

# Bloch's Theorem and Toy Models

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## Contents

<b>1</b>	<b>Definitions</b>	<b>1</b>
<b>2</b>	<b>Lattice definitions</b>	<b>2</b>
<b>3</b>	<b>Bloch's theorem</b>	<b>2</b>
<b>4</b>	<b>Schrodinger equation for Bloch waves</b>	<b>5</b>
<b>5</b>	<b>Nearly free electron model</b>	<b>8</b>
<b>6</b>	<b>Wannier Functions</b>	<b>11</b>
<b>7</b>	<b>Tight binding model</b>	<b>12</b>

## 1 Definitions

$a$	Bravais lattice basis vector
$\mathbf{R}$	Bravais lattice vector
$b_i$	reciprocal lattice basis vector
$\mathbf{G}$	reciprocal lattice vector
$\mathbf{k}$	Bloch k-vector restricted to the first Brillouin zone
$U_{\mathbf{G}}$	Fourier coefficient of the periodic potential $U(\mathbf{r})$
$c_{(\mathbf{k}-\mathbf{G})}$	Fourier coefficient of the Bloch wave function $\psi_{\mathbf{k}}(\mathbf{r})$ ; see (4.4)
$\mathbf{K}$	or $\mathbf{K}'$ or $\mathbf{K}_i$ a particular reciprocal lattice vector
$\psi_{n,\mathbf{k}}$	Bloch waves
$\phi_n(\mathbf{r}-\mathbf{R})$	Wannier function
$\psi_i(\mathbf{r}-\mathbf{R})$	an atomic orbital on lattice site $\mathbf{R}$

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## 2 Lattice definitions

The Bravais lattice is the set of all points lattice points generated by discrete translations by a set of primitive lattice vectors  $\mathbf{a}_i$ . The set of direct lattice points  $\mathbf{R}$  is defined

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad \text{where } n_i \in \mathbb{Z} \quad (2.1)$$

The lattice has three-dimensional spatial periodicity, and so we may expect that many lattice properties (e.g. the potential electrons in the solid experience excluding electron-electron interactions) to have a similar periodicity and a Fourier representation. For some lattice-periodic function  $f(\mathbf{r})$

$$f(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad \text{where } e^{\mathbf{G}\cdot\mathbf{R}} = 1 \quad (2.2)$$

Notice that if both  $e^{\mathbf{b}_1\cdot\mathbf{R}} = e^{\mathbf{b}_2\cdot\mathbf{R}} = 1$ , then  $e^{(m_1\mathbf{b}_1+m_2\mathbf{b}_2)\cdot\mathbf{R}} = 1$  where  $m_i$  are integers. Therefore, the set of reciprocal lattice vectors  $\mathbf{G}$  also form a Bravais lattice

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \quad \text{where } m_i \in \mathbb{Z} \quad (2.3)$$

We can relate  $\mathbf{a}_i$  and  $\mathbf{b}_j$  by requiring that<sup>1</sup>

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \quad (2.4)$$

We can check that the expression above is satisfied by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.5)$$

In reciprocal space, the Wigner-Seitz primitive cell of reciprocal lattice is called the first Brillouin zone and becomes relevant in our development of electronic bands.

## 3 Bloch's theorem

We consider a defect-free, infinite crystal to consist of stationary ions arranged in a periodic lattice and electrons that move through the potential generated by the ions  $U(\mathbf{r})$ . Ignoring electron-electron interactions (independent electrons approximation), we expect the potential to be periodic in the Bravais lattice

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \quad (3.1)$$

The Hamiltonian of an electron<sup>2</sup> in the crystal has the form

$$H = \frac{p^2}{2m} + U(\mathbf{r}) \quad (3.2)$$

Does the translation symmetry of the Hamiltonian provide constraints on the electronic wave function? Yes! To see this, first we define the translation operator. For any function  $f(\mathbf{r})$

$$T(\mathbf{R})f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}) \quad (3.3)$$

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<sup>1</sup>To check, substitute this into  $e^{i\mathbf{G}\cdot\mathbf{R}}$ .

<sup>2</sup>Note: we need only consider the wave function of a single electron rather than the full many-body wave function because of the independent electrons approximation.

Notice that by the definition above

$$T(\mathbf{R})T(\mathbf{R}') = T(\mathbf{R}')T(\mathbf{R}) = T(\mathbf{R} + \mathbf{R}') \quad (3.4)$$

Let  $\psi(\mathbf{r})$  be an eigenstate of  $T(\mathbf{R})$  with eigenvalue  $c(\mathbf{R})$

$$T(\mathbf{R})\psi(\mathbf{r}) = c(\mathbf{R})\psi(\mathbf{r}) \quad (3.5)$$

Then from (3.4)

$$c(\mathbf{R} + \mathbf{R}') = c(\mathbf{R})c(\mathbf{R}') \quad (3.6)$$

This is also a property of exponential functions. Without loss of generality, we can rewrite  $c(\mathbf{R})$  as,

$$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \quad \text{where } \mathbf{k} \in \mathbb{C}^3 \quad (3.7)$$

Therefore

$$T(\mathbf{R})\psi(\mathbf{r}) = c(\mathbf{R})\psi(\mathbf{r}) \quad (3.8)$$

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}) \quad (3.9)$$

Since Hamiltonian commutes with  $T(\mathbf{R})$ <sup>3</sup>, there exists a simultaneous eigenbasis of  $H$  and  $T(\mathbf{R})$ . Hence any solution to the Schrodinger equation  $\psi(\mathbf{r})$  must obey (3.9).

However the wave vector  $\mathbf{k}$  in (3.9) could be anything (e.g. it doesn't even have to be real!). To further constrain  $\mathbf{k}$ , we impose boundary conditions. We imagine that a physical crystal consists of  $N_1N_2N_3 = N$  lattice sites where  $N$  is very large. Rather than imposing a "hard" boundary condition, we impose periodic boundary condition on the wave function (Born-Von Karman boundary condition)

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}) \quad (3.10)$$

In one-dimension this corresponds to a chain of  $N$  atoms arranged in a closed loop. Applying the condition we found above (3.9) to (3.10), we find

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = e^{i\mathbf{k}\cdot(N_i\mathbf{a}_i)}\psi(\mathbf{r}) = \psi(\mathbf{r}) \quad (3.11)$$

Therefore,

$$e^{i\mathbf{k}\cdot(N_i\mathbf{a}_i)} = e^{iN_i(\mathbf{k}\cdot\mathbf{a}_i)} = 1 \quad (3.12)$$

The expression above is satisfied if and only if  $N_i(\mathbf{k}\cdot\mathbf{a}_i)$  is a multiple of  $2\pi$ . Recalling (2.4), this holds if and only if  $\mathbf{k} = (m_i/N_i)\mathbf{b}_i$  where  $m_i$  is an integer. Putting everything together, Bloch's theorem says that if  $\psi_{\mathbf{k}}(\mathbf{r})$  is an eigenstate of the Hamiltonian for an electron in a crystal lattice with periodic boundary conditions, then

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}) \quad \text{where } \mathbf{k} = \frac{m_i}{N_i}\mathbf{b}_i \text{ and } m_i \in \mathbb{Z} \quad (3.13)$$

Some remarks on Bloch's theorem:

- From Bloch's theorem, we know that  $|\psi_{\mathbf{k}}(\mathbf{r})|$  is periodic. Define  $u_{\mathbf{k}}(\mathbf{r})$  such that  $|\psi_{\mathbf{k}}(\mathbf{r})|^2 = |\psi_{\mathbf{k}}(\mathbf{r})|^2$ , then we see that  $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$  satisfies Bloch's theorem. Therefore, an alternative form of Bloch's theorem is that if  $\psi_{\mathbf{k}}(\mathbf{r})$  is an eigenstate of the Hamiltonian for an electron in a crystal lattice with periodic boundary conditions, then

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \quad \text{where } u_{\mathbf{k}}(\mathbf{r}) \text{ is periodic in } \mathbf{R} \quad (3.14)$$

<sup>3</sup>The Hamiltonian is invariant under translation operations, or  $T(\mathbf{R})H(\mathbf{r})\psi(\mathbf{r}) = H(\mathbf{r} + \mathbf{R})\psi(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})\psi(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})T(\mathbf{R})\psi(\mathbf{r})$

- The wave vector  $\mathbf{k}$  does not uniquely specify a Bloch wave  $\psi_{\mathbf{k}}(\mathbf{r})$  because for any  $\mathbf{k}$  in the first Brillouin zone and  $\mathbf{G}$  a reciprocal lattice vector

$$\begin{aligned}\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) &= e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}) \\ \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r} + \mathbf{R}) &= e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}}\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})\end{aligned}\quad (3.15)$$

Therefore, we can constrain  $\mathbf{k}$  to be in the first Brillouin zone without loss of generality.

$$\mathbf{k} \in \text{first Brillouin zone}$$

With this, we can also calculate the number of distinct  $\mathbf{k}$ . The volume of the first Brillouin zone is  $V_{\text{BZ}} = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$  and from (3.13) the reciprocal-space volume occupied by a single  $\mathbf{k}$  is  $(\mathbf{b}_1/N_1) \cdot (\mathbf{b}_2/N_2) \times (\mathbf{b}_3/N_3) = V_{\text{BZ}}/N$ . Therefore

$$\# \mathbf{k} \text{ in the first Brillouin zone} = N \quad (3.16)$$

- Plugging the Bloch wave into Schrodinger's equation,

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \left( e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \right) = \varepsilon_{\mathbf{k}} \left( e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \right) \quad (3.17)$$

$$\underbrace{\left[ \frac{\hbar^2}{2m} (k^2 - \nabla^2) + U(\mathbf{r}) \right]}_{H_{\text{eff}}} u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) \quad (3.18)$$

There are infinitely many solutions for  $u_{\mathbf{k}}(\mathbf{r})$  because  $\varepsilon_{\mathbf{k}}$  can be arbitrarily large. Furthermore, using the Bloch wave require imposing a periodic (Born-Von Karman) boundary condition

$$u_{\mathbf{k}}(\mathbf{r} + N_i \mathbf{a}_i) \quad (3.19)$$

and so we expect the set of solutions for  $u_{\mathbf{k}}(\mathbf{r})$  to be discrete, which we will label with the index  $n$ .

$$H_{\text{eff}} u_{n,\mathbf{k}} = \varepsilon_{n,\mathbf{k}} u_{n,\mathbf{k}} \quad (3.20)$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \quad (3.21)$$

Plotting the dispersion ( $\varepsilon_{n,\mathbf{k}}$  versus  $\mathbf{k}$ ), we find distinct bands of energy, each corresponding to an  $n$ . By the Pauli exclusion principle, at most two electrons<sup>4</sup> can have the same wave vector  $\mathbf{k}$ . Also recall from the previous remark that there are a total of  $N$  distinct  $\mathbf{k}$ <sup>5</sup>. Therefore, there can be at most  $2N$  electrons in a band.

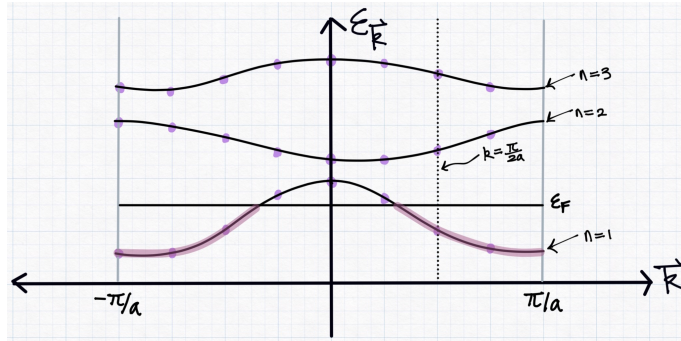


Figure 1: Example electronic band structure.

<sup>4</sup>Electrons have spin-1/2.

<sup>5</sup>That is,  $\mathbf{k}$  in the first Brillouin zone.

## 4 Schrodinger equation for Bloch waves

In the previous remark, we started to write out Schrodinger's equation for Bloch waves. Here, we will go through the algebra more thoroughly. The Schrodinger equation has the form

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) \quad (4.1)$$

Notice that we can make two Fourier expansions:

1.  $u_{\mathbf{k}}(\mathbf{r})$  is periodic in  $\mathbf{R}$ . Therefore

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \\ &= e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \\ &= \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \end{aligned} \quad (4.2)$$

where

$$\begin{aligned} c_{\mathbf{k},\mathbf{G}} &= \int_{\langle \mathbf{r} \rangle} d^3\mathbf{r} u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} \\ &= \int_{\langle \mathbf{r} \rangle} d^3\mathbf{r} (\psi_{\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}) e^{i\mathbf{G}\cdot\mathbf{r}} \\ &= \int_{\langle \mathbf{r} \rangle} d^3\mathbf{r} \psi_{\mathbf{k}}(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \\ &\equiv c_{\mathbf{k}-\mathbf{G}} \end{aligned} \quad (4.3)$$

Putting everything together,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \quad \text{where} \quad c_{\mathbf{k}-\mathbf{G}} = \int_{\langle \mathbf{r} \rangle} d^3\mathbf{r} \psi_{\mathbf{k}}(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \quad (4.4)$$

2. The potential  $U(\mathbf{r})$  is also periodic in  $\mathbf{R}$ . Therefore

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \quad \text{where} \quad U_{\mathbf{G}} = \int_{\langle \mathbf{r} \rangle} d^3\mathbf{r} U(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (4.5)$$

Since we are free to define  $U(\mathbf{r})$  up to a constant. We can always add a constant energy such that  $U_{\mathbf{0}} = 0$ . Furthermore, since  $U(\mathbf{r})$  is real,  $U_{\mathbf{k}}^* = U_{-\mathbf{k}}$ .

$$U_{\mathbf{0}} = 0, \quad U_{\mathbf{k}}^* = U_{-\mathbf{k}} \quad (4.6)$$

Now, we plug everything into Schrodinger's equation

$$\frac{\hbar^2}{2m} \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} |\mathbf{k} - \mathbf{G}|^2 e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \left( \sum_{\mathbf{G}'} U_{\mathbf{G}'} e^{-i\mathbf{G}'\cdot\mathbf{r}} \right) \left( \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \right) = \varepsilon_{\mathbf{k}} \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \quad (4.7)$$

$$\sum_{\mathbf{G}} \left[ \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon_{\mathbf{k}} \right] c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G}, \mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = 0 \quad (4.8)$$

To simplify the second term in the expression above, we define  $\mathbf{G}'' = \mathbf{G} + \mathbf{G}'$ . Then

$$\begin{aligned} \sum_{\mathbf{G}, \mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} &= \sum_{\mathbf{G}', \mathbf{G}''} U_{\mathbf{G}'} c_{\mathbf{k}+\mathbf{G}'-\mathbf{G}''} e^{i(\mathbf{k}-\mathbf{G}'')\cdot\mathbf{r}} \\ &= \sum_{\mathbf{G}''} \left[ e^{i(\mathbf{k}-\mathbf{G}'')\cdot\mathbf{r}} \sum_{\mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k}+\mathbf{G}'-\mathbf{G}''} \right] \\ (\text{redefine } \mathbf{G}'' \rightarrow \mathbf{G}) &= \sum_{\mathbf{G}} \left[ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \sum_{\mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k}-\mathbf{G}+\mathbf{G}'} \right] \\ (\text{define } \mathbf{G}'' = \mathbf{G} - \mathbf{G}') &= \sum_{\mathbf{G}} \left[ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \sum_{\mathbf{G}''} U_{(\mathbf{G}-\mathbf{G}'')} c_{(\mathbf{k}-\mathbf{G}'')} \right] \\ (\text{redefine } \mathbf{G}'' \rightarrow \mathbf{G}') &= \sum_{\mathbf{G}} \left[ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \sum_{\mathbf{G}'} U_{(\mathbf{G}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \right] \end{aligned} \quad (4.9)$$

Substituting this back into (4.8)

$$\sum_{\mathbf{G}} \left[ \left( \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon_{\mathbf{k}} \right) c_{(\mathbf{k}-\mathbf{G})} + \sum_{\mathbf{G}'} U_{(\mathbf{G}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \right] e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = 0 \quad (4.10)$$

For each  $\mathbf{G}$ , the term in the square bracket must vanish. So

$$\underbrace{\left( \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon_{\mathbf{k}} \right)}_{\varepsilon_{(\mathbf{k}-\mathbf{G})}^0} c_{(\mathbf{k}-\mathbf{G})} + \sum_{\mathbf{G}'} U_{(\mathbf{G}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} = 0 \quad \text{for fixed } \mathbf{k} \text{ and all } \mathbf{G} \quad (4.11)$$

We find that for a particular Bloch wave with wave vector  $\mathbf{k}$ , in a periodic potential, the Schrodinger equation becomes a set of coupled linear equations for  $c_{(\mathbf{k}-\mathbf{G})}$ . Note that  $\mathbf{G}$  is a reciprocal lattice vector not constrained to the first Brillouin zone!

Some remarks:

- This system of equations (4.11) is underdetermined because  $\varepsilon_{\mathbf{k}}$  is an additional unknown. We expect there to be a discrete and infinite set of  $\varepsilon_{\mathbf{k}}$  for which we can find  $c_{(\mathbf{k}-\mathbf{G})}$  that satisfies the coupled equations above. This set of eigenenergies  $\{\varepsilon_{n,\mathbf{k}}\}$  precisely correspond to the bands described in the previous section and each  $\varepsilon_{n,\mathbf{k}}$  yields a corresponding set of  $\{c_{n,(\mathbf{k}-\mathbf{G})}\}$  with which we can construct  $\psi_{n,\mathbf{k}}$  via (4.4).
- We can write (4.11) in matrix form; recalling  $U_0 = 0$  (4.6)

$$\begin{pmatrix} \varepsilon_{(\mathbf{k}-\mathbf{G}_0)}^0 - \varepsilon_{\mathbf{k}} & U_{(\mathbf{G}_0-\mathbf{G}_1)} & U_{(\mathbf{G}_0-\mathbf{G}_2)} & \cdots \\ U_{(\mathbf{G}_1-\mathbf{G}_0)} & \varepsilon_{(\mathbf{k}-\mathbf{G}_1)}^0 - \varepsilon_{\mathbf{k}} & U_{(\mathbf{G}_1-\mathbf{G}_2)} & \\ U_{(\mathbf{G}_2-\mathbf{G}_0)} & U_{(\mathbf{G}_2-\mathbf{G}_1)} & \varepsilon_{(\mathbf{k}-\mathbf{G}_2)}^0 - \varepsilon_{\mathbf{k}} & \\ \vdots & & & \ddots \end{pmatrix} \begin{pmatrix} c_{(\mathbf{k}-\mathbf{G}_0)} \\ c_{(\mathbf{k}-\mathbf{G}_1)} \\ c_{(\mathbf{k}-\mathbf{G}_2)} \\ \vdots \end{pmatrix} = 0 \quad (4.12)$$

- Notice that we have not made any approximations. If we knew  $U(\mathbf{r})$ , we could use (4.6) to find all of the  $U_{\mathbf{G}}$ <sup>6</sup>, then numerically solve (4.11) to find the bands structure  $\{\varepsilon_{n,\mathbf{k}}\}$  and corresponding Bloch waves  $\{c_{n,(\mathbf{k}-\mathbf{G})}\}$ .
- As a sanity check, let's examine (4.11) in the limiting case of the completely free electron:  $U(\mathbf{r}) = 0$ . Here,  $U_{\mathbf{G}} = 0$  for all  $\mathbf{G}$ , so

$$\left(\varepsilon_{(\mathbf{k}-\mathbf{G})}^0 - \varepsilon_{\mathbf{k}}\right) c_{(\mathbf{k}-\mathbf{G})} = 0 \quad (4.13)$$

To be explicit, there is no implied summation over  $(\mathbf{k} - \mathbf{G})$  on the LHS. Hence, for each  $\mathbf{G}$ , the expression above holds independently.

It must be true that at least one  $c_{\mathbf{k}-\mathbf{G}}$  is non-zero; otherwise  $\psi_{\mathbf{k}}(\mathbf{r}) = 0$ . Let  $\mathbf{K} \in \{\mathbf{G}\}$  and  $\mathbf{K}' \in \{\mathbf{G}\} \setminus \mathbf{K}$ , then

$$c_{\mathbf{k}-\mathbf{K}} = 0 \quad \text{which implies} \quad \varepsilon_{\mathbf{k}} = \varepsilon_{(\mathbf{k}-\mathbf{K})}^0 \quad (4.14)$$

Notice that  $\varepsilon_{\mathbf{k}}$  does not depend on  $\mathbf{G}$ . Therefore if  $\varepsilon_{\mathbf{k}}$  is

1. Non-degenerate<sup>7</sup>: then

$$\varepsilon_{(\mathbf{k}-\mathbf{K}') }^0 - \varepsilon_{\mathbf{k}} \neq 0 \quad \text{which implies} \quad c_{(\mathbf{k}-\mathbf{K}')} = 0 \quad (4.15)$$

From (4.4), this yields a plane wave solution

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2, \quad \psi_{\mathbf{k}}(\mathbf{r}) \propto e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} \quad (4.16)$$

2. Degenerate<sup>8</sup>: then let's first define  $\mathbf{K} = \mathbf{K}_1$  and  $\{\mathbf{K}_1, \dots, \mathbf{K}_m\}$  to be the set of all reciprocal lattice vectors for which  $\varepsilon_{\mathbf{k}} = \varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0$ . Furthermore, redefine  $\mathbf{K}' \in \{\mathbf{G}\} \setminus \{\mathbf{K}_i\}$ . It remains true that

$$\varepsilon_{(\mathbf{k}-\mathbf{K}') }^0 - \varepsilon_{\mathbf{k}} \neq 0 \quad \text{which implies} \quad c_{(\mathbf{k}-\mathbf{K}')} = 0 \quad (4.17)$$

But now

$$\varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0 - \varepsilon_{\mathbf{k}} = 0 \quad \text{which implies} \quad c_{(\mathbf{k}-\mathbf{K}_i)} = \text{anything} \quad (4.18)$$

By (4.4), this yields a solution that is a linear combination of plane waves

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2, \quad \psi_{\mathbf{k}}(\mathbf{r}) \propto \sum_i c_{(\mathbf{k}-\mathbf{K}_i)} e^{i(\mathbf{k}-\mathbf{K}_i)\cdot\mathbf{r}} \quad (4.19)$$

Regardless of if  $\varepsilon_{\mathbf{k}}$  is degenerate, we get the band structure (the set of all eigenenergies)

$$\varepsilon_{n,\mathbf{k}} = \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{G}_n) \quad (4.20)$$

If we were to solve Schrodinger's equation for a free electron normally, we would find the set of eigenstates

$$\varepsilon_{\mathbf{k}'} = \frac{\hbar^2}{2m}, \quad \psi_{\mathbf{k}'}(\mathbf{r}) \propto e^{i\mathbf{k}'\cdot\mathbf{r}} \quad (4.21)$$

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<sup>6</sup>There are infinitely many  $U_{\mathbf{G}}$ , but presumably, we may keep only a small subset of non-negligible terms for a numerical approximation. For numerics, this is the approximation!

<sup>7</sup>In other words  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0 \neq \varepsilon_{(\mathbf{k}-\mathbf{K}') }^0$

<sup>8</sup>There exists one or more  $\mathbf{K}'$  such that  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0 = \varepsilon_{(\mathbf{k}-\mathbf{K}') }^0$ .

where  $\mathbf{k}'$  is any vector in reciprocal space. Notice that (4.21) and (4.16, 4.19) become the same (as they must!) when

$$\mathbf{k}' = \mathbf{k} + \mathbf{G} \quad (4.22)$$

This makes sense because  $\mathbf{k}$  is constrained to the first Brillouin zone while  $\mathbf{k}'$  is free to span the entire reciprocal space. To further drive home this point, let's examine the eigenenergies in both pictures. To simplify things, we'll work in one-dimension with a lattice spacing of  $a$ .

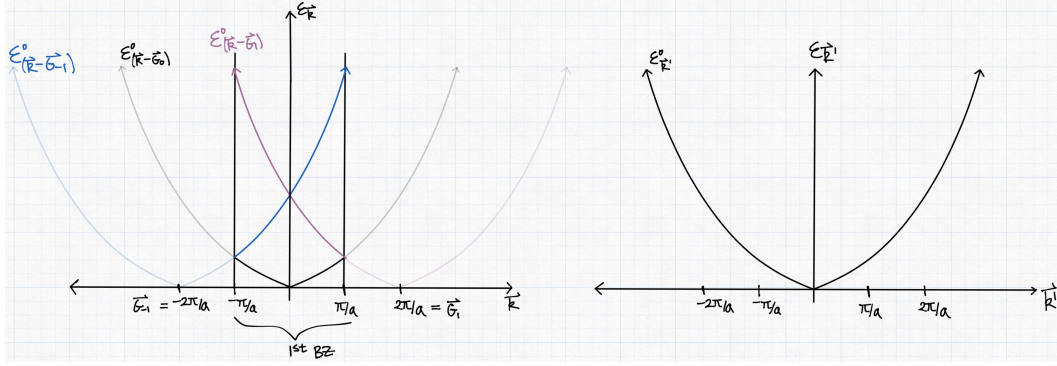


Figure 2: Left: the reduced zone scheme. Right: the normal dispersion.

As expected,  $\varepsilon_{\mathbf{k}'}$  is simply the energy of the free electron which depends quadratically on  $\mathbf{k}'$ . However, in the band structure picture,  $\mathbf{k}'$  outside the first Brillouin zone are mapped to  $\mathbf{k}$  within the first Brillouin zone with the subtraction of the reciprocal lattice vector  $\mathbf{G}$ . Each reciprocal lattice vector  $\mathbf{G}$  defines a band with dispersion  $\varepsilon_{(\mathbf{k}-\mathbf{G})}^0$ .

## 5 Nearly free electron model

Above we derived the exact form of Schrodinger's equation for Bloch states (4.11); however, the resulting expression can not in general be solved exactly. In the nearly free electron model, we approach (4.11) perturbatively by treating the Hamiltonian as that of a free electron with a small perturbation  $U(\mathbf{r})$ .

Like all perturbative approaches, our analysis splits into the case where the bare free-electron eigenenergies  $\varepsilon_{\mathbf{k}}$  are non-degenerate and degenerate.

**Case I (non-degenerate):** Let  $\mathbf{K}$  be a particular reciprocal lattice vector and  $\mathbf{K}' \in \{\mathbf{G}\} \setminus \mathbf{K}$ . For fixed  $\mathbf{k}$ , the band  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0$  is non-degenerate if

$$\varepsilon_{(\mathbf{k}-\mathbf{K})}^0 \neq \varepsilon_{(\mathbf{k}-\mathbf{K}')}^0 \quad \text{for all } \mathbf{K}' \quad (5.1)$$

We can treat  $U(\mathbf{r})$  as a small perturbation if

$$U(\mathbf{r}) \ll \varepsilon_{(\mathbf{k}-\mathbf{K})}^0 - \varepsilon_{(\mathbf{k}-\mathbf{K}')}^0 \quad \text{for fixed } \mathbf{k} \text{ and all } \mathbf{K}' \quad (5.2)$$

Recall that for a free electron,  $\mathbf{K}$  defines a band with dispersion  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0$  and  $c_{(\mathbf{k}-\mathbf{K}')} = 0$ . With a small perturbing potential, we expect the bare energy  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0$  to shift slightly and  $c_{(\mathbf{k}-\mathbf{K}')} = 0$  to be  $O(U)$ .



Equation (4.11) takes the form

$$\left(\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0\right) c_{(\mathbf{k}-\mathbf{G})} = \sum_{\mathbf{G}'} U_{(\mathbf{G}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \quad (5.3)$$

Solving for the  $c_{(\mathbf{k}-\mathbf{G})}$  terms

$$\begin{aligned} c_{(\mathbf{k}-\mathbf{G})} &= \frac{U_{(\mathbf{G}-\mathbf{K})} c_{(\mathbf{k}-\mathbf{K})}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0} + \sum_{\mathbf{K}'} \frac{U_{(\mathbf{G}-\mathbf{K}')} \overbrace{c_{(\mathbf{k}-\mathbf{K}')}^{O(U)}}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0} \\ &= \frac{U_{(\mathbf{G}-\mathbf{K})} c_{(\mathbf{k}-\mathbf{K})}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0} + O(U^2) \end{aligned} \quad (5.4)$$

Then

$$\begin{aligned} \left(\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K})}^0\right) c_{(\mathbf{k}-\mathbf{K})} &= \sum_{\mathbf{G}'} U_{(\mathbf{K}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \\ &= \sum_{\mathbf{G}'} U_{(\mathbf{K}-\mathbf{G}')} \left[ \frac{U_{(\mathbf{G}'-\mathbf{K})} c_{(\mathbf{k}-\mathbf{K})}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G}')}^0} + O(U^2) \right] \\ &= \sum_{\mathbf{G}'} \frac{U_{(\mathbf{K}-\mathbf{G}')} U_{(\mathbf{G}'-\mathbf{K})}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G}')}^0} c_{(\mathbf{k}-\mathbf{K})} + O(U^3) \\ &= \sum_{\mathbf{G}'} \frac{|U_{(\mathbf{K}-\mathbf{G}')}|^2}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G}')}^0} c_{(\mathbf{k}-\mathbf{K})} + O(U^3) \end{aligned} \quad (5.5)$$

$$\varepsilon_{\mathbf{k}} = \varepsilon_{(\mathbf{k}-\mathbf{K})}^0 + \sum_{\mathbf{G}'} \frac{|U_{(\mathbf{K}-\mathbf{G}')}|^2}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G}')}^0} + O(U^3) \quad (5.6)$$

Valid up to first order,  $\varepsilon_{\mathbf{k}} \approx \varepsilon_{(\mathbf{k}-\mathbf{K})}^0$ . Therefore

$$\varepsilon_{\mathbf{k}} = \varepsilon_{(\mathbf{k}-\mathbf{K})}^0 + \underbrace{\sum_{\mathbf{G}'} \frac{|U_{(\mathbf{K}-\mathbf{G}')}|^2}{\varepsilon_{(\mathbf{k}-\mathbf{K})}^0 - \varepsilon_{(\mathbf{k}-\mathbf{G}')}^0}}_{\text{energy shift}} + O(U^3) \quad (5.7)$$

From the expression above, we see that every band below  $\varepsilon_{(\mathbf{k}-\mathbf{K})}^0$  contributes a term that raises  $\varepsilon_{\mathbf{k}}$  and every band above contributes a term that lowers  $\varepsilon_{\mathbf{k}}$ . Therefore, non-degenerate bands repel each other under weak perturbation by a potential.

Importantly, the energy shift of the perturbation to be  $O(U^2)$ . Therefore, to leading order, we need only consider the energy shift of degenerate or nearly degenerate states.

**Case II (degenerate):** suppose now that for some fixed  $\mathbf{k}$ , there exists a set of reciprocal lattice vectors  $\mathbf{K}_i \in \{\mathbf{K}_1, \dots, \mathbf{K}_m\}$  such that  $\varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0$  are degenerate or nearly degenerate

$$\left| \varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0 - \varepsilon_{(\mathbf{k}-\mathbf{K}_j)}^0 \right| \ll U(\mathbf{r}) \quad (5.8)$$

Define  $\mathbf{K}' \in \{\mathbf{G}\} \setminus \{\mathbf{K}_i\}$ . Once again, (4.11) takes the form

$$\left(\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0\right) c_{(\mathbf{k}-\mathbf{G})} = \sum_{\mathbf{G}'} U_{(\mathbf{G}-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \quad (5.9)$$

In the free-electron case with degeneracies, recall  $c_{(\mathbf{k}-\mathbf{K}')} = 0$ . But with a small perturbation, we expect  $c_{(\mathbf{k}-\mathbf{K}')}$  to be at most  $O(U)$ . Solving for the  $c_{(\mathbf{k}-\mathbf{G})}$  terms

$$\begin{aligned} c_{(\mathbf{k}-\mathbf{G})} &= \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0} \left( \sum_{j=1}^m U_{(\mathbf{G}-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + \sum_{\mathbf{K}'} U_{(\mathbf{G}-\mathbf{K}')} \overbrace{c_{(\mathbf{k}-\mathbf{K}')}}^{O(U)} \right) \\ &= \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{G})}^0} \sum_{j=1}^m U_{(\mathbf{G}-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + O(U^2) \end{aligned} \quad (5.10)$$

Then for  $i = 1, \dots, m$ , the set of  $m$  coupled equations gives us the energy shifts

$$\begin{aligned} (\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0) c_{(\mathbf{k}-\mathbf{K}_i)} &= \sum_{\mathbf{G}'} U_{(\mathbf{K}_i-\mathbf{G}')} c_{(\mathbf{k}-\mathbf{G}')} \\ &= \sum_{j=1}^m U_{(\mathbf{K}_i-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + \sum_{\mathbf{K}'} U_{(\mathbf{K}_i-\mathbf{K}')} c_{(\mathbf{k}-\mathbf{K}')} \\ &= \sum_{j=1}^m U_{(\mathbf{K}_i-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + \sum_{\mathbf{K}'} U_{(\mathbf{K}_i-\mathbf{K}')} \left[ \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}')}^0} \sum_{j=1}^m U_{(\mathbf{K}'-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + O(U^2) \right] \\ &= \sum_{j=1}^m \left[ U_{(\mathbf{K}_i-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} + \sum_{\mathbf{K}'} \frac{U_{(\mathbf{K}_i-\mathbf{K}')} U_{(\mathbf{K}'-\mathbf{K}_j)}}{\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}')}^0} c_{(\mathbf{k}-\mathbf{K}_j)} + O(U^3) \right] \end{aligned} \quad (5.11)$$

To leading order in  $U$ ,

$$(\varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}_i)}^0) c_{(\mathbf{k}-\mathbf{K}_i)} = \sum_{j=1}^m U_{(\mathbf{K}_i-\mathbf{K}_j)} c_{(\mathbf{k}-\mathbf{K}_j)} \quad \text{where } i = 1, \dots, m \quad (5.12)$$

Solving the system of equations above yields new energies valid up to first-order in perturbation theory. In matrix form, the system becomes (recalling  $U_0 = 0$ )

$$\begin{pmatrix} \varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}_1)}^0 & -U_{(\mathbf{K}_1-\mathbf{K}_2)} & \cdots & -U_{(\mathbf{K}_1-\mathbf{K}_m)} \\ -U_{(\mathbf{K}_2-\mathbf{K}_1)} & \varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}_2)}^0 & \cdots & -U_{(\mathbf{K}_2-\mathbf{K}_m)} \\ \cdots & & \ddots & \vdots \\ -U_{(\mathbf{K}_m-\mathbf{K}_1)} & -U_{(\mathbf{K}_m-\mathbf{K}_2)} & \cdots & \varepsilon_{\mathbf{k}} - \varepsilon_{(\mathbf{k}-\mathbf{K}_m)}^0 \end{pmatrix} \begin{pmatrix} c_{k-\mathbf{K}_1} \\ c_{k-\mathbf{K}_2} \\ \cdots \\ c_{k-\mathbf{K}_m} \end{pmatrix} = 0 \quad (5.13)$$

If  $M$  is the matrix above, this is equivalent to  $\det(M) = 0$ .

Remarks:

- Returning to the one-dimension lattice from the previous section, let's find the band structure in the nearly free electron model.

We notice that there are no degeneracies in the band structure except for when  $k = 0, \pm\pi/a$ . Near these Bloch vectors, we find pairs of degenerate bands  $\varepsilon_{(k-K_i)}^0$  and  $\varepsilon_{(k-K_j)}^0$  and, under small perturbation  $U(r)$ , we expect the dispersion in these regions to be  $O(U)$ .

In particular, let's focus on the degeneracy at  $k = \pi/a$  and bands  $\varepsilon_{(k-G_0)}^0$  and  $\varepsilon_{(k-G_1)}^0$  where  $G_0 = 0$  and  $G_1 = \pi/a$ . To first-order in perturbation theory, (5.12) becomes

$$\begin{pmatrix} \varepsilon_k - \varepsilon_{(k-G_0)}^0 & -U_{(G_0-G_1)} \\ -U_{(G_1-G_0)} & \varepsilon_k - \varepsilon_{(k-G_1)}^0 \end{pmatrix} \begin{pmatrix} c_{(k-G_0)} \\ c_{(k-G_1)} \end{pmatrix} = 0 \quad (5.14)$$

Noticing  $U_{G_1} = U_{(G_0-G_1)}$  and using (4.6)

$$0 = \det \left\{ \begin{pmatrix} \varepsilon_k - \varepsilon_{(k-G_0)}^0 & -U_{G_1} \\ -U_{G_1}^* & \varepsilon_k - \varepsilon_{(k-G_1)}^0 \end{pmatrix} \right\} \quad (5.15)$$

$$= \varepsilon_k^2 - \varepsilon_k \left[ \varepsilon_{(k-G_0)}^0 - \varepsilon_{(k-G_1)}^0 \right] - |U_{G_1}|^2$$

$$\varepsilon_k = \frac{\varepsilon_{(k-G_0)}^0 - \varepsilon_{(k-G_1)}^0 \pm \sqrt{\left( \varepsilon_{(k-G_0)}^0 - \varepsilon_{(k-G_1)}^0 \right)^2 + 4|U_{G_1}|^2}}{2} \quad (5.16)$$

$$\varepsilon_k = \frac{\varepsilon_{(k-G_0)}^0 - \varepsilon_{(k-G_1)}^0}{2} \pm \left[ \left( \frac{\varepsilon_{(k-G_0)}^0 - \varepsilon_{(k-G_1)}^0}{2} \right)^2 + |U_{G_1}|^2 \right]^{1/2} \quad (5.17)$$

We see that at the degeneracy, where two bands overlap, the perturbation separates the bands, forming a band gap. From (5.17) magnitude this gap is  $2|U_{G_1}|$ . In three dimensions, the band structure exhibits similar behavior but in general can be more complicated.

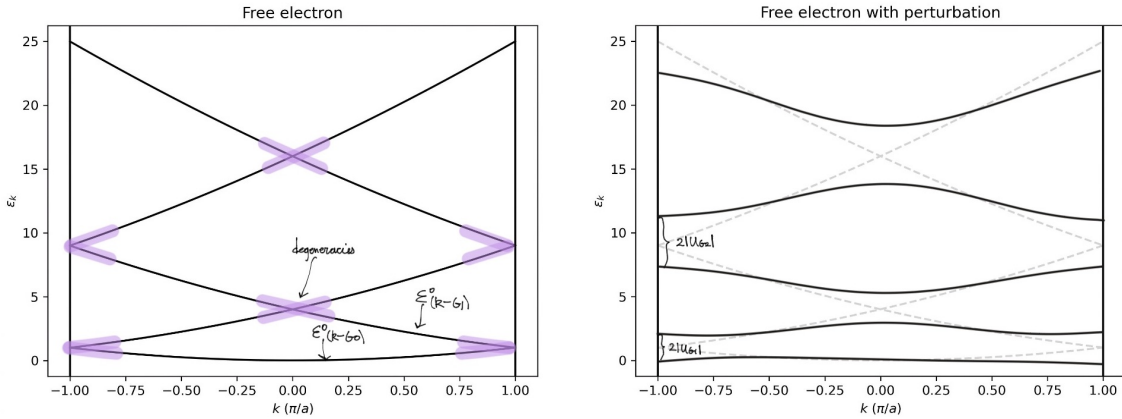


Figure 3: Left: bare free electron dispersion. Areas with degeneracies are highlighted. Right: perturbed bands from a weak potential.

## 6 Wannier Functions

Before exploring the tight binding model, let's develop the idea of Wannier functions. Wannier functions are a method of representing a general Bloch wave. These functions are not specific to the tight-binding model but are particularly relevant!

For fixed  $\mathbf{r}$ , if we consider  $\psi_{n,\mathbf{k}}$  as a function of  $\mathbf{k}$ , from (3.14) we see that  $\psi_{n,\mathbf{k}}$  is periodic in the reciprocal lattice. Therefore, we can write the Fourier expansion,

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} f_{n,\mathbf{R}}(\mathbf{r}) e^{i\mathbf{R}\cdot\mathbf{k}} \quad \text{where} \quad f_{n,\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{R}\cdot\mathbf{k}} \quad (6.1)$$

Notice that,

$$f_{n,0}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) \equiv \phi_n(\mathbf{r}) \quad (6.2)$$

by Bloch's theorem

$$\begin{aligned}
f_{n,\mathbf{R}}(\mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{R}\cdot\mathbf{k}} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r} - \mathbf{R}) \\
&= \phi_n(\mathbf{r} - \mathbf{R})
\end{aligned} \tag{6.3}$$

We call  $\phi_n(\mathbf{r} - \mathbf{R})$  the Wannier functions. Any Bloch vector can be expressed in the basis of Wannier functions

$$\begin{aligned}
\psi_{n,\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{+i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R}) && \text{for any Bloch function} \\
\phi_n(\mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) && \text{associated Wannier functions}
\end{aligned} \tag{6.4}$$

We can show that Wannier functions at different lattice sites or different band indices are orthogonal. First notice that the Bloch functions are orthogonal (they are eigenstates of the Hamiltonian, which is Hermitian)

$$\int \psi_{n',\mathbf{k}'}^*(\mathbf{r} - \mathbf{R}') \psi_{n,\mathbf{k}}(\mathbf{r} - \mathbf{R}) d\mathbf{r} = \delta_{n,n'} \delta_{\mathbf{k},\mathbf{k}'} \tag{6.5}$$

Then

$$\begin{aligned}
\int \phi_{n'}^*(\mathbf{r} - \mathbf{R}') \phi_n(\mathbf{r} - \mathbf{R}) d\mathbf{r} &= \int \left[ \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} e^{-i\mathbf{k}'\cdot\mathbf{R}'} \psi_{n',\mathbf{k}'}(\mathbf{r} - \mathbf{R}') \right]^* \left[ \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r} - \mathbf{R}) \right] d\mathbf{r} \\
&\propto \sum_{\mathbf{k},\mathbf{k}'} e^{-i(\mathbf{k}\cdot\mathbf{R} - \mathbf{k}'\cdot\mathbf{R}')} \int \psi_{n',\mathbf{k}'}^*(\mathbf{r} - \mathbf{R}') \psi_{n,\mathbf{k}}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\
&\propto \sum_{\mathbf{k},\mathbf{k}'} e^{-i(\mathbf{k}\cdot\mathbf{R} - \mathbf{k}'\cdot\mathbf{R}')} \delta_{n,n'} \delta_{\mathbf{k},\mathbf{k}'} \\
&\propto \delta_{n,n'} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R} - \mathbf{R}')} \\
&\propto \delta_{n,n'} \delta_{\mathbf{R},\mathbf{R}'}
\end{aligned} \tag{6.6}$$

$$\int \phi_{n'}^*(\mathbf{r} - \mathbf{R}') \phi_n(\mathbf{r} - \mathbf{R}) d\mathbf{r} \propto \delta_{n,n'} \delta_{\mathbf{R},\mathbf{R}'} \tag{6.7}$$

## 7 Tight binding model

Now we take an entirely different approach to a toy model of a solid. Rather than examining the case of a free electron, we by thinking about the case of a single atomic Hamiltonian,  $H_{\text{at}}$ , outside of the crystal lattice. In general,  $H_{\text{at}}$  will have a set of bound solutions  $\psi_j(\mathbf{r})$  which are the atomic orbitals.

$$H_{\text{at}} \psi_j(\mathbf{r}) = E_j \psi_j(\mathbf{r}) \tag{7.1}$$

Now the corresponding crystal Hamiltonian is

$$H = \sum_{\mathbf{R}} H_{\text{at}}(\mathbf{r} - \mathbf{R}) = H_{\text{at}}(\mathbf{r}) + \sum_{\mathbf{R} \neq 0} H_{\text{at}}(\mathbf{r} - \mathbf{R}) \tag{7.2}$$

$$H = H_{\text{at}}(\mathbf{r}) + \Delta U(\mathbf{r}) \quad \text{where} \quad \Delta U(\mathbf{r}) = \sum_{\mathbf{R} \neq 0} H_{\text{at}}(\mathbf{r} - \mathbf{R}) \quad (7.3)$$

**The ideal limit:** If atomic eigenstates are sufficiently localized so that the overlap between  $\psi_j(\mathbf{r})$  and  $\Delta U(\mathbf{r})$  is exactly zero, then the localized atomic wave functions are eigenstates of the full crystal Hamiltonian

$$H\psi_j(\mathbf{r}) = [H + \Delta U(\mathbf{r})]\psi_j(\mathbf{r}) = H\psi_j(\mathbf{r}) + 0 = E_j\psi_j(\mathbf{r}) \quad (7.4)$$

In this limit, for each atomic orbital  $\psi_j(\mathbf{r})$ , we obtain a set of  $N$  eigenstates  $\{\psi_j(\mathbf{r} - \mathbf{R})\}$  of the orbital localized on each site of the lattice. However, these eigenstates do not satisfy Bloch's theorem, nor the periodic (Born Von-Karman) boundary condition of the crystal. Instead, the wave functions of an electron in the crystal must be some linear combination of these eigenstates that do satisfy Bloch's theorem.

Recall we can write any Bloch function in a basis of Wannier functions (6.4). Conveniently, if we let the Wannier functions be the atomic orbitals,  $\phi_n(\mathbf{r}) = \psi_n(\mathbf{r})$ , then  $\psi_{n,\mathbf{k}}(\mathbf{r})$  is indeed a linear combination of atomic orbitals. Hence, the eigenstates of the Hamiltonian are

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \psi_n(\mathbf{r} - \mathbf{R}) \quad (7.5)$$

We can also directly solve for the band structure

$$\begin{aligned} H\psi_{n,\mathbf{k}}(\mathbf{r}) &= H \left[ \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \psi_n(\mathbf{r} - \mathbf{R}) \right] \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} [H\psi_n(\mathbf{r} - \mathbf{R})] \\ \text{(from (7.4))} \quad &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} [E_n\psi_n(\mathbf{r} - \mathbf{R})] \\ &= E_n\psi_{n,\mathbf{k}}(\mathbf{r}) \end{aligned} \quad (7.6)$$

The bands are simply flat (independent  $\mathbf{k}$ ) with energies of the atomic orbitals. This is quite boring and not informative.

**Tight binding:** unlike the ideal case, it is more realistic that the overlap of the bare atomic orbitals  $\psi_j(\mathbf{r})$  and  $\Delta U(\mathbf{r})$  is small but non-zero. Then  $\psi_j(\mathbf{r})$  are no longer eigenstates of the full Hamiltonian  $H$ .

However, we still know that the eigenstates must be Bloch functions and the expansion in Wannier functions is always valid. The eigenstates must be of the form

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_n(\mathbf{r} - \mathbf{R}) \quad (7.7)$$

While no longer eigenstates, the atomic orbitals nevertheless provide a complete basis. Therefore, we can express

$$\phi_n(\mathbf{r}) = \sum_j b_j \psi_j(\mathbf{r}) \quad (7.8)$$

and the Bloch function becomes

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sum_j e^{i\mathbf{k}\cdot\mathbf{R}} b_{n,j} \psi_j(\mathbf{r} - \mathbf{R}) \quad (7.9)$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_j b_{n,j} \underbrace{\left[ \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}) \right]}_{\Psi_{j,\mathbf{k}}(\mathbf{r})} \quad (7.10)$$

Let's plug this into the Schrodinger equation  $H\psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}}(\mathbf{r})$  and take the inner product with  $\phi_m(\mathbf{r})$ . First, expanding the RHS and LHS separately (we cancel the factor of  $1/\sqrt{N}$  on both sides)

$$\begin{aligned} & \int \psi_m^*(\mathbf{r}) \varepsilon_{n,\mathbf{k}} \left[ \sum_j b_{n,j} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}) \right] \\ &= \varepsilon_{n,\mathbf{k}} \sum_j b_{n,j} \left( \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \right) \end{aligned} \quad (7.11)$$

$$\begin{aligned} & \int \psi_m^*(\mathbf{r}) H \left[ \sum_j b_{n,j} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}) \right] \\ &= \int \psi_m^*(\mathbf{r}) [H_{\text{at}}(\mathbf{r}) + \Delta U(\mathbf{r})] \left[ \sum_j b_{n,j} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}) \right] \\ &= \sum_j b_{n,j} \left( \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) H_{\text{at}} \psi_j(\mathbf{r} - \mathbf{R}) \right) + \sum_j b_{n,j} \left( \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) \right) \\ &= E_m \sum_j b_{n,j} \left( \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) \right) + \sum_j b_{n,j} \left( \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) \right) \end{aligned} \quad (7.12)$$

Putting everything together

$$\sum_j \left[ (\varepsilon_{n,\mathbf{k}} - E_m) \gamma_{m,j}(\mathbf{R}) - t_{m,j}(\mathbf{R}) \right] b_{n,j} = 0 \quad \text{for fixed } \mathbf{k} \text{ and all } j \quad [\text{exact}] \quad (7.13)$$

where

$$\begin{aligned} \gamma_{m,j}(\mathbf{R}) &= \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ t_{m,j}(\mathbf{R}) &= \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \end{aligned} \quad (7.14)$$

Some remarks:

- We can write the expression above in matrix form

$$\begin{pmatrix} (\varepsilon_{n,\mathbf{k}} - E_1)\gamma_{1,1} - t_{1,1} & (\varepsilon_{n,\mathbf{k}} - E_1)\gamma_{1,2} - t_{1,2} & \cdots \\ (\varepsilon_{n,\mathbf{k}} - E_2)\gamma_{2,1} - t_{2,1} & (\varepsilon_{n,\mathbf{k}} - E_2)\gamma_{2,2} - t_{2,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} b_{n,1} \\ b_{n,2} \\ \vdots \end{pmatrix} = 0 \quad (7.15)$$

- We have not made any approximations in our derivation of (7.13). Here we present the standard assumptions for the tight-binding model:

1. Recall in the ideal case that when the overlap between the atomic orbital  $\psi_n(\mathbf{r})$  and  $\Delta U(\mathbf{r})$  is zero, the Wannier functions are exactly the atomic orbitals  $\phi_n(\mathbf{r}) = \psi_n(\mathbf{r})$ . Therefore, when the overlap is small, it is reasonable that  $\phi_n(\mathbf{r}) \approx \psi_n(\mathbf{r})$ .

While we exactly expanded the Wannier functions in the complete basis of atomic orbitals<sup>9</sup> (7.8), since  $\phi_n(\mathbf{r}) \approx \psi_n(\mathbf{r})$  we can restrict this expansion (7.8) to only include orbitals that are close in energy to the energy of the valence electrons.

Suppose that we consider only  $m$  orbitals  $\{\psi_{n_1}(\mathbf{r}), \dots, \psi_{n_m}(\mathbf{r})\}$  rather than the complete (infinite) set. Then the Bloch wave becomes (7.10) becomes a linear combination of atomic orbitals (LCAO)

$$\psi_{n,\mathbf{k}}(\mathbf{r}) \approx \sum_{j=1}^m b_n \Psi_{j,\mathbf{k}}(\mathbf{r}) \quad \text{where} \quad \Psi_{j,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}) \quad (7.16)$$

With this approximation (7.13) is unchanged except for the summation of  $n$  now runs to  $m$  and not infinity.

2. Since we assume that the atomic orbitals are well localized, we will take overlap between atomic orbitals located at different sites to be zero. Furthermore, recall that atomic orbitals (both at the same site) are orthonormal.

$$\int \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{m,j} \quad (7.17)$$

Therefore,  $\gamma_{m,j}$  becomes

$$\begin{aligned} \gamma_{m,j}(\mathbf{R}) &= \sum_{\mathbf{R}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ &= \int \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} + \sum_{\mathbf{R} \neq 0} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \\ &\approx \delta_{m,j} + 0 \end{aligned} \quad (7.18)$$

$$\gamma_{m,j} \approx \delta_{m,j} \quad (7.19)$$

3. Once again invoking well-localization of the atomic orbits, we argue that  $\Delta U(\mathbf{r})$  can at most couple atomic orbitals at the same site or nearest neighbors. Therefore

$$t_{m,j}(\mathbf{R}) \approx \sum_{\mathbf{R} \leq \text{N.N.}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \quad (7.20)$$

Putting everything together, (7.13) becomes

$$\begin{aligned} \sum_j [(\varepsilon_{n,\mathbf{k}} - E_m) \delta_{m,j} - \tilde{t}_{m,j}] b_{n,j} &= 0 \quad \text{for fixed } \mathbf{k} \text{ and } j = 1, \dots, m \\ \tilde{t}_{m,j} &= \sum_{\mathbf{R} \leq \text{N.N.}} \int e^{i\mathbf{k}\cdot\mathbf{R}} \psi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_j(\mathbf{r} - \mathbf{R}) d\mathbf{r} \quad [\text{tight-binding}] \end{aligned} \quad (7.21)$$

<sup>9</sup>Recall the complete basis of atom includes unbound states!

In matrix form, the tight-binding equations becomes

$$\begin{pmatrix} (\varepsilon_{n,\mathbf{k}} - E_1) - t_{1,1} & -\tilde{t}_{1,2} & \dots & -\tilde{t}_{1,m} \\ -\tilde{t}_{2,1} & (\varepsilon_{n,\mathbf{k}} - E_2) - \tilde{t}_{2,2} & \dots & -\tilde{t}_{2,m} \\ \vdots & & \ddots & \vdots \\ -\tilde{t}_{m,1} & -\tilde{t}_{m,2} & \dots & (\varepsilon_{n,\mathbf{k}} - E_m) - \tilde{t}_{m,m} \end{pmatrix} \begin{pmatrix} b_{n,1} \\ b_{n,2} \\ \vdots \\ b_{n,m} \end{pmatrix} = 0 \quad (7.22)$$

- TODO: S, Px, Py, Pz example in Girvan and Yang

## References

- [1] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*. Holt-Saunders, 1976.
- [2] Steven M Girvin and Kun Yang. *Modern condensed matter physics*. Cambridge University Press, 2019.