Chapter 3

Electrons in a periodic potential

3.1 Bloch's theorem.

We consider in this chapter electrons under the influence of a static, periodic potential $V(\boldsymbol{x})$, i.e. such that it fulfills $V(\boldsymbol{x}) = V(\boldsymbol{x}+\boldsymbol{R})$, where $\boldsymbol{R}$ is a lattice vector.

Bloch's theorem states that the one-particle states in a periodic potential can be chosen so that

$$\psi(\boldsymbol{x}) = u_{\boldsymbol{k}}(\boldsymbol{x}) \exp(i\boldsymbol{k}\cdot\boldsymbol{x}) \ , \tag{3.1}$$

where $u_{\boldsymbol{k}}(\boldsymbol{x})$ is a periodic function with the periodicity of the lattice, and $\boldsymbol{k}$ belongs to the Brillouin zone. This implies that

$$\psi(\boldsymbol{x}+\boldsymbol{R}) \ = \ \exp(i\boldsymbol{k}\cdot\boldsymbol{R}) \ \psi(\boldsymbol{x}) \ , \tag{3.2}$$

i.e. $\psi(\boldsymbol{x})$ is a periodic function up to a phase.

Proof
Let $\boldsymbol{R}$ be a lattice vector and $T_{\boldsymbol{R}}$ be a translation operator that acts as follows on any given function

$$T_{\boldsymbol{R}} f(\boldsymbol{x}) = f(\boldsymbol{x}+\boldsymbol{R}) \ . \tag{3.3}$$

By assumption, the Hamiltonian is translational invariant under translations by a lattice vector. It follows that

$$\begin{aligned} T_{\boldsymbol{R}} H(\boldsymbol{x}) \ \psi(\boldsymbol{x}) &= H(\boldsymbol{x}+\boldsymbol{R}) \ \psi(\boldsymbol{x}+\boldsymbol{R}) \\ &= H(\boldsymbol{x}) \ \psi(\boldsymbol{x}+\boldsymbol{R}) = H(\boldsymbol{x}) \ T_{\boldsymbol{R}} \psi(\boldsymbol{x}) \quad \forall\, \psi \ , \ \forall\, \boldsymbol{R} \ . \end{aligned} \tag{3.4}$$

This means that

$$\left[T_{\boldsymbol{R}}, H\right] = 0 \qquad \forall\, \boldsymbol{R} \ . \tag{3.5}$$

Since H and the translation operators commute for all translations $\boldsymbol{R}$, there is a common set of eigenfunctions for H and the set $\left\{T_{\boldsymbol{R}}\right\}$ of all translation operators of the lattice. Therefore, the one-particle states of the system obey an eigenvalue equation for the translation operators

$$\begin{aligned} \psi(\boldsymbol{x}+\boldsymbol{R}) &= T_{\boldsymbol{R}}\psi(\boldsymbol{x}) \\ &= c(\boldsymbol{R})\,\psi(\boldsymbol{x}) \; . \end{aligned} \tag{3.6}$$

Furthermore, since

$$T_{\boldsymbol{R}}T_{\boldsymbol{R}'} = T_{\boldsymbol{R}+\boldsymbol{R}'} \Longrightarrow c(\boldsymbol{R}+\boldsymbol{R}') = c(\boldsymbol{R}')\;c(\boldsymbol{R}) \; . \tag{3.7}$$

In the presence of periodic boundary conditions, we should have using the last result,

$$\left(T_{\boldsymbol{a}_i}\right)^{N_i}\;\psi(\boldsymbol{x}) = \psi(\boldsymbol{x}) \Longrightarrow \left[c(\boldsymbol{a}_i)\right]^{N_i} = 1 \; . \tag{3.8}$$

This is easily fulfilled by

$$c(\boldsymbol{R}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{R}) \; , \tag{3.9}$$

for some wavevector $\boldsymbol{k}$. Since $\boldsymbol{G}\cdot\boldsymbol{R} = 2\pi n$, with n integer, we can restrict $\boldsymbol{k}$ to the first Brillouin zone. Such a form also satisfies eq. (3.7), for any lattice translation vector.

Finally, let us consider a function

$$u_{\boldsymbol{k}}(\boldsymbol{x}) = \exp(-i\boldsymbol{k}\cdot\boldsymbol{x})\;\psi(\boldsymbol{x}) \; . \tag{3.10}$$

After a translation we have

$$\begin{aligned} u_{\boldsymbol{k}}(\boldsymbol{x}+\boldsymbol{R}) &= \exp(-i\boldsymbol{k}\cdot\boldsymbol{x})\;\exp(-i\boldsymbol{k}\cdot\boldsymbol{R})\;\psi(\boldsymbol{x}+R) \\ &= \exp(-i\boldsymbol{k}\cdot\boldsymbol{x})\;\psi(\boldsymbol{x}) = u_{\boldsymbol{k}}(\boldsymbol{x}) \; , \end{aligned} \tag{3.11}$$

i.e. $u_{\boldsymbol{k}}(\boldsymbol{x})$ is a periodic function with the periodicity of the lattice. This means that

$$\psi(\boldsymbol{x}) = u_{\boldsymbol{k}}(\boldsymbol{x})\;\exp(i\boldsymbol{k}\cdot\boldsymbol{x}) \; . \tag{3.12}$$

as stated at the beginning. Since the wavefunction is labeled by $\boldsymbol{k}$, we denote from now on the eigenfunction by

$$\psi(\boldsymbol{x}) \longrightarrow \psi_{\boldsymbol{k}}(\boldsymbol{x}) \; . \tag{3.13}$$

3.1.1 Consequences of Bloch's theorem. Bandstructure

The first direct consequence of Bloch's theorem is that the electronic density

$$n(\boldsymbol{x}) = \psi^*(\boldsymbol{x})\,\psi(\boldsymbol{x}) = u^*_{\boldsymbol{k}}(\boldsymbol{x})\,u_{\boldsymbol{k}}(\boldsymbol{x}) \tag{3.14}$$

is a periodic function with the periodicity of the lattice because it was demonstrated above that $u_{\boldsymbol{k}}(\boldsymbol{x})$ has this periodicity. Although this was expected, it is comforting to see that this is obtained on purely theoretical grounds, where the only assumption is that the Hamiltonian is periodic.

Since we are dealing with non-interacting electrons under the influence of a periodic potential, the Schrödinger equation looks a s follows

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V\left(\boldsymbol{x}\right)\right] \exp\left(i\boldsymbol{k}\cdot\boldsymbol{x}\right)\, u_{n,\boldsymbol{k}}\left(\boldsymbol{x}\right) = E_n\left(\boldsymbol{k}\right)\, \exp\left(i\boldsymbol{k}\cdot\boldsymbol{x}\right)\, u_{n,\boldsymbol{k}}\left(\boldsymbol{x}\right)\ , \tag{3.15}$$

that is, $u_{n,\boldsymbol{k}}$ itself is a solution of a Schrödinger equation,

$$\left[\frac{\hbar^2}{2m}\left(-i\boldsymbol{\nabla} + \boldsymbol{k}\right)^2 + V\left(\boldsymbol{x}\right)\right] u_{n,\boldsymbol{k}}\left(\boldsymbol{x}\right) = E_n\left(\boldsymbol{k}\right)\, u_{n,\boldsymbol{k}}\left(\boldsymbol{x}\right)\ , \tag{3.16}$$

The subindex n was introduced, since as we know already from a simple problem in quantum mechanics, like the particle in a box, more than one solution of Schrödingers equation can be found for a given wavevector $\boldsymbol{k}$. The subindex n denotes the bands in the solid. The set of eigenvalues $E_n\left(\boldsymbol{k}\right)$ is called usually the band-structure.

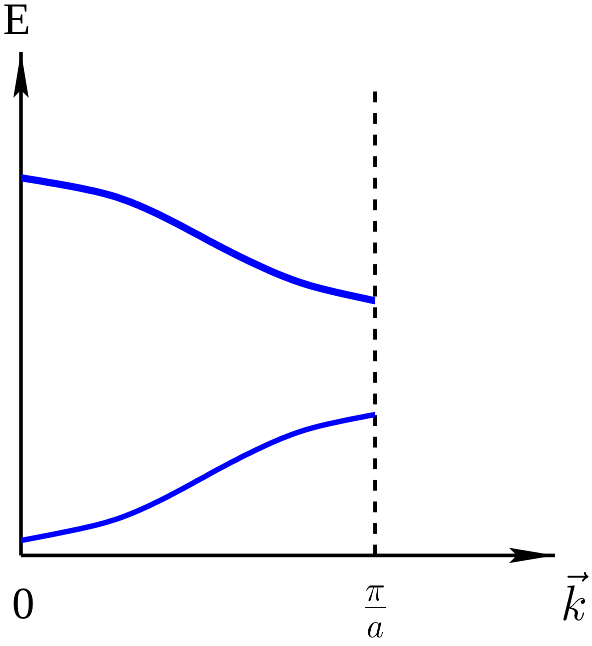

Figure 3.1: Sketch of a band-structure.

As already discussed in (3.9), we restricted $\boldsymbol{k}$ to the first Brillouin zone, since for any translation, the eigenvalue remains unchanged by an addition of a reciprocal lattice vector. Since this eigenfunction of the translation operator is at the same time an eigenfunction of the Hamiltonian, the eigenenergies are also insensitive with respect to a translation by a reciprocal lattice vector. Therefore, we have

$$E_n\left(\boldsymbol{k} + \boldsymbol{G}\right) = E_n\left(\boldsymbol{k}\right)\ . \tag{3.17}$$

This means that we can consider the energy bands in the first Brillouin zone (restricited zone scheme - Fig. 3.2) or beyond it (repeated zone scheme - Fig. 3.3).

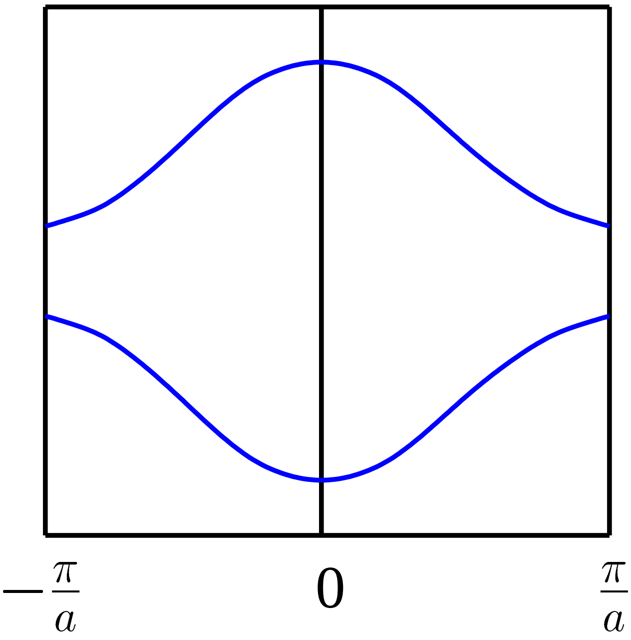

Figure 3.2: One dimensional band structure in the reduced zone scheme.

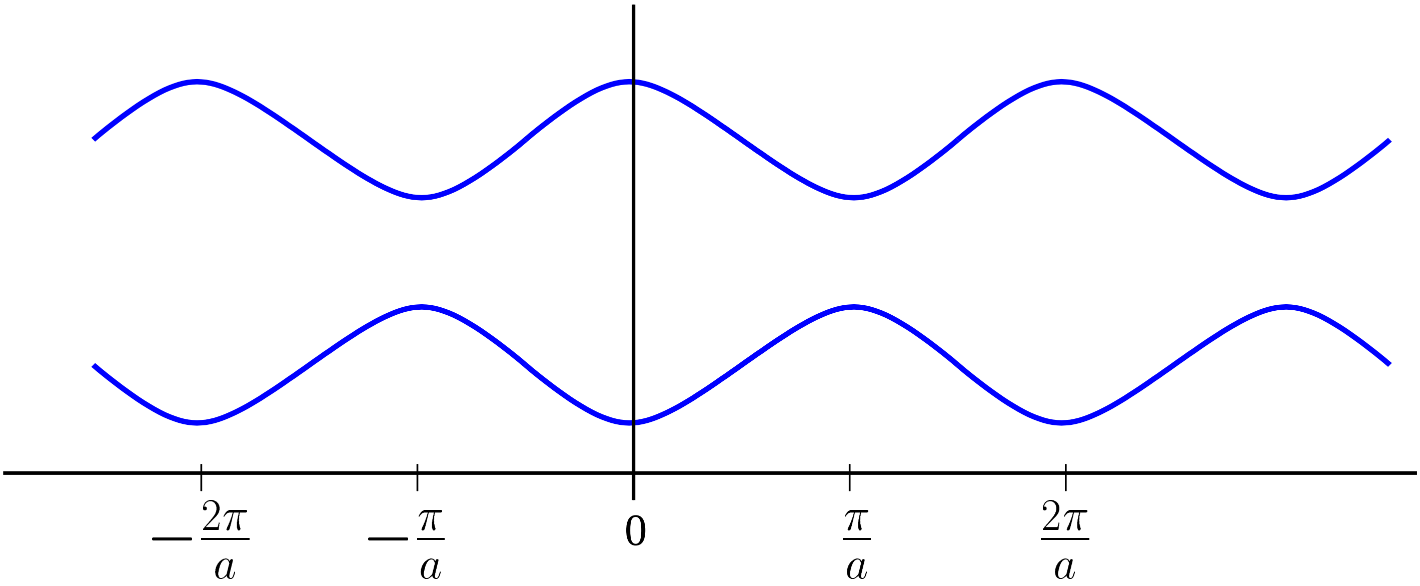

Figure 3.3: One dimensional band structure in the repeated zone scheme.

3.1.2 Fermi surface, metals, and insulators

At this stage, we have to begin to consider not only one electron but many of them, such that we will be able to distinguish between metals and insulators. Instead of developing the full theory at this point, let us just postulate some of their properties, and later try to view these postulates in a more general frame.

First, we postulate that electrons are *fermions*, i.e. particles that obey the Pauli-Dirac statistics. For us, at this point this means only that they obey Pauli's exclusion principle, that is, two fermions cannot occupy the same state. In order to specify the state of an electron, we have to recall also the fact that electrons have a spin, i.e. an intrinsic angular momentum, with possible projections along the z-axis $S^z = \frac{1}{2}, -\frac{1}{2}$. Denoting the possible states of the electron by the wavevector $\boldsymbol{k}$ and spin, we have two possible states available for each electron of wavevector $\boldsymbol{k}$.

Given a certain number of electrons in the solid, allways assuming them non-interacting, we can construct the ground state by filling the lowest energy states. By doing so, the last electron will be at an energy that is called the Fermi energy E_F. The set of points in the Brillouin zone corresponding to the energy surface with $E_{\boldsymbol{k}} = E_F$ is called the Fermi surface. In general, in order to provoke a change in the system like inducing a current, the distribution of electrons on the available states should be changed. Due to Pauli's exclusion principle this can only happen by promoting electrons across the Fermi surface. The bandstructure of Fig. 3.4 corresponds to the case, where such a change can be induced with a vanishingly small energy. This is the case of metals.

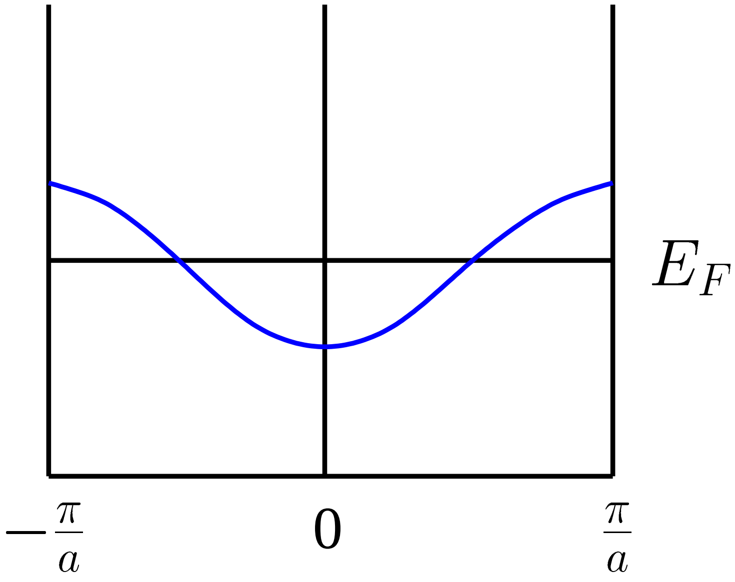

Figure 3.4: Partially filled band for a one-dimensional system. Occupied states correspond to those with energies lower than E_F.

If we continue to fill up the band with electrons, we will come to the point where a band is completely filled. In this situation, we have a completely filled band, and the next available state is at a finite energy Δ from the last occupied one, i.e. Δ is an *energy gap* between the bands. For temperatures such that $k_B T \ll \Delta$, we have an insulator, whereas for $k_B T \sim \Delta$ the system is a semiconductor. A general feature for a band insulator, i.e. an insulator where the appearance of a band gap is not induced by interaction, is that a band gap appears when there is an even number of electrons per elementary cell.

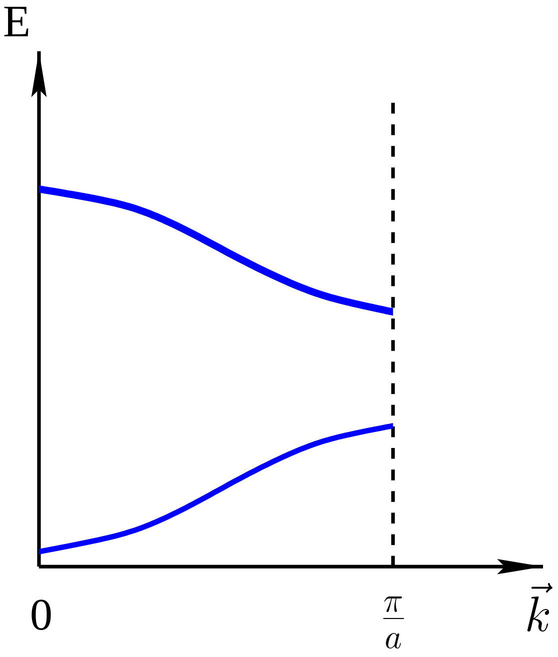

Figure 3.5: Filled band for a one-dimensional system. Δ denotes the energy gap between the occupied and unoccupied bands.

3.1.3 Density of states

As we have seen in the case of phonons, a number of physical quantities can be obtained from the knowledge of the density of states. It is therefore, in general of interest to calculate it for the one-particle states in an electronic system. In this case, it is defined as follows

$N(E)\,\mathrm{d}E$: number of energy eigenstates in the interval $[E, E+\mathrm{d}E]$ per unit volume and per spin

As before (Ch. 2, Sec. 3), we have

$$\begin{aligned} N(E) &= \frac{1}{V} \sum_{\substack{n \\ \boldsymbol{k} \in BZ}} \delta\left[E - E_n(\boldsymbol{k})\right] \\ &\xrightarrow{V \to \infty} \sum_n \int_{BZ} \frac{\mathrm{d}^3 k}{(2\pi)^3}\, \delta\left[E - E_n(\boldsymbol{k})\right] \end{aligned}$$

$$= \int_{BZ} \frac{\mathrm{d}S}{\mid \boldsymbol{\nabla}_{\boldsymbol{k}} E_n(\boldsymbol{k}) \mid} . \tag{3.18}$$

A more intuitive way of looking at this integral is shown in Fig. 3.6, where the number of states is just obtained by multiplying the volume in reciprocal space by the density of states in it, such that

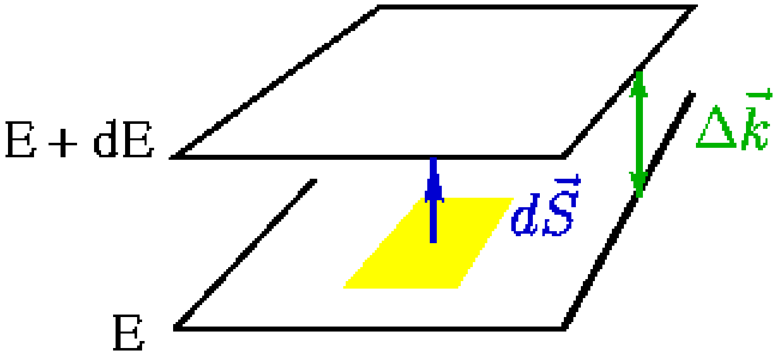

Figure 3.6: Schematic view of the volume in reciprocal space that enters in the calculation of the density of states.

$$N(E)\,\mathrm{d}E = \frac{1}{(2\pi)^3} \int \mathrm{d}S\,\Delta k . \tag{3.19}$$

On the other hand,

$$\mathrm{d}E = \left(\boldsymbol{\nabla}_{\boldsymbol{k}} E\right) \cdot \Delta\boldsymbol{k} = \mid \boldsymbol{\nabla}_{\boldsymbol{k}} E \mid \Delta k . \tag{3.20}$$

Deviding (3.19) by (3.20), we finally obtain (3.18). A clear consequence of (3.18) is that when $\boldsymbol{\nabla}_{\boldsymbol{k}} E(\boldsymbol{k}) = 0$, there are in general singularities in the density of states. These are Van Hove singularities.

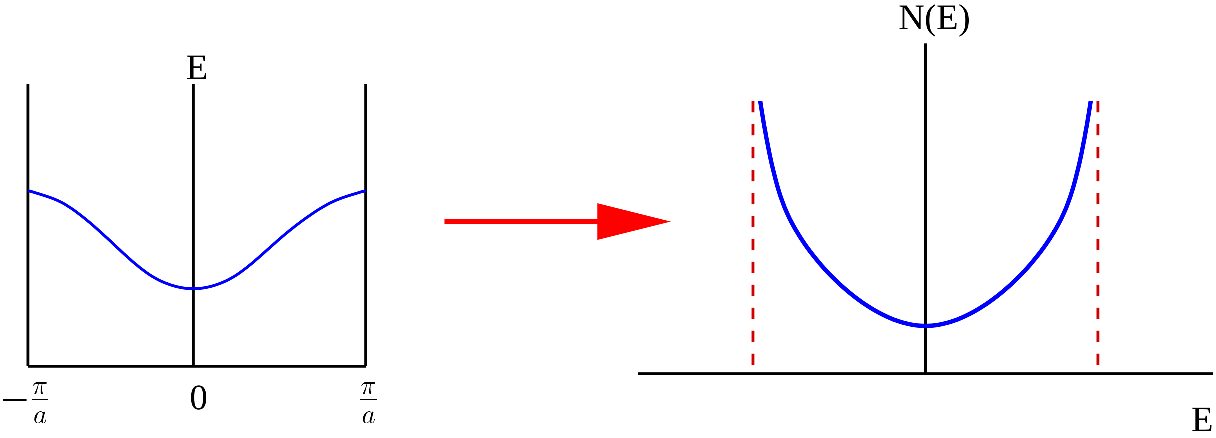

Figure 3.7: Van hove singularities in the one dimensional case.

3.2 Nearly free electrons

After having discussed some general features of the dispersion relation for electrons in a periodic potential, we consider in this and in the following section two limiting cases that will help us to iluminate some aspects of the band-structures of electrons.

We discuss here the case of a very weak periodic potential, $V(\boldsymbol{x}) \ll E_{kinetic}$ such that perturbation theory is applicable. This is a model that is suitable for simple metals like Li, Na, K, etc. Since the exact solution of the problem should fulfill Bloch's theorem, let us consider the general form of the eigenfunctions of this problem in more detail. The eigenfunctions should be of the form

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{x})\; u_{\boldsymbol{k}}(\boldsymbol{x}) \ , \tag{3.21}$$

where $u_{\boldsymbol{k}}(\boldsymbol{x})$ is periodic, such that this function can be expanded in a sum over reciprocal lattice vectors

$$u_{\boldsymbol{k}}(\boldsymbol{x}) \;=\; \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} v_{\boldsymbol{G}}(\boldsymbol{k}) \exp(i\boldsymbol{G}\cdot\boldsymbol{x}) \ , \tag{3.22}$$

leading to

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} v_{\boldsymbol{G}}(\boldsymbol{k}) \exp\left[i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{x}\right] \ . \tag{3.23}$$

Here we see that a Bloch electron (or particle actually, since the discussion until now was not really specific about the particle in question), does not posses a definite momentum, but is a superposition of plane waves with momentum $\boldsymbol{k}+\boldsymbol{G}$ where the respective amplitude is given by $v_{\boldsymbol{G}}(\boldsymbol{k})$. These amplitudes (i.e. the Fourier components of $u_{\boldsymbol{k}}$) can be obtained as we have already seen in Chapter 1.

$$\begin{aligned} v_{\boldsymbol{G}}(\boldsymbol{k}) &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} \mathrm{d}^3x\, u_{\boldsymbol{k}}(\boldsymbol{x}) \exp(-i\boldsymbol{G}\cdot\boldsymbol{x}) \\ &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} \mathrm{d}^3x \; \underbrace{\psi_{\boldsymbol{k}}(\boldsymbol{x})}_{\psi_{\boldsymbol{k}+\boldsymbol{G}}(\boldsymbol{x})} \exp\left[-i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{x}\right] \\ &= v(\boldsymbol{k}+\boldsymbol{G}) \ . \end{aligned} \tag{3.24}$$

The last line shows that $v_{\boldsymbol{G}}(\boldsymbol{k})$ does not depend separately on $\boldsymbol{G}$ and $\boldsymbol{k}$ but on their sum. We can therefore, rewrite the eigenfunctions as follows

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} v(\boldsymbol{k}-\boldsymbol{G}) \exp\left[i(\boldsymbol{k}-\boldsymbol{G})\cdot\boldsymbol{x}\right] \ . \tag{3.25}$$

On the other hand, since $V(\boldsymbol{x})$ is periodic, it can be also Fourier expanded

$$V(\boldsymbol{x}) \;=\; \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} \exp(i\boldsymbol{G}\cdot\boldsymbol{x}) \ , \tag{3.26}$$

Inserting (3.25) and (3.26) in the Schrödinger equation, we have

$$\left[\frac{\mid \boldsymbol{k}-\boldsymbol{G}\mid^2}{2m} - E(\boldsymbol{k})\right] v(\boldsymbol{k}-\boldsymbol{G}) + \sum_{\boldsymbol{G}'} V_{\boldsymbol{G}'-\boldsymbol{G}}\, v(\boldsymbol{k}-\boldsymbol{G}') = 0\,. \tag{3.27}$$

The equation above has to be solved for each $\boldsymbol{k}$.

We can consider the equation above in the frame of perturbation theory, since $V(\boldsymbol{x})$ is assumed to be weak.

a) Zero-th order ($V = 0 \longrightarrow$ 'empty lattice'). This correspond obviously to free electrons, but in the frame developed above, we can look at the solutions in different ways.

$$\hookrightarrow (3.27) \to \left[\frac{\mid \boldsymbol{k}-\boldsymbol{G}\mid^2}{2m} - E(\boldsymbol{k})\right] v(\boldsymbol{k}-\boldsymbol{G}) = 0\,. \tag{3.28}$$

The solutions have the form

$$E^0_{\boldsymbol{G}}(\boldsymbol{k}) = \frac{\mid \boldsymbol{k}-\boldsymbol{G}\mid^2}{2m}\,. \tag{3.29}$$

The solutions can be considered in two possible ways:

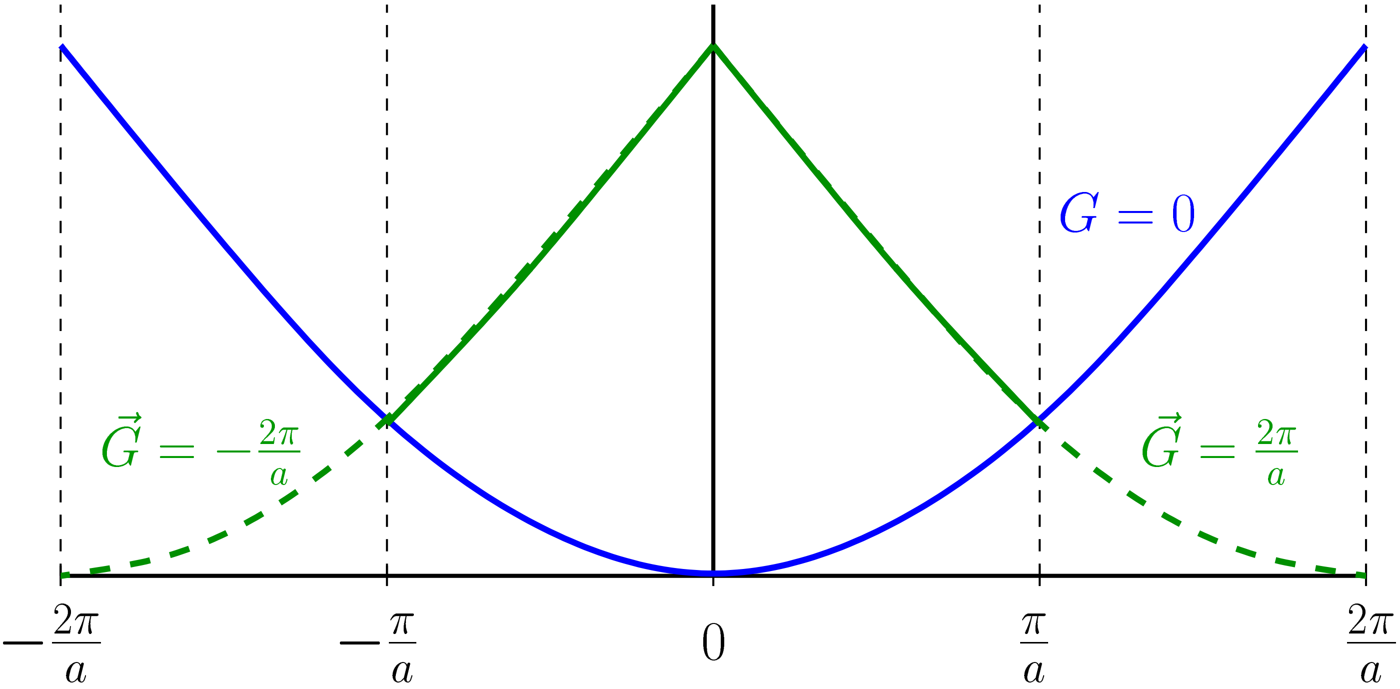

Figure 3.8: Band-structure of the empty lattice. Blue line: extended zone scheme, full green line: reduced zone scheme.

i) Extended zone scheme: here $E(\boldsymbol{k})$ is univocally defined for each $\boldsymbol{k}$-point, with $-\infty < k_i < \infty$, for $i = x, y, z$. In this case we just have the result for a free electron as anticipated above, but the convention is then, that $G = 0$, and, normalizing the plane wave for the volume V,

$$v(\boldsymbol{k} - \boldsymbol{G}) = \frac{1}{\sqrt{N}} \delta_{\boldsymbol{G},0} \, . \tag{3.30}$$

ii) Reduced zone scheme: here we consider the eigenvalues as given by (3.29) but with $\boldsymbol{k}$ restricted to the first Brillouin zone, so that for each value of $\boldsymbol{k}$ there is an infinite number of bands, each one corresponding to a different reciprocal lattice vector. The corresponding eigenfunctions are

$$v(\boldsymbol{k} - \boldsymbol{G}') = \frac{1}{\sqrt{N}} \delta_{\boldsymbol{G},\boldsymbol{G}'} \, . \tag{3.31}$$

Solutions for different reciprocal lattice vectors are degenerate at the boundary of the Brillouin zone and at the center ($\boldsymbol{k} = 0$).

A summary of the discussion above is given in Fig. (3.8), where the example corresponds to a one dimensional system.

b) First order. For the further discussion we concentrate on the reduced zone scheme. Then, the eigenfunctions in zero-th order are given by (3.31), such that eq. (3.27) becomes

$$\hookrightarrow (3.27) \rightarrow \left[\frac{|\, \boldsymbol{k} - \boldsymbol{G} \,|^2}{2m} - E(\boldsymbol{k}) \right] v(\boldsymbol{k} - \boldsymbol{G}) + V_0 \, v(\boldsymbol{k} - \boldsymbol{G}) = 0 \, , \tag{3.32}$$

where V_0 denotes the Fourier coefficient for $\boldsymbol{G} = 0$. This is just a constant

$$V_0 = \frac{1}{\sqrt{\Omega}} \int_\Omega \mathrm{d}^3x \, V(\boldsymbol{x}) \tag{3.33}$$

that corresponds to the average potential. The constant introduces only a shift of the energy scale, without physical consequences. For future convenience, let us shift the energy scale in such a way that $V_0 = 0$.

c) Second order. When calculating this contribution, we should recall the fact mentioned in *a.ii)*, that degeneracies can appear at particular values of $\boldsymbol{k}$. Let us first treat the case, where such degeneracies are absent, that is solutions for wavevectors $\boldsymbol{k}$ such that given $\boldsymbol{G}$,

$$\left| E^0_{\boldsymbol{G}}(\boldsymbol{k}) - E^0_{\boldsymbol{G}'}(\boldsymbol{k}) \right| \gg V \tag{3.34}$$

for all other reciprocal lattice vectors $\boldsymbol{G}'$. We examine then (3.27) for a given reciprocal lattice vector $\boldsymbol{G}$, and rewrite it as follows

$$\left[E(\boldsymbol{k}) - E^0_{\boldsymbol{G}}(\boldsymbol{k}) \right] v(\boldsymbol{k} - \boldsymbol{G}) = \sum_{\boldsymbol{G}'}{}' V_{\boldsymbol{G}'-\boldsymbol{G}} \, v(\boldsymbol{k} - \boldsymbol{G}') \, , \tag{3.35}$$

where the prime on the summation denotes the fact that $\boldsymbol{G}' \neq \boldsymbol{G}$, since we assume as discussed in *b*), that $V_0 = 0$. Next we discuss which contributions should enter in the rhs. of (3.35) in order to have a second order contribution in the energy. Since there is already a term of $\mathcal{O}(V)$, we may be tempted to use $v\left(\boldsymbol{k}-\boldsymbol{G}'\right)$ of zero-th order, but this leads back to the zero-th order result. We therefore iterate this equation once, using that

$$v\left(\boldsymbol{k}-\boldsymbol{G}'\right) = \frac{1}{E\left(\boldsymbol{k}\right) - E^0_{\boldsymbol{G}'}\left(\boldsymbol{k}\right)} \sum_{\boldsymbol{G}''}{}' V_{\boldsymbol{G}''-\boldsymbol{G}'}\, v\left(\boldsymbol{k}-\boldsymbol{G}''\right) \ , \tag{3.36}$$

and inserting it into (3.35), we have

$$\begin{aligned} &\left[E\left(\boldsymbol{k}\right) - E^0_{\boldsymbol{G}}\left(\boldsymbol{k}\right)\right] v\left(\boldsymbol{k}-\boldsymbol{G}\right) \\ &\quad = \sum_{\boldsymbol{G}'}{}' V_{\boldsymbol{G}'-\boldsymbol{G}} \frac{1}{E\left(\boldsymbol{k}\right) - E^0_{\boldsymbol{G}'}\left(\boldsymbol{k}\right)} \sum_{\boldsymbol{G}''}{}' V_{\boldsymbol{G}''-\boldsymbol{G}'}\, v\left(\boldsymbol{k}-\boldsymbol{G}''\right) \ , \end{aligned} \tag{3.37}$$

where, since we are already in second order in V, we can let $v\left(\boldsymbol{k}-\boldsymbol{G}''\right) \propto \delta_{\boldsymbol{G},\boldsymbol{G}''}$, having finally

$$E\left(\boldsymbol{k}\right) = E^0_{\boldsymbol{G}} + \sum_{\boldsymbol{G}'} \frac{\mid V_{\boldsymbol{G}'-\boldsymbol{G}} \mid^2}{E^0_{\boldsymbol{G}} - E^0_{\boldsymbol{G}'}} \ , \tag{3.38}$$

where in the denominator we replaced $E\left(\boldsymbol{k}\right)$ by $E^0_{\boldsymbol{G}}$ since that term is already of second order.

The perturbative calculation fails whenever $\mid E^0_{\boldsymbol{G}} - E^0_{\boldsymbol{G}'} \mid$ becomes of the order or smaller than $\mid V_{\boldsymbol{G}'-\boldsymbol{G}} \mid$. In particular it fails completely when

$$\begin{aligned} E^0_{\boldsymbol{G}} &= E^0_{\boldsymbol{G}'} \\ \hookrightarrow \left(\boldsymbol{k}-\boldsymbol{G}\right)^2 &= \left(\boldsymbol{k}-\boldsymbol{G}'\right)^2 \\ \hookrightarrow 2\left(\boldsymbol{k}-\boldsymbol{G}'\right)\cdot\left(\boldsymbol{G}-\boldsymbol{G}'\right) &= \left(\boldsymbol{G}-\boldsymbol{G}'\right)^2 \ , \end{aligned} \tag{3.39}$$

where to go from the second to the third line we used that $\boldsymbol{G}^2 - \boldsymbol{G}'^2 = \left(\boldsymbol{G}-\boldsymbol{G}'\right)^2 + 2\boldsymbol{G}'\cdot\left(\boldsymbol{G}-\boldsymbol{G}'\right)$. All this manipulation shows that the vector $\boldsymbol{k}-\boldsymbol{G}'$ fulfills the Bragg condition, that is the condition for Bragg scattering as in the case of X-rays. We recall that this condition is fulfilled when the wavevector lies on the bisector plane plane of a reciprocal lattice vector. This can be easily seen to be the case by setting $\boldsymbol{G}' = 0$ in eq. (3.39), that results in

$$\mid \boldsymbol{k} \mid \ \cos\theta = \frac{\mid \boldsymbol{G} \mid}{2} \tag{3.40}$$

as shown in Fig. 3.9.

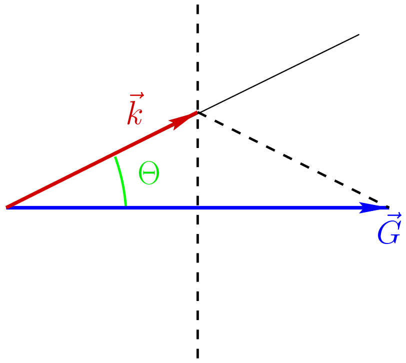

Figure 3.9: Sketch of wavevectors fulfilling the Bragg condition.

d) Case of degenerate levels. Here we consider the case where two free electron levels are degenerate and far apart from the others, as shown in Fig. 3.8. If the states correspond to $\boldsymbol{k}+\boldsymbol{G}$ and $\boldsymbol{k}+\boldsymbol{G}'$, the Hamiltonian in this subspace can be written as follows.

$$\tilde{H} = \begin{bmatrix} E^0_{\boldsymbol{G}} & V_{\boldsymbol{G}-\boldsymbol{G}'} \\ V_{\boldsymbol{G}'-\boldsymbol{G}} & E^0_{\boldsymbol{G}'} \end{bmatrix} \tag{3.41}$$

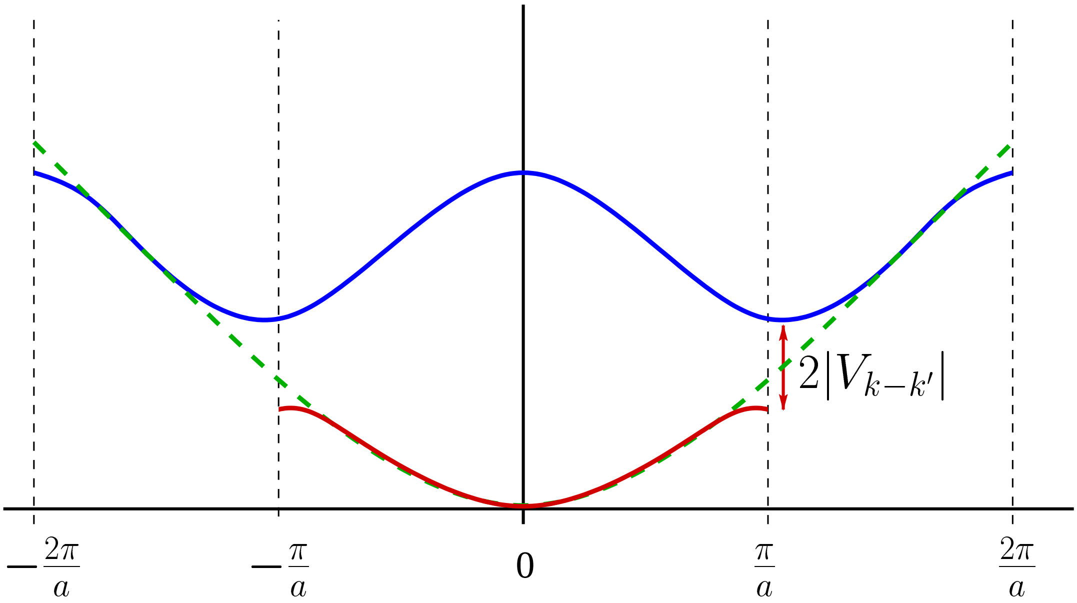

Figure 3.10: Opening of band gaps due to Bragg scattering.

The eigenvalues are

$$E_{1,2} = \frac{1}{2}\left[E^0_{\boldsymbol{G}} + E^0_{\boldsymbol{G}'} \pm \frac{1}{2}\sqrt{\left(E^0_{\boldsymbol{G}} - E^0_{\boldsymbol{G}'}\right)^2 + 4 \mid V_{\boldsymbol{G}-\boldsymbol{G}'} \mid^2}\right] . \quad (3.42)$$

As shown in Fig. 3.10, band gaps appear at the crossings of the free electron dispersion as a consequence of the scattering by the periodic potential. The scattering is maximal when the Bragg condition is fulfilled. This happens at the zone boundary and at the center of the Brillouin zone.

3.3 The tight-binding approximation

Here we consider the opposite case to the one in the precedent chapter. We assume here that the electronic wavefunction is rather localized around the atomic positions, such that the atomic orbitals give a good approximation to represent the electronic states. Let $\varphi_n(\boldsymbol{x} - \boldsymbol{R}_i)$ be the n-th atomic level at the lattice site i. With it, we can construct a Bloch wavefunction

$$\psi_{n\boldsymbol{k}}(\boldsymbol{x}) = \sum_i \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_i)\, \varphi_n(\boldsymbol{x} - \boldsymbol{R}_i) . \quad (3.43)$$

In order to see that this is indeed a Bloch wavefunction, we translate it by a lattice vector

$$\begin{aligned} \psi_{n\boldsymbol{k}}(\boldsymbol{x} + \boldsymbol{R}_j) &= \sum_i \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_i)\, \varphi_n(\boldsymbol{x} + \underbrace{\boldsymbol{R}_j - \boldsymbol{R}_i}_{\equiv -\boldsymbol{R}_\ell}) \\ &= \sum_\ell \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_j)\, \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_\ell)\, \varphi_n(\boldsymbol{x} - \boldsymbol{R}_\ell) \\ &= \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_j)\, \psi_{n\boldsymbol{k}}(\boldsymbol{x}) . \quad (3.44) \end{aligned}$$

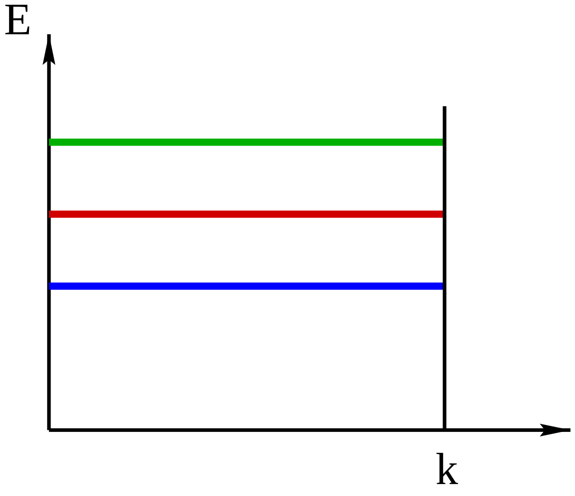

Figure 3.11: Dispersion for local levels.

In the case of extreme localization, the Hamiltonian is just given by the sum of local Hamiltonians

$$H = \sum_i H_{i\,atomic} \tag{3.45}$$

Applying the Hamiltonian to a local orbital gives just the eigenenergy of that orbital

$$H \varphi_n (\boldsymbol{x} - \boldsymbol{R}_i) = H_{i\,atomic}\, \varphi_n (\boldsymbol{x} - \boldsymbol{R}_i) = E_n \varphi_n (\boldsymbol{x} - \boldsymbol{R}_i) \ . \tag{3.46}$$

The same happens when the Hamiltonian is applied on a Bloch superposition of local orbitals

$$H\, \psi_{n\boldsymbol{k}} (\boldsymbol{x}) = \sum_i \exp (i\boldsymbol{k} \cdot \boldsymbol{R}_i)\ E_n\, \varphi_n (\boldsymbol{x} - \boldsymbol{R}_i) = E_n\, \psi_{n\boldsymbol{k}} (\boldsymbol{x}) \ . \tag{3.47}$$

This means that in the case of extreme localization, the eigenenergies have no dispersion, as depicted in Fig. 3.11. As the localization of orbitals decreases, the degeneracy is lifted by the overlap of the wavefunctions, leading to a situation as sketched in Fig. 3.12. Here r_0 corresponds to the radius of the atomic wavefunction and a to the lattice constant.

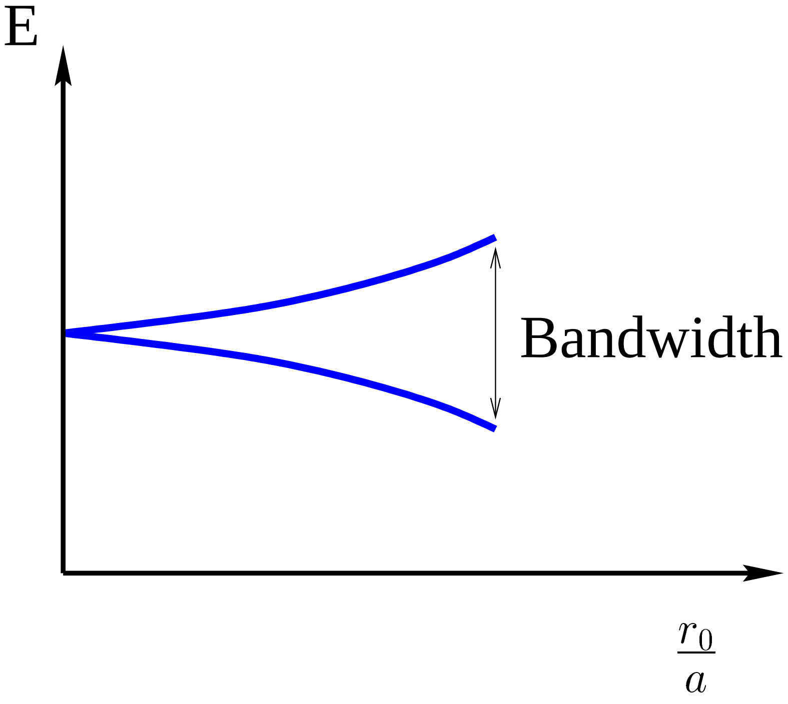

Figure 3.12: Broadening of levels as the overlap between neighboring atoms increases.

3.3.1 Tight-binding method for an ‘s-band’

We consider here the case of a single kind of atomic orbitals and for simplicity we choose them to be s-orbitals. We denote the corresponding state by $\mid i >$, such that

$$< \boldsymbol{x} \mid i >= \varphi (\boldsymbol{x} - \boldsymbol{R}_i) \ . \tag{3.48}$$

In this subspace, the matrix elements of the Hamiltonian are denoted as follows

$$< i \mid H \mid j >= H\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right) \ . \tag{3.49}$$

Furthermore, the overlap of the orbitals is given by

$$< i \mid j >= S\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right) \ , \tag{3.50}$$

and the normalization leads to $< i \mid i >= S(0) = 1$. Finally, the Bloch states look as follows

$$\mid \boldsymbol{k} >= \sum_i \exp\left(i\boldsymbol{k}\cdot\boldsymbol{R}_i\right) \mid i > \ . \tag{3.51}$$

Once we discuss the notation, we can consider the eigenvalues of the Hamiltonian in the considered subspace.

$$H \mid \boldsymbol{k} >= E\left(\boldsymbol{k}\right) \mid \boldsymbol{k} > \tag{3.52}$$

From the equation above, we have

$$\begin{aligned} E\left(\boldsymbol{k}\right) &= \frac{< \boldsymbol{k} \mid H \mid \boldsymbol{k} >}{< \boldsymbol{k} \mid \boldsymbol{k} >} \\ &= \frac{\sum_{i,j} \exp\left[i\boldsymbol{k}\cdot\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)\right] \overbrace{< i \mid H \mid j >}^{(3.49)}}{\sum_{i,j} \exp\left[i\boldsymbol{k}\cdot\left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)\right] \underbrace{< i \mid j >}_{(3.50)}} \\ &= \frac{N\sum_\ell \exp\left(i\boldsymbol{k}\cdot\boldsymbol{R}_\ell\right) \ H\left(\boldsymbol{R}_\ell\right)}{N\sum_\ell \exp\left(i\boldsymbol{k}\cdot\boldsymbol{R}_\ell\right) \ S\left(\boldsymbol{R}_\ell\right)} = \frac{\tilde{H}\left(\boldsymbol{k}\right)}{\tilde{S}\left(\boldsymbol{k}\right)} \ . \end{aligned} \tag{3.53}$$

Therefore, in order to calculate the energy eigenvalues in the tight-binding approximation, it is necessary to calculate the matrix elements of the Hamiltonian and of the overlap matrix, and then Fourier transform them.

Let us consider as an example a one-dimensional case with matrix elements and overlap of the orbitals only up to the next nearest neighbors.

$$\left.\begin{array}{rcll} < i \mid H \mid j > &=& 0 & \text{for} \quad \mid \boldsymbol{R}_i - \boldsymbol{R}_j \mid \geq 2a \\ < i \mid j > &=& 0 & \text{for} \quad \mid \boldsymbol{R}_i - \boldsymbol{R}_j \mid \geq 2a \\ < i \mid H \mid i > &=& E_0 & \\ < i \mid H \mid i \pm 1 > &=& -t & \\ < i \mid i > &=& 1 & \\ < i \mid i \pm 1 > &=& \delta & \end{array}\right\} \tag{3.54}$$

The Fourier sums are easily calculated

$$\tilde{H}\left(\boldsymbol{k}\right) = E_0 - t\left(\mathrm{e}^{ika} + \mathrm{e}^{-ika}\right) \tag{3.55}$$

$$\tilde{S}\left(\boldsymbol{k}\right) = 1 + \delta\left(\mathrm{e}^{ika} + \mathrm{e}^{-ika}\right) \tag{3.56}$$

Since taking into account the overlap merely redefines the off-diagonal matrix elements of H in the case that $\delta \ll 1$, it is generally disregarded, leading to

$$E(\boldsymbol{k}) \;=\; E_0 - 2t\cos ka\;. \tag{3.57}$$

The band-width in one dimension for nearest neighbor coupling is then $4t$.

3.3.2 Wannier functions

From the discussion in the previous section, it is seen that it would be in general advantageous to have at our disposition localized wavefunctions with vanishing overlap $< i \mid j >$, since this would allow us to disregard the overlap matrix S. It will be shown in this last section, that this is always possible, such that the Bloch wavefunctions can always be expressed in the form given in eq. (3.43), but with wavefunctions $\varphi(\boldsymbol{x}-\boldsymbol{R}_i)$ that constitute a localized basis.

In order to introduce the Wannier functions, let us recall the fact that Bloch wavefunctions are periodic in reciprocal space, i.e.

$$\psi_{n\boldsymbol{k}} = \psi_{n\boldsymbol{k}+\boldsymbol{G}}\;. \tag{3.58}$$

In fact, this was the reason to restrict $\boldsymbol{k}$ to the first Brillouin zone. We can then use the prescription given in (1.14), but with reversed roles, i.e. $\boldsymbol{x} \to \boldsymbol{k}$, $\Omega \to \Omega_B$, and $\boldsymbol{g} = \boldsymbol{R}$.

$$\begin{aligned} \tilde{\varphi}_{n\boldsymbol{R}}(\boldsymbol{x}) &= \frac{1}{\sqrt{\Omega_B}}\int_{\Omega_B} \mathrm{d}\boldsymbol{k}\,\psi_{n\boldsymbol{k}}(\boldsymbol{x})\exp(-i\boldsymbol{R}\cdot\boldsymbol{k}) \\ &= \underbrace{\sqrt{\frac{\Omega}{(2\pi)^3}\frac{(2\pi)^3}{V}}}_{\sqrt{\frac{(2\pi)^3}{\Omega}\frac{1}{N}}} \sum_{\boldsymbol{k}\,in\,BZ} \psi_{n\boldsymbol{k}}(\boldsymbol{x})\exp(-i\boldsymbol{R}\cdot\boldsymbol{k})\;. \end{aligned} \tag{3.59}$$

From the fundamental property (3.2), we can set in the expression above

$$\psi_{n\boldsymbol{k}}(\boldsymbol{x})\,\exp(-i\boldsymbol{R}\cdot\boldsymbol{k}) = \psi_{n\boldsymbol{k}}(\boldsymbol{x}-\boldsymbol{R})\;, \tag{3.60}$$

showing that $\tilde{\varphi}_{n\boldsymbol{R}}(\boldsymbol{x}) = \tilde{\varphi}_n(\boldsymbol{x}-\boldsymbol{R})$. Defining

$$\varphi_n(\boldsymbol{x}-\boldsymbol{R}) \equiv \sqrt{\frac{V}{(2\pi)^3}}\,\tilde{\varphi}_n(\boldsymbol{x}-\boldsymbol{R})\;, \tag{3.61}$$

we have a Wannier function as a Fourier transform of a Bloch function

$$\varphi_n(\boldsymbol{x}-\boldsymbol{R}) \;=\; \frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}\,in\,BZ} \psi_{n\boldsymbol{k}}(\boldsymbol{x})\,\exp(-i\boldsymbol{R}\cdot\boldsymbol{k})\;, \tag{3.62}$$

and also

$$\psi_{n\boldsymbol{k}}(\boldsymbol{x}) \;=\; \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}} \varphi_n(\boldsymbol{x}-\boldsymbol{R})\,\exp(i\boldsymbol{R}\cdot\boldsymbol{k})\;. \tag{3.63}$$

The localization of Wannier functions can be seen in a simple case. Let us take for simplicity free electrons in one dimension.

$$\begin{aligned}\psi_k &= \frac{1}{\sqrt{L}}\exp(ikx)\\ \hookrightarrow \varphi(x-R) &= \frac{1}{\sqrt{N}}\frac{L}{2\pi}\frac{1}{\sqrt{L}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\mathrm{d}k\ \exp\left[ik(x-R)\right]\\ &= \frac{\sqrt{a}}{\pi}\frac{\sin\left[\frac{\pi}{a}(x-R_i)\right]}{x-R_i}\ . \end{aligned} \tag{3.64}$$

Figure 3.13 shows that the largest amplitude is centered around zero. However, as shown by eq. 3.64, the wavefunction decays as a power law, such that it is actually not localized.

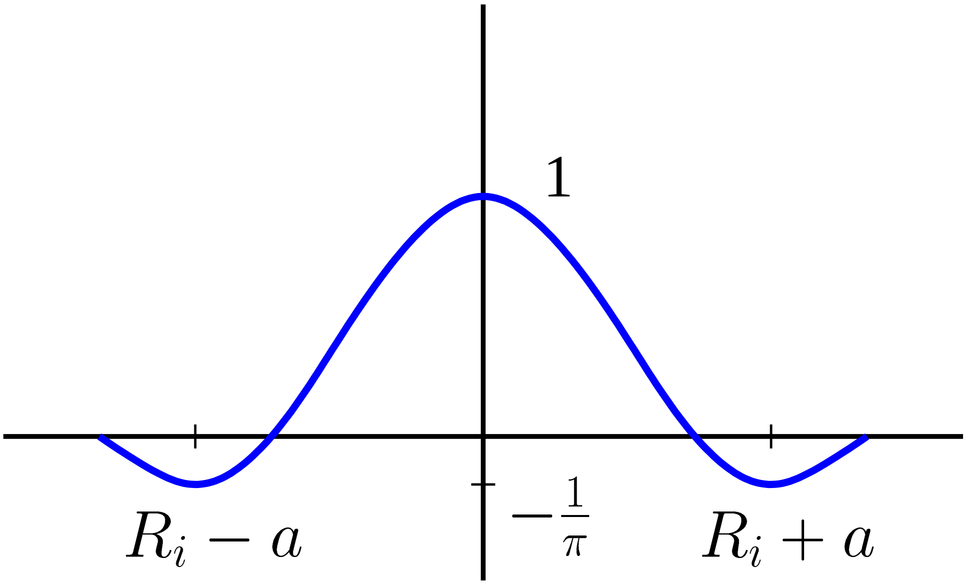

Figure 3.13: Sketch of the Wannier function in one dimension for a free electron.

Finally, we consider the overlap of two Wannier functions. For this, we just use (3.62):

$$\begin{aligned}&< \varphi_n(\boldsymbol{x}-\boldsymbol{R}_i) \mid \varphi_m(\boldsymbol{x}-\boldsymbol{R}_j) >\\ &\qquad = \frac{1}{N}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2}\exp\left[i\left(\boldsymbol{R}_i\cdot\boldsymbol{k}_1-\boldsymbol{R}_j\cdot\boldsymbol{k}_2\right)\right]\underbrace{< \psi_{n\boldsymbol{k}_1} \mid \psi_{m\boldsymbol{k}_2} >}_{\delta_{nm}\delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}}\\ &\qquad = \delta_{nm}\delta_{ij}\ . \end{aligned} \tag{3.65}$$

Therefore, Wannier functions constitute a complete set of orthonormal wavefunctions, where each one can be assigned to a given lattice site.