Lecture notes on elements of band theory and thermodynamics of the Fermi gas

Contents

1 Fermi gas

A Fermi gas is an idealised model of N non-interacting electrons confined in a volume $\mathscr{V} = L^3$ that we can use as a starting point to describe, in a first approximation, some thermodynamic properties of the delocalised electrons found in metallic solids (Cu, Ag, Fe, Al etc.). Neglecting all interactions with the crystalline lattice, impurities, other electrons, etc., the non-relativistic single-electron wavefunctions satisfy the time-independent Schroedinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}) \tag{1}$$

Whenever we are interested in bulk solid properties, it is useful to consider periodic boundary conditions

$$\psi(x+L, y, z) = \psi(x, y, x) \tag{2}$$

$$\psi(x, y+L, z) = \psi(x, y, x) \tag{3}$$

$$\psi(x, y, z+L) = \psi(x, y, x) \tag{4}$$

By direct computation, we can verify that the following wavefunction is a solution to the Schroedinger equation ($\mathscr{V} = L^3$)

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\mathscr{V}}}e^{i\mathbf{k}\cdot\mathbf{r}}} \tag{5}$$

with energy

$$\boxed{\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}} \tag{6}$$

The vector $\mathbf{k}$ conveniently labels wavefunctions by their wavevector $k = 2\pi/\lambda$, associated with the de Broglie wavelength $\lambda = h/p$ and momentum p. The periodic boundary conditions

$$e^{ik_x x} = e^{ik_x(x+L)} \tag{7}$$

$$e^{ik_y y} = e^{ik_y(y+L)} \tag{8}$$

$$e^{ik_z z} = e^{ik_z(z+L)} \tag{9}$$

limit the set of $\mathbf{k}$ vectors labelling a valid solution of the Schroedinger equation, to a subset that satisfies the condition

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1 \tag{10}$$

2

We remember that $e^z = 1$ only for $z = m(2\pi i)$, with m being an *integer* number ($m \in \mathbb{Z}$). Therefore the electronic states of the Fermi gas are limited to wavevectors of the form

$$k_x = m_x \frac{2\pi}{L} \tag{11}$$

$$k_y = m_y \frac{2\pi}{L} \tag{12}$$

$$k_z = m_z \frac{2\pi}{L} \tag{13}$$

with m_x, m_y and m_z as integer numbers. In k-space (reciprocal space) these vectors form a regular grid with spacing $2\pi/L$ (see the figure below for a 2D representation).
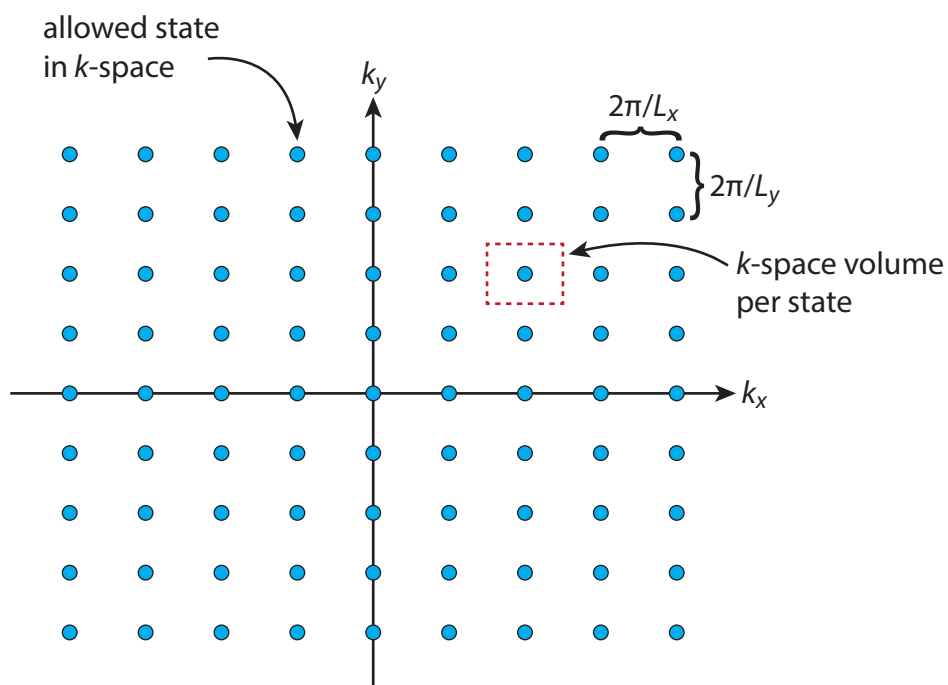
The density of (allowed) states in k-space is therefore (number of allowed states/volume)

$$1/(2\pi/L)^3 = \frac{\mathscr{V}}{(2\pi)^3} \tag{14}$$

In the continuous limit this reads

$$\boxed{\frac{d^3 N}{dk^3} = \frac{\mathscr{V}}{(2\pi)^3}} \tag{15}$$

Importantly, this result for the density in k-space turns out to be valid also in the presence of a periodic potential, as we will see below. N electrons in their ground state will fill these levels according to the Pauli exclusion principle (at most two electrons in each level considering their spin quantum number) starting from the lowest in energy and progressively occupying higher energy levels up to k_F, the Fermi wavevector.

In k-space the quantum states of a free electron system occupy a sphere of volume $V_{\mathrm{FS}} = (4/3)\pi k_F^3$: states within this sphere are occupied and states outside the sphere are unoccupied (also known as the Fermi sea, as illustrated in the figure below).
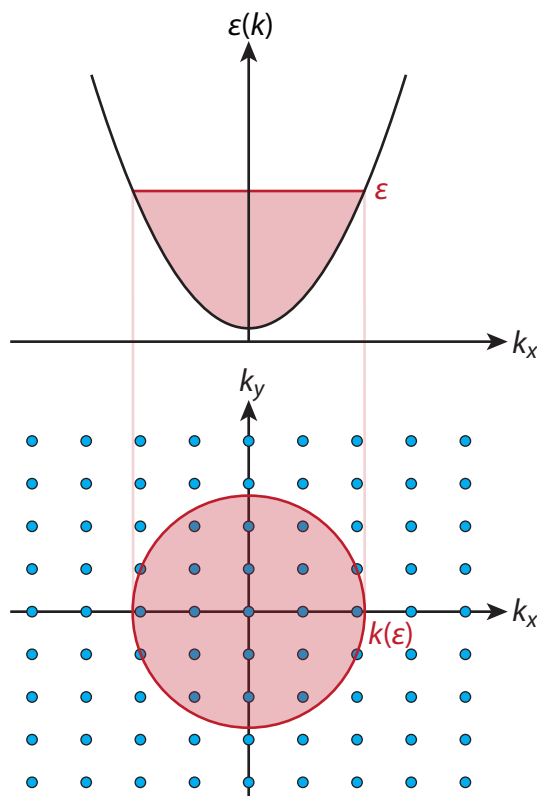
By using the result of eq. 14 we can calculate the number of states occupied by an electron gas with Fermi wavevector k_F (2 x volume occupied by the state x density, the factor 2 accounts for the spin degeneracy):

$$N = 2\left(\frac{4\pi k_F^3}{3}\right)\left(\frac{\mathscr{V}}{(2\pi)^3}\right) = \frac{k_F^3}{3\pi^2}\mathscr{V} \tag{16}$$

We have come to a very important result: in an electron gas the density $n = N/\mathscr{V}$ is

4

related to the Fermi wavevector by the relation

$$n = \frac{k_F^3}{3\pi^2} = 2\frac{V_{\text{FS}}}{(2\pi)^3} \qquad (17)$$

This is a beautiful and surprising result and we urge you to memorise it. Let's reflect on its meaning using a concrete example. Cu has a molar mass of 63.546 g mol^{-1}. This means that in 1 gram of Cu we find $9.47 \cdot 10^{21}$ atoms ($\mathcal{N}_A = 6.022 \cdot 10^{23}$ mol^{-1}). The density of Cu being 8.96 g/cm^3, results in an atomic density of Cu of $8.49 \cdot 10^{22}$ cm^{-3} $= 8.49 \cdot 10^{28}$ m^{-3}. In a typical metal each atom contributes with one electron to the Fermi gas responsible for its conducting properties. Therefore, we can take as electron density for the Fermi gas idealisation of the delocalised electrons in Cu, $n = 8.49 \cdot 10^{28}$ m^{-3}. The Fermi wavevector is related to the kinetic energy of the electron of highest energy by

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \qquad (18)$$

Plugging in the numbers for Cu we find, for the highest kinetic energy of free electrons *in their ground state* $(T = 0)$, $\epsilon = 7$ eV, an astonishingly large number.

   As we will see later, electrons occupying states in the vicinity of the Fermi energy mostly account for the thermodynamic properties of the Fermi gas. Here we have underscored that, even in their ground state, these electrons have kinetic energies associated with velocities of the order $v_F \sim 10^6$ m/s. A military rifle delivers bullets flying at a velocity of about 10^3 m/s. In ordinary metals in their ground state (the lowest possible energy state, reached at the coldest temperatures) we find electrons with velocities a thousand times faster than these bullets, as fast as a few percent of the speed of light. We have taken the concrete example of Cu ($E_F = 7$ eV) but the same considerations are valid for other common metals such as Ag (5.5 eV), Fe (11.1 eV) or Al (11.7 eV). These numbers are in stark contrast with the expectations of classical statistical mechanics that assigns kinetic energies to the particles of an ideal gas at temperature T of the order $(3/2)k_B T$, vanishing in the low temperature limit.

   As a consequence of the quantum nature of electrons (in this particular case the quantisation of the action in unit of h and of the Pauli exclusion principle), even a piece of ordinary metal has some amazing properties.
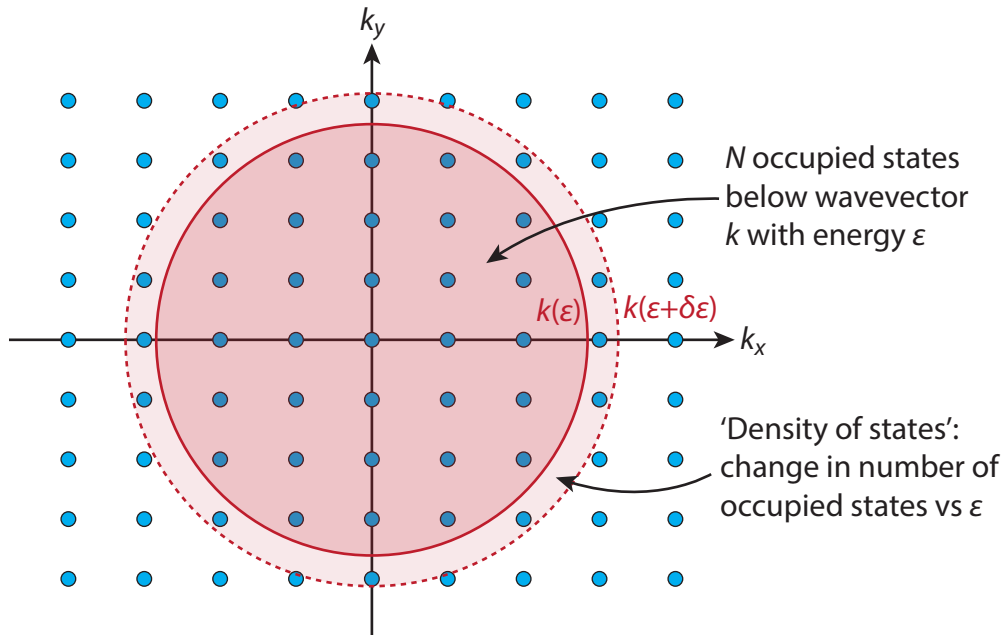
2   Density of states

A very important concept in condensed matter physics is the one-electron density of states, often indicated as DOS (density of states) or $g(\epsilon)$. It is defined as the density of levels per unit of volume and energy[1]: (see the figure below for a 2D representation)

$$g(\epsilon) = \frac{1}{\mathscr{V}} \frac{dN(\epsilon)}{d\epsilon} \tag{19}$$

with

$$N(\epsilon) = 2 \int_0^{k=k(\epsilon)} \frac{dN(k)}{dk} dk \tag{20}$$

On the surface it can appear just as a somewhat useful computational device, as it allows us to reformulate the integration in k-space of some functions of energy into an integration using the energy as a continuous variable. Indeed ϵ and k will be connected by a well-behaved dispersion relation that will allow us to calculate $k(\epsilon)$ and perform this operation. Apart from computational aspects, the DOS is full of important physical information on a condensed matter system, as it tells us about the amount of available quantum states in a given energy range. This is a typical quantity probed in experiments such as scanning tunneling spectroscopy, photoemission spectroscopy and other tools that will be discussed during the course. The calculation (and measurement) of the DOS for real condensed

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[1]not to be confused with the density of states in k-space discussed above

matter systems (that is, going beyond the free electron approximation considered here) is a central problem of theoretical (experimental) condensed matter physics. Its definition will be extended in the following lectures to include interacting electron systems. Here it is important to note that, even for a free Fermi gas, dimensionality is key.

For a 3D electron gas ($\mathcal{V}_{3D} = L^3$) we have

$$N^{3D}(\epsilon) = 2 \int_{|\mathbf{k}|<\mathbf{k_F}} \frac{\mathcal{V}}{(2\pi)^3} d\mathbf{k} = 2 \int_0^{\sqrt{2m\epsilon/\hbar^2}} \frac{\mathcal{V}}{(2\pi)^3} 4\pi k^2 dk = \frac{\mathcal{V}}{\pi^2} \frac{1}{3} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2} \tag{21}$$

$$g^{3D}(\epsilon) = \frac{d}{d\epsilon} N^{3D}(\epsilon)/\mathcal{V} = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\epsilon} \tag{22}$$

In a 2D electron gas ($\mathcal{V}_{2D} = L^2$) we have

$$N^{2D}(\epsilon) = 2 \int_{|\mathbf{k}|<\mathbf{k_F}} \frac{L^2}{(2\pi)^2} d\mathbf{k} = 2 \int_0^{\sqrt{2m\epsilon/\hbar^2}} \frac{L^2}{(2\pi)^2} 2\pi k dk = \frac{L^2}{\pi} \frac{1}{2} \left(\frac{2m\epsilon}{\hbar^2} \right) = \frac{L^2}{\pi} \frac{m\epsilon}{\hbar^2} \tag{23}$$

$$g^{2D}(\epsilon) = \frac{d}{d\epsilon} N^{2D}(\epsilon)/L^2 = \frac{m}{\pi\hbar^2} \tag{24}$$

Finally in 1D ($\mathcal{V}_{1D} = L$) we find

$$N^{1D}(\epsilon) = 2 \int_{|k|<k_F} \frac{L}{2\pi} dk = 2 \frac{L}{\pi} \sqrt{2m\epsilon/\hbar^2} \tag{25}$$

$$g^{1D}(\epsilon) = \frac{d}{d\epsilon} N^{1D}(\epsilon)/L = \frac{1}{\pi} \sqrt{2m/\hbar^2} \frac{1}{\sqrt{\epsilon}} \tag{26}$$

Please note that

$$g^{3D}(\epsilon) \propto \sqrt{\epsilon} \tag{27}$$

$$g^{2D}(\epsilon) \propto \text{const} \tag{28}$$

$$g^{1D}(\epsilon) \propto 1/\sqrt{\epsilon} \tag{29}$$

Considering density of states in reduced dimensions might feel like a pure intellectual exercise. In reality, low dimensional electron systems (2D and 1D) can be created in the lab and are a subject of great interest in condensed matter physics.

3 Thermodynamic properties of the Fermi gas

At finite temperatures, the probability of occupation of an energy level for a system of electrons (fermions) is provided by the Fermi distribution:

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \tag{30}$$

In this expression μ is the chemical potential, the thermodynamic variable that accounts for changes in energy related to a change in the number of particles (energy cost of adding or removing particles). It is in general a temperature dependent quantity that we will calculate below. Through the Fermi distribution, we are able to compute all relevant thermodynamic quantities of the free electron gas, for example the specific heat (at constant volume, u internal energy density) defined as

$$C = \left(\frac{\partial u}{\partial T}\right)_{\mathscr{V}} \tag{31}$$

the magnetic susceptibility or the chemical potential.

3.1 Chemical potential

We have previously seen that the density of available states in k-space is $\mathscr{V}/(2\pi)^3$. Therefore, in a continuous limit, the internal energy density is given by

$$u = 2 \int \frac{d\mathbf{k}}{(2\pi)^3} \epsilon(\mathbf{k}) f\left[\epsilon(\mathbf{k})\right] \tag{32}$$

For clarity, the factor 2 arising from the spin degeneracy is explicitly noted. Using the density of state we can now write down a simple expression for the internal energy density

$$u = \int_0^\infty g(\epsilon)\epsilon f(\epsilon) d\epsilon \tag{33}$$

and for the electron density

$$n = \int_0^\infty g(\epsilon) f(\epsilon) d\epsilon \tag{34}$$

Evaluating integrals containing the Fermi distribution is a task that is aided by a mathematical device called Sommerfeld expansion. This is illustrated in details in Ashcroft and Mermin, Appendix C. In a nutshell: typically one needs to calculate expressions of the kind

$$\int_0^\infty h(\epsilon) f(\epsilon) d\epsilon \tag{35}$$

Since in most cases $h(\epsilon)$ is a slowly varying function around the Fermi energy compared to the Fermi distribution, the following approximations are generally valid up to order T^2

$$\int_0^\infty h(\epsilon)f(\epsilon)d\epsilon \sim \int_0^\mu h(\epsilon)d\epsilon + \frac{\pi^2 k_B^2 T^2}{6}\frac{\partial h}{\partial \epsilon}\bigg|_{\epsilon=\mu} \tag{36}$$

as well as

$$\int_0^\mu h(\epsilon)d\epsilon = \int_0^{\epsilon_F} h(\epsilon)d\epsilon + (\mu - \epsilon_F)h(\epsilon_F) \tag{37}$$

Using this methodology, we find for the electron density

$$n \simeq \int_0^\mu g(\epsilon)d\epsilon + \frac{\pi^2 k_B^2 T^2}{6}\frac{\partial g(\epsilon)}{\partial \epsilon}\bigg|_{\epsilon=\mu} \tag{38}$$

Using the equation 37 and replacing μ by ϵ_F in the terms of order T^2, we obtain

$$n \simeq \int_0^{\epsilon_F} g(\epsilon)d\epsilon + (\mu - \epsilon_F)g(\epsilon_F) + \frac{\pi^2 k_B^2 T^2}{6}\frac{\partial g(\epsilon)}{\partial \epsilon}\bigg|_{\epsilon=\epsilon_F} \tag{39}$$

The term $\int_0^{\epsilon_F} g(\epsilon)d\epsilon$ counts the electron density in the ground state. When considering a Fermi gas at constant density this last equation reduces to

$$(\mu - \epsilon_F)g(\epsilon_F) = -\frac{\pi^2 k_B^2 T^2}{6}\frac{\partial g(\epsilon)}{\partial \epsilon}\bigg|_{\epsilon=\epsilon_F} \tag{40}$$

Therefore the temperature dependence of the chemical potential of a Fermi gas (at constant electron density) is given by

$$\mu = \epsilon_F - \frac{\pi^2 k_B^2 T^2}{6}\frac{1}{g(\epsilon_F)}\frac{\partial g(\epsilon)}{\partial \epsilon}\bigg|_{\epsilon=\epsilon_F} \tag{41}$$

Using the conventional 3D expression for the DOS derived above we find

$$\boxed{\mu = \epsilon_F\left[1 - \frac{\pi^2 k_B^2 T^2}{12\epsilon_F^2}\right]} \tag{42}$$

This result is very important. Let's reflect on its meaning. The chemical potential is found to be mainly set by the Fermi energy (a constant, temperature-independent parameter, defined by a fixed electron density) plus a temperature dependent term $\propto (k_B T/\epsilon_F)^2$. As we have seen before, in most realistic scenarios in which we will consider the Fermi gas picture, $(k_B T/\epsilon_F)^2$ is a very small number, for Cu at room temperature $(k_B T/\epsilon_F)^2 \sim 1.3 \cdot 10^{-5}$. Therefore, in many practical situations and conventional condensed matter systems, the chemical potential can be approximated as independent of temperature and set by the

Fermi energy. Here the energy cost that we need to pay in order to add a particle to our system is naturally set by the Fermi energy, since we are forbidden by the Pauli principle to occupy states below this edge. For this reason, you will often see in the literature the term Fermi level being used as a synonym of the chemical potential.

However, there are interesting scenarios in which this approximation breaks down, for example whenever a chemical potential is in close proximity to a band crossing with a strong variation of the density of states. This situation may arise in solids characterised by multiple orbital quantum numbers, as we will discuss below.

3.2 Specific heat

We will now follow the same approach in order to calculate a temperature dependent internal energy and hence the heat capacity.

$$u \simeq \int_0^\mu \epsilon g(\epsilon) d\epsilon + \frac{\pi^2 k_B^2 T^2}{6} \left[\mu \frac{\partial g(\epsilon)}{\partial \epsilon} \bigg|_{\epsilon=\mu} + g(\epsilon)|_{\epsilon=\mu} \right] \tag{43}$$

Using the temperature dependence of the chemical potential obtained above, leads to the simplified expression, valid at constant electron density,

$$u \simeq \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon + \frac{\pi^2}{6} k_B^2 T^2 g(\epsilon_F) \tag{44}$$

that can be rewritten as

$$u \simeq u_0 + \frac{\pi^2}{6} k_B^2 T^2 g(\epsilon_F) \tag{45}$$

where u_0 is a T-independent ground state contribution to the internal energy. Therefore the specific heat of a Fermi gas, at constant electron density, is given by

$$\boxed{C = \left(\frac{\partial u}{\partial T} \right)_{\mathscr{V}} = \frac{\pi^2}{3} k_B^2 T g(\epsilon_F)} \tag{46}$$

where $g(\epsilon_F)$ is the density of states found at the Fermi energy. We have outlined a very important result here. The specific heat is measurable in experiments and relates the energy added to a condensed matter system to a change in its temperature. What our result tells us is that, for a Fermi gas, this is entirely determined by the thermal excitations of electrons above the Fermi energy in a narrow energy window of the order $k_B T$. The sea of electrons beneath this narrow strip is thermodynamically silent as a consequence of the Pauli exclusion principle. This result will be used extensively throughout the course.

4   Electrons in periodic crystals: Bloch's theorem

4.1   Boundary conditions for periodic crystals and Luttinger theorem

We will now go beyond the Fermi gas analysis and start considering the effects of a periodic crystal lattice, with $\mathbf{T} = m_x \mathbf{a}_x + m_y \mathbf{a}_y + m_z \mathbf{a}_z$ ($m_i \in \mathbb{Z}$) lattice sites.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}) \quad (47)$$

with $V(\mathbf{r})$ being a periodic real space function

$$V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r}) \quad (48)$$

The solutions of the Schroedinger equation can be expressed as an expansion in plane waves

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (49)$$

with coefficients $C_{\mathbf{k}}$ to be determined. The periodic boundary conditions (compare with the above discussion for the Fermi gas) limit the set of $\mathbf{k}$ vectors contributing to the expansion to those identified by the condition

$$\psi(\mathbf{r} + N_j\mathbf{a}_j) = \psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i(\mathbf{k}\cdot\mathbf{r} + \mathbf{k}\cdot N_j\mathbf{a}_j)} = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (50)$$

$$e^{iN_j\mathbf{k}\cdot\mathbf{a}_j} = 1 \quad (51)$$

$$\mathbf{k}\cdot\mathbf{a}_j = m_j\frac{2\pi}{N_j} \quad (52)$$

with m_j being an integer number ($m_j \in \mathbb{Z}$) and N_j is the total number of unit cells available in the crystal along the direction j ($N = N_x N_y N_z$ is the total number of unit cells). The valid solutions of the Schroedinger equation will be labeled by the following collection of quantum numbers

$$k_x = m_x\frac{2\pi}{N_x a_x} \quad (53)$$

$$k_y = m_y\frac{2\pi}{N_y a_y} \quad (54)$$

$$k_z = m_z\frac{2\pi}{N_z a_z} \quad (55)$$

generalizing the results obtained for the Fermi gas, on the density of allowed states in k-space

$$\frac{1}{(2\pi)^3/(Na_x a_y a_z)} = \frac{\mathscr{V}}{(2\pi)^3} \quad (56)$$

or

$$\frac{dN(k)}{dk} = \frac{\mathscr{V}}{(2\pi)^3} \tag{57}$$

We express this allowed set of vectors as a linear combination of primitive vectors of the reciprocal space $\mathbf{b}_i$ defined as

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \tag{58}$$

$$\mathbf{k} = \sum_{i=x,y,z} \frac{m_i}{N_i}\mathbf{b}_i \tag{59}$$

Therefore, within the volume of one primitive cell in reciprocal space $(2\pi/a_x \times 2\pi/a_y \times 2\pi/a_z = N(2\pi)^3/\mathscr{V})$ we find a number of allowed states equal to the number of lattice site. For a generic Fermi surface of volume V_{FS}, the result

$$N/\mathscr{V} = n = 2\frac{V_{\text{FS}}}{(2\pi)^3} \tag{60}$$

continues to be valid even in the presence of a periodic potential. It turns out that this important equation is even more general. According to a central result of many-body theory, known as Luttinger theorem, this relationship continues to be valid even in the presence of many-body interactions, provided that the Fermi surface is not broken by interactions. This concept will be developed in our lecture on Fermi liquid theory. Certain interactions will lead to the formation of energy gaps at the Fermi surface, invalidating this argument. We will give a concrete example later in the course, during our investigation of the superconducting instability. However, if the Fermi surface is simply reshaped by interactions and not gapped, then it may change its shape but not its volume.

4.2   Bloch's functions and quasimomentum

The solutions of the Schroedinger equation in the presence of a periodic potential can be expressed as an expansion in plane waves

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{61}$$

We have already established the constraints imposed by the periodic boundary conditions on the possible $\mathbf{k}$ vectors of this expansion. Bloch's theorem further constrains the properties of this expansion, specifying the nature of its coefficients. We call the solutions Bloch's functions. They are characterised by the following form:

$$\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}} \tag{62}$$

As motivated below, the possible vectors $\mathbf{k}$ are limited to the first Brillouin zone (the primitive cell of the reciprocal lattice described above, in 1D $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, for simplicity also

called Brillouin zone). These wavefunctions resemble plane waves with one important difference: the function $u_\mathbf{k}(\mathbf{r})$ modulates their amplitude with the same periodicity as the crystal lattice.

$$u_\mathbf{k}(\mathbf{r} + \mathbf{T}) = u_\mathbf{k}(\mathbf{r}) \tag{63}$$

Therefore, for any translation of the real space lattice spacing $\mathbf{T}$ (the basic symmetry operation of this system), we obtain

$$\psi_\mathbf{k}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_\mathbf{k}(\mathbf{r}) \tag{64}$$

In other words, the wavefunciton will acquire a phase factor $\mathbf{k} \cdot \mathbf{T}$. We note that the vector $\mathbf{k}$ is defined only modulo (i.e. to within) an arbitrary reciprocal lattice vector $\mathbf{G}$:

$$e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{T}} = e^{i\mathbf{k}\cdot\mathbf{T}}e^{i\mathbf{G}\cdot\mathbf{T}} = e^{i\mathbf{k}\cdot\mathbf{T}}e^{i2\pi m} = e^{i\mathbf{k}\cdot\mathbf{T}} \tag{65}$$

For this reason, the vector $\mathbf{k}$ is also called quasimomentum and the whole expansion of the wavefunction is limited to the first Brillouin zone. This is a consequence of the discrete translational lattice symmetry.

4.3   Proof of Bloch's theorem

We will now outline a basic proof of Bloch's theorem. As discussed above, the solutions of the Schroedinger equation are expanded as plane waves

$$\psi(\mathbf{r}) = \sum_\mathbf{k} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{66}$$

with coefficients $C_\mathbf{k}$ to be determined and constrained by the periodic boundary conditions. The next step consists in writing the periodic crystal potential as a Fourier expansion

$$V(\mathbf{r}) = \sum_\mathbf{G} V_\mathbf{G} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{67}$$

with $\mathbf{G}$ being the ensemble of reciprocal space vectors and $V_\mathbf{G}$ the Fourier coefficients of the expansion.

   The objective of our calculation is to find a system of equations for the coefficients of the expansion $C_\mathbf{k}$ that characterise the wavefunctions. In order to do so, we can now plug the two expansions (for the wavefunction and for the potential) into the Schroedinger equation, to obtain

$$\left[\frac{(i\hbar\nabla)^2}{2m} + \sum_\mathbf{G} V_\mathbf{G} e^{i\mathbf{G}\cdot\mathbf{r}}\right] \sum_\mathbf{k} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} = \epsilon \sum_\mathbf{k} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{68}$$

$$\sum_\mathbf{k} \frac{\hbar^2 k^2}{2m} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} + \left(\sum_\mathbf{G} V_\mathbf{G} e^{i\mathbf{G}\cdot\mathbf{r}}\right)\left(\sum_\mathbf{k} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}}\right) = \epsilon \sum_\mathbf{k} C_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{69}$$

13

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{G},\mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} = \epsilon \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{70}$$

We define $\mathbf{G} + \mathbf{k} = \mathbf{k}'$

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{G},\mathbf{k}'} V_{\mathbf{G}} C_{\mathbf{k}'-\mathbf{G}} e^{i\mathbf{k}'\cdot\mathbf{r}} = \epsilon \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{71}$$

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} \right] = 0 \tag{72}$$

Since the plane waves form an orthogonal basis, the only way to satisfy the equation above is for each term to be individually zero:

$$\left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0 \tag{73}$$

We write now $\mathbf{k} = \mathbf{q} - \mathbf{G}'$, where the vector q is limited to the first Brillouin zone and $\mathbf{G}'$ is a vector of the reciprocal space:

$$\left(\frac{\hbar^2 (\mathbf{q} - \mathbf{G}')^2}{2m} - \epsilon \right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}'-\mathbf{G}} = 0 \tag{74}$$

We translate by one reciprocal space vector $\mathbf{G} + \mathbf{G}' = \mathbf{G}^\star$

$$\left(\frac{\hbar^2 (\mathbf{q} - \mathbf{G}')^2}{2m} - \epsilon \right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}^\star} V_{\mathbf{G}^\star-\mathbf{G}'} C_{\mathbf{q}-\mathbf{G}^\star} = 0 \tag{75}$$

We rename the indexes ($\mathbf{G}' \rightarrow \mathbf{G}$ and $\mathbf{G}^\star \rightarrow \mathbf{G}'$)

$$\left(\frac{\hbar^2 (\mathbf{q} - \mathbf{G})^2}{2m} - \epsilon \right) C_{\mathbf{q}-\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}} C_{\mathbf{q}-\mathbf{G}'} = 0 \tag{76}$$

Please note that we have come to a system of equations for the coefficients $C_{\mathbf{k}}$ of $\psi(\mathbf{r})$. We have found out that, for each allowed wavevector within the first Brillouin zone (as limited by the boundary conditions), the coefficients of its expansion are a linear combination of the type

$$\sum_{\mathbf{G}'} V_{\mathbf{G}'-\mathbf{G}} C_{\mathbf{q}-\mathbf{G}'} \tag{77}$$

extending across only vectors of the reciprocal lattice. Therefore, if we choose any value of $\mathbf{q}$, the corresponding Bloch's function can be expressed as

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{i(\mathbf{q}-\mathbf{G})\cdot\mathbf{r}} \tag{78}$$

14

which consists of a plane wave modulated by a periodic function that has the same periodicity as the crystal lattice

$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} = u_{\mathbf{q}}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}} \tag{79}$$

5   Tight-binding model

A useful model to characterize the properties of electrons in a solid, taking into account the interaction with the crystalline lattice, is the tight-binding theory, an approach to compute the solutions of a general hamiltonian $H = \frac{p^2}{2m} + V$, that describes electrons hopping between lattice sites in a periodic potential V.

We assume to have N lattice sites and τ orbitals per atomic lattice site. We identify an electronic state localised at the atomic site n as the state $|n\rangle$. These states can be represented as so-called Wannier orbitals $\phi_\tau(\mathbf{r})$, functions that decay spatially very rapidly around the lattice site and strongly resemble local orbitals. These orbital states are assumed to be orthonormal (negligible direct overlap between different lattice sites)

$$\langle n|m\rangle = \delta_{nm} \tag{80}$$

and to form a basis set that we can use to expand the electronic wavefunction as a linear combination of atomic orbitals

$$|\psi\rangle = \sum_n c_n |n\rangle \tag{81}$$

We ensure that this wavefunction satisfies Bloch's theorem (being characterised by the appropriate translational symmetry)

$$\psi_{\tau\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{\tau\mathbf{k}}(\mathbf{r}) \tag{82}$$

by choosing the following form of the expansion

$$\boxed{\psi_{\tau\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_\tau(\mathbf{r} - \mathbf{T})} \tag{83}$$

The factor $\frac{1}{\sqrt{N}}$ ensures the normalisation of the states, as shown here:

$$\int \psi^*_{\tau\mathbf{k}}(\mathbf{r})\psi_{\tau\mathbf{k}}(\mathbf{r})d\mathbf{r} = \tag{84}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T'}} \int e^{-i\mathbf{k}\cdot\mathbf{T}} \phi^*_\tau(\mathbf{r} - \mathbf{T}) e^{i\mathbf{k}\cdot\mathbf{T'}} \phi_\tau(\mathbf{r} - \mathbf{T'})d\mathbf{r} \tag{85}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T'}} e^{i\mathbf{k}\cdot(\mathbf{T'}-\mathbf{T})} \int \phi^*_\tau(\mathbf{r} - \mathbf{T})\phi_\tau(\mathbf{r} - \mathbf{T'})d\mathbf{r} \tag{86}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T'}} e^{i\mathbf{k}\cdot(\mathbf{T'}-\mathbf{T})}\delta(\mathbf{T} - \mathbf{T'}) \tag{87}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} 1 = \frac{1}{N}N = 1 \tag{88}$$

where we used the orthonormality of the Wannier functions ($\int \phi_\tau^*(\mathbf{r})\phi_\tau(\mathbf{r} - \mathbf{T})d\mathbf{r} = \delta(\mathbf{T})$).
We can show that this wavefunction satisfies Bloch's theorem by direct computation. If
we translate this state by a generic lattice vector $\mathbf{T}'$ we obtain

$$\psi_{\tau\mathbf{k}}(\mathbf{r} + \mathbf{T}') = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\phi_\tau(\mathbf{r} - (\mathbf{T} - \mathbf{T}')). \tag{89}$$

However, $\mathbf{T} - \mathbf{T}' = \mathbf{T}''$ is another lattice vector, therefore

$$\psi_{\tau\mathbf{k}}(\mathbf{r} + \mathbf{T}') = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\phi_\tau(\mathbf{r} - \mathbf{T}'') \tag{90}$$

$$= \frac{1}{\sqrt{N}} \sum_{\mathbf{T}''} e^{i\mathbf{k}\cdot(\mathbf{T}'+\mathbf{T}'')}\phi_\tau(\mathbf{r} - \mathbf{T}'') \tag{91}$$

$$= e^{i\mathbf{k}\cdot\mathbf{T}'} \frac{1}{\sqrt{N}} \sum_{\mathbf{T}''} e^{i\mathbf{k}\cdot\mathbf{T}''}\phi_\tau(\mathbf{r} - \mathbf{T}'') \tag{92}$$

$$= e^{i\mathbf{k}\cdot\mathbf{T}'}\psi_{\tau\mathbf{k}}(\mathbf{r}) \tag{93}$$

showing that, indeed, translational invariance is properly implemented by the choice of
Bloch wavefunction outlined in equation 83.

5.1   Single orbital 1D atomic chain

We will start by describing a one-dimensional ($T = na_x$) hopping model with single orbitals
($\tau = 1$), directly solving the time-independent Schroedinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi(x) + V(x)\psi(x) = \epsilon\psi(x) \tag{94}$$

According to Bloch's theorem, we should be looking for solutions of the form

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n} e^{ikna_x}\phi(x - na_x) \tag{95}$$

This will help us identify the coefficients of the linear combination of atomic orbitals

$$|\psi\rangle = \sum_{n} c_n|n\rangle \tag{96}$$

Here we will directly solve the time-independent Schroedinger equation

$$H|\psi\rangle = \epsilon(k)|\psi\rangle \tag{97}$$

17

for the eigenvalues $\epsilon(k)$. The action of the hamiltonian is specified by its matrix elements

$$H_{nm} = \langle n|H|m\rangle = \langle n|\frac{p^2}{2m} + V|m\rangle \tag{98}$$

$$\sum_m H_{nm}c_m = \epsilon(k)c_n \tag{99}$$

We assume that this hamiltonian only allows for hopping over neighbouring lattice sites. In this scenario we have the following matrix elements:

$$\langle n|H|m\rangle = \eta_\tau \text{ for } n = m \tag{100}$$

$$\langle n|H|m\rangle = t \text{ for } n = m \pm 1 \tag{101}$$

$$\langle n|H|m\rangle = 0 \text{ otherwise} \tag{102}$$

that can be written in the compact form

$$\langle n|H|m\rangle = \eta_\tau \delta_{nm} + t(\delta_{nm+1} + \delta_{nm-1}) \tag{103}$$

The parameter η_τ accounts for the energy associated with electron localisation on the atomic lattice sites on state τ, while $t = \langle \phi_0|\frac{p^2}{2m} + V|\phi_a\rangle$ describes the energy associated with hopping through the crystal from site to site. With this choice of parameters we can solve for the eigenvalues $\epsilon(k)$ of the time-independent Schroedinger equation

$$\sum_m H_{nm}c_m = \epsilon(k)c_n \tag{104}$$

$$\sum_m \eta_\tau \delta_{nm}c_m + t\sum_m (\delta_{nm+1} + \delta_{nm-1})c_m = \epsilon(k)c_n \tag{105}$$

$$\eta_\tau c_n + t(c_{n-1} + c_{n+1}) = \epsilon(k)c_n \tag{106}$$

As emphasised previously, the coefficients c_n of the wavefunction expansion $|\psi\rangle = \sum_n c_n|n\rangle$ are identified by the Bloch form of the solutions

$$\psi_{\tau\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\phi_\tau(\mathbf{r} - \mathbf{T}) \tag{107}$$

In one dimension ($T = na_x$, a_x being the lattice parameter) and for one orbital, we have

$$\psi_k(x) = \frac{1}{\sqrt{N}}\sum_n e^{ikna_x}\phi(x - na_x) \tag{108}$$

that allows us to identify the coefficients c_n as

$$c_n = \frac{e^{ikna_x}}{\sqrt{N}} \tag{109}$$

We can now finally solve for the electron dispersion $\epsilon(k)$

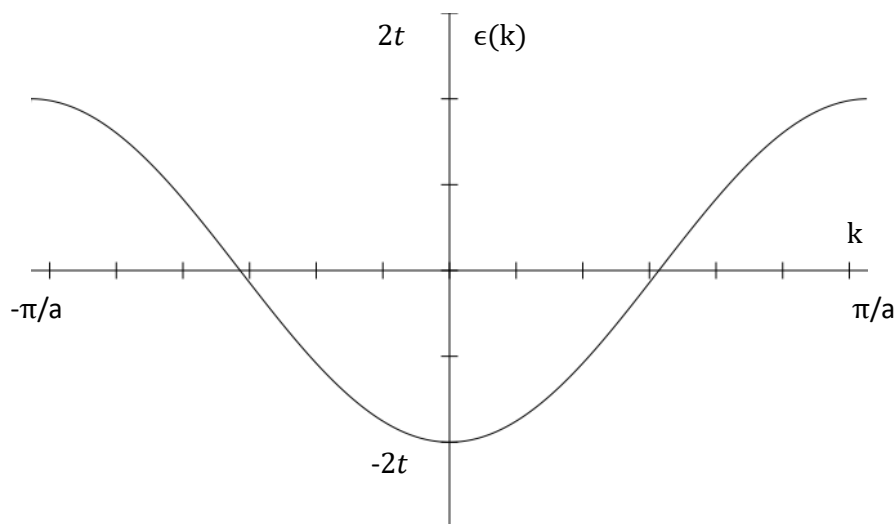$$\epsilon(k)c_n = \eta_\tau c_n + t(c_{n-1} + c_{n+1}) \tag{110}$$

$$\epsilon(k)\frac{e^{ikna_x}}{\sqrt{N}} = \eta_\tau \frac{e^{ikna_x}}{\sqrt{N}} + t\left(\frac{e^{ik(n-1)a_x}}{\sqrt{N}} + \frac{e^{ik(n+1)a_x}}{\sqrt{N}}\right) \tag{111}$$

$$\epsilon(k)\frac{e^{ikna_x}}{\sqrt{N}} = \frac{e^{ikna_x}}{\sqrt{N}}[\eta_\tau + t(e^{-ika_x} + e^{ika_x})] \tag{112}$$

$$\epsilon(k) = \eta_\tau + t(e^{-ika_x} + e^{ika_x})] \tag{113}$$

$$\boxed{\epsilon(k) = \eta_\tau + 2t\cos(ka_x)} \tag{114}$$

The 1D dispersion along k_x is plotted below for a hopping integral $t < 0$.

By reflecting on this picture we can take home some very important points

1. As we have learnt from the Bloch's theorem, the only portion of k-space that we should consider is $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, the Brillouin zone. Here we find that the allowed electronic states are distributed in an energy band whose width is $W = 4t$, set by the hopping amplitude.

2. For computational simplicity we have considered in our model only a limited subset of hopping channels leading to the formation of a single band of allowed states. In real solids we find a number of weakly coupled or decoupled orbital groups that lead to the formation of various electronic bands separated by band gaps, energy intervals in which no electronic states are available. The position of the chemical potential within this landscape of electronic bands separated by gaps will determine whether the solid behaves as an insulator, semiconductor or a metal.

19

3. At the bottom of our energy band the electron dispersion looks a lot like a parabola. Indeed by Taylor expansion we find

$$\epsilon(k) \propto \frac{\hbar^2 k^2}{2m^\star} \tag{115}$$

with $m^\star = \hbar/2ta^2$, which strongly resemble the free electron dispersion albeit with a modified mass. A more general 3D expression for this approximation, valid for isotropic bands, reads

$$\epsilon(\mathbf{k}) \sim \epsilon_0 + \frac{\hbar^2}{2m^\star}(\mathbf{k} - \mathbf{k}_0)^2 \tag{116}$$

This is telling us something very important: for wavefunctions having long wavelengths compared to the crystal spacing, in this particular example states close to the Γ point ($k = 0$) of the Brillouin zone, the electron dispersion is well approximated by a free dispersion with a mass of the electrons renormalised by the hopping integral t: the stronger the hopping amplitude (stronger interaction, larger matrix element of the hamiltonian coupling adjacent orbital states) the lighter the Bloch wave will be.

4. The quantum mechanical wave nature of the electrons has a number of interesting consequences that pertain to transport phenomena. Electron wave packets propagating in a solid state medium will be characterised by a group velocity

$$v(k) = \hbar^{-1}\nabla_k\epsilon(k) \tag{117}$$

We seek to describe, using the language of Newtonian dynamics (forces leading to accelerations through an inertial mass), the evolution of wave packets in solids. With this intent, we write for the work $\Delta\epsilon$ performed by a force F acting on an electron for a time Δt

$$\Delta\epsilon = Fv\Delta t \tag{118}$$

Moreover we can describe the changes in kinetic energy of particles in solids as

$$\Delta\epsilon = \frac{d\epsilon}{dk}\Delta k \tag{119}$$

In the context of parabolic bands we have

$$\frac{d\epsilon}{dk} = \frac{h^2 k}{m} = \hbar v \tag{120}$$

Therefore we obtain two expressions for this quantity that we can equate

$$\Delta\epsilon = \hbar v \Delta k = Fv\Delta t \tag{121}$$

From this expression we infer a description of force acting on an electron in a solid in the continuous limit

$$\mathbf{F} = \hbar \frac{d\mathbf{k}}{dt} \tag{122}$$

Here, we can also define an effective mass through the expressions

$$F = m^\star \frac{dv}{dt} = \frac{m^\star}{\hbar} \frac{d^2\epsilon}{dt\,dk} = \hbar \frac{dk}{dt} \tag{123}$$

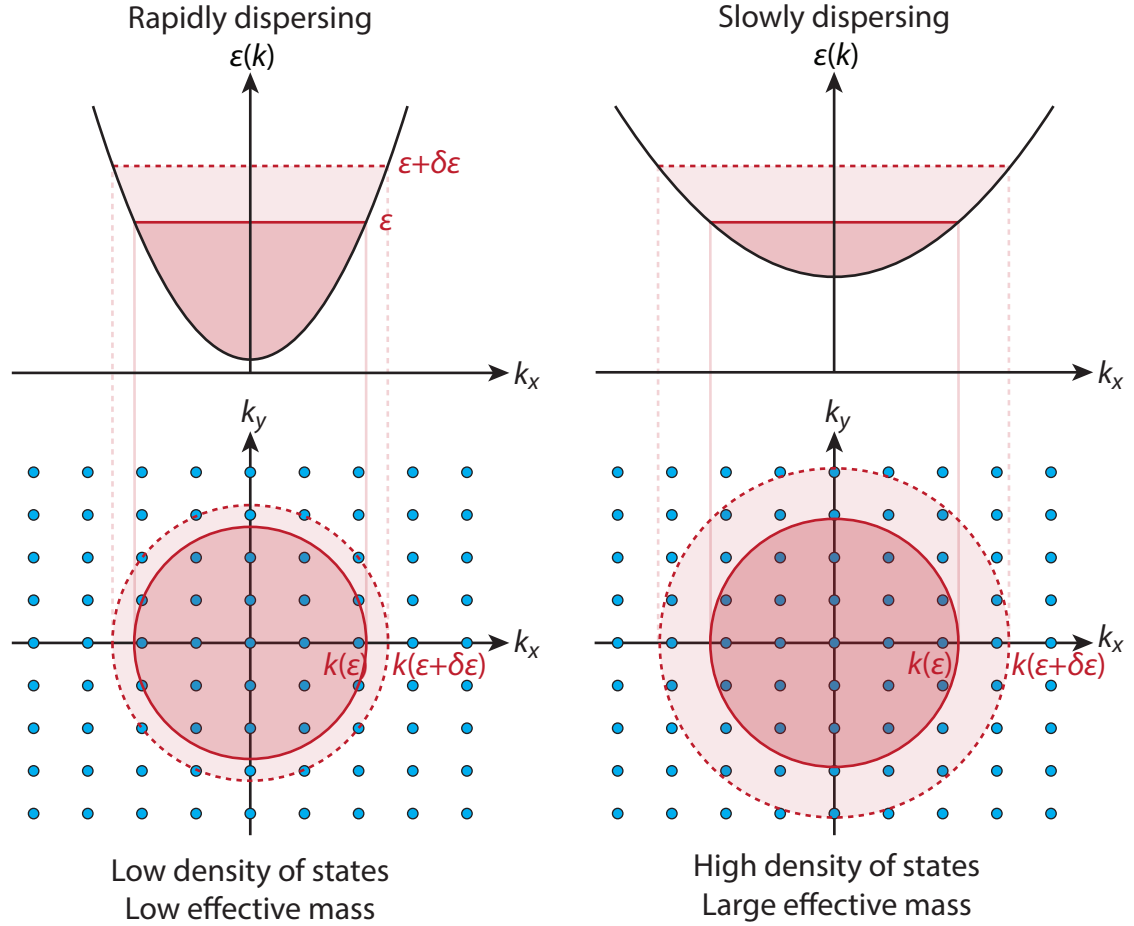$$\boxed{m^\star(k) = \hbar^2 \left[\nabla_k^2 \epsilon(k)\right]^{-1}} \tag{124}$$

Note that in this generalised picture the effective mass depends on k and can be positive or negative. Therefore we should be prepared for some surprising phenomena in the electrodynamics of solids. The concept of effective mass also gives us a very practical language to characterise the density of states. For example for a 3D isotropic parabolic band we can write

$$N(\epsilon) = 2 \int_0^{k=k(\epsilon)} \frac{dN(k)}{dk} dk = 2 \int_0^{\sqrt{2m^\star(\epsilon-\epsilon_0)/\hbar^2}} \frac{\mathscr{V}}{(2\pi)^3} d\mathbf{k} = \tag{125}$$

$$= 2 \int_0^{\sqrt{2m^\star(\epsilon-\epsilon_0)/\hbar^2}} \frac{\mathscr{V}}{(2\pi)^3} 4\pi k^2 dk = \frac{\mathscr{V}}{\pi^2} \frac{1}{3} \left[\frac{2m^\star(\epsilon-\epsilon_0)}{\hbar^2}\right]^{3/2} \tag{126}$$

$$g(\epsilon) = \frac{1}{\mathscr{V}} \frac{dN(\epsilon)}{d\epsilon} = \frac{1}{2\pi^2} \left(\frac{2m^\star}{\hbar^2}\right)^{3/2} \sqrt{\epsilon - \epsilon_0} \tag{127}$$

that extends our previous result of the density of states of the Fermi gas to this more general case. Since for a given region of k-space we have a well defined number of available states (recall our discussion on the periodic boundary conditions), a rapidly dispersing electron band (high curvature, light effective mass) will result in the spreading of k levels in a wide energy range (low density of states). On the contrary, a slowly dispersing electron band (small curvature, heavy effective mass) will result in the packing of many k levels in a small energy rage. This establishes a convenient direct link between density of states and effective mass (see figure below).

Rapidly dispersing
$\varepsilon(k)$

$\varepsilon+\delta\varepsilon$

ε

k_x

k_y

$k(\varepsilon)$ $k(\varepsilon+\delta\varepsilon)$ k_x

Low density of states
Low effective mass

Slowly dispersing
$\varepsilon(k)$

k_x

k_y

$k(\varepsilon)$ $k(\varepsilon+\delta\varepsilon)$ k_x

High density of states
Large effective mass

5. At the edge of the Brillouin zone we see an interesting flattening of the dispersion. This fact implies that the electronic state in this region find it difficult to transport energy (small curvature corresponding to heavy effective masses). At the edge of the Brillouin zone, we also typically observe the opening of band gaps in the density of states. Let's consider an important clue that helps us understand the physical origin of the band gaps. We ask ourselves: what is so special about the edge of the Brillouin zone? This is a region of k-space defined as

$$k = \pm\frac{1}{2}G = \pm n\frac{\pi}{a} \tag{128}$$

where $G = 2\pi n/a$ is a vector of the reciprocal lattice and n is an integer. In other words, these k states are integer multiples of a reciprocal space vector. We make an important step forward by realising that this is the condition for Bragg diffraction of waves from the crystal lattice. Therefore these states at the edge of the Brillouin

zone corrispond to electrons that undergo Bragg reflections from the crystal. In a one dimensional picture, a wave travelling to the left will be reflected into a wave travelling to the right while a wave travelling to the right will be reflected into a wave travelling to the left. This process will inevitably lead to the formation of a standing wave. The most simple standing waves that we can construct from a linear combination of propagating k states (in a 1D representation) are

$$\psi^+ = e^{ix\pi/a} + e^{-ix\pi/a} = 2\cos(x\pi/a) \tag{129}$$

$$\psi^- = e^{ix\pi/a} - e^{-ix\pi/a} = 2i\sin(x\pi/a) \tag{130}$$

Their corresponding densities are

$$\rho^+ = |\psi^+|^2 \propto \cos^2(x\pi/a) \tag{131}$$

$$\rho^- = |\psi^-|^2 \propto \sin^2(x\pi/a) \tag{132}$$

From a direct inspection of these functions, we understand that the wave ψ^+ distributes electron probability density in correspondence with the lattice sites while the wave ψ^- distributes electron probability density between lattice sites. The energy of the wavefunction ψ^+ is obviously lower than ψ^-: the negative electron charge feels the attraction of the ionised lattice sites and sits more comfortably when being in tune with the crystal. The difference between the energy of these wavefunction sets the energy scale of the band gap.

In summary, at the edge of the Brillouin zone we are unable to construct propagating electronic states because of Bragg elastic diffusion. The resulting electronic states in this region of k space are standing waves. These do not form a continuous of states but will form a discrete spectrum with wide gaps in between. The energy scale of these gaps is set by the different electrostatic interaction of these standing waves with the crystal lattice.

5.2   Single orbital 2D square lattice

We will now describe the tight binding model on a 2D lattice using the occupation number representation (also known as second quantization). If this formalism is not (yet) known to you, we encourage you to came back to this final part of the notes later in the course. The tight-binding hamiltonian reads (V is a periodic potential describing the crystal lattice)

$$H = \sum_{nm} \langle \phi_n | \frac{p^2}{2m} + V | \phi_m \rangle c_n^\dagger c_m \tag{133}$$

Here the operators $c_n^\dagger$ (c_n) create (annihilate) a particle on site n and the ϕ_n are the quantum states at site n forming an orthonormal basis (Wannier orbitals). Thanks to this property we can take advantage of translational invariance

$$\phi_{\mathbf{R}_n}(\mathbf{r}) = \phi_{\mathbf{0}}(\mathbf{r} - \mathbf{R}_n) \tag{134}$$

allowing us to write the hamiltonian as

$$H = \sum_{nm} \langle \phi_0 | \frac{p^2}{2m} + V | \phi_m \rangle c^\dagger_{\mathbf{R}_n} c_{\mathbf{R}_n + \mathbf{R}_m} \tag{135}$$

where we have a set of on-site matrix elements valid for the whole crystal that we call hopping amplitudes. It is wise to limit the possible hopping channels to the nearest neighbours

$$t = \langle \phi_0 | \frac{p^2}{2m} + V | \phi_{\mathbf{d}} \rangle \tag{136}$$

where $\mathbf{d} = \pm a\mathbf{x}, \pm a\mathbf{y}$. For isotropic hopping the hamiltonian becomes

$$H = \sum_n t \, c^\dagger_{\mathbf{R}_n} \left(c_{\mathbf{R}_n + a\mathbf{x}} + c_{\mathbf{R}_n - a\mathbf{x}} + c_{\mathbf{R}_n + a\mathbf{y}} + c_{\mathbf{R}_n - a\mathbf{y}} \right) \tag{137}$$

This hamiltonian is beautifully descriptive as it allows us to see all the hopping processes that contribute to the kinetic energy of our electron as it propagates through the crystal lattice. Unfortunately this hamiltonian is not in a diagonal form and therefore we cannot directly see at this point its eigenvalues and evaluate the accessible energy levels to our electrons. At this point, we would like to diagonalise this hamiltonian in order to make its eigenvalues explicit. In order to do this, we need to use the translational invariance of our system and transform the creation and annihilation operators in a k-space basis. We seek a relation between the operator $c^\dagger_{\mathbf{r}}$ that creates a particle in state $\phi_{\mathbf{r}}(\mathbf{r}_1) = \delta(\mathbf{r} - \mathbf{r}_1)$ and the operator $c^\dagger_{\mathbf{k}}$ that creates a particle state $\phi_{\mathbf{k}}(\mathbf{r}_1) = (1/\sqrt{\mathcal{V}})e^{i\mathbf{k}\cdot\mathbf{r}_1}$. This takes the general form of a unitary transformation

$$c^\dagger_{\mathbf{k}} = \int W_{\mathbf{k}\mathbf{r}} c^\dagger_{\mathbf{r}} d\mathbf{r} \tag{138}$$

The matrix elements $W_{\mathbf{k}\mathbf{r}}$ can be calculated by creating on the vacuum Φ a state in basis $\mathbf{k}$ and projecting on state $\mathbf{r}_1$

$$\langle \mathbf{r}_1 | c^\dagger_{\mathbf{k}} | \Phi \rangle = \int W_{\mathbf{k}\mathbf{r}} \langle \mathbf{r}_1 | c^\dagger_{\mathbf{k}} | \Phi \rangle d\mathbf{r} = \int W_{\mathbf{k}\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_1) d\mathbf{r} = W_{\mathbf{k}\mathbf{r}_1} = \phi_{\mathbf{k}}(\mathbf{r}_1) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\mathbf{k}\cdot\mathbf{r}_1} \tag{139}$$

Therefore the transformation we are looking for is

$$c^\dagger_{\mathbf{k}} = \frac{1}{\sqrt{\mathcal{V}}} \int e^{i\mathbf{k}\cdot\mathbf{r}} c^\dagger_{\mathbf{r}} d\mathbf{r} \tag{140}$$

and by conjugation we obtain the corresponding transformation for annihilation operators

$$c_{\mathbf{k}} = \frac{1}{\sqrt{\mathcal{V}}} \int e^{-i\mathbf{k}\cdot\mathbf{r}} c_{\mathbf{r}} d\mathbf{r} \tag{141}$$

The inverse operators are given by

$$c_{\mathbf{r}}^{\dagger} = \frac{1}{\sqrt{\mathscr{V}}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} c_{\mathbf{k}}^{\dagger} \tag{142}$$

and by conjugation

$$c_{\mathbf{r}} = \frac{1}{\sqrt{\mathscr{V}}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} c_{\mathbf{k}} \tag{143}$$

Now we are fully equipped in order to diagonalise our tight binding hamiltonian through the transformation

$$c_{\mathbf{R}_n}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_n} c_{\mathbf{k}}^{\dagger} \tag{144}$$

and

$$c_{\mathbf{R}_m} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{R}_m} c_{\mathbf{k}'} \tag{145}$$

The volume $\mathscr{V}$ is replaced here by a discrete number of sites N. Our tight binding hamiltonian becomes diagonal through the following

$$H = \sum_{n} \frac{1}{N} \sum_{\mathbf{k}\mathbf{k}'} e^{-i\mathbf{k}\cdot\mathbf{R}_n} c_{\mathbf{k}}^{\dagger} e^{i\mathbf{k}'\cdot\mathbf{R}_n} t \left(e^{i\mathbf{k}'\cdot a\mathbf{x}} + e^{-i\mathbf{k}'\cdot a\mathbf{x}} + e^{i\mathbf{k}'\cdot a\mathbf{y}} + e^{-i\mathbf{k}'\cdot a\mathbf{y}} \right) c_{\mathbf{k}'} \tag{146}$$

$$= \sum_{\mathbf{k}\mathbf{k}'} \frac{1}{N} \sum_{n} e^{i(\mathbf{k}'-\mathbf{k})\mathbf{R}_n} t \left(e^{ik_x'a} + e^{-ik_x'a} + e^{ik_y'a} + e^{-ik_y'a} \right) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}'} \tag{147}$$

$$= \sum_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{k}\mathbf{k}'} t \left(e^{ik_x'a} + e^{-ik_x'a} + e^{ik_y'a} + e^{-ik_y'a} \right) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}'} \tag{148}$$

$$\sum_{\mathbf{k}} t \left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} \right) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \tag{149}$$

$$\sum_{\mathbf{k}} 2\, t \left[\cos(k_x a) + \cos(k_y a) \right] c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \tag{150}$$

We have obtained the diagonal form

$$\sum_{\mathbf{k}} \epsilon(\mathbf{k}) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \tag{151}$$

that highlights the eigenvalues

$$\boxed{\epsilon(\mathbf{k}) = 2\, t \left[\cos(k_x a) + \cos(k_y a) \right]} \tag{152}$$

called the dispersion relation. The hopping amplitude t can be calculated for a specific material-dependent choice of Wannier states and description of the crystal lattice potential, but here we will limit ourselves to consider it a parameter of our model. It describes the kinetic energy associated with electron delocalisation through the crystal. In our calculation we have neglected in the sum the on-site matrix element that only results in a shift of chemical potential and does not influence the dispersion relation.

5.3 Single orbital 3D lattice

Having analysed the 1D and 2D cases using two different formalisms, the generalisation to 3D is straightforward. We again consider solutions of the Bloch form

$$\psi_{\tau\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_\tau(\mathbf{r} - \mathbf{T}) \tag{153}$$

and we calculate the eigenvalues of the Schroedinger equation by direct computation of the expectation values of the hamiltonian

$$\epsilon(\mathbf{k}) = \int \psi_{\tau\mathbf{k}}^*(\mathbf{r}) H \psi_{\tau\mathbf{k}}(\mathbf{r}) d\mathbf{r} \tag{154}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T}'} \int e^{-i\mathbf{k}\cdot\mathbf{T}} \phi_\tau^*(\mathbf{r} - \mathbf{T}) H e^{i\mathbf{k}\cdot\mathbf{T}'} \phi_\tau(\mathbf{r} - \mathbf{T}') d\mathbf{r} \tag{155}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T}'} e^{i\mathbf{k}\cdot(\mathbf{T}'-\mathbf{T})} \int \phi_\tau^*(\mathbf{r} - \mathbf{T}) H \phi_\tau(\mathbf{r} - \mathbf{T}') d\mathbf{r} \tag{156}$$

We make use of the invariance for translations of $\mathbf{T}$ to rewrite this expression as

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T}'} e^{i\mathbf{k}\cdot(\mathbf{T}'-\mathbf{T})} \int \phi_\tau^*(\mathbf{r}) H \phi_\tau(\mathbf{r} - (\mathbf{T}' - \mathbf{T})) d\mathbf{r} \tag{157}$$

$$= \frac{1}{N} \sum_{\mathbf{T}} \sum_{\mathbf{T}''} e^{i\mathbf{k}\cdot\mathbf{T}''} \int \phi_\tau^*(\mathbf{r}) H \phi_\tau(\mathbf{r} - \mathbf{T}'') d\mathbf{r} \tag{158}$$

$$= \sum_{\mathbf{T}''} e^{i\mathbf{k}\cdot\mathbf{T}''} \int \phi_\tau^*(\mathbf{r}) H \phi_\tau(\mathbf{r} - \mathbf{T}'') d\mathbf{r} \tag{159}$$

For the term $\mathbf{T}'' = 0$ we obtain

$$\int \phi_\tau^*(\mathbf{r}) H \phi_\tau(\mathbf{r}) d\mathbf{r} = \eta_\tau \tag{160}$$

Just like discussed before, the parameter η_τ accounts for the energy associated with electron localisation on the atomic lattice sites on state τ. We limit the sum to the nearest neighbours $\boldsymbol{\alpha}$

$$\epsilon(\mathbf{k}) = \eta_\tau + \sum_{\boldsymbol{\alpha}} e^{i\mathbf{k}\cdot\boldsymbol{\alpha}} \int \phi_\tau^*(\mathbf{r}) H \phi_\tau(\mathbf{r} - \boldsymbol{\alpha}) d\mathbf{r} \tag{161}$$

The hopping integral is often indicated with the parameter $t(\boldsymbol{\alpha})$, leading to our final expression:

$$\boxed{\epsilon(\mathbf{k}) = \eta_\tau + \sum_{\boldsymbol{\alpha}} t(\boldsymbol{\alpha}) e^{i\mathbf{k}\cdot\boldsymbol{\alpha}}} \tag{162}$$

This equation is very useful as it is the starting point of a typical tight-binding calculation of the electronic structure of a material with known chemical composition and structure. The hopping integral t can be derived from a microscopic theory or taken as a parameter to be adjusted according to experimental data. The experimental methods used for mapping out the electronic structure of materials will be introduced later in the course.