governed by the free electrons and we therefore focus our attention on those electrons. For accurate results we need to treat the solid quantum mechanically and

¹ The Brillouin zone is at half the reciprocal vector spacing; the wavevectors within the Brillouin zone uniquely define the electron properties, such as energy.

therefore use the Fermi-Dirac distribution. Figure 1b shows that the Fermi-Dirac distribution is very different from the classical Maxwell-Boltzmann distribution. In particular, the electron energies are much higher in the former due to the Pauli Exclusion principle, which only allows two electrons per electronic state.

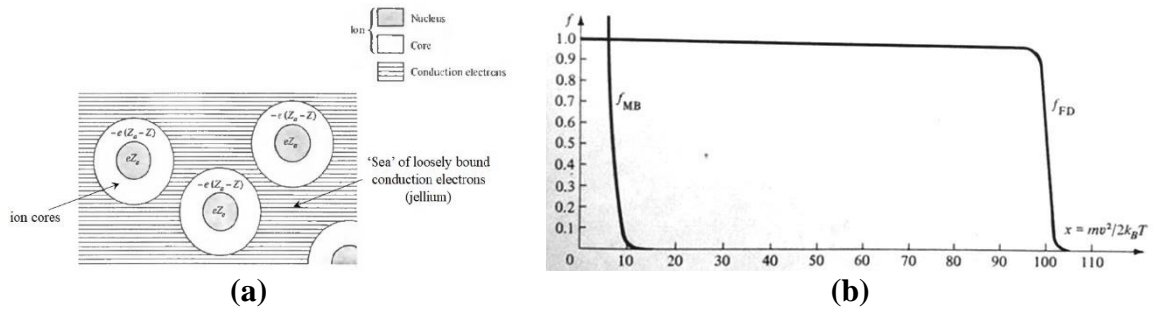


Figure 1: (a) structure of a free electron solid and (b) comparison of Maxwell-Boltzmann (MB) and Fermi-Dirac (FD) distributions.

The electrons must obey the Schrödinger equation $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$. For a free electron solid we assume that the potential energy V is constant and arbitrarily set it to zero (we are mainly interested in differences in energies, rather than absolute values). This can be justified by the fact that the bound electrons shield the nuclei and Coulomb interaction between the free electrons is minimised by the Pauli Exclusion principle. The electron wavefunction therefore takes the form of a plane wave $\psi = \exp(i\mathbf{k}\cdot\mathbf{r})$ with energy $E = \frac{(\hbar k)^2}{2m}$.

The wavevector \mathbf{k} can only take discrete values due to the **boundary conditions**, which are defined for a travelling wave in the crystal (cf. standing wave solutions in the case of ‘particle in a box’ problem). Travelling waves are selected since we are interested in problems related to electrical, thermal conductivity etc where electrons travel over large distances. For a cube of length L the boundary conditions are $\psi(x, y, z) = \psi(x + L, y + L, z + L)$; these are also known as *periodic boundary conditions*, since mathematically they are equivalent to a solid that is infinitely repeating. For a free electron wavefunction this results in \mathbf{k} vectors that are integer multiples of $(2\pi/L)$ along any one of the x, y, z -directions. The volume of a \mathbf{k} -point in reciprocal space is therefore $(2\pi/L)^3$ or $(2\pi)^3$ per unit volume (i.e. cube of side length $L=1$).

An important concept that will be useful later on is the **density of states**, $g(E)dE$, which is defined as the number of electronic levels between energies E and $E+dE$ per unit volume of solid. For a free electron material $E \propto k^2$ and therefore all states for a given energy will lie on a spherical surface in reciprocal space (see Figure 2). The density of states in reciprocal space $g(k)dk$ is therefore equal to the volume of the thin shell (i.e. $4\pi k^2 dk$) on the surface of the sphere divided by the volume of a single \mathbf{k} -point (i.e. $(2\pi)^3$) with a factor of ‘2’ to take into account spin degeneracy (i.e. spin up and spin down electrons):

$$g(k)dk = 2 \frac{(4\pi k^2)dk}{(2\pi)^3}$$

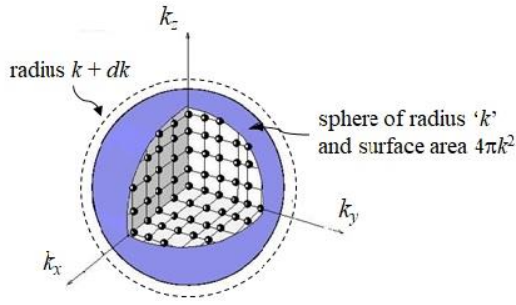


Fig 2: Fermi surface for an idealised free electron solid

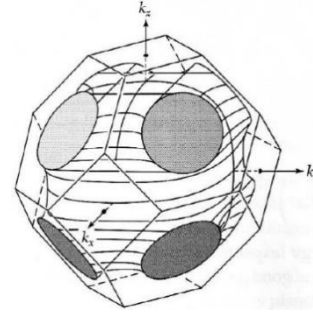


Fig 3: Fermi surface for copper

From $E = \frac{(\hbar k)^2}{2m}$ we have $\frac{dE}{dk} = \frac{\hbar^2 k}{m}$, so that:

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

Since energy must be minimised at absolute zero all electronic states within a sphere, also known as the **Fermi sphere**, will be fully occupied². If k_F is the wavenumber of the Fermi surface (i.e. radius of the Fermi sphere in reciprocal space) it is easy to show that $n = \frac{k_F^3}{3\pi^2}$, where n is the electron density. Using copper as an example we can calculate n based on the valence of the atoms and lattice parameters of the unit cell. Hence k_F , and consequently energy of the electrons at the Fermi surface, can be determined. The Fermi energy in copper is ~ 7 eV, equivalent to 81,290 K in temperature, with the electrons moving at $\sim 1\%$ the speed of light! (cf. Fig 1b).

Nearly-free electron model

Real materials do not always conform to the highly idealised free electron model. For example, the Fermi surface for copper is nearly spherical, but shows substantial deviations close to the Brillouin zone boundaries (Figure 3). Furthermore, the free electron model does not predict why some materials are electrical conductors and other insulators. To explain these phenomena, we need to take into account the electron-nuclear interactions, in what is called the *nearly-free electron theory*. Here we will only give a qualitative account, and reserve the quantitative description for the next lecture.

We can think of electron-nuclear interactions in terms of Bragg scattering of the electron plane waves from the crystal planes (Figure 4a). Constructive interference occurs when the path difference is equal to an integer number of wavelengths (i.e. $n\lambda = 2d\sin\theta$). This condition can also be expressed as $(\mathbf{k} + \mathbf{G})^2 = k^2$, where \mathbf{G} is a reciprocal vector. Here the Bragg diffracted beam has wavevector $(\mathbf{k} + \mathbf{G})$ for incident wavevector \mathbf{k} . A potential solution is $\mathbf{k} = -\mathbf{G}/2$, so that the diffracted wavevector $= +\mathbf{G}/2$. There are now two plane waves in the crystal, an incident and Bragg diffracted wave, which can interfere with one another in one of two ways:

$$\begin{aligned}\psi(+) &= \exp(i\mathbf{G} \cdot \mathbf{r}/2) + \exp(-i\mathbf{G} \cdot \mathbf{r}/2) = 2\cos(\mathbf{G} \cdot \mathbf{r}/2) \\ \psi(-) &= \exp(i\mathbf{G} \cdot \mathbf{r}/2) - \exp(-i\mathbf{G} \cdot \mathbf{r}/2) = 2i\sin(\mathbf{G} \cdot \mathbf{r}/2)\end{aligned}$$

² At temperatures above 0 K some ‘smearing’ of the Fermi sphere takes place, due to the Fermi-Dirac distribution deviating from an ideal step function. However, the smearing is small, even at room temperature.

The first solution has maximum electron intensity $|\psi(+)|^2$ at the positively charged nuclei which are potential wells. Therefore, the energy of $\psi(+)$ is lowered. Conversely $\psi(-)$ has maximum electron intensity between the nuclei and hence has higher energy (Figure 4b). Therefore, the electron energy becomes *non-degenerate* at the Brillouin zone boundary $\mathbf{k} = \pm \mathbf{G}/2$.

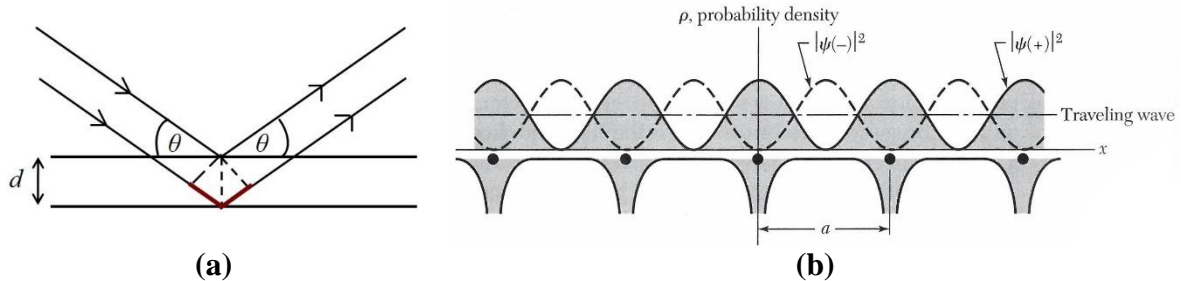


Figure 4: (a) Bragg diffraction from a crystal and (b) the two wave solutions at the Brillouin zone boundary

The **energy dispersion** (i.e. E vs k) diagram for the free electron and nearly free electron models are shown in Figure 5. Note that the two curves are similar for small wavenumbers; it is only close to the Brillouin zone boundary, where the condition for Bragg diffraction is satisfied, that the two curves deviate from one another. In the nearly-free electron model there is a low and high energy band (i.e. $\psi(+)/\psi(-)$) separated by a forbidden band or **band gap** which contains no electronic states. The electron group velocity $v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$ is also zero at the Brillouin zone boundary. This indicates that the electron forms stationary waves, as opposed to travelling planar waves, due to interference of the incident wave with its Bragg scattered wave.

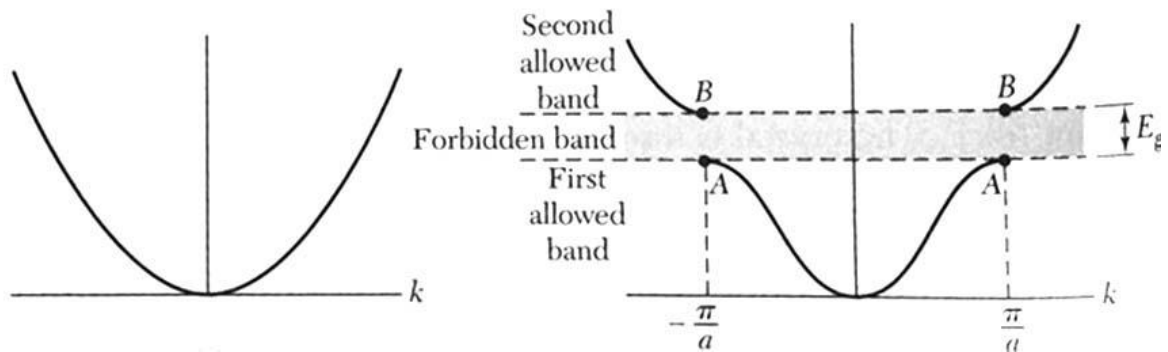


Figure 5: Energy dispersion curves for the free electron (left) and nearly-free electron models (right).