



CHAPTER 3

BAND STRUCTURE

3.1 INTRODUCTION

Much of solid-state physics concerns the calculation of the energy eigenstates and eigenvalues of a system of interacting electrons and nuclei. In principle, the system is described by the many-particle Hamiltonian:

$$\hat{H} = \sum_l \frac{\hat{p}_l^2}{2m_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}$$

Here, the sums run over all charged particles—electrons and nuclei—of the solid; m_l it is the mass of the electron or nucleus, q_l it is its charge.

Despite its compact form, this Hamiltonian is extremely difficult to solve. Even numerical solutions become impractical for systems containing more than a few tens of interacting particles. A mole of material contains approximately 10^{23} particles, so a tractable description requires a hierarchy of approximations, many of which can be systematically controlled.

The goal of solid-state theory is therefore to construct simplified models that retain the relevant physics while allowing the resulting equations to be solved analytically or numerically. Their validity must ultimately be assessed by comparison with experiment.



3.1 INTRODUCTION

3.2.1 Single-electron model

The simplest model of a metal is the free-electron gas, also called the ideal Fermi gas.

In this model, the conduction electrons are treated as non-interacting particles moving freely inside a box. Electron–electron interactions and the periodic potential generated by the ion cores are neglected. The Pauli exclusion principle is retained.

When this model is applied to a metal, only the valence electrons that participate in electrical conduction are considered. The ion cores provide a uniform neutralising background.

The free-electron gas accounts for several important properties of simple metals, but it cannot describe all solids. In particular, it is inadequate for insulators, semiconductors, and magnetic materials.

A key feature of the model is that the total energy is the sum of the energies of independent electrons

$$E = \sum_i \varepsilon_i .$$

Many results can therefore be derived from the more general independent-electron, or single-particle, model.

3.2 FREE ELECTRON GAS

3.2.1 Single-electron model

Let us start from the independent-electron Hamiltonian:

$$\hat{H}\Psi = \sum_{l=1}^N \left[-\frac{\hbar^2 \nabla_l^2}{2m} + U(\vec{r}_l) \right] \Psi(\vec{r}_1 \dots \vec{r}_N) = \varepsilon \Psi(\vec{r}_1 \dots \vec{r}_N)$$

This equation describes N conduction electrons moving independently in an external potential $U(\vec{r}_l)$. Electron–electron interactions are neglected.

The one-electron eigenfunctions are obtained from:

$$\left(-\frac{\hbar^2 \nabla_l^2}{2m} + U(\vec{r}_l) \right) \psi_l(\vec{r}_l) = \varepsilon_l \psi_l(\vec{r}_l)$$

The wavefunction of the N -electron system is constructed by antisymmetrizing the occupied one-electron states, yielding a Slater determinant. This antisymmetry accounts for the Pauli exclusion principle. Therefore, within the independent-electron approximation, the total energy is:

$$E = \sum_{l \in \text{occupied}} \varepsilon_l$$

3.2 FREE ELECTRON GAS

3.2.1 Single-electron model

Although the independent-electron approximation can be applied to a large number of electrons, the problem reduces to solving a one-electron equation.

For a general potential $U(\vec{r}_l)$, however, the Schrödinger equation cannot usually be solved analytically..

In the free-electron-gas model, both the electron–ion potential and electron–electron interactions are neglected. Therefore, $U(\mathbf{r}) = 0$ and the Hamiltonian becomes::

$$\hat{H} = - \sum_{l=1}^N \frac{\hbar^2}{2m} \nabla_l^2$$

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

This Hamiltonian describes N noninteracting electrons moving freely inside the crystal volume. Its eigenfunctions and eigenvalues can be determined analytically once suitable boundary conditions are specified.

A wavefunction that vanishes at the boundaries would describe electrons confined in a box. This is not appropriate for a bulk crystal, which is instead described by periodic boundary conditions.

3.2 FREE ELECTRON GAS

3.2.1 Single-electron model

We impose Born–von Kármán periodic boundary conditions by considering a cubic box of side L , with volume $V = L^3$:

$$\Psi(\dots, x_j + L, y_j, z_j, \dots) = \Psi(\dots, x_j, y_j, z_j, \dots)$$

$$\Psi(\dots, x_j, y_j + L, z_j, \dots) = \Psi(\dots, x_j, y_j, z_j, \dots)$$

$$\Psi(\dots, x_j, y_j, z_j + L, \dots) = \Psi(\dots, x_j, y_j, z_j, \dots)$$

These conditions make the finite system equivalent to an infinite periodic repetition of the same volume. They remove surface effects and provide an appropriate description of a crystal. For a free-electron gas, the one-electron eigenstates are plane waves:

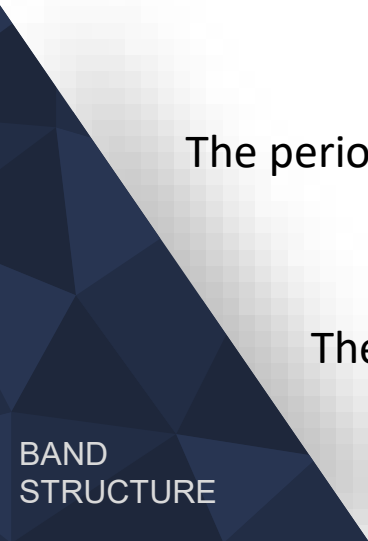
$$\psi_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

The periodic boundary conditions restrict the allowed wavevectors to:

$$\mathbf{k} = \frac{2\pi}{L} (n_x \hat{\mathbf{x}} + n_y \hat{\mathbf{y}} + n_z \hat{\mathbf{z}}), \quad n_x, n_y, n_z \in \mathbb{Z}$$

The factor $1/\sqrt{V}$ ensures normalization over the crystal volume:

$$\int_V |\psi_{\mathbf{k}}(\mathbf{r})|^2 d^3r = 1$$



3.2 FREE ELECTRON GAS

3.2.2 Fermi sphere

The energy eigenvalue of a free electron with wavevector $\mathbf{k}$ is:

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

The many-electron ground state is obtained by filling the available one-electron states in order of increasing energy. Because electrons are fermions, the many-electron wavefunction must be antisymmetric under the exchange of two electrons.

According to the Pauli exclusion principle, each spatial state labelled by $\mathbf{k}$ can be occupied by at most two electrons, provided that they have opposite spin.

The filling starts from the state $\mathbf{k} = 0$, followed by the degenerate states with the smallest nonzero values of $|\mathbf{k}|$. Since the energy depends only on $k = |\mathbf{k}|$,

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m},$$

all states with the same value of k have the same energy. Therefore, at zero temperature, the occupied states fill a sphere in $\mathbf{k}$ -space, called the Fermi sphere. Its radius is the Fermi wavevector k_F .

3.2 FREE ELECTRON GAS

3.2.2 Fermi sphere

For each one-electron spin state $(\mathbf{k}, \sigma)$, the occupation number is defined as.

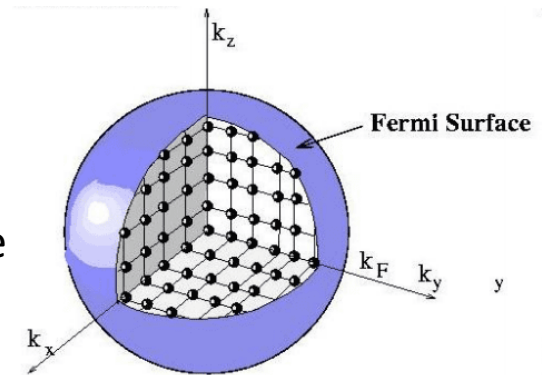
$$f_{\mathbf{k}\sigma} = \begin{cases} 1, & \text{if the state is occupied,} \\ 0, & \text{if the state is empty.} \end{cases}$$

At zero temperature, the ground state of a system containing N electrons is obtained by filling all the lowest-energy states. Thus.

$$\begin{aligned} f_{\mathbf{k}\sigma} &= 1 & \text{for } |\mathbf{k}| \leq k_F, \\ f_{\mathbf{k}\sigma} &= 0 & \text{for } |\mathbf{k}| > k_F. \end{aligned}$$

The quantity k_F is called the Fermi wavevector. The surface defined by

$$|\mathbf{k}| = k_F$$



is the Fermi surface; for a free-electron gas, it is a sphere, called the Fermi sphere. Each allowed $\mathbf{k}$ -value corresponds to two one-electron states, one for each spin orientation. At zero temperature, all the states inside the Fermi sphere are occupied, whereas all states outside it are empty.

The spherical shape minimizes the total energy because the single-electron energy depends only on k^2 :

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

3.2 FREE ELECTRON GAS

3.2.3 Density of states

For a free-electron gas confined to a cubic volume $V = L^3$, the periodic boundary conditions allow only the wavevectors

$$\mathbf{k} = \frac{2\pi}{L} (n_x \hat{\mathbf{x}} + n_y \hat{\mathbf{y}} + n_z \hat{\mathbf{z}}), \quad n_x, n_y, n_z \in \mathbb{Z}.$$

The allowed $\mathbf{k}$ -points form a cubic grid in $\mathbf{k}$ -space, with spacing $2\pi/L$ along each direction. Therefore, each allowed $\mathbf{k}$ -value occupies a volume

$$\Delta k_x \Delta k_y \Delta k_z = \left(\frac{2\pi}{L} \right)^3 = \frac{(2\pi)^3}{V}$$

At zero temperature, all states inside the Fermi sphere are occupied. Taking into account the two possible spin states for each $\mathbf{k}$ -value, the number of electrons is

$$N = 2 \frac{\frac{4}{3} \pi k_F^3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3.$$

From the relation between the electron density and the Fermi wavevector,

$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

3.2 FREE ELECTRON GAS

3.2.3 Density of states

we obtain:

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} = (3\pi^2 n)^{1/3}$$

$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

The electron velocity at the Fermi surface is the Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3}$$

The energy of a state on the Fermi surface is called the Fermi energy:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}.$$

At zero temperature, E_F is the energy of the highest occupied one-electron state. The Fermi surface is the set of wavevectors satisfying

$$\varepsilon_{\mathbf{k}} = E_F.$$

For a free-electron gas, the Fermi surface is a sphere of radius k_F .

Combining the expressions for k_F and E_F , we obtain:

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3},$$

3.2 FREE ELECTRON GAS

3.2.3 Density of states

Let $\mathcal{N}(E)$ be the number of one-electron states with energy less than or equal to E . For a free-electron gas,

$$\mathcal{N}(E) = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

The density of states is defined as the number of states per unit energy:

$$D(E) = \frac{d\mathcal{N}(E)}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

Equivalently,

$$D(E) = \frac{3}{2} \frac{\mathcal{N}(E)}{E}$$

Thus, apart from the numerical factor $3/2$, the density of available one-electron states at the Fermi energy is of the order of $\mathcal{N}(E)$.

The Fermi temperature is defined by

$$T_F = \frac{E_F}{k_B},$$

where k_B is the Boltzmann constant. It is the temperature scale associated with the Fermi energy.

3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

Typical orders of magnitude for conduction electrons in metals are:

$$n \sim 10^{28} \text{ m}^{-3}; \quad k_F \sim 10^{10} \text{ m}^{-1}; \quad v_F \sim 10^6 \text{ m s}^{-1}; \quad E_F \sim \text{a few eV}; \quad T_F \sim 10^4\text{--}10^5 \text{ K}$$

The ground state described above corresponds to a system of N electrons at absolute zero temperature. At $T = 0$, the occupation number is

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < E_F, \\ 0, & \varepsilon > E_F. \end{cases}$$

At finite temperature, electrons can be thermally excited from states below the Fermi energy to initially empty states above it. The sharp occupation step is therefore broadened over an energy range of the order of $k_B T$.

At thermal equilibrium, the probability that a one-electron state of energy ε is occupied is given by the Fermi–Dirac distribution:

$$f(\varepsilon, T) = \frac{1}{\exp \left[\frac{\varepsilon - \mu(T)}{k_B T} \right] + 1}.$$

where $\mu(T)$ represents the chemical potential.

3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

The number of one-electron states per unit volume with energies between ε and $\varepsilon + d\varepsilon$ is $g(\varepsilon) d\varepsilon$, with $g(\varepsilon) = \frac{D(\varepsilon)}{V}$ defined as the density of state per unit of volume. Since each state is occupied with probability $f(\varepsilon, T)$, the electron density is:

$$n = \int_0^{\infty} g(\varepsilon) f(\varepsilon, T) d\varepsilon$$

For a free-electron gas, the energy origin is chosen at the bottom of the band, so that $\varepsilon \geq 0$. This equation determines the chemical potential $\mu(T)$ for a given electron density n .

At absolute zero, the Fermi–Dirac distribution becomes:

$$f(\varepsilon, 0) = \begin{cases} 1, & \varepsilon < E_F, \\ 0, & \varepsilon > E_F. \end{cases}$$

$$f(\varepsilon, T) = \frac{1}{\exp\left[\frac{\varepsilon - \mu(T)}{k_B T}\right] + 1}$$

For the discontinuity, the density equation reduces to $n = \int_0^{\mu(0)} g(\varepsilon) f d\varepsilon$

At $T = 0$, the electron gas is in its ground state. All one-electron states with energies between 0 and E_F are occupied. Therefore,

$$n = \int_0^{E_F} g(\varepsilon) d\varepsilon.$$

3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

Comparing the two expressions, we obtain

$$\mu(0) = E_F.$$

At any temperature, the Fermi–Dirac distribution satisfies

$$f(\mu, T) = \frac{1}{2}$$

Thus, the chemical potential is the energy at which the occupation probability is one half.

For $T > 0$, the chemical potential is determined by imposing particle-number conservation:

$$n = \int_0^\infty g(\varepsilon) \frac{1}{\exp\left[\frac{\varepsilon - \mu(T)}{k_B T}\right] + 1} d\varepsilon.$$

For ordinary metals, $T \ll T_F$, or equivalently $k_B T \ll E_F$

In this regime, the Sommerfeld expansion gives, for a three-dimensional free-electron gas,

$$\mu(T) \simeq E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right]$$

$$n = \int_0^{\mu(0)} g(\varepsilon) f d\varepsilon$$

$$n = \int_0^{E_F} g(\varepsilon) f d\varepsilon$$

$$f(\varepsilon, T) = \frac{1}{\exp\left[\frac{\varepsilon - \mu(T)}{k_B T}\right] + 1}$$

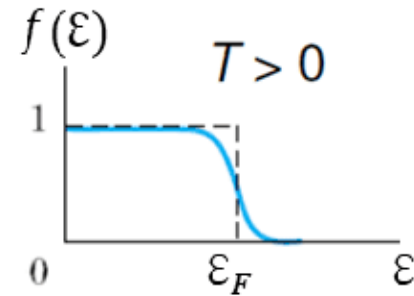
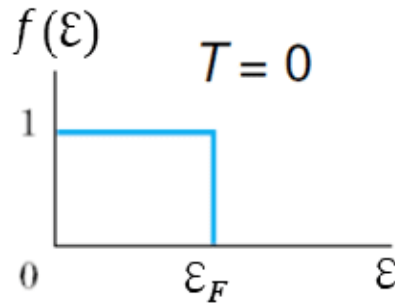
3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

Therefore, in ordinary metals, the chemical potential remains very close to the Fermi energy over a broad temperature range.

$$\mu(T) \simeq E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right]$$

At $T = 0$, the Fermi–Dirac distribution is a sharp step.



For $0 < T \ll T_F$, the step is smoothed over an energy range of the order of $k_B T$, centred at the chemical potential $\mu(T)$:

$$f(\mu(T), T) = \frac{1}{2}$$

Thus, only electrons in an energy interval of a few $k_B T$ around the Fermi energy are thermally redistributed; states far below E_F remain almost fully occupied.

3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

Far above the chemical potential, the occupation probability is much smaller than one:

$$f(\varepsilon, T) \ll 1.$$

$$f(\varepsilon, T) = \frac{1}{\exp\left[\frac{\varepsilon - \mu(T)}{k_B T}\right] + 1}$$

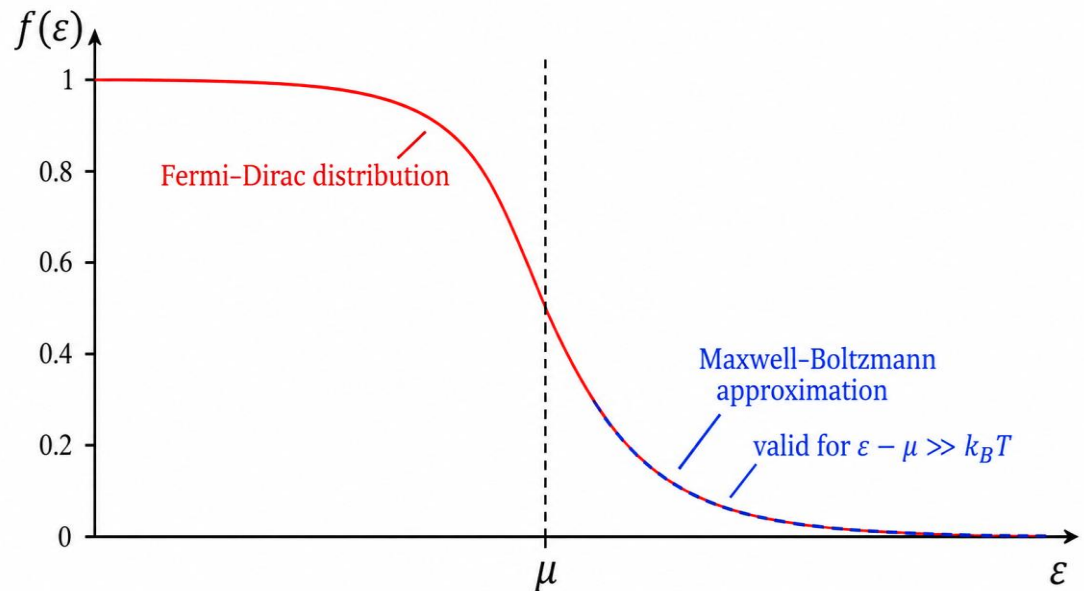
In this limit, $\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) \gg 1$,

and the Fermi–Dirac distribution reduces to the Maxwell–Boltzmann form:

$$f(\varepsilon, T) \simeq \exp\left[-\frac{\varepsilon - \mu}{k_B T}\right]$$

This is the non-degenerate limit, valid only for states whose occupation probability is much smaller than one.

It describes the high-energy tail of the Fermi–Dirac distribution.



3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

A first application of the free-electron model is the calculation of the electronic heat capacity.

For a classical three-dimensional ideal gas, equipartition gives the mean energy per particle.

$$\langle \varepsilon \rangle = \frac{3}{2} k_B T,$$

and therefore

$$U_{\text{cl}} = \frac{3}{2} N k_B T, \quad C_{V,\text{cl}} = \frac{3}{2} N k_B.$$

If each of N atoms contributed one classical free electron, one would therefore expect an electronic heat capacity equal to $\frac{3}{2} N k_B$. Experimentally, however, the electronic contribution is much smaller at ordinary temperatures.

The reason is the Pauli exclusion principle: at $T \ll T_F$, only electrons within an energy range of the order of $k_B T$ around the Fermi energy can be thermally excited. Electrons far below E_F cannot absorb energy because all nearby states are already occupied.

3.2 FREE ELECTRON GAS

3.2.4 Fermi Distribution

If N is the total number of conduction electrons, only a fraction of the order of

$$\frac{T}{T_F} = \frac{k_B T}{E_F}$$

can be thermally excited at temperature T .

The number of thermally active electrons is therefore of the order of

$$N_{\text{active}} \sim N \frac{T}{T_F}.$$

Each excitation involves an energy of the order of $k_B T$. Thus, the temperature-dependent correction to the electronic energy scales as:

$$\Delta U_e \sim N \frac{T}{T_F} k_B T = N k_B \frac{T^2}{T_F}.$$

Consequently, the electronic heat capacity has the order of magnitude

$$C_{V,e} = \frac{\partial U_e}{\partial T} \sim N k_B \frac{T}{T_F}.$$

A full low-temperature calculation gives $C_{V,e} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$, $T \ll T_F$.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.1 The periodic potential

The free-electron model provides a useful first description of several properties of metals, including their electronic heat capacity and electrical transport. However, it cannot explain the origin of energy bands or the distinction between metals, semimetals, semiconductors, and insulators.

In the free-electron model, the electrons move independently inside a uniform positive background. The periodic potential generated by the ionic cores is neglected.

In 1928, Bloch introduced a more realistic independent-electron model in which electrons move in the static potential created by the periodic array of ions. Electron–electron interactions are still neglected.

The corresponding one-electron Hamiltonian is: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})$.

Although the Schrödinger equation cannot generally be solved explicitly for an arbitrary potential, the crystal potential satisfies the translational symmetry

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

for every Bravais-lattice vector $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, n_1, n_2, n_3 \in \mathbb{Z}$.

This periodicity is the key assumption underlying Bloch's theorem and the formation of electronic energy bands.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.1 The periodic potential

The one-electron Hamiltonian is: $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r})$.

The main consequences of a periodic potential can be illustrated in one dimension. Let us consider the stationary Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = \varepsilon \psi(x)$$

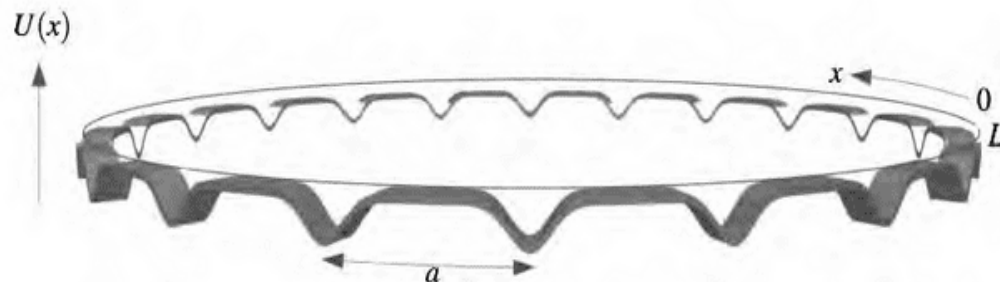
The potential has the periodicity of the one-dimensional lattice:

$$U(x + a) = U(x)$$

where a is the lattice constant.

We consider a chain containing N unit cells, with total length $L = Na$.

The one-dimensional model retains the essential consequences of translational symmetry while allowing the derivation to remain simple.



3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

To eliminate surface effects, we impose the Born–von Kármán boundary condition:

$$\psi(x) = \psi(x + L)$$

In the absence of a periodic potential, $U(x) = 0$, the normalized eigenstates are plane waves:

$$\psi_k(x) = \frac{e^{ikx}}{\sqrt{L}}$$

When the potential is periodic, $U(x + a) = U(x)$, Bloch's theorem states that the eigenfunctions can be written as:

$$\psi_k(x) = e^{ikx} u_k(x)$$

where $u_k(x)$ has the periodicity of the lattice:

$$u_k(x + a) = u_k(x).$$

Equivalently, a Bloch wave satisfies $\psi_{nk}(x + a) = e^{ika} \psi_{nk}(x)$.

The boundary condition over the whole crystal quantizes the allowed wavevectors:

$$e^{ikL} = 1, k = \frac{2\pi m}{L}, m \in \mathbb{Z}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

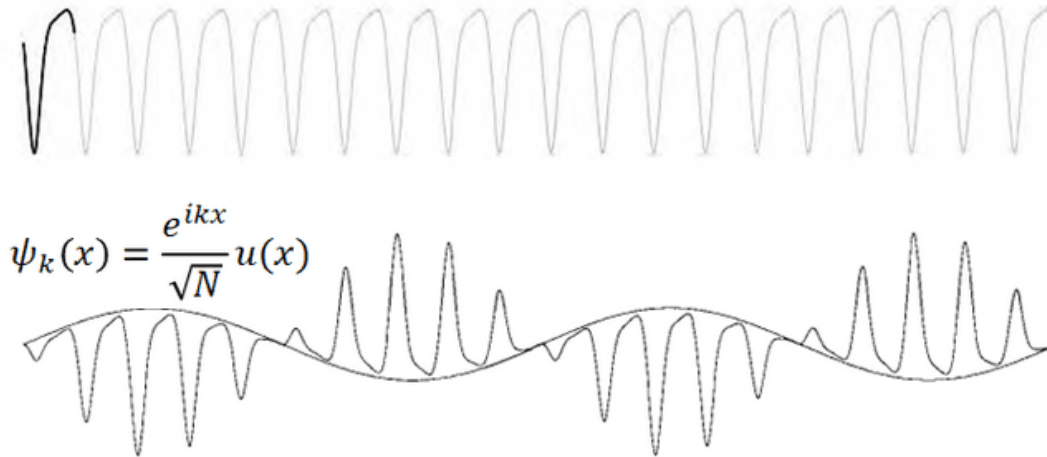
If $u_k(x)$ is normalized over one unit cell,

$$\int_0^a |u_k(x)|^2 dx = 1$$

then $\psi_k(x)$ is normalized over the entire crystal of length $L = Na$:

$$\int_0^L |\psi_k(x)|^2 dx = 1$$

$$\psi_k(x) = \frac{e^{ikx}}{\sqrt{N}} u(x)$$



The periodic lattice-scale modulation is described by $u_k(x)$, whereas the factor e^{ikx} determines the phase variation of the Bloch wave across the crystal.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

Let us derive Bloch's theorem in three dimensions. A crystal potential has the periodicity of the Bravais lattice:

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

Therefore, it can be expanded in a Fourier series over reciprocal-lattice vectors:

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \quad \text{with} \quad U_{\mathbf{G}} = \frac{1}{V_c} \int_{V_c} U(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d^3r$$

Since the zero of potential energy is arbitrary, we may choose the additive constant such that the spatial average of the periodic potential over one primitive cell vanishes:

$$U_0 = \frac{1}{V_c} \int_{V_c} U(\mathbf{r}) d^3r = 0$$

Because the crystal potential is real, its Fourier coefficients satisfy

$$U_{-\mathbf{G}} = U_{\mathbf{G}}^*, \quad \forall \mathbf{G}$$

If the crystal has inversion symmetry, the origin can be chosen at an inversion centre and the potential satisfies

$$U(\mathbf{r}) = U(-\mathbf{r})$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$U_{-G} = U_G^*, \quad \forall G$$

$$U(\mathbf{r}) = U(-\mathbf{r})$$

This implies also that the Fourier coefficients satisfy

$$U_{-G} = U_G$$

Combining the two relations gives

$$U_G = U_G^*$$

so that all Fourier coefficients are real $U_G \in \mathbb{R}$.

Expand the eigenfunction and the periodic potential in plane waves:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}, \quad U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

The kinetic-energy term is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \sum_{\mathbf{q}} \frac{\hbar^2 q^2}{2m} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}$$

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

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

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

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \sum_{\mathbf{q}} \frac{\hbar^2 q^2}{2m} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}$$

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

The potential-energy term is

$$U(\mathbf{r})\psi(\mathbf{r}) = \sum_{\mathbf{G}, \mathbf{q}} U_{\mathbf{G}} c_{\mathbf{q}} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}}$$

Introducing

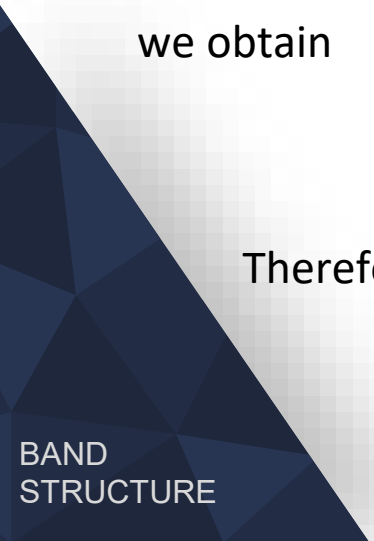
$$\mathbf{q}' = \mathbf{q} + \mathbf{G}$$

we obtain

$$U(\mathbf{r})\psi(\mathbf{r}) = \sum_{\mathbf{q}'} \left(\sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q}' - \mathbf{G}} \right) e^{i\mathbf{q}' \cdot \mathbf{r}}.$$

Therefore, the Schrödinger equation becomes:

$$\sum_{\mathbf{q}} \left[\frac{\hbar^2 q^2}{2m} c_{\mathbf{q}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q} - \mathbf{G}} \right] e^{i\mathbf{q} \cdot \mathbf{r}} = \varepsilon \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}.$$



3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$\sum_{\mathbf{q}} \left[\frac{\hbar^2 q^2}{2m} c_{\mathbf{q}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} \right] e^{i\mathbf{q}\cdot\mathbf{r}} = \varepsilon \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

By collecting the coefficients of the same plane wave $e^{i\mathbf{q}\cdot\mathbf{r}}$, the Schrödinger equation becomes

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left[\left(\frac{\hbar^2 q^2}{2m} - \varepsilon \right) c_{\mathbf{q}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} \right] = 0$$

Since the plane waves $e^{i\mathbf{q}\cdot\mathbf{r}}$ are linearly independent, the coefficient of each plane wave must vanish:

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon \right) c_{\mathbf{q}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} = 0, \quad \forall \mathbf{q}.$$

This is the Schrödinger equation in momentum space. The periodic potential couples a plane-wave component with wavevector $\mathbf{q}$ only to components whose wavevectors differ from $\mathbf{q}$ by a reciprocal-lattice vector $\mathbf{G}$.

$$\mathbf{q} \leftrightarrow \mathbf{q} - \mathbf{G}.$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon \right) c_{\mathbf{q}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} = 0$$

The original differential equation has therefore been transformed into an infinite homogeneous system of linear equations for the coefficients $c_{\mathbf{q}}$. Nontrivial solutions exist only for specific eigenvalues ε .

Every wavevector $\mathbf{q}$ can be written uniquely as

$$\mathbf{q} = \mathbf{k} - \mathbf{G}$$

where $\mathbf{k}$ lies in the first Brillouin zone and $\mathbf{G}$ is a reciprocal-lattice vector.

The periodic potential couples only plane-wave components whose wavevectors differ by a reciprocal-lattice vector. Therefore, the coefficients

$$c_{\mathbf{k}-\mathbf{G}}$$

are coupled to one another, whereas coefficients belonging to different values of $\mathbf{k}$ are not coupled.

The original problem separates into independent problems, one for each $\mathbf{k}$ in the first Brillouin zone.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

For a fixed $\mathbf{k}$, the Bloch eigenstate is expanded as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}.$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\mathbf{q} = \mathbf{k} - \mathbf{G}$$

Factoring out the plane-wave term $e^{i\mathbf{k}\cdot\mathbf{r}}$, we obtain

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}$$

Defining

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}$$

the eigenfunction assumes the Bloch form

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

Because $\mathbf{G} \cdot \mathbf{R} = 2\pi m$, with $m \in \mathbb{Z}$, the function $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

This is Bloch's theorem: in a periodic potential, every one-electron eigenstate is a plane wave modulated by a lattice-periodic function.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_{\mathbf{q}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{q}-\mathbf{G}'} = 0$$

$$\mathbf{q} = \mathbf{k} - \mathbf{G}$$

Let's recall the momentum-space Schrödinger equation. The substitution gives:

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon\right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k}-\mathbf{G}-\mathbf{G}'} = 0$$

Since the difference of two reciprocal-lattice vectors is itself a reciprocal-lattice vector, we may define

$$\mathbf{G}'' = \mathbf{G} - \mathbf{G}'$$

The equation can therefore be written as

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon\right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}''} U_{\mathbf{G}-\mathbf{G}''} c_{\mathbf{k}-\mathbf{G}''} = 0$$

For each fixed $\mathbf{k}$, this is an infinite matrix equation in the coefficients $c_{\mathbf{k}-\mathbf{G}}$.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

We have seen that the wavevector $\mathbf{k}$ appearing in Bloch's theorem can be chosen within the first Brillouin zone. We now show that this restriction entails no loss of generality.

Let us consider a wavevector $\mathbf{k}'$ outside the first Brillouin zone. According to Bloch's theorem,

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

$$\psi_{\mathbf{k}'}(\mathbf{r}) = u'(\mathbf{r}) e^{i\mathbf{k}'\cdot\mathbf{r}}$$

There is always a reciprocal-lattice vector $\mathbf{G}'$ such that

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

where $\mathbf{k}$ lies in the first Brillouin zone. Hence,

$$\psi_{\mathbf{k}'}(\mathbf{r}) = u'(\mathbf{r}) e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} [u'(\mathbf{r}) e^{i\mathbf{G}'\cdot\mathbf{r}}].$$

We can expand $u'(\mathbf{r})$ as

$$u'(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}'-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}$$

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left[\sum_{\mathbf{G}} c_{\mathbf{k}'-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}'\cdot\mathbf{r}} \right] = e^{i\mathbf{k}\cdot\mathbf{r}} \left[\sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}'-\mathbf{G}} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \right]$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left[\sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}'-\mathbf{G}} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \right]$$

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

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}$$

By defining

$$\mathbf{G}'' = \mathbf{G} - \mathbf{G}'$$

We obtain

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left[\sum_{\mathbf{G}''} c_{\mathbf{k}-\mathbf{G}''} e^{-i\mathbf{G}''\cdot\mathbf{r}} \right] = \psi_{\mathbf{k}}(\mathbf{r}).$$

Therefore, $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}'$ describe the same Bloch state. The wavevector $\mathbf{k}$ can thus be restricted to the first Brillouin zone.

It remains to be shown that choosing two wavevectors related by a reciprocal-lattice vector,

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

leads to exactly the same system of equations for the Fourier coefficients.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.2 Bloch's Theorem

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}''} U_{\mathbf{G}-\mathbf{G}''} c_{\mathbf{k}-\mathbf{G}''} = 0$$

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

Substituting, we obtain

$$\left[\frac{\hbar^2}{2m} |\mathbf{k}' - \mathbf{G}' - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}'-\mathbf{G}'-\mathbf{G}} + \sum_{\mathbf{G}''} U_{\mathbf{G}-\mathbf{G}''} c_{\mathbf{k}'-\mathbf{G}'-\mathbf{G}''} = 0$$

Let us introduce $\tilde{\mathbf{G}} = \mathbf{G}' + \mathbf{G}$, $\tilde{\mathbf{G}}' = \mathbf{G}' + \mathbf{G}''$

and we have:

$$\left[\frac{\hbar^2}{2m} |\mathbf{k}' - \tilde{\mathbf{G}}|^2 - \varepsilon \right] c_{\mathbf{k}'-\tilde{\mathbf{G}}} + \sum_{\tilde{\mathbf{G}}'} U_{\tilde{\mathbf{G}}-\tilde{\mathbf{G}}'} c_{\mathbf{k}'-\tilde{\mathbf{G}}'} = 0$$

Since $\tilde{\mathbf{G}}$ and $\tilde{\mathbf{G}}'$ span all reciprocal-lattice, this system is identical to that obtained for $\mathbf{k}$.

Therefore, the eigenvalues and eigenstates associated with $\mathbf{k}' = \mathbf{k} + \mathbf{G}''$ are identical to those associated with $\mathbf{k}$. Wavevectors that differ by a reciprocal-lattice vector label the same physical Bloch state.

It is thus sufficient to solve the problem for $\mathbf{k}$ restricted to the first Brillouin zone. This convention is known as the reduced-zone scheme. 32

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.3 Band Index

Let us consider one-electron Schrödinger equation in real space:

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

For a fixed wavevector $\mathbf{k}$, we seek solutions in the Bloch form:

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

where the function $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the Bravais lattice:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

Substitution into the Schrödinger equation gives the eigenvalue problem

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

For a fixed wavevector $\mathbf{k}$, the equation for the lattice-periodic function $u_{\mathbf{k}}(\mathbf{r})$ can be solved within a single primitive cell, subject to periodic boundary conditions.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.3 Band Index

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

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

Because the problem is defined over a finite volume, it has an infinite discrete set of eigenvalues.

For each fixed $\mathbf{k}$, these eigenvalues can be labelled by an integer n :

$$\varepsilon_{1\mathbf{k}}, \varepsilon_{2\mathbf{k}}, \varepsilon_{3\mathbf{k}}, \dots$$

As $\mathbf{k}$ is varied continuously, each eigenvalue $\varepsilon_{n\mathbf{k}}$ changes continuously.

Moreover, wavevectors that differ by a reciprocal-lattice vector describe the same physical state.

Hence, the energy spectrum is periodic in reciprocal space:

$$\varepsilon_n(\mathbf{k} + \mathbf{G}) = \varepsilon_n(\mathbf{k}).$$

The integer n is called the band index. It is therefore sufficient to consider $\mathbf{k}$ within the first Brillouin zone.

— $n = 4$

— $n = 3$

— $n = 2$

— $n = 1$

— $n = 4$

— $n = 3$

— $n = 2$

— $n = 1$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.3 Band Index

$$\varepsilon_n(\mathbf{k} + \mathbf{G}) = \varepsilon_n(\mathbf{k})$$

The one-electron energy spectrum in a periodic potential is therefore described by a family of continuous functions $\varepsilon_n(\mathbf{k})$, each defined within the first Brillouin zone.

The complete set of these functions constitutes the band structure of the solid.

For a fixed value of n , the set of energies

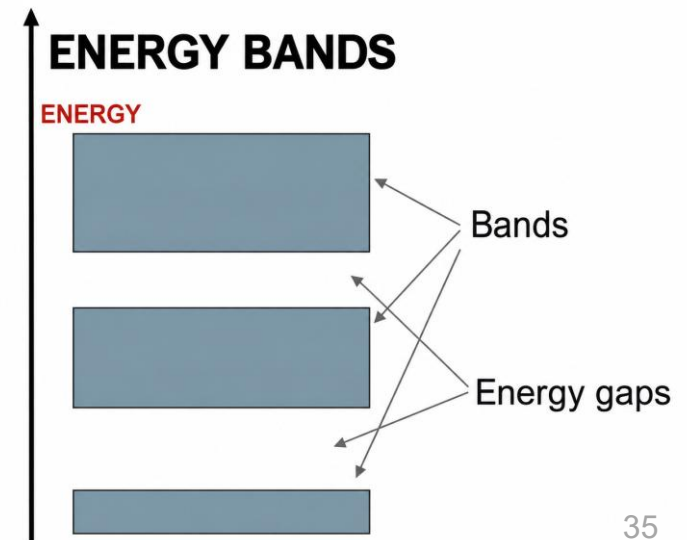
$$\mathcal{B}_n = \{\varepsilon_n(\mathbf{k}) : \mathbf{k} \in \text{BZ}\}$$

is called the n -th energy band.

Because $\varepsilon_n(\mathbf{k})$ is a continuous function and the first Brillouin zone is connected, the allowed energies of a given band fill a continuous interval:

$$\varepsilon_n^{\min} \leq \varepsilon_n(\mathbf{k}) \leq \varepsilon_n^{\max}.$$

This continuous range of allowed energies is the origin of the term “energy band”.



3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.4 Fermi surface

At zero temperature, the ground state of a free-electron gas is obtained by filling all one-electron states with

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} < E_F$$

The Fermi energy E_F is fixed by the total number of electrons. Each spatial state labelled by $\mathbf{k}$ can accommodate two electrons with opposite spin.

The ground state of N Bloch electrons is constructed in the same way, with the following differences:

1. The one-electron energy levels are labelled by a band index n and a crystal wavevector $\mathbf{k}$: $\varepsilon_n(\mathbf{k})$.
2. In general, the dispersion relation $\varepsilon_n(\mathbf{k})$ does not have the simple parabolic form of the free-electron gas.
3. The wavevector $\mathbf{k}$ is restricted to the first Brillouin zone, so that every physical Bloch state is counted only once.

At zero temperature, the Bloch states are filled in order of increasing energy up to the Fermi energy.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.4 Fermi surface

If an integer number of bands is completely filled and the next band is empty, the energy difference between the top of the highest occupied band and the bottom of the lowest empty band is called the band gap:

$$E_g = \min_{\mathbf{k}} \varepsilon_{\text{empty}}(\mathbf{k}) - \max_{\mathbf{k}} \varepsilon_{\text{occupied}}(\mathbf{k}).$$

Materials with a large band gap have negligible electrical conductivity at ordinary temperatures and are classified as insulators.

Materials with a smaller band gap can generate a measurable concentration of charge carriers through thermal excitation or doping and are classified as semiconductors.

A band may be partially filled. In this case, at zero temperature, the Fermi energy lies within the energy range of that band.

The set of wavevectors separating occupied from empty states defines the Fermi surface. It is the generalization of the Fermi sphere of a free-electron gas.

A solid with a partially filled band has metallic behaviour. The Fermi surface in the n -th band is defined by

$$\varepsilon_n(\mathbf{k}) = E_F$$

Therefore, the Fermi surface is a constant-energy surface in reciprocal space, restricted to the first Brillouin zone.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.5 Kronig-Penney model

In 1931, Kronig and Penney introduced a solvable one-dimensional model that illustrates the origin of electronic energy bands in a periodic potential.

Consider a one-dimensional lattice with lattice constant a , Bravais-lattice vectors :

$$R_n = na, \quad n \in \mathbb{Z}$$

and reciprocal-lattice vectors

$$G = \frac{2\pi m}{a}, m \in \mathbb{Z}$$

The periodic potential is modelled as a Dirac-comb potential:

$$U(x) = U_0 a \sum_{n=-\infty}^{+\infty} \delta(x - na)$$

where U_0 has the dimensions of energy.

The Fourier coefficients of this potential are independent of G :

$$U_G = \frac{1}{a} \int_0^a U(x) e^{-iGx} dx = U_0$$

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$
$$U_{\mathbf{G}} = \frac{1}{V_c} \int_{V_c} U(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d^3r$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.5 Kronig-Penney model

Since $U_G = U_0$, the momentum-space Schrödinger equation is therefore:

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_q + U_0 \sum_G c_{q-G} = 0.$$

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_q + \sum_G U_G c_{q-G} = 0$$

Define:

$$Q_q = \sum_G c_{q-G}$$

The Schrödinger equation can then be written as:

$$\left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) c_q + U_0 Q_q = 0$$

Solving for c_q , we obtain

$$c_q = -\frac{U_0}{\frac{\hbar^2 q^2}{2m} - \varepsilon} Q_q$$

For a given Bloch wavevector k , the coupled plane-wave components have wavevectors

$$q = k - G$$

where G is a reciprocal-lattice vector.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.5 Kronig-Penney model

$$q = k - G$$

$$Q_q = \sum_G c_{q-G}$$

$$c_q = -\frac{U_0}{\frac{\hbar^2 q^2}{2m} - \varepsilon} Q_q$$

Therefore:

$$c_{k-G} + \frac{U_0}{\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon} Q_{k-G} = 0.$$

Summing the equation over all reciprocal-lattice vectors G , we obtain:

$$\sum_G \left[c_{k-G} + \frac{U_0}{\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon} Q_{k-G} \right] = 0$$

Moreover: $Q_{k-G} = \sum_{G'} c_{k-G-G'} = \sum_{G''} c_{k-G''} = Q_k$ where $G'' = G + G'$

Since G'' spans all reciprocal-lattice vectors when G' does, Q_{k-G} is independent of G . Therefore, it can be taken outside the summation:

$$Q_k + U_0 Q_k \sum_G \frac{1}{\left[\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon \right]} = 0$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.5 Kronig-Penney model

For the branch of solutions with $Q_k \neq 0$, the secular equation becomes

$$-\frac{1}{U_0} = \sum_G \frac{1}{\left[\frac{\hbar^2}{2m} (k - G)^2 - \mathcal{E} \right]}$$

$$Q_k + U_0 Q_k \sum_G \frac{1}{\left[\frac{\hbar^2}{2m} (k - G)^2 - \mathcal{E} \right]} = 0$$

For a one-dimensional lattice of period a , the reciprocal-lattice vectors are:

$$G_n = \frac{2\pi n}{a}, \quad n \in \mathbb{Z}$$

The summation over reciprocal-lattice vectors can therefore be written as a summation over all integers n . For each wavevector

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a},$$

the secular equation is solved for the allowed energies $\varepsilon_n(k)$. Repeating the procedure for all values of k in the first Brillouin zone yields the energy bands.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.5 Kronig-Penney model

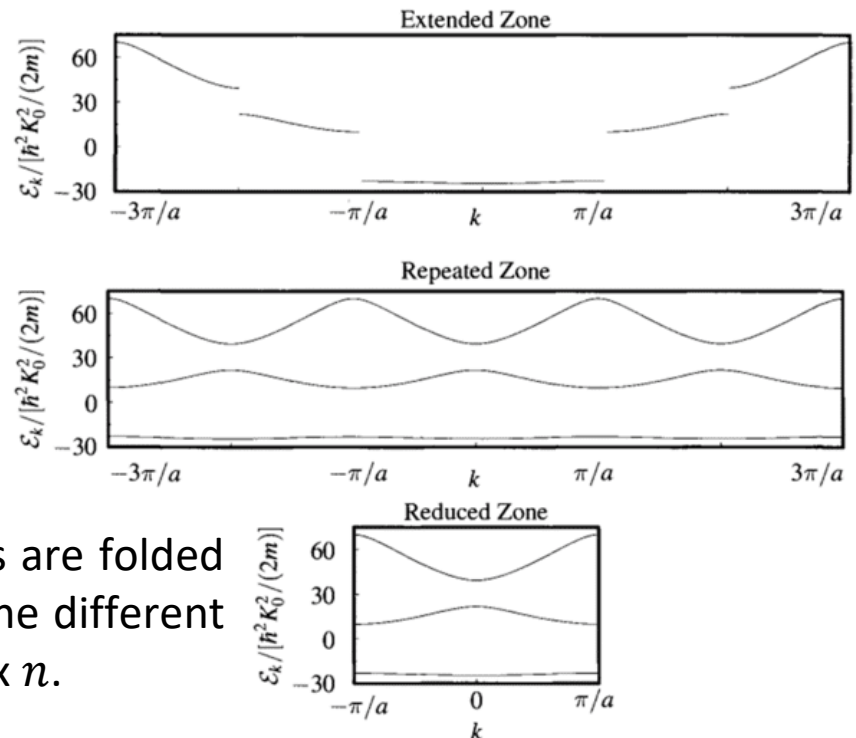
The secular equation determines the allowed energies $\varepsilon_n(k)$ for each wavevector k . Solving it throughout reciprocal space yields the band structure shown below.

The same energy spectrum can be represented using three equivalent schemes.

Extended-zone scheme: the dispersion is displayed over several Brillouin zones. Energy gaps open at the Brillouin-zone boundaries, where the effect of the periodic potential is strongest.

Repeated-zone scheme: the energy spectrum is repeated in each reciprocal-lattice cell.

Reduced-zone scheme: all wavevectors are folded back into the first Brillouin zone, and the different branches are labelled by the band index n .



In the reduced-zone scheme, each continuous branch $\varepsilon_n(k)$ represents an energy band. The gaps between adjacent branches are forbidden energy intervals.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

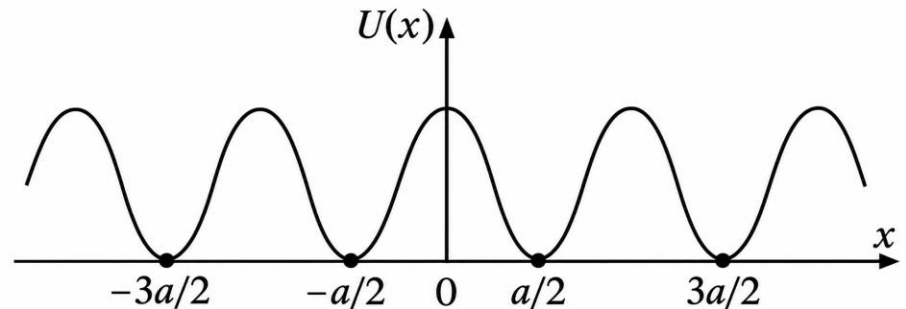
3.3.6 Bands in a 1D periodic potential

Having obtained the energy bands from the Kronig–Penney model, we now introduce a simple scattering picture that provides an intuitive physical origin of band formation.

We consider a one-dimensional periodic array of identical potential barriers. Each barrier partially reflects and partially transmits an incident electron wave:

$$U(x) = \sum_{n=-\infty}^{+\infty} v(x - na)$$

where a is the lattice constant and $v(x)$ is the potential profile of a single barrier, localized within a region of width $b < a$.



The barriers are centred at the Bravais-lattice sites

$$R_n = na, \quad n \in \mathbb{Z}.$$

The purpose of this exercise is to determine how the coherent superposition of the reflected and transmitted waves from successive barriers gives rise to allowed energy bands and forbidden energy gaps. 43

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

The function $v(x - na)$ represents a single localized scattering barrier centred at the lattice site $x = na$. The periodic potential is obtained by repeating this barrier at all lattice sites.

$$U(x) = \sum_{n=-\infty}^{+\infty} v(x - na)$$

An electron can propagate from one region to the next either by transmission above the barrier or, when its energy is below the barrier height, by quantum tunnelling.

We assume that the single-barrier potential is inversion symmetric:

$$v(x) = v(-x)$$

Apart from this symmetry and its localization around $x = 0$, no specific form of $v(x)$ is assumed. The purpose of the following derivation is to relate the scattering properties of one barrier to the allowed energies of the periodic chain.

Consider an electron incident from the left on a single barrier $v(x)$. In the regions where the potential vanishes, its energy is

$$\mathcal{E} = \frac{h^2 K^2}{2m}$$

Here, K is the wavevector of the scattering state for the isolated barrier. It is a continuous variable determined by the electron energy and must not be confused with the Bloch wavevector k .



3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

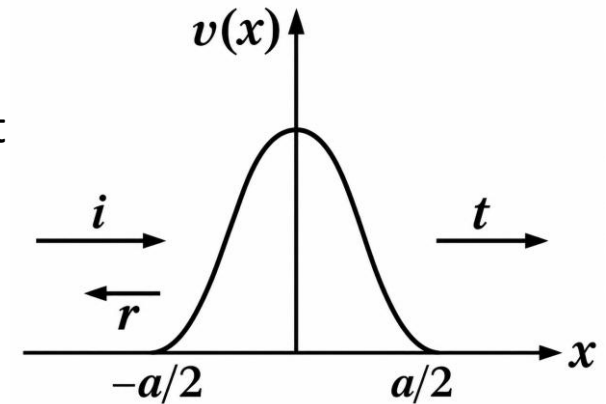
3.3.6 Bands in a 1D periodic potential

For the isolated barrier, let

$$v(x) = 0 \text{ for } |x| \geq \frac{a}{2}$$

Outside the barrier region, an electron incident from the left is described by

$$\psi_L(x) = \begin{cases} e^{iKx} + r(K)e^{-iKx}, & x \leq -\frac{a}{2}, \\ t(K)e^{iKx}, & x \geq \frac{a}{2}. \end{cases}$$



The incident wave has unit amplitude. The quantities $r(K)$ and $t(K)$ are the complex reflection and transmission amplitudes, respectively.

Since the potential is real and the wavevector has the same magnitude on both sides of the barrier, the reflection and transmission probabilities are

$$R(K) = |r(K)|^2, \quad T(K) = |t(K)|^2, \quad R(K) + T(K) = 1$$

Both amplitudes depend on the wavevector K and on the specific shape of the barrier. In the following, we will obtain qualitative features of the band structure without specifying $v(x)$ explicitly, using only the general properties of $r(K)$ and $t(K)$.

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

Since the single-barrier potential is inversion symmetric,

$$v(x) = v(-x),$$

if $\psi_L(x)$ is a solution of the Schrödinger equation with energy ε , then

$$\psi_R(x) = \psi_L(-x)$$

is also a solution with the same energy. It describes a wave incident on the barrier from the right.

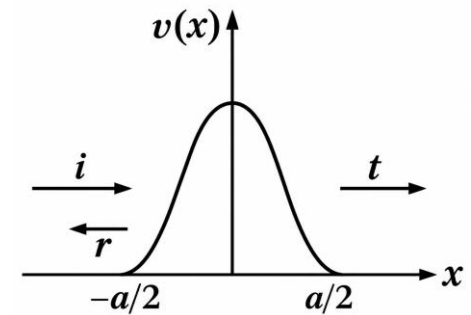
By replacing x with $-x$ in $\psi_L(x)$, we obtain

$$\psi_R(x) = \begin{cases} t e^{-iKx}, & x \leq -\frac{a}{2}, \\ e^{-iKx} + r e^{iKx}, & x \geq \frac{a}{2}. \end{cases}$$

a wave incident on the barrier from the right.

The functions $\psi_L(x)$ and $\psi_R(x)$ are two linearly independent solutions at the same energy.

$$\psi_L(x) = \begin{cases} e^{iKx} + r e^{-iKx} & x \leq -\frac{a}{2} \\ t e^{iKx} & x \geq \frac{a}{2} \end{cases}$$



3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

Therefore, any solution at this energy can be written as

$$\psi(x) = A\psi_L(x) + B\psi_R(x).$$

In particular, this representation can be used inside the barrier region

$$-\frac{a}{2} \leq x \leq \frac{a}{2}$$

$$\psi_L(x) = \begin{cases} e^{iKx} + re^{-iKx} & x \leq -\frac{a}{2} \\ te^{iKx} & x \geq \frac{a}{2} \end{cases}$$
$$\psi_R(x) = \begin{cases} te^{-iKx} & x \leq -\frac{a}{2} \\ e^{-iKx} + re^{iKx} & x \geq \frac{a}{2} \end{cases}$$

For an electron moving in the periodic potential, the wavefunction must satisfy Bloch's condition:

$$\psi_k(x + a) = e^{ika}\psi_k(x), \quad \text{where } k \text{ is the Bloch wavevector.}$$

Applying this condition at the boundaries of the barrier region gives

$$\psi_k\left(\frac{a}{2}\right) = e^{ika}\psi_k\left(-\frac{a}{2}\right).$$

Using the two scattering solutions, outside the barrier we have

$$\psi_k(x) = \begin{cases} Ae^{iKx} + (Ar + Bt)e^{-iKx}, & x \leq -\frac{a}{2}, \\ (At + Br)e^{iKx} + Be^{-iKx}, & x \geq \frac{a}{2}. \end{cases}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

Evaluating the wavefunction at the two boundaries of the barrier region, we obtain:

$$\psi_k\left(-\frac{a}{2}\right) = Ae^{-iK\frac{a}{2}} + (Ar + Bt)e^{iK\frac{a}{2}}$$

$$\psi_k\left(\frac{a}{2}\right) = (At + Br)e^{iK\frac{a}{2}} + Be^{-iK\frac{a}{2}}$$

$$\psi_k(x) = \begin{cases} Ae^{iKx} + (Ar + Bt)e^{-iKx}, & x \leq -\frac{a}{2}, \\ (At + Br)e^{iKx} + Be^{-iKx}, & x \geq \frac{a}{2}. \end{cases}$$

Applying Bloch's condition for $x = -\frac{a}{2}$:

$$\psi_k(x + a) = e^{ika}\psi_k(x)$$

$$\psi_k\left(\frac{a}{2}\right) = e^{ika}\psi_k\left(-\frac{a}{2}\right)$$

gives:

$$(At + Br)e^{iK\frac{a}{2}} + Be^{-iK\frac{a}{2}} = e^{ika}\left[Ae^{-iK\frac{a}{2}} + (Ar + Bt)e^{iK\frac{a}{2}}\right]$$

Dividing both sides by $e^{-iK\frac{a}{2}}$, we find:

$$e^{ika}\left[A + (Ar + Bt)e^{iKa}\right] = B + (At + Br)e^{iKa}$$

Collecting separately the terms proportional to **A** and **B**, we obtain:

$$\left[e^{ika}(1 + re^{iKa}) - te^{iKa}\right]\mathbf{A} + (te^{iKa}e^{iKa} - re^{iKa} - 1)\mathbf{B} = 0$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

We now derive the second boundary condition by differentiating Bloch's condition:

$$\psi'_k(x + a) = e^{ika}\psi'_k(x)$$

Evaluating this condition at $x = -a/2$, we obtain :

$$\psi'_k\left(\frac{a}{2}\right) = e^{ika}\psi'_k\left(-\frac{a}{2}\right)$$

$$\psi_k(x) = \begin{cases} Ae^{iKx} + (Ar + Bt)e^{-iKx}, & x \leq -\frac{a}{2}, \\ (At + Br)e^{iKx} + Be^{-iKx}, & x \geq \frac{a}{2}. \end{cases}$$

Differentiating the expressions for $\psi_k(x)$, we find :

$$\psi'_k(x) = \begin{cases} iKAe^{iKx} - iK(Ar + Bt)e^{-iKx} & x \leq -\frac{a}{2} \\ iK(At + Br)e^{iKx} - iKBe^{-iKx} & x \geq \frac{a}{2} \end{cases}$$

Therefore:

$$\psi'_k\left(-\frac{a}{2}\right) = iKAe^{-iK\frac{a}{2}} - iK(Ar + Bt)e^{iK\frac{a}{2}}$$

$$\psi'_k\left(\frac{a}{2}\right) = iK(At + Br)e^{iK\frac{a}{2}} - iKBe^{-iK\frac{a}{2}}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

Applying the derivative form of Bloch's condition gives:

$$(At + Br)e^{iK\frac{a}{2}} - Be^{-iK\frac{a}{2}} = e^{ika} [Ae^{-iK\frac{a}{2}} - (Ar + Bt)e^{iK\frac{a}{2}}]$$

Dividing both sides by $e^{-iKa/2}$, we obtain:

$$e^{ika} [A - (Ar + Bt)e^{iKa}] = -B + (At + Br)e^{iKa}$$

Collecting separately the terms proportional to $\mathbf{A}$ and $\mathbf{B}$, we find:

$$[e^{ika}(1 - re^{iKa}) - te^{iKa}]\mathbf{A} + (-te^{ika}e^{iKa} - re^{iKa} + 1)\mathbf{B} = 0$$

Together with the equation obtained from the wavefunction itself, we have the homogeneous system:

$$\begin{cases} [e^{ika}(1 + re^{iKa}) - te^{iKa}]\mathbf{A} + (te^{ika}e^{iKa} - re^{iKa} - 1)\mathbf{B} = 0 \\ [e^{ika}(1 - re^{iKa}) - te^{iKa}]\mathbf{A} + (-te^{ika}e^{iKa} - re^{iKa} + 1)\mathbf{B} = 0 \end{cases}$$

For this system to have a nontrivial solution, the determinant of its coefficient matrix must vanish.

$$\psi'_k(x + a) = e^{ika}\psi'_k(x)$$

$$\psi'_k\left(-\frac{a}{2}\right) = iKAe^{-iK\frac{a}{2}} - iK(Ar + Bt)e^{iK\frac{a}{2}}$$

$$\psi'_k\left(\frac{a}{2}\right) = iK(At + Br)e^{iK\frac{a}{2}} - iKBe^{-iK\frac{a}{2}}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

Setting the determinant of the coefficient matrix equal to zero gives:

$$\left[e^{ika}(1 + re^{iKa}) - te^{iKa} \right] \cdot (-te^{ika}e^{iKa} - re^{iKa} + 1) - (te^{ika}e^{iKa} - re^{iKa} - 1) \cdot [e^{ika}(1 - re^{iKa}) - te^{iKa}] = 0$$

After simplifying, we obtain:

$$e^{2iKa}(t^2 - r^2)e^{ika} - t(1 + e^{2ika})e^{iKa} + e^{ika} = 0$$

Multiplying both sides by $e^{-ika}e^{-iKa}$, we find :

$$e^{iKa}(t^2 - r^2) - t(e^{-ika} + e^{ika}) + e^{-iKa} = 0$$

Using $e^{-ika} + e^{ika} = 2 \cos(ka)$, the result can be written as:

$$2t \cos(ka) = e^{iKa}(t^2 - r^2) + e^{-iKa}$$

This is the dispersion relation connecting the Bloch wavevector k of the periodic lattice to the scattering wavevector K of the single-barrier problem, with

$$\varepsilon = \frac{\hbar^2 K^2}{2m}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

For a real and inversion-symmetric barrier, the transmission and reflection amplitudes can be written as:

$$t(K) = |t(K)| e^{i\delta(K)}, \\ r(K) = \pm i |r(K)| e^{i\delta(K)}$$

Here, $\delta(K)$ is the transmission phase shift relative to the incident wave. The reflection amplitude differs in phase from the transmission amplitude by $\pm\pi/2$.

Conservation of probability current implies:

$$|t(K)|^2 + |r(K)|^2 = 1$$

Substituting these expressions into the dispersion relation, we obtain

$$2t \cos(ka) = e^{iKa}(t^2 - r^2) + e^{-iKa}$$

$$2 |t(K)| e^{i\delta(K)} \cos(ka) = e^{iKa} [|t(K)|^2 + |r(K)|^2] e^{2i\delta(K)} + e^{-iKa}$$

Using the probability-conservation condition, this reduces to:

$$2 |t(K)| e^{i\delta(K)} \cos(ka) = e^{iKa+2i\delta(K)} + e^{-iKa}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

$$2 |t(K)| e^{i\delta(K)} \cos(ka) = e^{iKa+2i\delta(K)} + e^{-iKa}$$

Multiplying both sides by $e^{-i\delta(K)}$, we obtain:

$$2 |t(K)| \cos(ka) = e^{i[Ka+\delta(K)]} + e^{-i[Ka+\delta(K)]}$$

Using $e^{i\alpha} + e^{-i\alpha} = 2 \cos \alpha$, we find:

$$\cos(ka) = \frac{\cos[Ka + \delta(K)]}{|t(K)|} \quad \text{with} \quad \mathcal{E} = \frac{\hbar^2 K^2}{2m}$$

The transmission amplitude satisfies

$$0 < |t(K)| \leq 1$$

The phase shift $\delta(K)$ and the transmission amplitude $|t(K)|$ both depend on the scattering wavevector K , and therefore on the electron energy.

For a localized barrier, $|t(K)| \rightarrow 1$ as $K \rightarrow \infty$.

The left-hand side is a periodic function of K , with an amplitude equal to

$$\frac{1}{|t(K)|}$$

3.3 NON-INTERACTING ELECTRONS IN A PERIODIC POTENTIAL

3.3.6 Bands in a 1D periodic potential

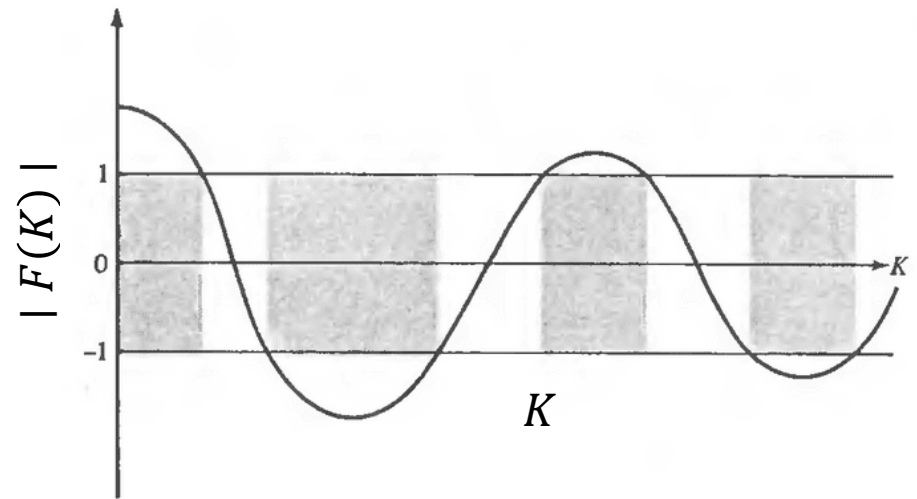
$$\cos(ka) = \frac{\cos[Ka + \delta(K)]}{|t(K)|}$$

Since the left-hand side satisfies

$$-1 \leq \cos(ka) \leq 1$$

a real Bloch wavevector k exists only when

$$|F(K)| = \frac{\cos[Ka + \delta(K)]}{|t(K)|} \leq 1$$



Therefore, the allowed values of the scattering wavevector K are the intervals for which the curve $|F(K)|$ lies between the horizontal lines $+1$ and -1 .

For each allowed value of K , the electron energy is $\varepsilon = \frac{\hbar^2 K^2}{2m}$

The corresponding energy intervals form the allowed energy bands.

Conversely, when $|F(K)| > 1$ no real value of the Bloch wavevector k satisfies the dispersion relation. The corresponding energy intervals are forbidden and constitute energy gaps.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

Electrons in a periodic crystal potential can be described using different approximation schemes. Two complementary limits are particularly important: the nearly-free-electron model and the tight-binding model.

The nearly-free-electron model applies when the periodic potential experienced by the valence electrons is weak compared with their kinetic energy. It starts from the free-electron gas and treats the periodic crystal potential as a perturbation.

Although the bare Coulomb potential of the ionic cores is strong, the effective potential acting on valence electrons can be substantially weaker for two main reasons:

1. Core electrons, together with the ionic cores, can be described by an effective pseudopotential. The orthogonality of valence-electron states to core states strongly modifies the short-range ionic potential.
2. The response of the valence electrons screens the electrostatic field of the ions, reducing the Fourier components of the effective periodic potential.

Even a weak periodic potential can have an important effect near Brillouin-zone boundaries, where it opens energy gaps.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

When the periodic potential is zero, the eigenstates of the Schrödinger equation are plane waves. In the nearly-free-electron approximation, a weak periodic potential is treated as a perturbation of this free-electron solution.

The wavefunction of a Bloch state with wavevector $\mathbf{k}$ is written as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}$$

The coefficients $c_{\mathbf{k}-\mathbf{G}}$ and the allowed energies ε are determined by the system of equations:

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'} = 0$$

For each fixed $\mathbf{k}$, this is an infinite homogeneous system, with one equation for each reciprocal-lattice vector $\mathbf{G}$. Its distinct solutions are labelled by the band index n .

The wavevector $\mathbf{k}$ can be restricted to the first Brillouin zone.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

For a free electron, the periodic potential vanishes, so that:

$$U_{\mathbf{G}} = 0 \quad \forall \mathbf{G}$$

Equation then reduces to

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}-\mathbf{G}} = 0$$

$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'} = 0$$

Introducing the free-electron energy: $\varepsilon_{\mathbf{q}}^0 = \frac{\hbar^2 q^2}{2m}$

we can rewrite this equation as:

$$[\varepsilon_{\mathbf{k}-\mathbf{G}}^0 - \varepsilon] c_{\mathbf{k}-\mathbf{G}} = 0$$

For a nontrivial solution, a coefficient $c_{\mathbf{k}-\mathbf{G}}$ can be nonzero only if

$$\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}}^0$$

Two cases may occur:

1. There is only one reciprocal-lattice vector $\mathbf{G}_1$ for which $\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0$

Then only $c_{\mathbf{k}-\mathbf{G}_1}$ is nonzero, whereas

$$c_{\mathbf{k}-\mathbf{G}} = 0 \quad \text{for } \mathbf{G} \neq \mathbf{G}_1$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

2. Several reciprocal-lattice vectors $\mathbf{G}_1, \dots, \mathbf{G}_m$ satisfy

$$\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 = \dots = \varepsilon_{\mathbf{k}-\mathbf{G}_m}^0$$

When ε is equal to the common value of these free-electron energies, there are m linearly independent degenerate plane-wave solutions. Any linear combination of these degenerate solutions is also a solution; therefore, the coefficients

$$c_{\mathbf{k}-\mathbf{G}_j}, \quad j = 1, \dots, m$$

are not determined in the free-electron limit.

This observation becomes crucial when a weak periodic potential, with nonzero Fourier coefficients $U_{\mathbf{G}}$, is introduced. We distinguish between non-degenerate and degenerate solutions.

CASE 1 — NON-DEGENERATE SOLUTIONS

There is only one reciprocal-lattice vector $\mathbf{G}_1$ for which

$$\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0$$

The coefficient $c_{\mathbf{k}-\mathbf{G}_1}$ may be nonzero, whereas all other coefficients vanish in the free-electron limit.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

Let us fix $\mathbf{k}$ and consider a reciprocal-lattice vector $\mathbf{G}_1$ such that the free-electron energy $\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0$ is well separated from all other free-electron energies:

$$|\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 - \varepsilon_{\mathbf{k}-\mathbf{G}}^0| \gg |U_{\mathbf{G}-\mathbf{G}_1}|, \quad \mathbf{G} \neq \mathbf{G}_1$$

We now investigate the effect of the periodic potential on the free-electron state

$$\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0, \quad c_{\mathbf{k}-\mathbf{G}_1} \neq 0$$

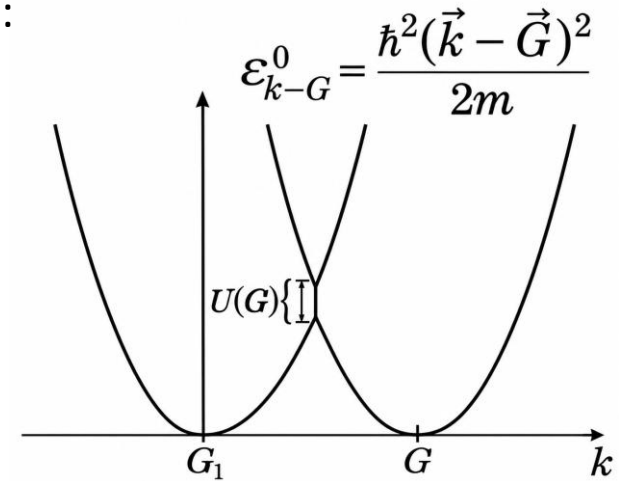
while, in the free-electron limit,

$$c_{\mathbf{k}-\mathbf{G}} = 0, \quad \mathbf{G} \neq \mathbf{G}_1$$

As a first approximation, we assume that $c_{\mathbf{k}-\mathbf{G}_1}$ is the only nonzero coefficient.

Setting $\mathbf{G} = \mathbf{G}_1$ in the equation, we obtain

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0] c_{\mathbf{k}-\mathbf{G}_1} = \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}_1} c_{\mathbf{k}-\mathbf{G}'}$$



$$\left[\frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2 - \varepsilon \right] c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'} = 0$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0] c_{\mathbf{k}-\mathbf{G}_1} = \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}_1} c_{\mathbf{k}-\mathbf{G}'}$$

$$c_{\mathbf{k}-\mathbf{G}} = 0, \quad \mathbf{G} \neq \mathbf{G}_1$$

$$c_{\mathbf{k}-\mathbf{G}_1} \neq 0$$

Let us examine the right-hand side. The term with $\mathbf{G}' = \mathbf{G}_1$ contains U_0 , which vanishes because the average value of the potential has been chosen to be zero.

For $\mathbf{G}' \neq \mathbf{G}_1$, the coefficients $c_{\mathbf{k}-\mathbf{G}'}$ are first order in the weak potential, as are the Fourier coefficients $U_{\mathbf{G}'-\mathbf{G}_1}$. Their products are therefore of second order.

For $\mathbf{G} \neq \mathbf{G}_1$, we isolate in the sum the term containing the dominant coefficient $c_{\mathbf{k}-\mathbf{G}_1}$

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0] c_{\mathbf{k}-\mathbf{G}} = U_{\mathbf{G}_1-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}_1} + \sum_{\mathbf{G}' \neq \mathbf{G}_1} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'}$$

Therefore,

$$c_{\mathbf{k}-\mathbf{G}} = \frac{U_{\mathbf{G}_1-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}_1}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} + \sum_{\mathbf{G}' \neq \mathbf{G}_1} \frac{U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0}$$

The second term is of second order in the weak potential, because it contains the product of a Fourier coefficient $U_{\mathbf{G}'-\mathbf{G}}$ and a coefficient $c_{\mathbf{k}-\mathbf{G}'}$ that is already first order in U .

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

$$c_{\mathbf{k}-\mathbf{G}} = \frac{U_{\mathbf{G}_1-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}_1}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} + \sum_{\mathbf{G}' \neq \mathbf{G}_1} \frac{U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0}$$

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0] c_{\mathbf{k}-\mathbf{G}_1} = \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}_1} c_{\mathbf{k}-\mathbf{G}'}$$

Thus, to first order,

$$c_{\mathbf{k}-\mathbf{G}} = \frac{U_{\mathbf{G}_1-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}_1}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} + \mathcal{O}(U^2), \quad \mathbf{G} \neq \mathbf{G}_1$$

Substituting the first-order expression for $c_{\mathbf{k}-\mathbf{G}}$ into the equation corresponding to $\mathbf{G}_1$:

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0] c_{\mathbf{k}-\mathbf{G}_1} = \sum_{\mathbf{G} \neq \mathbf{G}_1} \frac{U_{\mathbf{G}-\mathbf{G}_1} U_{\mathbf{G}_1-\mathbf{G}}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} c_{\mathbf{k}-\mathbf{G}_1}.$$

To evaluate the energy shift to second order in the weak potential, ε in the denominator may be replaced by its zeroth-order value $\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0$

$$\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 + \sum_{\mathbf{G} \neq \mathbf{G}_1} \frac{U_{\mathbf{G}-\mathbf{G}_1} U_{\mathbf{G}_1-\mathbf{G}}}{\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} + \mathcal{O}(U^3)$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

$$\varepsilon = \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 + \sum_{\mathbf{G} \neq \mathbf{G}_1} \frac{U_{\mathbf{G}-\mathbf{G}_1} U_{\mathbf{G}_1-\mathbf{G}}}{\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} + \mathcal{O}(U^3)$$

Being the potential real,

$$U_{\mathbf{G}-\mathbf{G}_1} U_{\mathbf{G}_1-\mathbf{G}} = |U_{\mathbf{G}-\mathbf{G}_1}|^2$$

The result shows that weakly perturbed non-degenerate levels repel each other. A free-electron level lying below $\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0$ gives a positive contribution to the energy shift, whereas a level lying above it gives a negative contribution.

The energy shift with respect to the free-electron value is therefore of second order in the periodic potential.

CASE 2 —DEGENERATE SOLUTIONS

Suppose that a group of reciprocal-lattice vectors, $\mathbf{G}_1, \dots, \mathbf{G}_m$, gives the same free-electron energy:

$$\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 = \dots = \varepsilon_{\mathbf{k}-\mathbf{G}_m}^0 \equiv \varepsilon_d^0.$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

$$\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 = \dots = \varepsilon_{\mathbf{k}-\mathbf{G}_m}^0 \equiv \varepsilon_d^0$$

Assume that this degenerate group is well separated from all the remaining free-electron levels:

$$|\varepsilon_d^0 - \varepsilon_{\mathbf{k}-\mathbf{G}}^0| \gg |U_{\mathbf{G}-\mathbf{G}_i}|,$$

$$\mathbf{G} \notin \{\mathbf{G}_1, \dots, \mathbf{G}_m\}, i = 1, \dots, m.$$

Proceeding as in the non-degenerate case, for each $i = 1, \dots, m$ we obtain

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0] c_{\mathbf{k}-\mathbf{G}} = U_{\mathbf{G}_1-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}_1} + \sum_{\mathbf{G}' \neq \mathbf{G}_1} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'}$$

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0] c_{\mathbf{k}-\mathbf{G}_i} = \sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j} + \sum_{\mathbf{G} \notin \{\mathbf{G}_1, \dots, \mathbf{G}_m\}} U_{\mathbf{G}-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}}.$$

Equivalently,

$$c_{\mathbf{k}-\mathbf{G}_i} = \frac{1}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0} \left[\sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j} + \sum_{\mathbf{G} \notin \{\mathbf{G}_1, \dots, \mathbf{G}_m\}} U_{\mathbf{G}-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}} \right]$$

Unlike the non-degenerate case, the first summation must be retained: it couples the degenerate plane-wave states already at first order in the periodic potential.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.1 General approach to the Schrodinger equation

Equivalently, for $i = 1, \dots, m$,

$$c_{\mathbf{k}-\mathbf{G}_i} = \frac{1}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0} \left[\sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j} + \mathcal{O}(U^2) \right].$$

Substituting this expression for the coefficients outside the degenerate subspace into the original equation gives

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0] c_{\mathbf{k}-\mathbf{G}_i} = \sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j} + \sum_{\mathbf{G} \notin \{\mathbf{G}_1, \dots, \mathbf{G}_m\}} U_{\mathbf{G}-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}}.$$

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0] c_{\mathbf{k}-\mathbf{G}_i} = \sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j} + \sum_{j=1}^m \sum_{\mathbf{G} \notin \{\mathbf{G}_1, \dots, \mathbf{G}_m\}} \frac{U_{\mathbf{G}-\mathbf{G}_i} U_{\mathbf{G}_j-\mathbf{G}}}{\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}}^0} c_{\mathbf{k}-\mathbf{G}_j}$$

The second term on the right-hand side is of second order in the weak periodic potential. Retaining only first-order terms, the equations reduce to

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0] c_{\mathbf{k}-\mathbf{G}_i} = \sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j}, \quad i = 1, \dots, m.$$

These are the coupled first-order equations for the m degenerate free-electron states.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.2 Energy levels near a Bragg plane

$$[\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_i}^0] c_{\mathbf{k}-\mathbf{G}_i} = \sum_{j=1}^m U_{\mathbf{G}_j-\mathbf{G}_i} c_{\mathbf{k}-\mathbf{G}_j}, \quad i = 1, \dots, m.$$

For a fixed wavevector $\mathbf{k}$, suppose that two reciprocal-lattice vectors $\mathbf{G}_1$ and $\mathbf{G}_2$ give degenerate free-electron energies:

$$\varepsilon_{\mathbf{k}-\mathbf{G}_1}^0 = \varepsilon_{\mathbf{k}-\mathbf{G}_2}^0$$

The first-order system then reduces to two coupled equations:

$$\begin{aligned} [\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_1}^0] c_{\mathbf{k}-\mathbf{G}_1} &= U_{\mathbf{G}_2-\mathbf{G}_1} c_{\mathbf{k}-\mathbf{G}_2}, \\ [\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{G}_2}^0] c_{\mathbf{k}-\mathbf{G}_2} &= U_{\mathbf{G}_1-\mathbf{G}_2} c_{\mathbf{k}-\mathbf{G}_1}. \end{aligned}$$

To simplify the notation, define $\mathbf{q} = \mathbf{k} - \mathbf{G}_1$,
 $\mathbf{G} = \mathbf{G}_2 - \mathbf{G}_1$.

Thus, $\mathbf{k} - \mathbf{G}_2 = \mathbf{q} - \mathbf{G}$.

The two equations become $[\varepsilon - \varepsilon_{\mathbf{q}}^0] c_{\mathbf{q}} = U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}}$,
 $[\varepsilon - \varepsilon_{\mathbf{q}-\mathbf{G}}^0] c_{\mathbf{q}-\mathbf{G}} = U_{-\mathbf{G}} c_{\mathbf{q}} = U_{\mathbf{G}}^* c_{\mathbf{q}}.$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.2 Energy levels near a Bragg plane

$$\begin{aligned} [\varepsilon - \varepsilon_{\mathbf{q}}^0] c_{\mathbf{q}} &= U_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}}, \\ [\varepsilon - \varepsilon_{\mathbf{q}-\mathbf{G}}^0] c_{\mathbf{q}-\mathbf{G}} &= U_{-\mathbf{G}} c_{\mathbf{q}} = U_{\mathbf{G}}^* c_{\mathbf{q}} \end{aligned}$$

The degeneracy condition is

$$\varepsilon_{\mathbf{q}}^0 = \varepsilon_{\mathbf{q}-\mathbf{G}}^0.$$

Since

$$\varepsilon_{\mathbf{q}}^0 = \frac{\hbar^2 q^2}{2m},$$

this is equivalent to

$$|\mathbf{q}| = |\mathbf{q} - \mathbf{G}|.$$

Equivalently, $\Delta\mathbf{q} = \mathbf{G}$

This defines a Bragg plane in reciprocal space: it is the plane perpendicular to $\mathbf{G}$ and halfway between the origin and the reciprocal-lattice point $\mathbf{G}$.

Thus, degeneracy occurs for an electron wavevector that can be Bragg-reflected from $\mathbf{q}$ to $\mathbf{q} - \mathbf{G}$. Since degenerate levels are strongly mixed by the periodic potential, the largest effects of a weak periodic potential occur near Bragg planes.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.2 Energy levels near a Bragg plane

Let us now determine the energy levels in the vicinity of a single Bragg plane. The system has nontrivial solutions only if

$$\det \begin{vmatrix} \varepsilon - \varepsilon_{\mathbf{q}}^0 & -U_{\mathbf{G}} \\ -U_{\mathbf{G}}^* & \varepsilon - \varepsilon_{\mathbf{q}-\mathbf{G}}^0 \end{vmatrix} = 0$$

$$\begin{aligned} [\varepsilon - \varepsilon_{\mathbf{q}}^0]c_{\mathbf{q}} &= U_{\mathbf{G}}c_{\mathbf{q}-\mathbf{G}}, \\ [\varepsilon - \varepsilon_{\mathbf{q}-\mathbf{G}}^0]c_{\mathbf{q}-\mathbf{G}} &= U_{-\mathbf{G}}c_{\mathbf{q}} = U_{\mathbf{G}}^*c_{\mathbf{q}} \end{aligned}$$

The determinant condition leads to the quadratic equation

$$(\varepsilon - \varepsilon_{\mathbf{q}}^0)(\varepsilon - \varepsilon_{\mathbf{q}-\mathbf{G}}^0) = |U_{\mathbf{G}}|^2$$

Its two solutions are

$$\varepsilon_{\pm} = \frac{1}{2}(\varepsilon_{\mathbf{q}}^0 + \varepsilon_{\mathbf{q}-\mathbf{G}}^0) \pm \sqrt{\left[\frac{\varepsilon_{\mathbf{q}}^0 - \varepsilon_{\mathbf{q}-\mathbf{G}}^0}{2}\right]^2 + |U_{\mathbf{G}}|^2}$$

These energies describe the effect of the periodic potential on the two free-electron levels $\varepsilon_{\mathbf{q}}^0$ and $\varepsilon_{\mathbf{q}-\mathbf{G}}^0$ in the vicinity of a Bragg plane.

On the Bragg plane, $\varepsilon_{\mathbf{q}}^0 = \varepsilon_{\mathbf{q}-\mathbf{G}}^0$, the two solutions then reduce to

$$\varepsilon_{\pm} = \varepsilon_{\mathbf{q}}^0 \pm |U_{\mathbf{G}}|.$$

Thus, at the Bragg plane, one level is shifted upward by $|U_{\mathbf{G}}|$, whereas the other is shifted downward by the same amount.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.2 Energy levels near a Bragg plane

To visualise the two branches, let $\mathbf{q}$ vary along the direction of $\mathbf{G}$, $\mathbf{q} = q \hat{\mathbf{G}}$.

The two energies obtained from the coupled-state problem are

$$\varepsilon_{\pm}(q) = \frac{1}{2} [\varepsilon_{\mathbf{q}}^0 + \varepsilon_{\mathbf{q}-\mathbf{G}}^0] \pm \sqrt{\left[\frac{\varepsilon_{\mathbf{q}}^0 - \varepsilon_{\mathbf{q}-\mathbf{G}}^0}{2} \right]^2 + |U_{\mathbf{G}}|^2}$$

In the absence of the periodic potential, the two free-electron parabolas would cross at the Bragg plane

$$q = \frac{G}{2}$$

The periodic potential couples the two degenerate plane waves $\mathbf{q}$ and $\mathbf{q} - \mathbf{G}$. As a consequence, the crossing is removed: the two energy branches repel each other and an energy gap opens.

The upper branch corresponds to the sign $+$, whereas the lower branch corresponds to the sign $-$.

At the Bragg plane $q = \frac{G}{2}$,

$$\varepsilon_{\pm} = \varepsilon_{G/2}^0 \pm |U_{\mathbf{G}}|$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.2 Energy levels near a Bragg plane

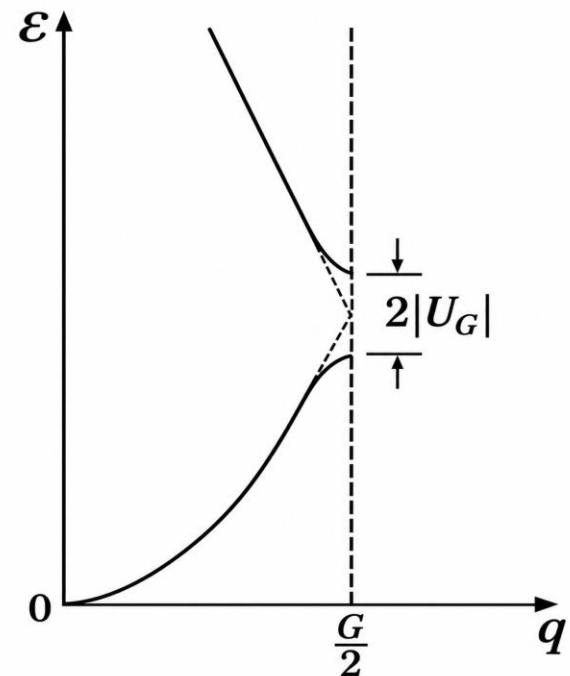
$$\varepsilon_{\pm}(q) = \frac{1}{2}[\varepsilon_q^0 + \varepsilon_{q-G}^0] \pm \sqrt{\left[\frac{\varepsilon_q^0 - \varepsilon_{q-G}^0}{2}\right]^2 + |U_G|^2}$$

$$\text{At the Bragg plane } q = \frac{G}{2}, \quad \varepsilon_{\pm} = \varepsilon_{G/2}^0 \pm |U_G|$$

Therefore, the energy separation between the two branches is:

$$E_g = \varepsilon_+ - \varepsilon_- = 2 |U_G|$$

Far from the Bragg plane, the free-electron levels are no longer nearly degenerate. The coupling due to the weak periodic potential then produces only a small correction, and the two branches approach the unperturbed free-electron parabolas.



3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

Summarizing the results obtained so far, a nearly free electron is only weakly affected by the periodic potential, except near a degeneracy of two free-electron states.

$$\varepsilon_{\mathbf{q}}^0 = \varepsilon_{\mathbf{q}-\mathbf{G}}^0$$

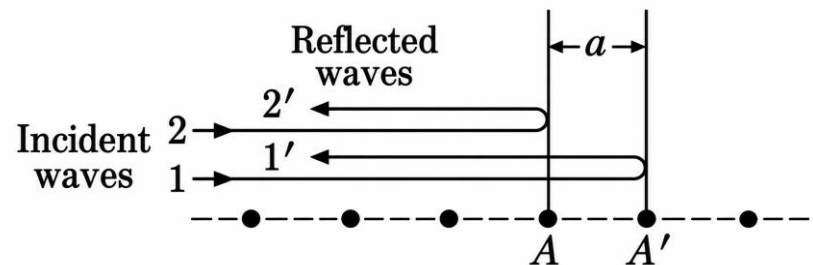
In a one-dimensional lattice, the reciprocal-lattice vectors are $G_n = \frac{2n\pi}{a}$ and the degeneracy condition becomes

$$q^2 = (q - G_n)^2 \Rightarrow q = \frac{G_n}{2} = \frac{n\pi}{a}$$

Equivalently, including reciprocal-lattice vectors of both signs, the Bragg points are located at

$$q = \pm \frac{n\pi}{a}$$

At these wavevectors, the electron waves reflected by neighbouring lattice sites interfere constructively. This is the one-dimensional Bragg condition.



The constructive interference is illustrated in the Figure: the extra path travelled by the wave reflected at the neighbouring site produces a phase difference equal to an integer multiple of 2π . Consequently, the reflected waves add coherently.

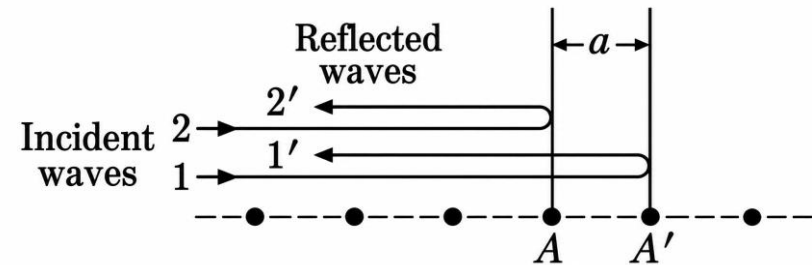
3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

When the Bragg condition

$$k = \pm \frac{n\pi}{a}$$

is satisfied, the two free-electron waves e^{ikx} and e^{-ikx} have the same energy and are coupled by Bragg reflection from the periodic lattice.



The stationary eigenstates are therefore standing waves, given by the two independent linear combinations:

$$\psi_+(x) \propto e^{ikx} + e^{-ikx} = 2\cos(kx) = 2\cos\left(\frac{n\pi}{a}x\right),$$
$$\psi_-(x) \propto e^{ikx} - e^{-ikx} = 2i\sin(kx) = 2i\sin\left(\frac{n\pi}{a}x\right).$$

The two standing waves have different spatial distributions.

At the lattice sites $x = ma$, with m integer,

$$|\psi_+(ma)|^2 \text{ is maximum,} \quad |\psi_-(ma)|^2 = 0.$$

Thus, the two electron states sample the periodic potential differently and acquire different potential energies. The degeneracy of the free-electron levels is removed: an energy gap opens at the Bragg points.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

The probability density associated with an electron wavefunction is

$$\rho(x) = \psi^*(x)\psi(x) = |\psi(x)|^2$$

For a single travelling plane wave, $\psi(x) \propto e^{ikx}$ the probability density is spatially uniform

$$\rho(x) \propto e^{-ikx}e^{ikx} = \text{constant}$$

The situation is different for the standing-wave states at the first Bragg point, $k = \pi/a$

$$\rho_+(x) = |\psi_+(x)|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$$

$$\psi_+ \propto 2\cos\left(\frac{\pi}{a}x\right)$$

Therefore, ρ_+ is maximum at the ion positions $x = ma$, where m is an integer. The electron density is concentrated near the positive ions, where the electron potential energy is lowest.

$$\text{For the other standing wave, } \rho_-(x) = |\psi_-(x)|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$$

$$\psi_- \propto 2i\sin\left(\frac{\pi}{a}x\right)$$

At the ion positions $x = ma$,

$$\rho_+(ma) \text{ is maximum, } \rho_-(ma) = 0$$

Hence, the two standing-wave states sample different regions of the periodic potential and have different energies.

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

The figure compares the probability densities of the two standing-wave states with the periodic potential created by the positive ions.

For the state

$$\psi_+(x) \propto \cos\left(\frac{\pi x}{a}\right)$$

the probability density is maximum at the ion positions. The electron is therefore more likely to be found close to the positive ions, where its potential energy is lowest. Consequently, the energy of the ψ_+ state is lowered with respect to the free-electron energy.

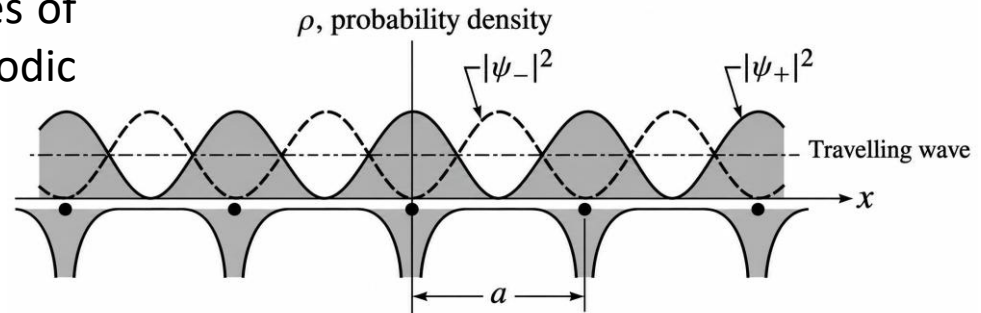
Conversely, for the state $\psi_-(x) \propto \sin\left(\frac{\pi x}{a}\right)$

the probability density vanishes at the ion positions and is concentrated between neighbouring ions. This state is less stabilized by the attractive ionic potential; its energy is therefore increased.

Thus, the two states that were degenerate for a free electron at the Bragg points

$$k = \pm \frac{n\pi}{a}$$

acquire different energies in the periodic potential.



3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

Their separation defines an energy gap:

$$E_g = \varepsilon_- - \varepsilon_+.$$

Let us evaluate the size of the energy gap at the first Brillouin-zone boundary, $k = \frac{\pi}{a}$

Let the periodic potential be described by its first Fourier component:

$$U(x) = 2U_G \cos \left(\frac{2\pi x}{a} \right)$$

The energy separation between the two standing-wave states is

$$E_g = \left| \int_0^a dx U(x) [|\psi_-(x)|^2 - |\psi_+(x)|^2] \right|$$

$$\psi_+(x) = \sqrt{\frac{2}{a}} \cos \left(\frac{\pi x}{a} \right)$$

$$\psi_-(x) = \sqrt{\frac{2}{a}} \sin \left(\frac{\pi x}{a} \right)$$

Substituting the explicit expressions gives

$$E_g = \left| \frac{2}{a} \int_0^a dx 2U_G \cos \left(\frac{2\pi x}{a} \right) \left[\sin^2 \left(\frac{\pi x}{a} \right) - \cos^2 \left(\frac{\pi x}{a} \right) \right] \right| = 2 |U_G|.$$

Therefore, the energy gap at the boundary of the first Brillouin zone is twice the magnitude of the Fourier component of the crystal potential:

$$E_g = 2 |U_G|$$

3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

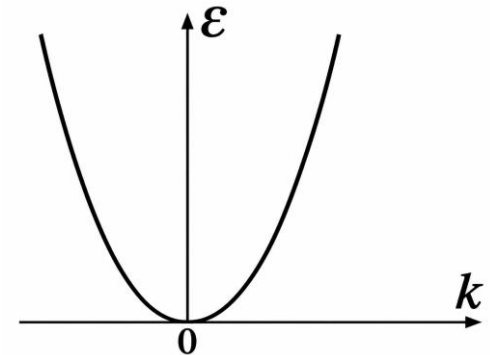
3.4.3 Energy levels for a one-dimensional lattice

Let us now construct the band structure $\varepsilon(k)$ for a one-dimensional lattice.

STEP 1 — Start from the free-electron dispersion relation:

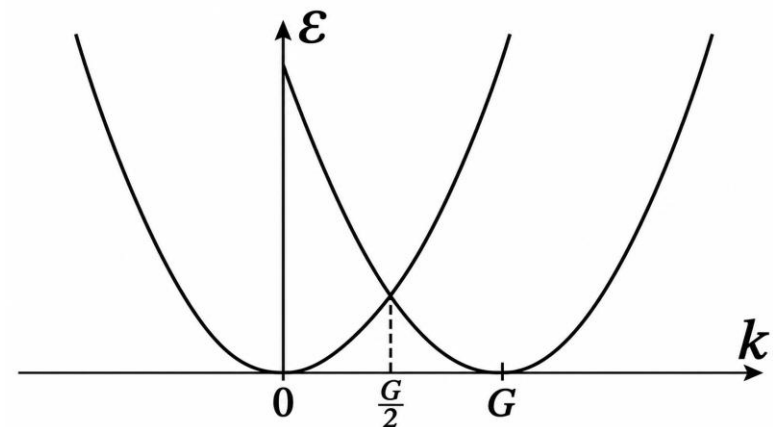
$$\varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$$

It is represented by a parabola centred at $k = 0$.



STEP 2 — Consider the effect of a weak periodic potential near a Bragg point. If the Bragg point is associated with the reciprocal-lattice vector G , we must also consider the free-electron state with wavevector $k - G$. Its energy is

$$\varepsilon_{k-G}^0 = \frac{\hbar^2 (k - G)^2}{2m}.$$

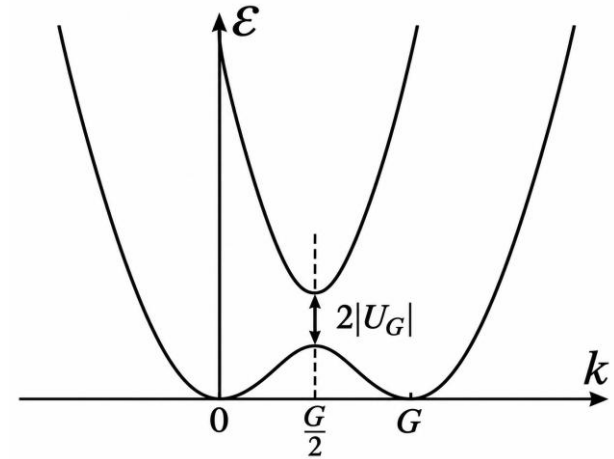


This dispersion relation is represented by a second parabola centred at $k = G$. The two free-electron parabolas intersect at the Bragg point $k = \frac{G}{2}$.

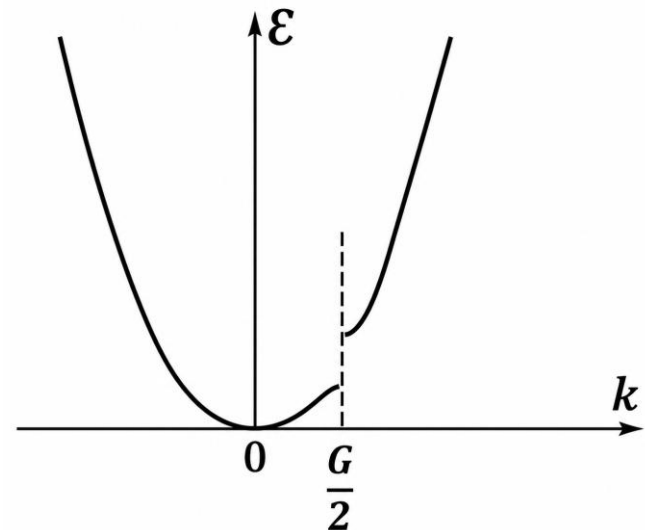
3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

STEP 3 — Lift the degeneracy at the crossing point. The weak periodic potential couples the two free-electron states and replaces their crossing with an avoided crossing. At the Bragg point, the two energy branches are separated by the energy gap $E_g = 2 |U_G|$. Moreover, both branches have zero slope at $k = \frac{G}{2}$.



STEP 4 — Retain the free-electron-like portions of the perturbed branches that evolve from a given free-electron parabola. At the Bragg point $k = G/2$, these portions are separated by the energy gap $2 |U_G|$.



3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

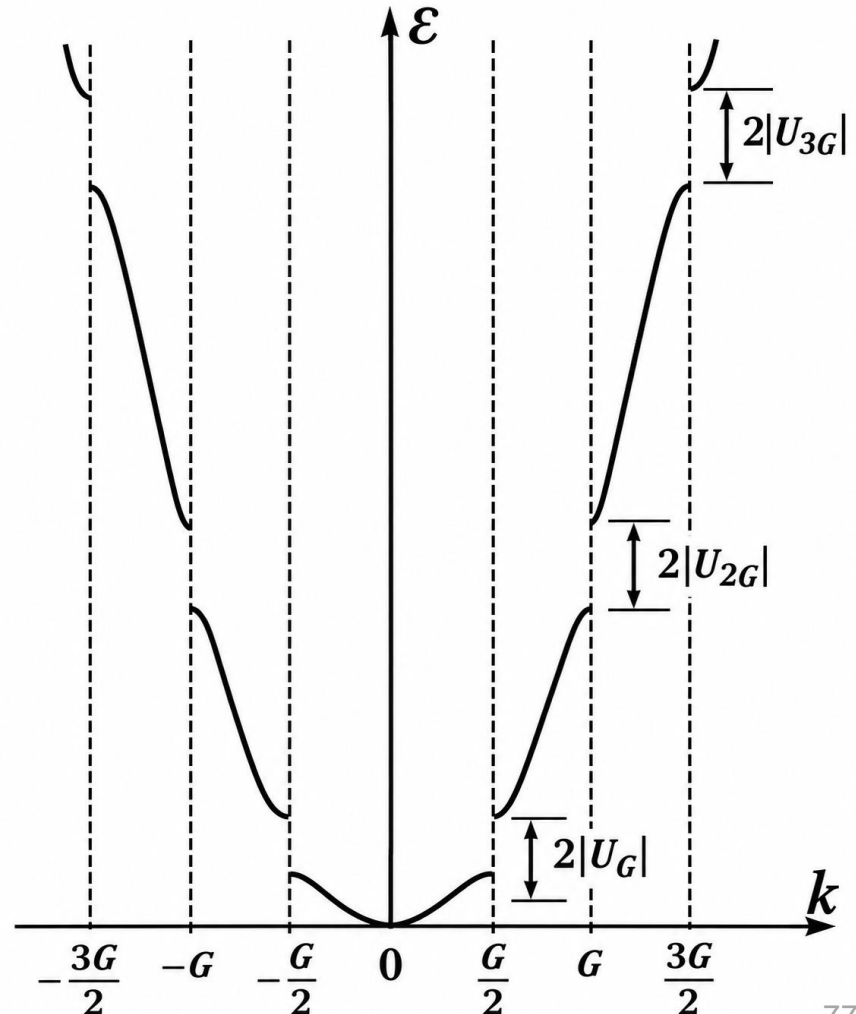
3.4.3 Energy levels for a one-dimensional lattice

STEP 5 — Repeat the same construction at all the other Bragg points, associated with the reciprocal-lattice vectors

$$G_n = \frac{2\pi n}{a}.$$

For each G_n , the periodic potential couples the corresponding degenerate free-electron states and opens a gap whose size is determined by the Fourier component U_{G_n} .

When all Bragg points and the associated Fourier components are included, the resulting dispersion relation is obtained as shown in the next figure. This is called as extended area scheme



3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

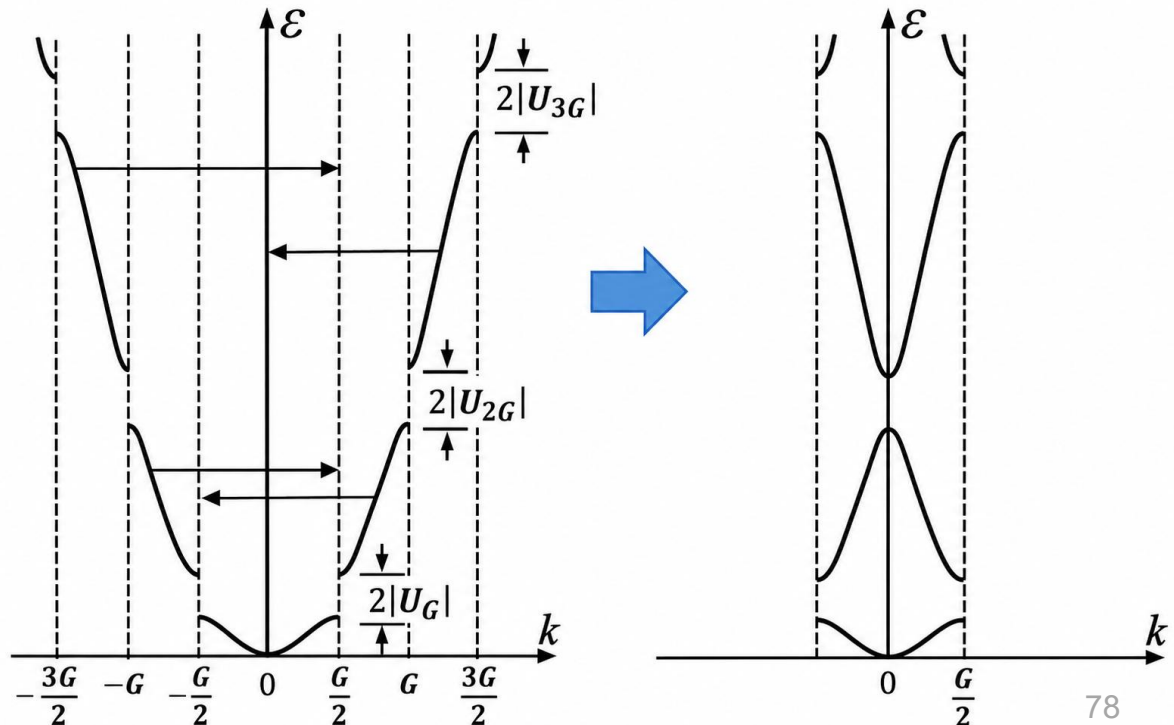
If we translate each branch of the extended-zone scheme by an appropriate reciprocal-lattice vector, all wavevectors can be brought into the first Brillouin zone:

$$-\frac{G}{2} \leq k \leq \frac{G}{2}.$$

We thereby obtain the reduced-zone scheme.

In this representation, the different branches are labelled by a band index n , while the crystal wavevector k is always restricted to the first Brillouin zone.

$$\varepsilon_n(k), -\frac{G}{2} \leq k \leq \frac{G}{2}.$$

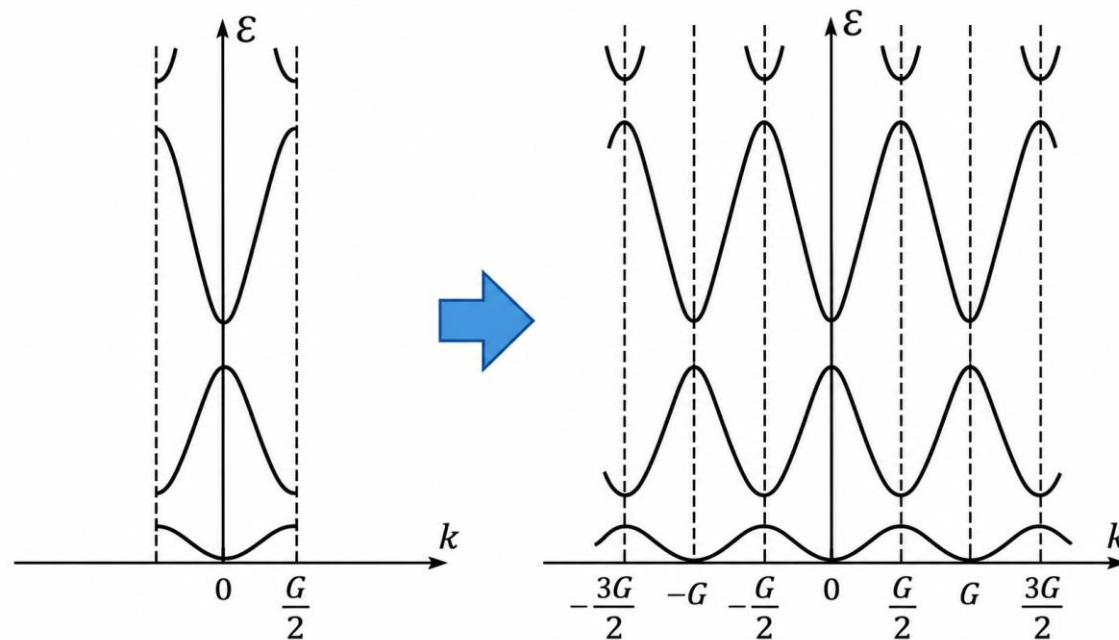


3.4 WEAK PERIODIC POTENTIAL – NEARLY FREE ELECTRONS

3.4.3 Energy levels for a one-dimensional lattice

The equivalence of crystal wavevectors that differ by a reciprocal-lattice vector can be illustrated by repeating the reduced-zone pattern in successive Brillouin zones.

This representation is known as the repeated-zone scheme.



For each band n , the energy is periodic in reciprocal space:

$$\epsilon_n(k + G) = \epsilon_n(k).$$

Thus, the wavevectors k and $k + G$ describe equivalent Bloch states.

3.5 TIGHT-BINDING MODEL

3.5.1 General approach

Up to this point, the free-electron gas has provided the main conceptual starting point for the description of electrons in solids.

This may seem surprising, since a solid is made of atoms. From an atomic point of view, a crystal might appear to have little in common with a free-electron gas.

We may instead start from the opposite limit: imagine forming a crystal by bringing isolated atoms together. In this picture, the electronic states of the solid are constructed from the atomic wavefunctions of the constituent atoms.

This approach complements, rather than contradicts, the free-electron model. It is known as the tight-binding model.

The tight-binding approximation is most appropriate when the valence-electron wavefunctions are strongly localized around their parent atoms and overlap only weakly with those centred on neighbouring sites.

The following discussion concerns the valence electrons. Core electrons are assumed to remain localized around their parent atoms and do not contribute significantly to chemical bonding.

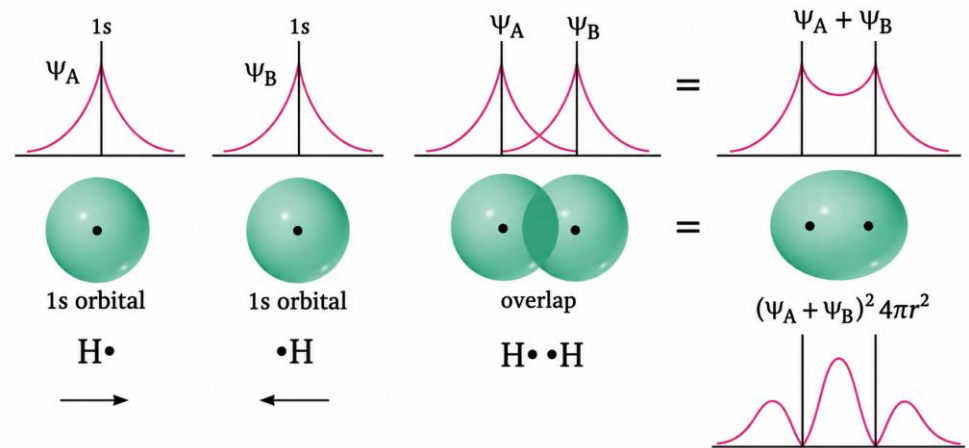


3.5 TIGHT-BINDING MODEL

3.5.1 General approach

The tight-binding model can be regarded as the extension of the linear combination of atomic orbitals (LCAO) approach from molecules to solids.

In this approach, the electronic wavefunction is expressed as a linear combination of atomic orbitals centred on the lattice sites. The method is particularly effective when the relevant atomic orbitals are strongly localized and only a small number of neighbouring orbitals contribute appreciably to the linear combination.



Consider a one-dimensional lattice of N atoms located at positions $\mathbf{R}_n$, with one atomic orbital φ_s on each atom.

We write the electronic wave function as a linear combination of atomic orbitals centered on the different lattice sites:

$$\psi(\mathbf{r}) = \sum_n c_s^n \varphi_s(\mathbf{r} - \mathbf{R}_n).$$

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

Here, $\varphi_s(\mathbf{r} - \mathbf{R}_n)$ is an eigenfunction of the isolated atom centered at $\mathbf{R}_n$, with eigenvalue E_s :

$$\psi(\mathbf{r}) = \sum_n c_s^n \varphi_s(\mathbf{r} - \mathbf{R}_n)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{at}}(\mathbf{r} - \mathbf{R}_n) \right] \varphi_s(\mathbf{r} - \mathbf{R}_n) = E_s \varphi_s(\mathbf{r} - \mathbf{R}_n)$$

Since $\psi(\mathbf{r})$ describes an electron in a crystal, it must satisfy Bloch's theorem.

Therefore, for a Bloch state with wavevector $\mathbf{k}$, the coefficients must have the form

$$c_s^n = \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_n}$$

where N is the number of unit cells in the crystal.

Let us verify that, with these coefficients, the wave function is a Bloch function:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \varphi_s(\mathbf{r} - \mathbf{R}_n) = e^{i\mathbf{k} \cdot \mathbf{r}} \underbrace{\frac{1}{\sqrt{N}} \sum_n e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R}_n)} \varphi_s(\mathbf{r} - \mathbf{R}_n)}_{u_{\mathbf{k}}(\mathbf{r})}.$$

The function $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. Therefore,

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

is a Bloch function.

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

Near the site $\mathbf{R}_n$, the crystal potential can be written as the potential of the isolated atom at that site plus a correction:

$$U(\mathbf{r}) = U_{\text{at}}(\mathbf{r} - \mathbf{R}_n) + \Delta U_n(\mathbf{r})$$

Accordingly, in the vicinity of site n , the Hamiltonian becomes

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) = \underbrace{\left[-\frac{\hbar^2}{2m} \nabla^2 + U_{\text{at}}(\mathbf{r} - \mathbf{R}_n) \right]}_{\hat{\mathcal{H}}_{\text{at}}^{(n)}} + \Delta U_n(\mathbf{r}).$$

The term $\Delta U_n(\mathbf{r})$ accounts for the modification of the isolated-atom energy levels caused by the presence of the other atoms in the crystal.

Let us recall the expression for the Bloch wave function and analyze its representation:

$$\psi(\vec{r}) = \frac{1}{\sqrt{N}} e^{i\vec{k} \cdot \vec{r}} \sum_n e^{-i\vec{k} \cdot (\vec{r} - \vec{R}_n)} \varphi_s(\vec{r} - \vec{R}_n)$$

Lattice-periodic function

Plane wave

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

$$\psi(\vec{r}) = \underbrace{\frac{1}{\sqrt{N}} e^{i\vec{k} \cdot \vec{r}}}_{\text{Plane wave}} \underbrace{\sum_n e^{-i\vec{k} \cdot (\vec{r} - \vec{R}_n)} \varphi_s(\vec{r} - \vec{R}_n)}_{\text{Lattice-periodic function}}$$

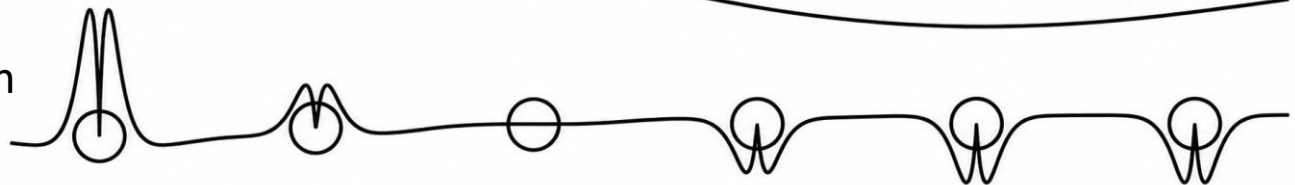
Atomic wave function



Plane wave



Tight-binding Bloch wave function



The tight-binding Bloch function retains the localized shape of the atomic orbital at each lattice site.

From site to site, its amplitude and phase are modulated by the plane-wave factor $e^{i\vec{k} \cdot \vec{r}}$.

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

In the limit in which the overlap between orbitals centered on different sites is negligible, the N states derived from the same atomic orbital remain degenerate at the atomic energy E_s . The band therefore collapses to a single N -fold degenerate energy level.

If the overlap between orbitals on neighboring sites is small but nonzero, the perturbation $\Delta U(\mathbf{r})$ produces only a small change in the atomic energy. The tight-binding wave function $\psi_{\mathbf{k}}(\mathbf{r})$ then provides a good approximation to the electronic wave function.

Let us substitute $\psi_{\mathbf{k}}(\mathbf{r})$ into the Schrödinger equation:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \varphi_s(\mathbf{r} - \mathbf{R}_n)$$

$$[\hat{\mathcal{H}}_{\text{at}} + \Delta U(\mathbf{r})] \sum_n \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_n} \varphi_s(\mathbf{r} - \mathbf{R}_n) = E_s(\mathbf{k}) \sum_n \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_n} \varphi_s(\mathbf{r} - \mathbf{R}_n)$$

We multiply on the left by the complex conjugate of the atomic orbital at the reference site, $\varphi_s^*(\mathbf{r})$, with $\mathbf{R}_0 = 0$, and integrate over $\mathbf{r}$:

$$\sum_n \frac{e^{i\mathbf{k} \cdot \mathbf{R}_n}}{\sqrt{N}} \int \varphi_s^*(\mathbf{r}) [\hat{\mathcal{H}}_{\text{at}} + \Delta U(\mathbf{r})] \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r = E_s(\mathbf{k}) \sum_n \frac{e^{i\mathbf{k} \cdot \mathbf{R}_n}}{\sqrt{N}} \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r.$$

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

$$\sum_n \frac{e^{i\mathbf{k}\cdot\mathbf{R}_n}}{\sqrt{N}} \int \varphi_s^*(\mathbf{r}) [\hat{\mathcal{H}}_{\text{at}} + \Delta U(\mathbf{r})] \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r = E_s(\mathbf{k}) \sum_n \frac{e^{i\mathbf{k}\cdot\mathbf{R}_n}}{\sqrt{N}} \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r$$

We note that: $\int \varphi_s^*(\mathbf{r}) \hat{\mathcal{H}}_{\text{at}}^{(n)} \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r = E_s \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r$

Therefore:

$$\begin{aligned} \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} E_s \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r + \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \Delta U_n(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r \\ = E_s(\mathbf{k}) \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r \end{aligned}$$

Consequently

$$\begin{aligned} [E_s - E_s(\mathbf{k})] \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r \\ + \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \Delta U_n(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r = 0 \end{aligned}$$

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

$$[E_s - E_s(\mathbf{k})] \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r + \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \int \varphi_s^*(\mathbf{r}) \Delta U_n(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_n) d^3r = 0$$

This approximation is justified when the overlap between atomic orbitals centered on different lattice sites is small.

In this limit, only the term with $\mathbf{R}_n = 0$ is retained in the first summation. In the second summation, we retain the on-site contribution, $\mathbf{R}_n = 0$, together with the contributions from the nearest-neighbor sites.

With this approximation, the previous equation becomes:

$$[E_s - E_s(\mathbf{k})] + \int \varphi_s^*(\mathbf{r}) \Delta U_0(\mathbf{r}) \varphi_s(\mathbf{r}) d^3r \\ + \sum_{\text{n.n.}} e^{i\mathbf{k} \cdot \mathbf{R}_{\text{n.n.}}} \int \varphi_s^*(\mathbf{r}) \Delta U_{\text{n.n.}}(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_{\text{n.n.}}) d^3r$$

where the sum runs over the nearest-neighbor sites, and $\mathbf{R}_{\text{n.n.}}$ denotes the lattice vectors connecting the reference site to its nearest neighbors.

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

$$[E_s - E_s(\mathbf{k})] + \int \varphi_s^*(\mathbf{r}) \Delta U_0(\mathbf{r}) \varphi_s(\mathbf{r}) d^3r + \sum_{\mathbf{n.n.}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{n.n.}}} \int \varphi_s^*(\mathbf{r}) \Delta U_{\mathbf{n.n.}}(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_{\mathbf{n.n.}}) d^3r$$

Defining:

$$\beta = - \int \varphi_s^*(\mathbf{r}) \Delta U_0(\mathbf{r}) \varphi_s(\mathbf{r}) d^3r, \quad \gamma(\mathbf{R}_{\mathbf{n.n.}}) = - \int \varphi_s^*(\mathbf{r}) \Delta U_{\mathbf{n.n.}}(\mathbf{r}) \varphi_s(\mathbf{r} - \mathbf{R}_{\mathbf{n.n.}}) d^3r$$

Then:
$$E_s(\mathbf{k}) = E_s - \beta - \sum_{\mathbf{n.n.}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{n.n.}}} \gamma(\mathbf{R}_{\mathbf{n.n.}})$$

In this approximation, β shifts the atomic energy by a $\mathbf{k}$ -independent amount, whereas the dispersion of $E_s(\mathbf{k})$ is determined by the transfer integrals $\gamma(\mathbf{R}_{\mathbf{n.n.}})$.

For a linear chain with lattice constant a , $\mathbf{R}_n = na \hat{\mathbf{x}}$, the nearest neighbors of the site at the origin are located at

$$\mathbf{R}_{\pm} = \pm a \hat{\mathbf{x}}.$$

Assuming equivalent nearest-neighbor transfer integrals,

$$\gamma \equiv \gamma(+a\hat{\mathbf{x}}) = \gamma(-a\hat{\mathbf{x}}),$$

we obtain
$$E_s(k_x) = E_s - \beta - \gamma(e^{ik_x a} + e^{-ik_x a}).$$

3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

Defining $E_0 = E_s - \beta$,

the energy dispersion becomes

$$E_s(k_x) = E_s - \beta - 2\gamma \cos(k_x a) = E_0 - 2\gamma \cos(k_x a).$$

The resulting energy band is shown in the Figure.

The bandwidth, defined as the energy range spanned by the electronic states in the band, is

$$W = 4 |\gamma|.$$

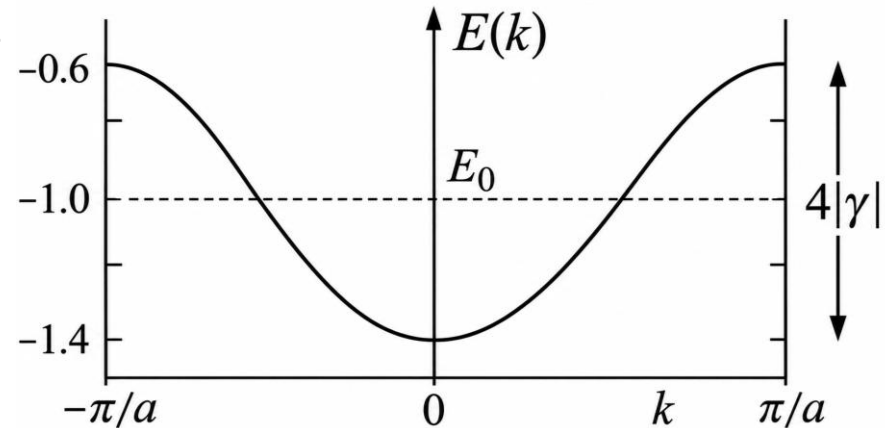
As the distance between neighboring atoms decreases, the overlap between their atomic orbitals generally increases.

Consequently, $|\gamma|$ increases and the band becomes broader.

In the limit of widely separated atoms, the overlap between atomic orbitals vanishes and $\gamma \rightarrow 0$. The band then collapses into a single N -fold degenerate atomic level: a flat band.

Thus, the bandwidth provides a measure of the degree of electron delocalization in the crystal: a wider band corresponds to stronger intersite coupling and more delocalized electrons.

$$E_s(k_x) = E_s - \beta - \gamma(e^{ik_x a} + e^{-ik_x a})$$



3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

$$E_{\alpha}(k_x + G) = E_{\alpha}(k_x), \quad G = \frac{2\pi m}{a}, m \in \mathbb{Z}.$$

As discussed in connection with Bloch's theorem, wavevectors that differ by a reciprocal-lattice vector describe the same crystal momentum. Therefore, it is sufficient to consider k_x within the first Brillouin zone,

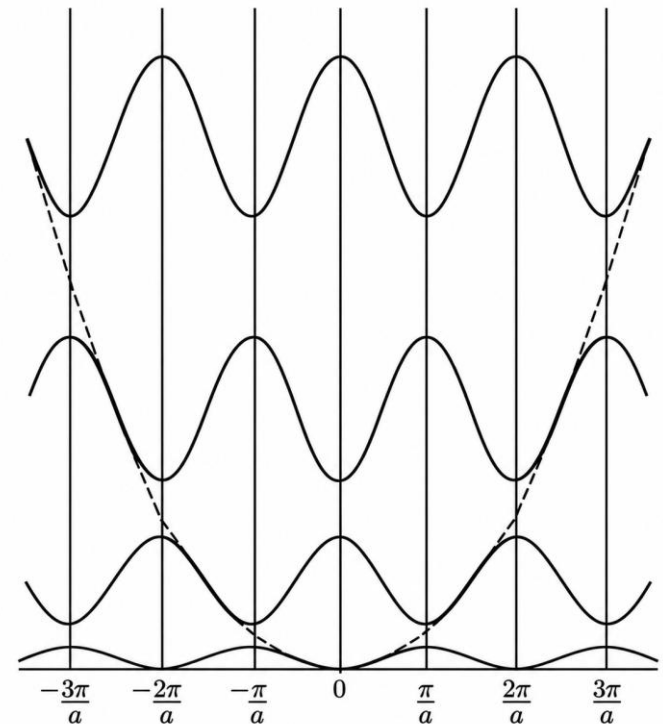
$$-\frac{\pi}{a} \leq k_x \leq \frac{\pi}{a}$$

If several atomic orbitals contribute to the electronic states, each orbital φ_{α} gives rise to a band of the form

$$E_{\alpha}(k_x) = E_{0\alpha} - 2\gamma_{\alpha} \cos(k_x a) \text{ where } E_{0\alpha} = E_{\alpha} - \beta_{\alpha}$$

Thus:

- β_{α} shifts the center of the band derived from orbital φ_{α} ;
- the relative values of $E_{0\alpha}$ determine the energy separation between bands arising from different atomic orbitals;
- γ_{α} determines the bandwidth, $W_{\alpha} = 4 |\gamma_{\alpha}|$.

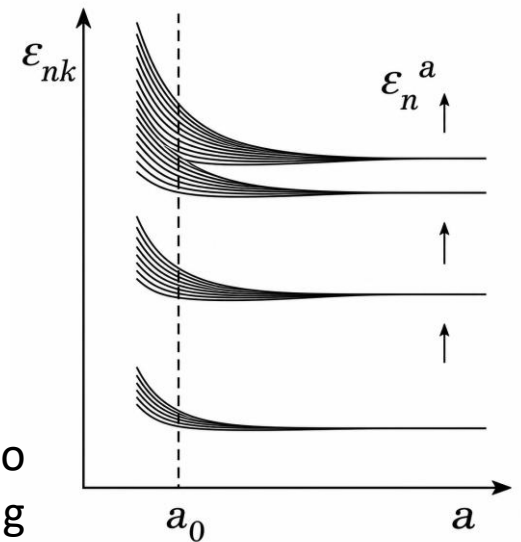


3.5 TIGHT-BINDING MODEL

3.5.2 One-dimensional lattice

The discrete energy levels of isolated atoms evolve into energy bands when the atoms form a crystal. For each orbital, a crystal with N unit cells generate N closely spaced electronic states. Because different isolated-atom levels are separated in energy, the corresponding bands may remain separated when their broadening is not large enough to make them overlap. The energy intervals between such bands are forbidden gaps.

The Figure shows the evolution of the energy levels in the tight-binding limit as a function of the interatomic distance a . At the equilibrium distance a_0 , the atomic levels have broadened into allowed energy bands separated by energy gaps.



For a band derived from an atomic orbital φ_α ,

$$E_\alpha(k_x) = E_\alpha - \beta_\alpha - 2\gamma_\alpha \cos(k_x a).$$

The parameter β_α shifts the centre of the band relative to the isolated-atom energy E_α , whereas the hopping integral γ_α determines its width.

As the atoms approach one another, the overlap between nearest-neighbor atomic orbitals increases, $|\gamma_\alpha|$ becomes larger, and the bands broaden. This effect is generally more pronounced for outer, more spatially extended atomic orbitals.

3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.1 Introduction

In three dimensions, the energy bands are described by the functions $E_n(\mathbf{k})$, defined throughout reciprocal space. Because $\mathbf{k}$ has three components, a complete representation of a band requires a three-dimensional energy surface.

For this reason, band structures are usually displayed as $E_n(\mathbf{k})$ along selected high-symmetry paths within the first Brillouin zone, i.e. in the reduced-zone scheme.

Even for free electrons, the dispersion relation is defined in three-dimensional $\mathbf{k}$ -space. Restricting the representation to high-symmetry paths provides a compact and physically meaningful description of the band structure..

The selected paths typically connect the centre of the first Brillouin zone to points and lines with high symmetry on its boundary.

High-symmetry points and lines are conventionally denoted as follows:

- The centre of the first Brillouin zone is denoted by Γ .
- High-symmetry lines inside the Brillouin zone are commonly denoted by Greek letters.
- High-symmetry points on the Brillouin-zone boundary are commonly denoted by Roman letters.

3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.2 High-symmetry points

We now define the high-symmetry points of the first Brillouin zone.

High-symmetry points and lines are points and lines in reciprocal space that remain invariant under a nontrivial subgroup of the crystal point group. For cubic lattices, they occur along, or at the intersections with the Brillouin-zone boundary of, directions related to the principal crystallographic axes and to other equivalent low-index directions.

Let us consider the case of a simple cubic lattice.

The primitive lattice vectors are:

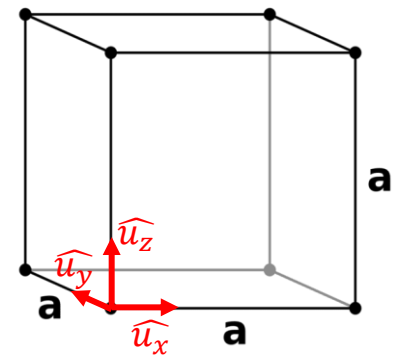
$$\mathbf{a}_1 = a \hat{\mathbf{u}}_x,$$
$$\mathbf{a}_2 = a \hat{\mathbf{u}}_y,$$
$$\mathbf{a}_3 = a \hat{\mathbf{u}}_z,$$

where $\hat{\mathbf{u}}_x$, $\hat{\mathbf{u}}_y$, and $\hat{\mathbf{u}}_z$ are mutually orthogonal unit vectors.

The primitive vectors of the reciprocal lattice are

$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{u}}_x, \quad \mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{u}}_y, \quad \mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{u}}_z.$$

Therefore, the reciprocal lattice is also a simple cubic lattice, with lattice constant $\frac{2\pi}{a}$.



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.2 High-symmetry points

The first Brillouin zone of a simple cubic lattice is a cube centred at Γ , defined by

$$-\frac{\pi}{a} \leq k_x, k_y, k_z \leq \frac{\pi}{a}.$$

For a simple cubic reciprocal lattice, the high-symmetry points of the first Brillouin zone are obtained by following the shortest inequivalent crystallographic directions from Γ to its boundary:

$[100]$, $[110]$, $[111]$.

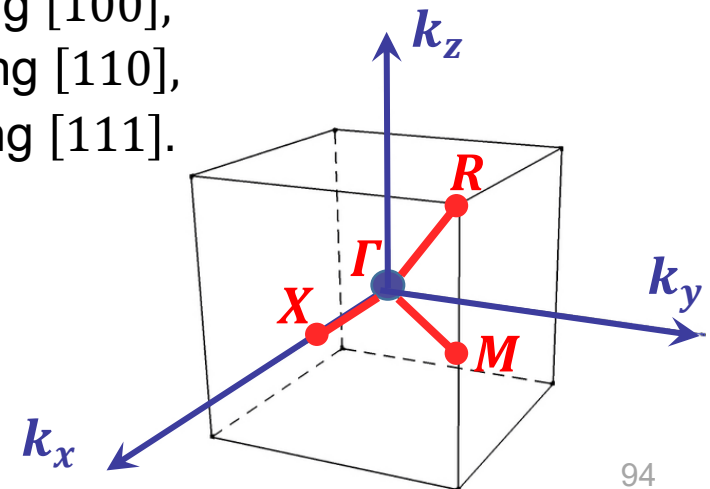
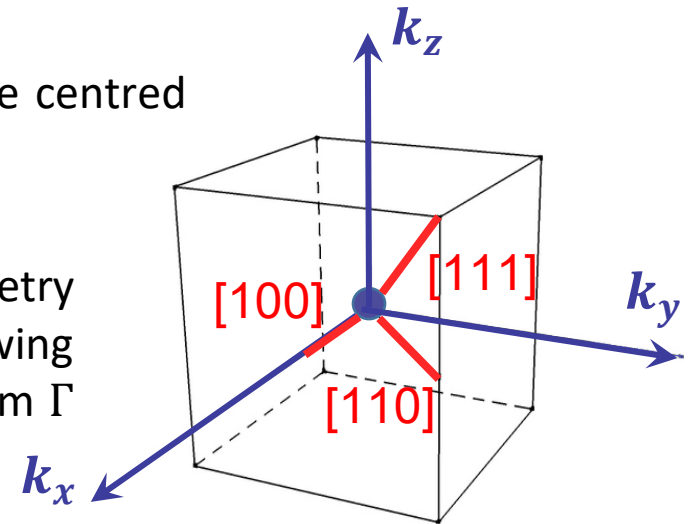
The intersections of these directions with the first Brillouin-zone boundary define the conventional high-symmetry points:

$\Gamma \rightarrow X$ along $[100]$,
 $\Gamma \rightarrow M$ along $[110]$,
 $\Gamma \rightarrow R$ along $[111]$.

Their coordinates are $X = \left(\frac{\pi}{a}, 0, 0\right)$,

$$M = \left(\frac{\pi}{a}, \frac{\pi}{a}, 0\right),$$

$$R = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right).$$



3.6 BAND STRUCTURES IN THREE DIMENSIONS

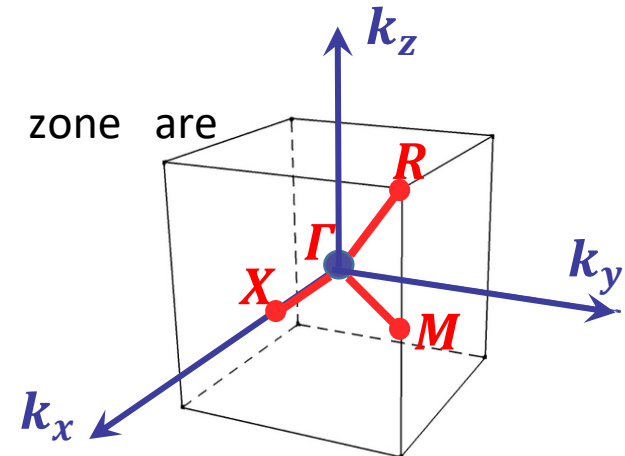
3.6.2 High-symmetry points

The high-symmetry paths of the simple cubic Brillouin zone are conventionally denoted as follows:

$\Gamma \rightarrow X$ is denoted by Δ ,

$\Gamma \rightarrow M$ is denoted by Σ ,

$\Gamma \rightarrow R$ is denoted by Λ .



For body-centred cubic and face-centred cubic lattices, the shapes of the first Brillouin zones and the conventional labels of their high-symmetry points and paths are different.

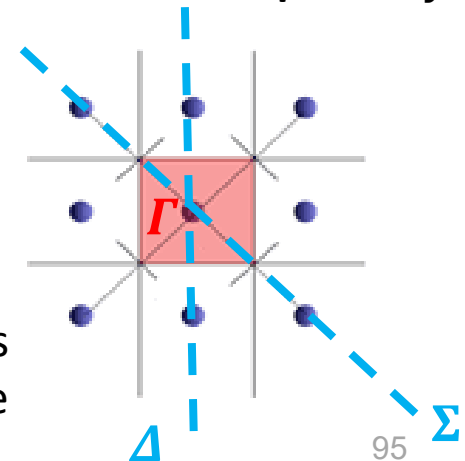
Why are these high-symmetry directions special?

Along Δ , the corresponding real-space direction is $[100]$. It contains a one-dimensional chain of lattice sites with nearest-neighbour spacing a .

Along Σ , the corresponding real-space direction is $[110]$. It contains a one-dimensional chain of lattice sites with nearest-neighbour spacing $\sqrt{2}a$.

Along Λ , the corresponding real-space direction is $[111]$. It contains a one-dimensional chain of lattice sites with nearest-neighbour spacing $\sqrt{3}a$.

Projection onto the plane xy



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.3 Energy bands of a simple cubic lattice

In the free-electron approximation, the energy branches are:

$$\varepsilon_{\mathbf{k}-\mathbf{G}}^0 = \frac{\hbar^2}{2m} |\mathbf{k} - \mathbf{G}|^2$$

In the reduced-zone scheme, $\mathbf{k}$ is restricted to the first Brillouin zone. We now consider the free-electron dispersion along selected high-symmetry directions in reciprocal space.

Let us consider the $[100]$ direction, corresponding to the path:

$$\Gamma \rightarrow X (\Delta)$$

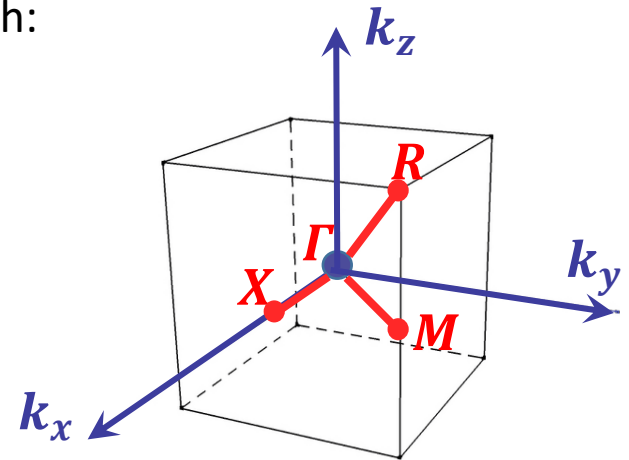
Along this direction, $\mathbf{k}$ can be written as:

$$\mathbf{k}(\chi) = \chi \frac{\pi}{a} \hat{\mathbf{u}}_x, 0 \leq \chi \leq 1$$

where a is the lattice constant.

The free-electron branches along Δ are therefore

$$\varepsilon_{\mathbf{k}(\chi)-\mathbf{G}}^0 = \frac{\hbar^2}{2m} \left| \chi \frac{\pi}{a} \hat{\mathbf{u}}_x - \mathbf{G} \right|^2$$



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.3 Energy bands of a simple cubic lattice

We now consider the different reciprocal-lattice vectors $\mathbf{G}$ and determine the corresponding free-electron branches along the Δ direction.

For $\mathbf{G} = \mathbf{0}$,

the dispersion relation becomes

$$\varepsilon_{\mathbf{k}(\chi)}^0 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \chi \right)^2 = C \chi^2,$$

where

$$C = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2, \quad 0 \leq \chi \leq 1.$$

This branch starts from zero energy at Γ and reaches the energy C at the point X .

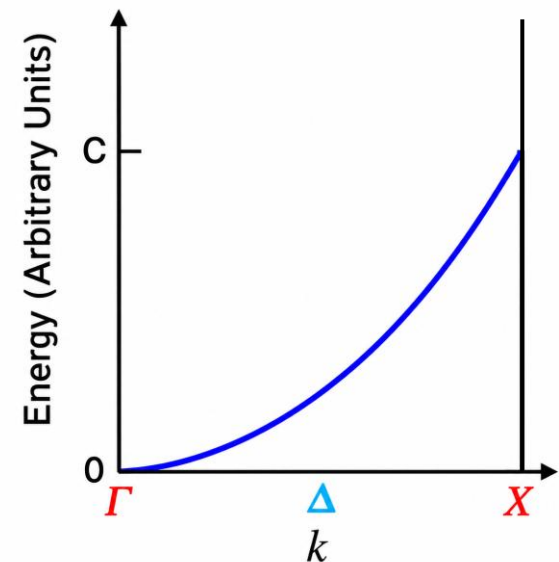
We now consider the non-zero reciprocal-lattice vector

$$\mathbf{G} = [1, 0, 0]$$

We first express $\mathbf{G}$ in terms of the reciprocal primitive vectors:

$$\mathbf{G} = \mathbf{b}_1$$

$$\varepsilon_{\mathbf{k}(\chi)-\mathbf{G}}^0 = \frac{\hbar^2}{2m} \left| \chi \frac{\pi}{a} \hat{\mathbf{u}}_x - \mathbf{G} \right|^2$$



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.3 Energy bands of a simple cubic lattice

Therefore,

$$\mathbf{G} = \mathbf{b}_1$$

$$\mathbf{G} = \frac{2\pi}{a} \hat{\mathbf{u}}_x$$

$$\begin{aligned}\vec{b}_1 &= \frac{2\pi}{a} \hat{u}_x \\ \vec{b}_2 &= \frac{2\pi}{a} \hat{u}_y \\ \vec{b}_3 &= \frac{2\pi}{a} \hat{u}_z\end{aligned}$$

Substituting $\mathbf{k}(\chi)$ and $\mathbf{G}$ in the free-electron dispersion relation, we obtain

$$\varepsilon_{[1,0,0]}^0(\chi) = \frac{\hbar^2}{2m} \left| \chi \frac{\pi}{a} \hat{\mathbf{u}}_x - \frac{2\pi}{a} \hat{\mathbf{u}}_x \right|^2$$

$$\varepsilon_{\mathbf{k}(\chi)-\mathbf{G}}^0 = \frac{\hbar^2}{2m} \left| \chi \frac{\pi}{a} \hat{\mathbf{u}}_x - \mathbf{G} \right|^2$$

which gives:

$$\varepsilon_{[1,0,0]}^0(\chi) = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2 (\chi - 2)^2$$

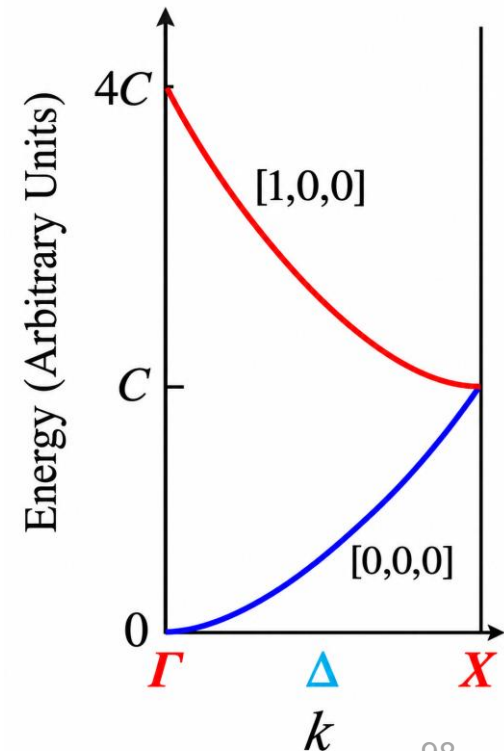
$$\mathbf{k}(\chi) = \chi \frac{\pi}{a} \hat{\mathbf{u}}_x, 0 \leq \chi \leq 1$$

The corresponding branch becomes

$$C = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2$$

$$\varepsilon_{[1,0,0]}^0(\chi) = C(\chi - 2)^2$$

At the endpoints of the Δ path,
 $\varepsilon_{[1,0,0]}^0(0) = 4C$, and $\varepsilon_{[1,0,0]}^0(1) = C$.



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.3 Energy bands of a simple cubic lattice

By considering the relevant reciprocal-lattice vectors $\mathbf{G}$ and repeating the calculation along the main high-symmetry directions, we obtain the free-electron band structure of a simple cubic lattice:

The energy branches are plotted along the high-symmetry path

$$\Gamma - X - R - \Gamma - M - X$$

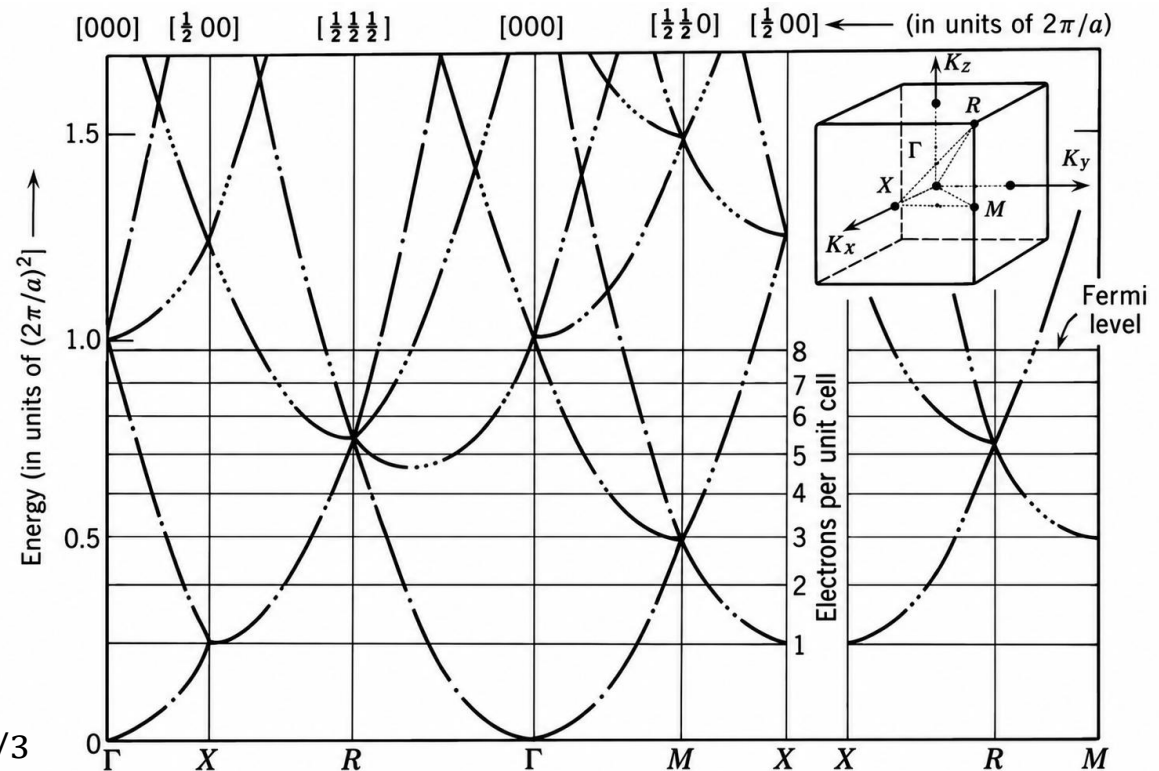
in the first Brillouin zone.

If z is the number of electrons per primitive cell of volume a^3 , then

$$n = \frac{z}{a^3}$$

and the Fermi energy is

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 z}{a^3} \right)^{2/3}$$



The horizontal lines in the diagram indicate the Fermi energies corresponding to different values of z , i.e. to different numbers of electrons per primitive cell.

3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.4 Energy bands of a body-centered lattice

For a body-centered cubic (BCC) lattice, the reciprocal lattice is face-centered cubic (FCC). Therefore, the first Brillouin zone is a rhombic dodecahedron

The intersection of the $[100]$ direction with the boundary of the first Brillouin zone defines the point H .

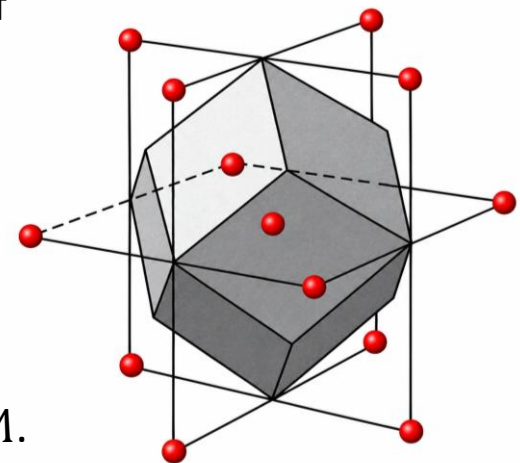
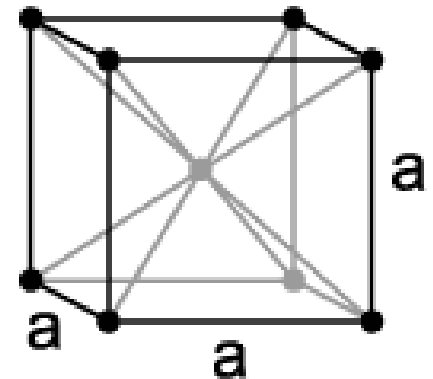
The intersection of the $[110]$ direction with the boundary of the first Brillouin zone defines the point N .

The intersection of the $[111]$ direction with the boundary of the first Brillouin zone defines the point P .

The high-symmetry line from Γ to H is denoted by Δ .

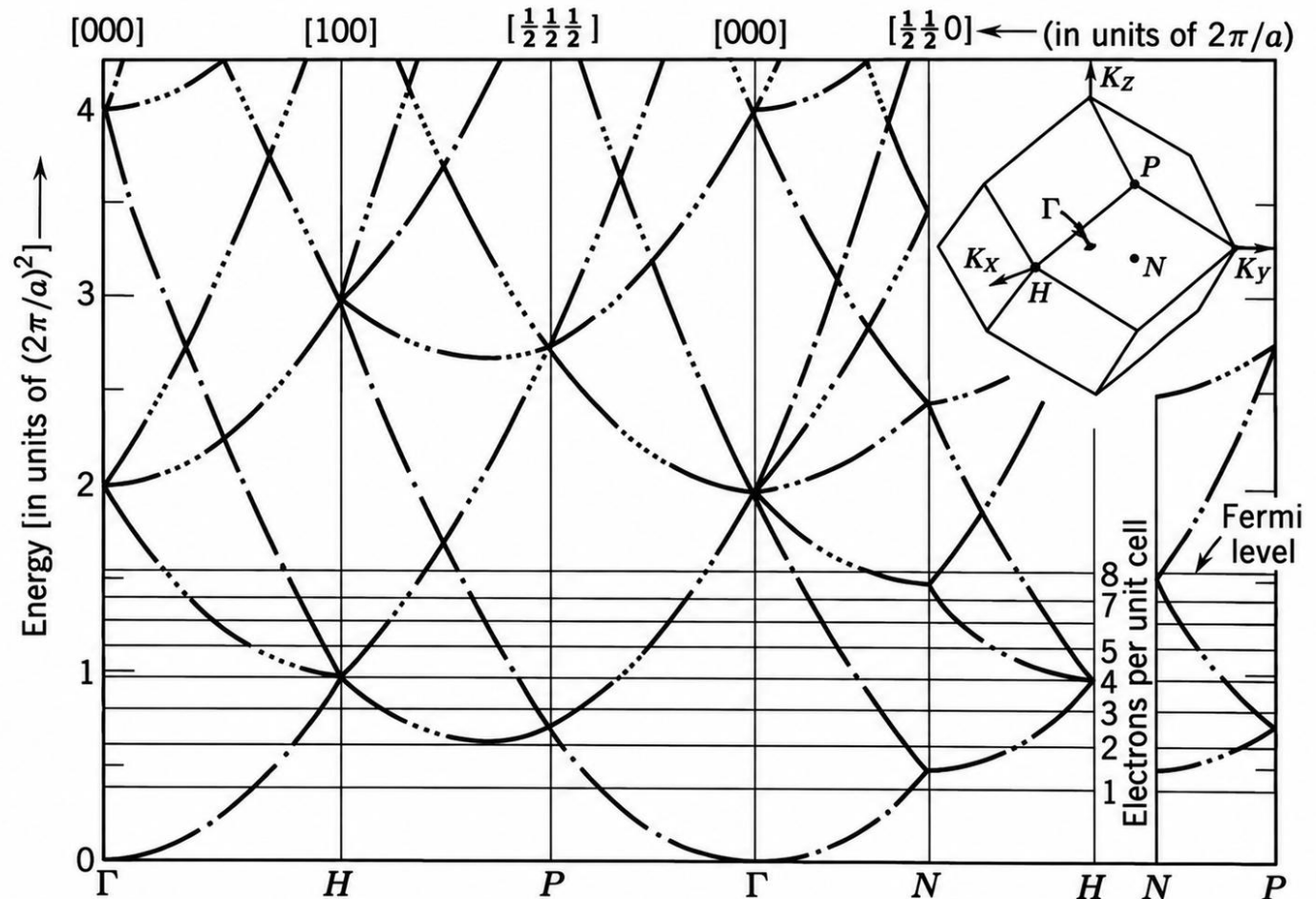
The high-symmetry line from Γ to N is denoted by Σ .

The high-symmetry line from Γ to P is denoted by Λ .



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.4 Energy bands of a body-centered lattice



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.5 Energy bands of a face-centered lattice

For a face-centered cubic (FCC) lattice, the reciprocal lattice is body-centered cubic (BCC). Therefore, the first Brillouin zone is a truncated octahedron.

The intersection of the $[100]$ direction with the boundary of the first Brillouin zone defines the point X .

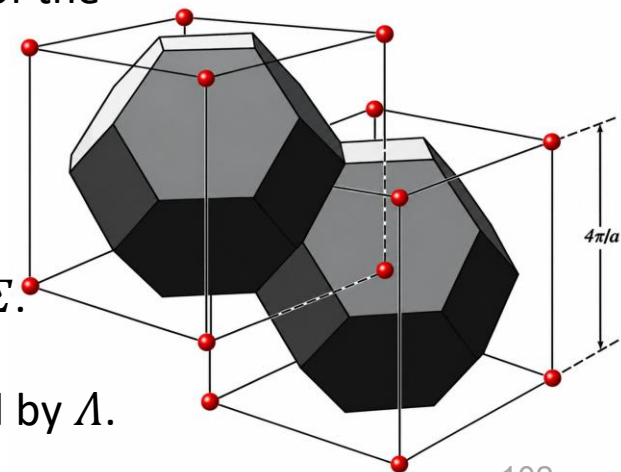
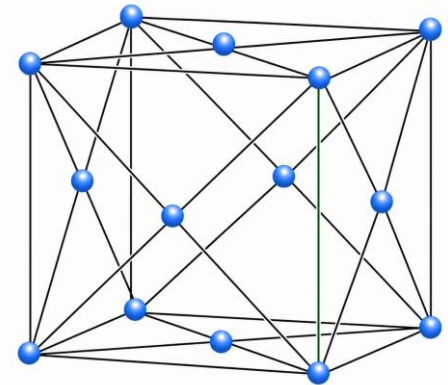
The intersection of the $[110]$ direction with the boundary of the first Brillouin zone defines the point K .

The intersection of the $[111]$ direction with the boundary of the first Brillouin zone defines the point L .

The high-symmetry line from Γ to X is denoted by Δ .

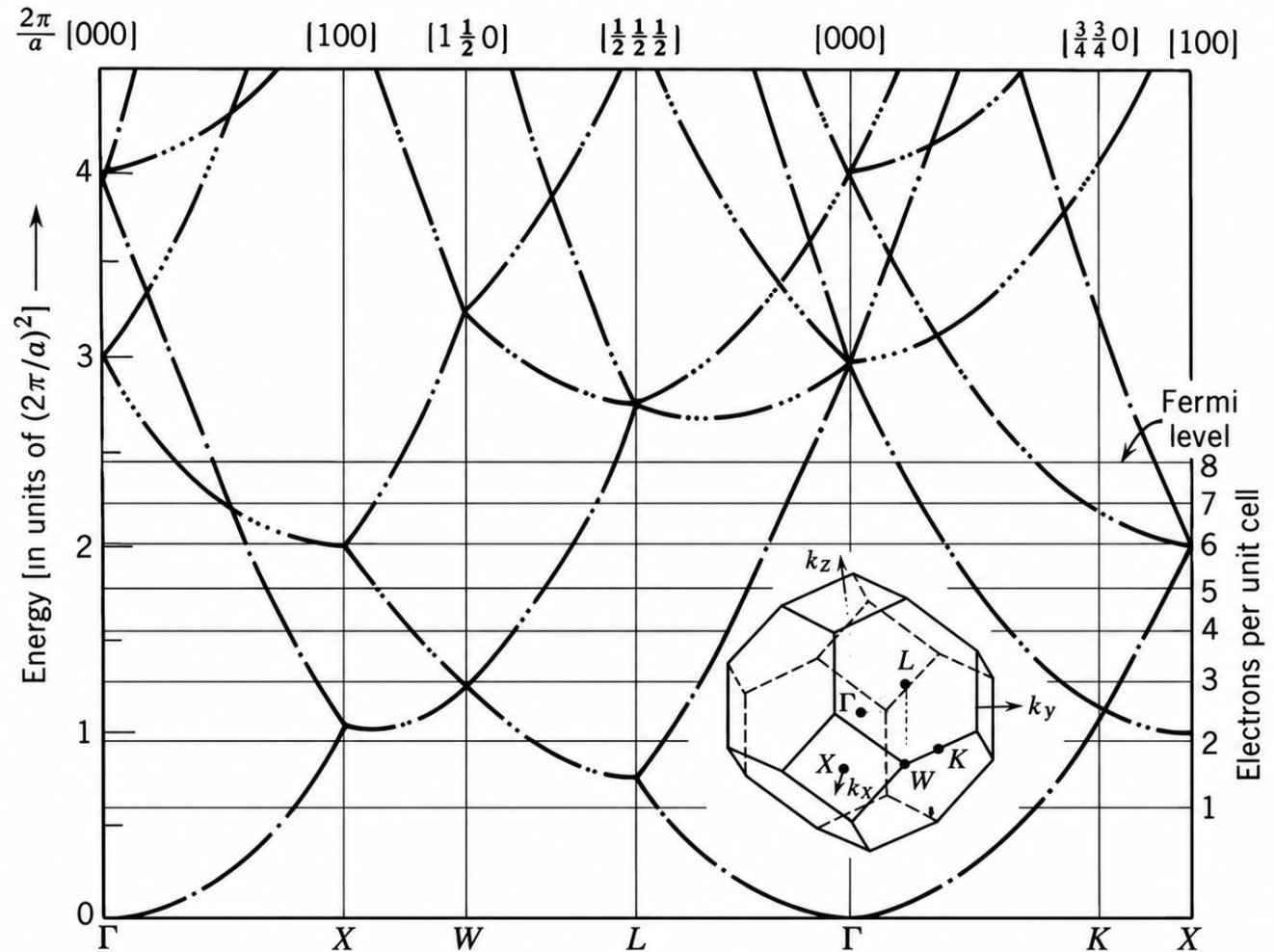
The high-symmetry line from Γ to K is denoted by Σ .

The high-symmetry line from Γ to L is denoted by Λ .



3.6 BAND STRUCTURES IN THREE DIMENSIONS

3.6.5 Energy bands of a face-centered lattice



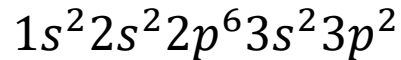
3.7 ORTHOGONALIZED PLANE WAVES

Let us begin by explicitly distinguishing between core and valence electrons.

Core-electron wave functions are strongly localized around the atomic nuclei.

Valence electrons, on the other hand, have a significant probability of being found in the interstitial regions between neighbouring atoms. In these regions, their wave functions can often be represented accurately by a relatively small number of plane waves.

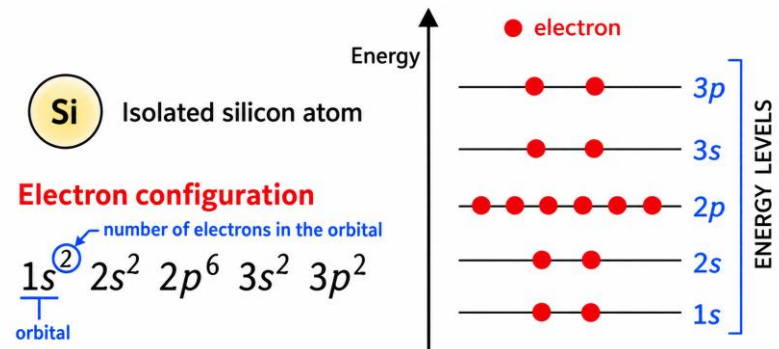
For an isolated silicon atom, the electron configuration is:



The core electrons $1s^2 2s^2 2p^6$ are treated as localized states that do not participate directly in chemical bonding or in the formation of the valence bands.

The valence electrons, $3s^2 3p^2$, determine the bonding properties of the crystal and play the main role in the formation of its energy bands.

Silicon crystallizes in the diamond-cubic structure. The atomic $3s$ and $3p$ orbitals hybridize to form four sp^3 hybrid orbitals.



These orbitals have the same shape, energy, and spatial orientation relative to the tetrahedral bonding geometry. Each silicon atom forms four equal covalent bonds with four nearest-neighbour atoms.

3.7 ORTHOGONALIZED PLANE WAVES

Why can a nearly-free-electron approximation be reasonable for valence electrons, even though they are involved in chemical bonds?

Away from the atomic cores, the nuclear potential is strongly screened by the core electrons. In the interstitial regions, the effective potential experienced by valence electrons is therefore relatively weak and smooth.

For this reason, valence-electron wave functions can often be approximated by a small number of plane waves in the interstitial region.

Close to the nuclei, however, valence-electron wave functions must remain orthogonal to the occupied core-electron states.

From now on, we use the superscript c to indicate core states and the superscript v to indicate valence states.

How do we describe the orthogonality of electronic wave functions?

A set of complex wave functions is said to be orthonormal if

$$\int \psi_n^*(\mathbf{r}) \psi_m(\mathbf{r}) d^3r = \delta_{nm}$$

As a zeroth-order approximation, we describe the valence electrons as free electrons and represent them by plane waves of the form

$$\frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

3.7 ORTHOGONALIZED PLANE WAVES

A more refined approximation, introduced by Herring, is to require that the valence-electron wave functions be orthogonal to all occupied core states.

The valence-electron wave functions can therefore be represented by orthogonalized plane waves (OPWs) of the form

$$\phi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_c b_{\mathbf{k}c} \psi_{\mathbf{k}}^c(\mathbf{r})$$

The sum runs over all core bands c at the same Bloch wave vector $\mathbf{k}$.

The core wave functions $\psi_{\mathbf{k}}^c(\mathbf{r})$ are assumed to be known. They are commonly constructed from localized atomic core orbitals.

The coefficients $b_{\mathbf{k}c}$ are determined by requiring that the OPW $\phi_{\mathbf{k}}^{\text{OPW}}$ be orthogonal to every core state:

$$\int [\psi_{\mathbf{k}}^c(\mathbf{r})]^* \phi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r}) d^3r = 0$$

Substituting the OPW expansion,

$$\phi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{c'} b_{\mathbf{k}c'} \psi_{\mathbf{k}}^{c'}(\mathbf{r})$$

and using the orthonormality of the core states

$$\int [\psi_{\mathbf{k}}^c(\mathbf{r})]^* \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r + \sum_{c'} b_{\mathbf{k}c'} \delta_{cc'} = 0$$

$$\int [\psi_{\mathbf{k}}^c(\mathbf{r})]^* \psi_{\mathbf{k}}^{c'}(\mathbf{r}) d^3r = \delta_{cc'}$$

3.7 ORTHOGONALIZED PLANE WAVES

Therefore

$$b_{\mathbf{k}c} = - \int [\psi_{\mathbf{k}}^c(\mathbf{r})]^* \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r$$

$$\int [\psi_{\mathbf{k}}^c(\mathbf{r})]^* \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r + \sum_{c'} b_{\mathbf{k}c'} \delta_{cc'} = 0$$

Since the core wave functions are strongly localized near the nuclei, their contribution to the OPW is negligible in the interstitial region. There, the orthogonalized plane wave is therefore very close to a single plane wave.

Since the core Bloch functions $\psi_{\mathbf{k}}^c(\mathbf{r})$ satisfy Bloch's theorem, the orthogonalized plane waves $\phi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r})$ also satisfy Bloch's theorem. Indeed, both terms entering the OPW construction have the same Bloch wave vector $\mathbf{k}$.

Therefore, the eigenstates of the Schrödinger equation can be expanded in the OPW basis as

$$\phi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_c b_{\mathbf{k}c} \psi_{\mathbf{k}}^c(\mathbf{r})$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \phi_{\mathbf{k}-\mathbf{G}}^{\text{OPW}}(\mathbf{r})$$

where the sum runs over all reciprocal-lattice vectors $\mathbf{G}$.

The coefficients $c_{\mathbf{k}-\mathbf{G}}$ and the energy bands $\varepsilon(\mathbf{k})$ are determined by solving the corresponding secular equation.

The crystal potential $U(\mathbf{r})$ enters the secular equation through the matrix elements

$$U_{\mathbf{G}\mathbf{G}'}^{\text{OPW}}(\mathbf{k}) = \int [\phi_{\mathbf{k}-\mathbf{G}}^{\text{OPW}}(\mathbf{r})]^* U(\mathbf{r}) \phi_{\mathbf{k}-\mathbf{G}'}^{\text{OPW}}(\mathbf{r}) d^3r.$$

3.8 PSEUDOPOTENTIAL

Pseudopotential theory builds on the orthogonalized plane-wave method and provides a widely used framework for electronic-structure calculations in periodic solids.

We introduce the method in its simplest form.

Let us expand a valence eigenstate as a linear combination of orthogonalized plane waves:

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \phi_{\mathbf{k}-\mathbf{G}}^{\text{OPW}}(\mathbf{r})$$

Each OPW consists of a plane-wave contribution and a linear combination of core states:

$$\phi_{\mathbf{k}-\mathbf{G}}^{\text{OPW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \sum_c b_{\mathbf{k}-\mathbf{G},c} \psi_{\mathbf{k}-\mathbf{G}}^c(\mathbf{r})$$

Substituting this expression into the valence-state expansion gives

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G}} \sum_c c_{\mathbf{k}-\mathbf{G}} b_{\mathbf{k}-\mathbf{G},c} \psi_{\mathbf{k}-\mathbf{G}}^c(\mathbf{r}).$$

Since $\mathbf{k} - \mathbf{G}$ and $\mathbf{k}$ describe equivalent Bloch wave vectors, the core states in the second term can be labeled by $\mathbf{k}$. Defining

$$B_{\mathbf{k}c} = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} b_{\mathbf{k}-\mathbf{G},c}$$

we can write

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \sum_c B_{\mathbf{k}c} \psi_{\mathbf{k}}^c(\mathbf{r})$$

3.8 PSEUDOPOTENTIAL

We isolate the plane-wave expansion of the valence state and denote it by $\phi_{\mathbf{k}}^v(\mathbf{r})$:

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}} + \sum_c B_{\mathbf{k}c} \psi_{\mathbf{k}}^c(\mathbf{r})$$

$$\phi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}}$$

Using the OPW construction, the valence wave function can then be written as

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int [\psi_{\mathbf{k}}^c(\mathbf{r}')]^* \phi_{\mathbf{k}}^v(\mathbf{r}') d^3r' \right] \psi_{\mathbf{k}}^c(\mathbf{r})$$

Since $\psi_{\mathbf{k}}^v(\mathbf{r})$ is a valence-electron wave function, it satisfies the Schrödinger equation with eigenvalue $\varepsilon_{\mathbf{k}}^v$:

$$\hat{H} \psi_{\mathbf{k}}^v(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \psi_{\mathbf{k}}^v(\mathbf{r})$$

Substituting the expression above for $\psi_{\mathbf{k}}^v(\mathbf{r})$, we obtain

$$\begin{aligned} & \hat{H} \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int [\psi_{\mathbf{k}}^c(\mathbf{r}')]^* \phi_{\mathbf{k}}^v(\mathbf{r}') d^3r' \right] \hat{H} \psi_{\mathbf{k}}^c(\mathbf{r}) \\ &= \varepsilon_{\mathbf{k}}^v \left\{ \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int [\psi_{\mathbf{k}}^c(\mathbf{r}')]^* \phi_{\mathbf{k}}^v(\mathbf{r}') d^3r' \right] \psi_{\mathbf{k}}^c(\mathbf{r}) \right\}. \end{aligned}$$

3.8 PSEUDOPOTENTIAL

$$\hat{H}\phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int [\psi_{\mathbf{k}}^c(\mathbf{r}')]^* \phi_{\mathbf{k}}^v(\mathbf{r}') d^3r' \right] \hat{H}\psi_{\mathbf{k}}^c(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \left\{ \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int [\psi_{\mathbf{k}}^c(\mathbf{r}')]^* \phi_{\mathbf{k}}^v(\mathbf{r}') d^3r' \right] \psi_{\mathbf{k}}^c(\mathbf{r}) \right\}$$

For core electrons:

$$H\psi_{\mathbf{k}}^c(\mathbf{r}) = \varepsilon_{\mathbf{k}}^c \psi_{\mathbf{k}}^c(\mathbf{r})$$

Substituting this into the previous expression gives

$$H\phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int d^3r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') \right] \varepsilon_{\mathbf{k}}^c \psi_{\mathbf{k}}^c(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \left\{ \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left[\int d^3r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') \right] \psi_{\mathbf{k}}^c(\mathbf{r}) \right\}$$

Bringing the second term on the right-hand side to the left-hand side, we obtain

$$H\phi_{\mathbf{k}}^v(\mathbf{r}) + \sum_c (\varepsilon_{\mathbf{k}}^v - \varepsilon_{\mathbf{k}}^c) \left[\int d^3r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') \right] \psi_{\mathbf{k}}^c(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v(\mathbf{r})$$

Let us define the operator V^R , acting on a generic function φ , as

$$V^R\varphi = \sum_c (\varepsilon_{\mathbf{k}}^v - \varepsilon_{\mathbf{k}}^c) \left[\int d^3r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \varphi(\mathbf{r}') \right] \psi_{\mathbf{k}}^c(\mathbf{r})$$

The previous equation can therefore be written as

$$(H + V^R)\phi_{\mathbf{k}}^v(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v(\mathbf{r})$$

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$$(H + V^R)\phi_{\mathbf{k}}^v(\mathbf{r}) = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v(\mathbf{r})$$

We have thus obtained a Schrödinger equation for $\phi_{\mathbf{k}}^v(\mathbf{r})$, namely the plane-wave, or smooth, part of the Bloch function describing a valence electron.

If $\phi_{\mathbf{k}}^v(\mathbf{r})$ can be approximated by a superposition of only a few plane waves, the valence energy levels of the effective operator $H + V^R$ can be determined within the nearly-free-electron approach.

The pseudopotential V^{pseudo} is defined by combining the real periodic potential $U(\mathbf{r})$ with the operator V^R :

$$V^{\text{pseudo}} = U + V^R$$

V^{pseudo} is generally non-local and energy-dependent through V^R .

Since

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U$$

we can write

$$H + V^R = -\frac{\hbar^2}{2m}\nabla^2 + V^{\text{pseudo}}$$

The central assumption is that V^{pseudo} is sufficiently weak for the valence levels to be calculated using the nearly-free-electron method. 111

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$$H + V^R = -\frac{\hbar^2}{2m}\nabla^2 + V^{\text{pseudo}}$$

$$V^{\text{pseudo}} = U + V^R$$

Since the ionic part of the real periodic potential $U(\mathbf{r})$ is strongly attractive near the nuclei, it is negative in the core region.

On the other hand, the valence-state energy lies above the energy of each core state:

$$\varepsilon_{\mathbf{k}}^v > \varepsilon_{\mathbf{k}}^c$$

Therefore, the operator V^R provides a positive, repulsive contribution in the core region.

When V^R is added to U , a substantial cancellation occurs near the nuclei.

As a result, the pseudopotential is much weaker than the original ionic potential. This justifies treating V^{pseudo} as a weak perturbation and applying the nearly-free-electron model to the smooth function $\phi_{\mathbf{k}}^v(\mathbf{r})$.

Qualitative interpretation

The pseudopotential may be viewed qualitatively as the result of combining a long-range attractive potential with a short-range repulsive contribution. Their partial cancellation strongly reduces the potential in the core region, making it much smoother and weaker than the bare Coulomb potential.

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Although V^R is generally non-local, simple band-structure calculations often replace the effective pseudopotential with a local model potential.

One of the simplest examples is the empty-core pseudopotential. It reproduces the Coulomb potential outside a core radius r_c , while it is set equal to zero inside the core region:

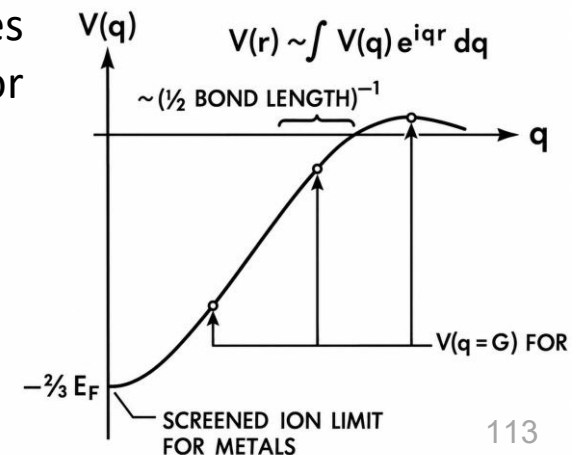
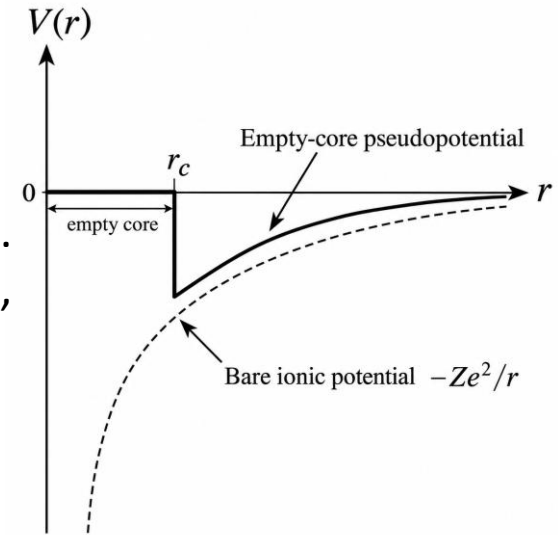
$$V^{\text{pseudo}}(r) = \begin{cases} 0, & 0 \leq r \leq r_c, \\ -\frac{Ze^2}{r}, & r > r_c. \end{cases}$$

Here, Z is the valence of the atomic species ($Z = 4$ for silicon), and r_c is the core radius. This parameter is chosen to reproduce selected experimental or atomic properties.

For band-structure calculations, the relevant quantities are the Fourier components of the pseudopotential. For the empty-core model, they are

$$V^{\text{pseudo}}(q) = -\frac{4\pi Ze^2}{q^2} \cos(qr_c), \quad q \neq 0$$

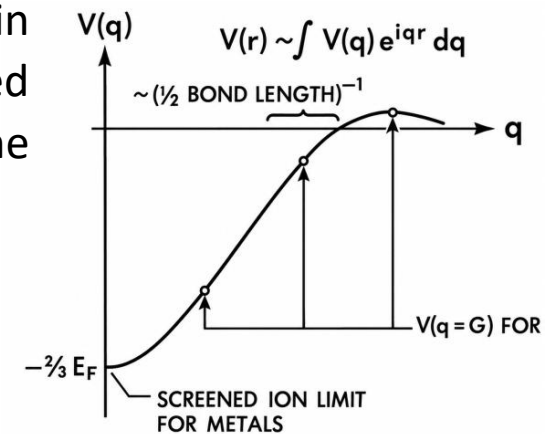
Thus, the single parameter r_c determines the Fourier components that couple plane waves in the nearly-free-electron description.



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The Fourier components of the pseudopotential decrease in magnitude at large wave vectors q . Consequently, only a limited number of plane waves is generally required to represent the smooth valence function $\phi_{\mathbf{k}}^v(\mathbf{r})$.

Let us now return to the general OPW pseudopotential and make two important observations:



$$V^R \varphi = \sum_c (\varepsilon_{\mathbf{k}}^v - \varepsilon_{\mathbf{k}}^c) \left[\int d^3 r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \varphi(\mathbf{r}') \right] \psi_{\mathbf{k}}^c(\mathbf{r})$$

- The operator V^R , and hence the general pseudopotential $V^{\text{pseudo}} = U + V^R$, is non-local. Its action on a generic function $\varphi(\mathbf{r})$ is not simply given by multiplication by a function of position.
- The operator V^R explicitly depends on the valence energy $\varepsilon_{\mathbf{k}}^v$. Therefore, the effective Hamiltonian $H + V^R$ is energy-dependent. As a consequence, some standard results for energy-independent Hermitian Hamiltonians—such as the usual orthogonality relation between eigenfunctions with different eigenvalues—cannot be applied without further consideration.

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The energy dependence of V^R can be removed by replacing the valence-state energy $\varepsilon_{\mathbf{k}}^v$ appearing in its definition with a fixed reference energy. For metals, a natural choice is the Fermi energy E_F .

We then define
$$V_{E_F}^R \varphi(\mathbf{r}) = \sum_c (E_F - \varepsilon_{\mathbf{k}}^c) \left[\int d^3 r' \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \varphi(\mathbf{r}') \right] \psi_{\mathbf{k}}^c(\mathbf{r}).$$

The effective Hamiltonian

$$H + V_{E_F}^R$$

is now energy-independent. Its eigenvalues do not, in general, coincide exactly with those of the original Hamiltonian; however, the approximation preserves the states at the reference energy E_F and is therefore particularly suitable for describing the electronic structure close to the Fermi level.

For example, by determining all wave vectors $\mathbf{k}$ for which $\varepsilon_{n\mathbf{k}} = E_F$, one can reconstruct the Fermi surface.

Pseudopotential methods have become central tools for calculating the electronic band structures of crystals.

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Application of the Orthogonalized Plane-Wave Method to Silicon Crystal*

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Approximate solutions for $\mathbf{k}=0$ of the Hartree-Fock-Slater equations for a perfect silicon crystal have been obtained by the orthogonalized plane-wave method. Estimates of the energy eigenvalues of the valence and conduction states for $\mathbf{k}=0$ are given. A simple method for obtaining a first approximation to the crystal potential and its Fourier coefficients was used. Approximate analytic wave functions and corresponding energy eigenvalues for the $1s$, $2s$, and $2p$ states in the isolated silicon atom were determined by a variational technique.