

Electronic Energy Bands

The complex problem of calculating the properties of electrons in perfect crystals is reduced to an investigation of a one-electron Hamiltonian.

Bloch's theorem and symmetry considerations are essential to simplify our calculations.

Bloch's Theorem

The Hamiltonian of a single electron in a periodic potential yields the Schrödinger equation

$$H(\vec{r})\Psi(\vec{r}) \equiv \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \Psi(\vec{r}) = E \Psi(\vec{r}) \quad (1)$$

where $V(\vec{r} + \vec{R}_n) = V(\vec{r})$.

Because of the periodic nature of $V(\vec{r})$, the wave functions have distinct properties and are called **Bloch wavefunctions**.

The theorem that states the properties of the Bloch wavefunctions is referred to as **Bloch's Theorem or the Bloch condition**.

There are 3-standard ways of stating Bloch's Theorem

1. The solution to the Hamiltonian in (1) can be expressed as a plane-wave $e^{i\vec{k} \cdot \vec{r}}$ times a function having the periodicity of the lattice, hence

$$\Psi_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \text{ where } U_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r} + \vec{R}_n).$$

The wavevector \vec{k} is used as a quantum # to label the electronic states.

Latter we will show that the energy levels group into bands. We are

going to index the bands by a letter (say n). Then a specific state will be assigned the label (n, \vec{k}) . We suppress the band index for now.

2. Bloch functions satisfy the periodic translational symmetry condition

$$\psi_{\vec{k}}(\vec{r} + \vec{R}\vec{n}) = e^{i\vec{k} \cdot \vec{R}\vec{n}} \psi_{\vec{k}}(\vec{r})$$

This condition relates a lattice translation to a wavefunction phase-factor. This condition is very useful for illustrating the consequences of lattice periodicity on the wavefunction and matrix elements involving Bloch functions.

3. Since functions having the same periodicity can be expressed in a discrete Fourier sum

→ Recall $u(\vec{r}) = \sum_m b_m e^{i\vec{q}_m \cdot \vec{r}}$ for $u(\vec{r}) = u(\vec{r} + \vec{R}\vec{n})$.

The periodic part of the Bloch wavefunction can be written as

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{q}} b_{\vec{k}}(\vec{q}) e^{i(\vec{k} + \vec{q}) \cdot \vec{r}}$$

This results in a useful and common form of the Bloch wavefunction

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{q}} b_{\vec{k}}(\vec{q}) e^{i(\vec{k} + \vec{q}) \cdot \vec{r}}$$

→ It is possible to use any of the 3 descriptions to obtain benefits of periodic translation symmetry via Bloch theorem.

→ The 3 statements describe the same physical properties.

→ One-dimensional proofs of Bloch's theorem are called Floquet

theorem.

Proof of Bloch's Theorem:

Discrete translation operators $\hat{T}_{\vec{n}}$: $\hat{T}_{\vec{n}} f(\vec{r}) = f(\vec{r} + \vec{R}_{\vec{n}})$.

where $f(\vec{r})$ is an arbitrary function and $\vec{n} = (n_1, n_2, n_3)$ where $n_{i=1,2,3} \in \mathbb{Z}$. Hence $\vec{R}_{\vec{n}} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$.

We can describe $\hat{T}_{\vec{n}}$ as an operator that takes $\vec{r} \rightarrow \vec{r}' - \vec{R}_{\vec{n}}$ and then relabel $\vec{r}' = \vec{r}$ where $\vec{r} = (x, y, z)$ and $\vec{r}' = (x', y', z')$.

If the operator $\hat{T}_{\vec{n}}$ acts on $H(\vec{r})$ in (1)

$$H(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

it leaves $H(\vec{r})$ invariant!

This is obvious for $V(\vec{r})$ since $\hat{T}_{\vec{n}} V(\vec{r}) = V(\vec{r} + \vec{R}_{\vec{n}}) = V(\vec{r})$

Now we examine the action of $\hat{T}_{\vec{n}}$ on the kinetic term. We first look at the x -component of \vec{r}

$$\hat{T}_{\vec{n}} \left[\frac{d^2}{dx^2} f(\vec{r}) \right] = \frac{d^2}{dx'^2} f(\vec{r}') = \frac{d^2}{dx^2} f(\vec{r} + \vec{R}_{\vec{n}}) = \frac{d}{dx^2} \hat{T}_{\vec{n}} f(\vec{r}).$$

Similarly for y and z . Therefore $\hat{T}_{\vec{n}}$ commutes ∇^2 and thus with $H(\vec{r})$

$$[\hat{T}_{\vec{n}}, H(\vec{r})] = 0$$

The action of two translation operators $\hat{T}_{\vec{n}}$ and $\hat{T}_{\vec{l}}$ on $f(\vec{r})$ yields

$$\hat{T}_{\vec{n}} \hat{T}_{\vec{l}} f(\vec{r}) = f(\vec{r} + \vec{R}_{\vec{n}} + \vec{R}_{\vec{l}}) = \hat{T}_{\vec{l}} \hat{T}_{\vec{n}} f(\vec{r}) = \hat{T}_{\vec{l} + \vec{n}} f(\vec{r}).$$

Therefore, $\{\hat{T}_{\vec{n}}\}$ is a set of commuting operators that also commute with $H(\vec{r})$. Hence, we can diagonalize all $\hat{T}_{\vec{n}}$ and $H(\vec{r})$ simultaneously.

Choosing $\Theta_{\vec{n}}$ to be the eigenvalue corresponding to the action of the translation operator on an eigenfunction of $H(\vec{r})$, $\Psi_{\vec{n}}(\vec{r})$ we have

$$\hat{T}_{\vec{n}} \Psi_{\vec{n}}(\vec{r}) = \Theta_{\vec{n}} \Psi_{\vec{n}}(\vec{r}).$$

Also using $\hat{T}_{\vec{n}} \hat{T}_{\vec{l}} f(\vec{r}) = \hat{T}_{\vec{n}+\vec{l}} f(\vec{r})$ we have $\Theta_{\vec{n}} \Theta_{\vec{l}} = \Theta_{\vec{n}+\vec{l}}$.

We now break up the translation operator into components

$$\hat{T}_{\vec{n}} = \hat{T}_{(n_1, n_2, n_3)} = [\hat{T}_{a_1}^{n_1}] [\hat{T}_{a_2}^{n_2}] [\hat{T}_{a_3}^{n_3}] \text{ and}$$

$$\Theta_{(n_1, n_2, n_3)} = \Theta_{a_1}^{n_1} \Theta_{a_2}^{n_2} \Theta_{a_3}^{n_3}.$$

Since \hat{T} is a translation operator and the electronic wave function is normalized, Θ can be only a unimodular complex #. Then

$$\Theta_{a_1}^n = e^{i n \alpha_1}, \quad \Theta_{a_2}^m = e^{i m \alpha_2}, \text{ and } \Theta_{a_3}^s = e^{i s \alpha_3}, \text{ yielding to}$$

$$\Theta_{\vec{n}} = \Theta_{(n_1, n_2, n_3)} = e^{i(n_1 \alpha_1 + n_2 \alpha_2 + n_3 \alpha_3)}$$

Now, recall that $\vec{p}_{\vec{m}} = m_1 \vec{g}_1 + m_2 \vec{g}_2 + m_3 \vec{g}_3$, $\vec{p}_{\vec{m}} \cdot \vec{R}_{\vec{n}} = 2\pi v$ and with

$$\vec{g}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3} \quad (i \rightarrow j \rightarrow k) = (1, 2, 3) \text{ in cyclic order}$$

we have $v = n_1 m_1 + n_2 m_2 + n_3 m_3$. Then

$$\vec{g}_i \cdot \vec{R}_{\vec{n}} = 2\pi n_i,$$

then we may write $\Theta_{\vec{n}} = e^{i \vec{k} \cdot \vec{R}_{\vec{n}}}$ with $\vec{k} \equiv \left(\frac{\alpha_1}{2\pi}\right) \vec{g}_1 + \left(\frac{\alpha_2}{2\pi}\right) \vec{g}_2 + \left(\frac{\alpha_3}{2\pi}\right) \vec{g}_3$.

Since α_i 's are defined between $0 \leq \alpha \leq 2\pi$, \vec{k} is a vector in reciprocal space.

cal space and maybe taken confined to the 1st B.Z.

We then can use \vec{k} as a quantum #, labeling the states that simultaneously diagonalize $H(\vec{r})$ and all $T_{\vec{n}}$'s, then

$$\hat{T}_{\vec{n}} \Psi_{\vec{k}}(\vec{r}) = \theta_{\vec{n}} \Psi_{\vec{k}}(\vec{r}) \text{ becomes}$$

$$\hat{T}_{\vec{n}} \Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}_{\vec{n}}} \Psi_{\vec{k}}(\vec{r})$$

which gives the standard form of Bloch's Theorem

$$\Psi_{\vec{k}}(\vec{r} + \vec{R}_{\vec{n}}) = e^{i\vec{k} \cdot \vec{R}_{\vec{n}}} \Psi_{\vec{k}}(\vec{r})$$

Arbitrariness of the \vec{k} -vector and reduction of the B.Z.

Because of the properties of the Bloch functions we can write

$$\begin{aligned} \Psi_{\vec{k}}(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} \Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{G}} b_{\vec{k}}(\vec{G}) e^{i\vec{G} \cdot \vec{r}} = e^{i(\vec{k} - \vec{G}_0) \cdot \vec{r}} \sum_{\vec{G}} b_{\vec{k}}(\vec{G}) e^{i(\vec{G} + \vec{G}_0) \cdot \vec{r}} \\ &= e^{i(\vec{k} - \vec{G}_0) \cdot \vec{r}} \sum_{\vec{G}'} b_{\vec{k}}(\vec{G}' - \vec{G}_0) e^{i\vec{G}' \cdot \vec{r}} = e^{i(\vec{k} - \vec{G}_0) \cdot \vec{r}} \Psi_{\vec{k} - \vec{G}_0}(\vec{r}) = \Psi_{\vec{k} - \vec{G}_0}(\vec{r}), \end{aligned}$$

where \vec{G}_0 is any specific reciprocal lattice vector, $\vec{G}' = \vec{G} + \vec{G}_0$, and $\Psi_{\vec{k} - \vec{G}_0}$ is a periodic function with properties similar to those of $\Psi_{\vec{k}}(\vec{r})$.

The equations above state that \vec{k} and $\vec{k} - \vec{G}_0$ are equally acceptable labels for describing the translation properties of Ψ .

This also means that any vector \vec{k}' in reciprocal space that differs from \vec{k} by a reciprocal lattice vector \vec{G} can be chosen to represent the plane wave part of a Bloch function; the choice is arbitrary.

This is because $(\vec{k}' - \vec{G}_0) \cdot \vec{R}_{\vec{n}} = \vec{k} \cdot \vec{R}_{\vec{n}} - 2\pi v$, $v \in \mathbb{Z}$, then \vec{G}_0 has

no physical consequences.

This indeterminacy is resolved by imposing extra conditions on \vec{k} . The most common one is to require the magnitude $|\vec{k}|$ to be the smallest possible. This restricts \vec{k} to the interior of the B.Z. and leaves a small # of choices if \vec{k} is on the boundary of the B.Z. These choices are left to the individual.

for example in 1D $\vec{G}\vec{n} = (2\pi/a)\vec{n} \rightarrow \vec{k}$ is restricted to $-\frac{\pi}{a} < k < \frac{\pi}{a}$.

→ Now that we have seen Bloch's theorem we will focus on electronic structure.

→ We begin by the free electron model, then we analyze the effects of symmetries on the band structure. Then we introduce the Kronig-Penney model to the existence of energy bands and bandgaps. We conclude this part with the nearly free and the tight-binding models.

The free electron model

Consider the Schrödinger Equation

$$\left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \Psi(\vec{r}) = E \Psi(\vec{r})$$

with $V(\vec{r}) = V(\vec{r} + \vec{R})$.

Here we explore the case where $V(\vec{r}) \ll \hat{p}^2/2m$. But we enforce the translation boundary conditions on the electronic wavefunction. This means we still have Bloch waves, but beyond this the potential has a small effect on the electrons.

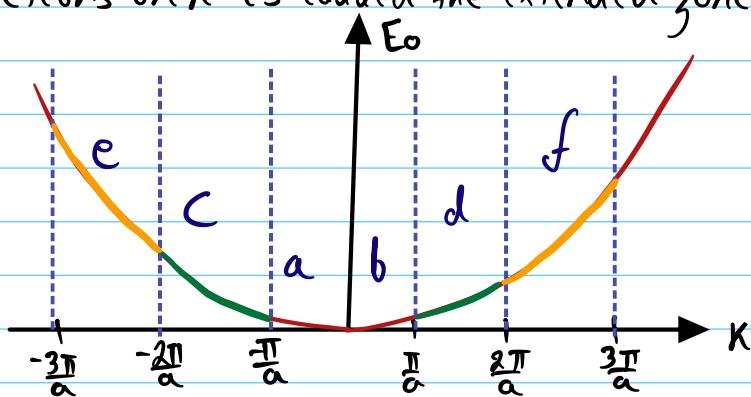
Consider electrons in 1D in a sample of length L , and as a first approximation set $V(x) = 0$. This leads to the free electron model or free electron gas, where

$$\frac{\hat{p}^2}{2m} \Psi_k^\circ = E_0(k) \Psi_k^\circ \quad (k=k_x).$$

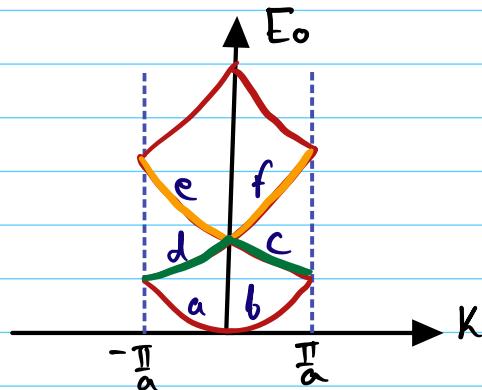
The solution of this equation is straight forward

$$\Psi_k^\circ = \frac{1}{\sqrt{L}} e^{ikx} \text{ and } E_0(k) = \frac{\hbar^2 k^2}{2m}$$

The wavevector \vec{k} is not restricted and goes from $-\infty$ to ∞ . If we plot $E_0(\vec{k})$ with no restrictions on \vec{k} is called the "extended zone scheme!"



When the $E_0(\vec{k})$ curve is mapped back to the 1st B.Z. this is called the "reduced zone scheme!"



→ The extended zone scheme is appropriate for free electrons, since the B.Z. has no real significance

→ In the reduced zone scheme the $E_0(\vec{k})$ is mapped into the 1st B.Z. in anticipation to restoring the potential. The mapping is done by

$K' = K - \frac{2n\pi}{a}$, $n \in \mathbb{Z}$ or $K' = K - G$. This gives the mapping for Ψ_K^o and $E_o(K)$ as $E_o(nK') = E_o\left(K + \frac{2n\pi}{a}\right)$.

There is another quantum # n in addition to K' that is restricted to the 1st B.Z.

These 2 plots are called dispersion curves or band structure for the free electron model.

A periodic potential can introduce gaps between the energy bands, at the points of degeneracy $K=0, K=\pm\pi/a$.

Symmetries in Energy Bands

Since translational symmetry lead to the Bloch functions and Bloch's theorem.

Let us assume the Bloch form of the wavefunctions

$$\Psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}}(\vec{r}) \quad (1)$$

and then we insert them in the one-electron Hamiltonian

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \Psi_{n,\vec{k}}(\vec{r})$$

to arrive at an equation for $u_{n,\vec{k}}(\vec{r})$ part of the Bloch functions

$$\left[\frac{1}{2m} (\vec{p}^2 + 2\hbar\vec{k} \cdot \vec{p} + \hbar^2 k^2) + V(\vec{r}) \right] u_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) u_{n,\vec{k}}(\vec{r}) \quad (2)$$

→ Since this is an eigenvalue problem with periodic boundary conditions, the eigenvalues take discrete values of n .

→ Once this equation is solved, the band structure $E_n(\vec{k})$, which gives the electronic energy for each state labeled by the band index n , and wave-vector \vec{k} .

→ The full Bloch wavefunction can be constructed using parts obtained from (2) using (1).

→ The lattice could have point-group symmetries in addition to translation.

Point group: The group of rotations, reflections, and combinations of the two. These symmetries are obtained by keeping one point fixed.

Space group: Point group operations together with translation symmetry operations of the crystal.

Non-Symmorphic Operations: Point group operation plus a translation that is not a translation vector.

→ The energy bands have the same symmetry as the crystal.

for example: Consider an operator Θ which can be a rotation such that

$$\vec{r}' = \Theta \vec{r}$$

In order to show that $E_n(\vec{k}') = E_n(\vec{k})$ where $\vec{k}' = \Theta \vec{k}$, we apply Θ to the wave equation for $u_{\vec{k}}(\vec{r})$ (2).

$\vec{p}'^2 = (\Theta \vec{p} \Theta \vec{p}) = \vec{p}^2$, $\vec{k}'^2 = \vec{k}^2$, and $\vec{k}' \cdot \vec{p}' = \vec{k} \cdot \vec{p}$, since scalar products are invariant under rotations. Therefore

$$\left[\frac{1}{2m} (\vec{p}^2 + 2\hbar \vec{k} \cdot \vec{p} + \hbar^2 \vec{k}^2) + V(\vec{r}) \right] u_{n,\vec{k}'}(\Theta \vec{r}) = E_n(\vec{k}') u_{n,\vec{k}'}(\Theta \vec{r})$$

$U_{n,\vec{k}'}(\theta \vec{r})$ satisfies the same equation as $U_{n,\vec{k}}(\vec{r})$. Hence, a situation similar to

$$\Psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R} n} U_{\vec{k}}(\vec{r})$$

exists, and a band index n can be chosen such that $E_n(\vec{k}') = E_n(\vec{k})$, where $\vec{k}' = \theta \vec{k}$.

Schematically $\theta E_n(\vec{k}) = E_n(\vec{k}')$, and $E_n(\vec{k}')$ possesses the full rotational symmetry of the crystal structure.

The translational symmetry is assured by the B.Z. scheme, and beyond this $E_n(\vec{k})$ is taken to have the spare symmetry of the lattice.

Another example, let us consider inversion since in the spinless case its consequences are related to time-reversal.

All Bravais lattices (without basis) have inversion symmetry. In some cases inversion symmetry remains even with basis.

Then if $V(\vec{r}) = V(-\vec{r})$ then $E_n(\vec{k}) = E_n(-\vec{k})$. However, even without inversion symmetry, if the system contains no magnetic fields and the forces are time-reversal invariant (such as Coulomb force), we can show that $E_n(\uparrow \vec{k}) = E_n(\downarrow -\vec{k})$, where \uparrow and \downarrow are related by time reversal symmetry.

Without spin-orbit interactions (Spin degenerate case) the time reversal operator is simply the conjugation operator. Applying this operator to the Bloch wave function

$$T \Psi_{n,\vec{k}}(\vec{r}) = \Psi_{n,\vec{k}}^T(\vec{r}) = e^{i(-\vec{k}).\vec{r}} U_{n,\vec{k}}^*(\vec{r})$$

Then Eq (2) becomes

$$\left[\frac{1}{2m} (\hat{p}^2 - 2\hbar \vec{k} \cdot \hat{p} + \hbar^2 \vec{k}^2) + V(\vec{r}) \right] U_{n,\vec{k}}^*(\vec{r}) = E_n(\vec{k}) U_{n,\vec{k}}^*(\vec{r}).$$

So $\psi_{n,\vec{k}}(\vec{r})$ and $\psi_{n,-\vec{k}}(\vec{r})$ satisfy the same equation if \vec{k} is replaced by $-\vec{k}$, then

$$\psi_{n,\vec{k}}^* = \psi_{n,-\vec{k}} \text{ and}$$

$E_n(\uparrow \vec{k}) = E_n(\downarrow -\vec{k})$. This is also called the Kramers Degeneracy, we are going to see it soon in the 2nd quantum review.

Some important concepts when discussing bands in the 1st B.Z.

Degeneracy : More than one state with the same \vec{k} and E . We do not call the states $\psi_{n,\vec{k}}$ and $\psi_{n,\vec{k}'}$ such that $\vec{k}' = \theta \vec{k}$ and in the case where we consider $\psi_{n,\vec{k}}$ and $\psi_{n,\vec{k}+\vec{G}}$ degenerate. In the case $\psi_{n,\vec{k}}$ and $\psi_{n,\vec{k}+\vec{G}}$ the states are identical.

→ Most degeneracies result from symmetry while others are called accidental.

→ Symmetry considerations save a lot of effort when calculating the band structure.

for example, if $E_n(\vec{k})$ for the FCC. The calculation only needs to be done on 1/48 of the B.Z., because of space group symmetry and $E_n(\vec{k}) = E_n(-\vec{k})$, and other states in the extended B.Z. are identical to those in 1/48 of the 1st B.Z., and are obtained by a mapping.

Symmetries and Energy Bands in 1D.

Several features of $E(k)$ with k in the 1st B.Z. ($-\pi/a < k \leq \pi/a$) are easily deduced from symmetry principles.

We can show that: 1) $E(k)$ is non-degenerate

2) $E(k=0)$ is a maximum or a minimum.

3) $E(k)$ approaches $\pm \pi/a$ with a zero slope.

4) $E(k)$ has a max. or a min. only at $k=0$ and $\pm \pi/a$.

1) $E(k)$ is non-degenerate. For 1D, the one electron schrodinger Eqn.

$\left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \Psi = E \Psi$, is just an ordinary linear differential eqn, so

there are at most 2-independent solutions $\Psi(x)$ for a given E , which are labeled by n and K .

Without spin time-reversal and inversion require $E(K) = E(-K)$, but we exclude the K and $-K$ pair from our definition by degeneracy.

Therefore, 1D bands are non-degenerate and do not overlap.

2) $E(K=0)$ is a max or a min. Since $E(K)=E(-K)$, assuming the derivative can be defined

$$\frac{dE}{dK} \Big|_{K=0} = \lim_{\delta K \rightarrow 0} \frac{E(\delta K) - E(-\delta K)}{2\delta K} = 0$$

Therefore, $E(K)$ is a max or a min at $K=0$.

3) $E(K)$ approaches, $K=\pm\pi/a$ with zero slope.

Translational symmetry requires that

$$E(-\pi/a + \delta K) = E(-\pi/a + \delta K + 2\pi/a) = E(\pi/a + \delta K).$$

from time reversal

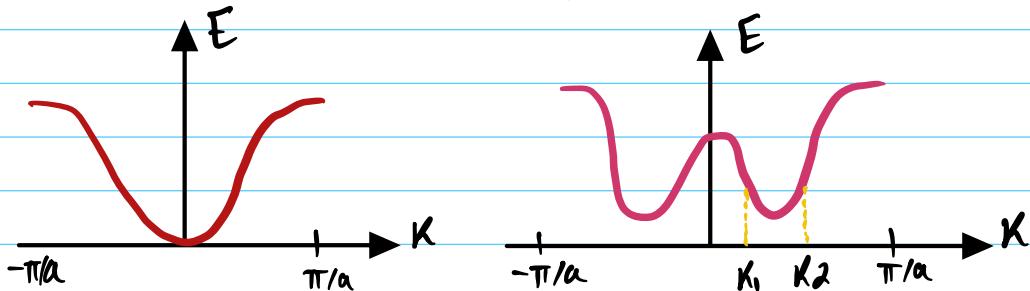
$$E(\pi/a + \delta K) = E(-\pi/a - \delta K)$$

then

$$\frac{dE(K)}{dK} \Big|_{K=\pm\frac{\pi}{a}} = \lim_{\delta K \rightarrow 0} \frac{E(\pm\pi/a + \delta K) - E(\pm\pi/a - \delta K)}{2\delta K} = 0.$$

So, $E(K)$ is a max or min at $K=\pm\pi/a$

4) $E(K)$ has a max or min only at $K=0, \pm\pi/a$.



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If we had another max or min a situation where $E(K_1) = E(K_2)$ with $K_1 \neq K_2$ could exist. This condition will exceed the max # of degenerate solutions that we could have. Then 1D conductors can only have electron or hole states at $K=0$ and $K=\pm\pi/a$.

In these proofs the system is assumed to be spinless, with inversion or time reversal, and that the 1D system is embedded in 3D with external symmetries

Energy Bands and Gaps : The Kronig-Penney Model

from symmetry we anticipated the existence of separated energy bands and bandgaps

- The gaps are regions of energy where electronic states do not exist.
- Gaps separate the states into bands.
- Neglecting strong electronic correlations, the interaction of the electrons with the periodic crystalline potential gives rise to bandgaps.
- The Kronig-Penney model is a 1D-model of a periodic potential that is exactly solvable and demonstrates the existence of separated energy bands and bandgaps. This is a toy model that gives deep insights into the consequences of

periodic potentials.

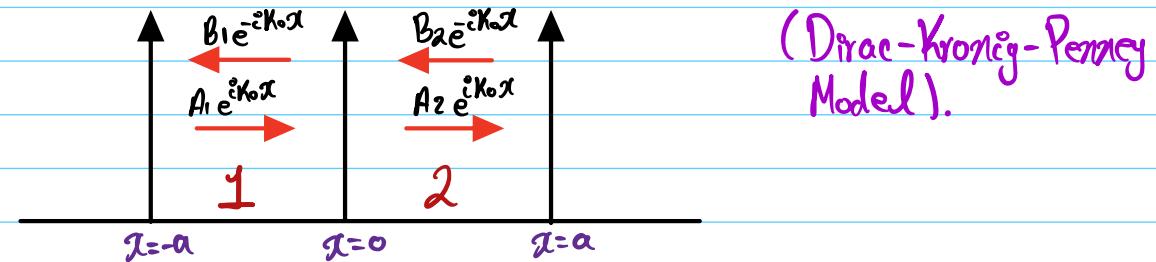
The model: Consider an infinite array of δ -function potentials of integrated strength aV and separated by a distance a .

The potential can be written as

$$V(x) = aV \sum_{n=-\infty}^{\infty} \delta(x-na).$$

This is the simplest periodic 1-D potential we can consider.

Now let us look at the regions on either side of the δ -potential that is placed at $x=0$.



In regions 1 and 2 (and any region with $V=0$) the eigenfunctions are linear combinations of the planewave solutions with $k k_0 = \sqrt{2mE}$. Then

$$\Psi_1(x) = A_1 e^{ik_0 x} + B_1 e^{-ik_0 x} \quad \text{and} \quad \Psi_2(x) = A_2 e^{ik_0 x} + B_2 e^{-ik_0 x}$$

In general Bloch's Theorem Requires

$$\Psi(x) = e^{ikx} \Psi(x-a) \quad \text{where } k \text{ is the crystal's momentum}$$

Then for $0 \leq x \leq a$

$$\Psi_2(x) = e^{ikx} \Psi_1(x-a), \text{ and}$$

$$A_2 e^{ik_0 x} + B_2 e^{-ik_0 x} = e^{ikx} (A_1 e^{ik_0 (x-a)} + B_1 e^{-ik_0 (x-a)})$$

Since, e^{ik_0x} and \bar{e}^{ik_0x} are linear independent, then the coefficients of $e^{\pm ix}$ on both sides must be equal, which yields to

$$A_2 = A_1 e^{i(K-K_0)a} \quad \text{and} \quad B_2 = B_1 \bar{e}^{i(K+K_0)a}$$

Then we can rewrite $\Psi_2(x)$

$$\Psi_2(x) = e^{ixa} (A_1 e^{iK_0(x-a)} + B_1 \bar{e}^{iK_0(x-a)})$$

Now we can apply the well known boundary conditions

$$\Psi_1(0) = \Psi_2(0)$$

$$A_1 + B_1 = e^{ixa} [A_1 e^{iK_0a} + B_1 \bar{e}^{iK_0a}] \quad \text{--- (1)}$$

Also, due to the presence of the δ -functions we have the discontinuity in the derivative

$$\left(\frac{d\Psi_2(x)}{dx} \Big|_{x=0} - \frac{d\Psi_1(x)}{dx} \Big|_{x=0} \right) - \frac{2maV}{\hbar^2} \Psi_1(0) = 0$$

$$\left[iK_0 e^{ixa} (A_1 \bar{e}^{iK_0a} - B_1 e^{iK_0a}) - iK_0 (A_1 - B_1) \right] - \frac{2maV}{\hbar^2} (A_1 + B_1) = 0 \quad \text{--- (2)}$$

Then reorganize eqs (1) and (2) in a matrix form

$$\begin{pmatrix} (1 - e^{i(K-K_0)a}) & (1 - e^{i(K+K_0)a}) \\ (e^{i(K-K_0)a} - 1 + i\beta) & (-e^{i(K+K_0)a} + 1 + i\beta) \end{pmatrix} \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad \text{--- (3).}$$

Recall that for a system of the form $\hat{M}\vec{x} = \vec{0}$, there are non-trivial solutions if $|\hat{M}| = 0$.

Evaluating the determinant of the matrix in Eq (3) we get

$$\cos(ka) = \cos(k_0 a) + \frac{B}{2} \sin(k_0 a), \text{ where } B = \frac{2maV}{\hbar^2 k_0}$$

$$\rightarrow \boxed{\cos(ka) = \cos(k_0 a) + \left(\frac{maV^2}{\hbar^2}\right) \frac{\sin(ka)}{k_0 a}} \quad (4)$$

Remember that the goal is to find $E(K)$, but since $E(K)$ is not explicit we need to solve Eq (4) graphically or numerically.

Let us redefine some variables $P = \frac{B}{2}a = \frac{Vma^2}{\hbar^2}$, $K = ka$, and

$\alpha^2 = k_0^2 a^2 = \frac{2mE}{\hbar^2} \alpha^2$, then the right hand side of the equation is

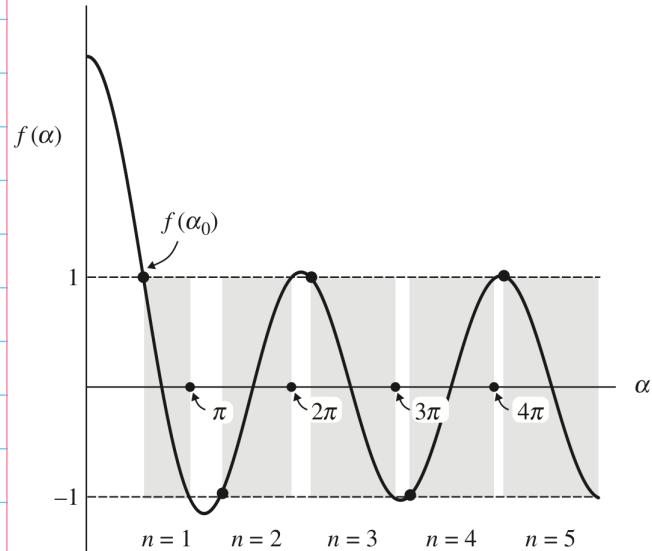
$$f(\alpha) = \cos(\alpha) + P \frac{\sin(\alpha)}{\alpha}, \text{ and}$$

$$g(K) = f(\alpha), \text{ where } g(K) = \cos(K).$$

→ Let us start by considering a repulsive potential.

for this case $P > 0$ since $V > 0 \rightarrow E > 0$ and $\alpha^2 > 0$, then α is a real #.

We take $\alpha > 0$ and solve for $g(K) = f(\alpha)$ graphically.



→ Since $|g(K)| \leq 1$ only values of α that satisfy $g(K) = f(\alpha)$ must also satisfy $|f(\alpha)| \leq 1$

→ The shaded regions represent the acceptable values of α

→ The white regions are forbidden regions (no-solution regions).

→ for a given K there is an infinite # of solutions for $f(\alpha)$. These solutions are given by the intersection of $\cos(K)$ and $f(\alpha)$.

→ When $\alpha \rightarrow \infty$ the forbidden regions get smaller, since

$$\lim_{\alpha \rightarrow \infty} f(\alpha) = \lim_{\alpha \rightarrow \infty} \left[\cos(\alpha) + \frac{P \sin(\alpha)}{\alpha} \right] = \cos(\alpha)$$

and in this limit $\cos(K) = \cos(\alpha)$ when $K = \alpha$ which also means that $K_0 = K$.

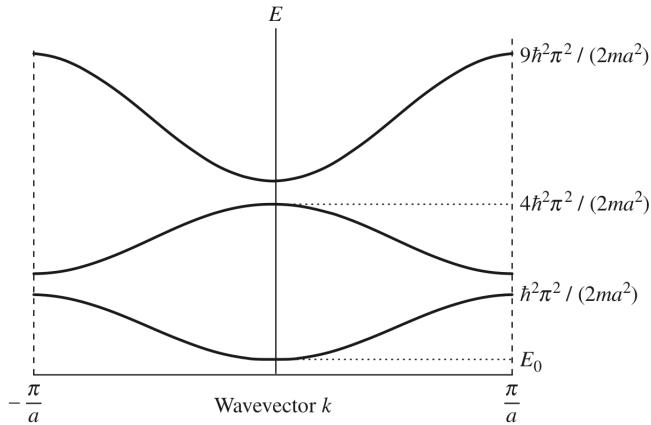
The conclusion above indicates that when energy of the particle becomes very large the potential has less of an effect.

→ The regions with acceptable α s are labeled by band index.

→ Since $\alpha^2 = \frac{2mE^2a^2}{\hbar^2}$, the acceptable $\alpha(K)$ yield acceptable values of $E(K)$.

→ This model preserves symmetry properties. Since $\cos(K) = \cos(-K)$, then $\alpha(K) = \alpha(-K)$ and $E(K) = E(-K)$.

→ Also $\cos(K + 2n\pi)$ is the same as the solution for $\cos(K)$, so we only need the reduced zone $-\pi < K \leq \pi \rightarrow -\pi/a < K \leq \pi/a$.



→ These are the first 3-bands of the Dirac-Kronig-Penney model

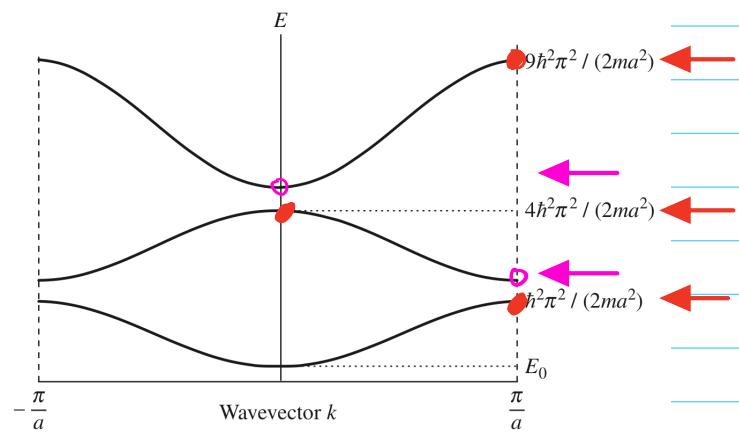
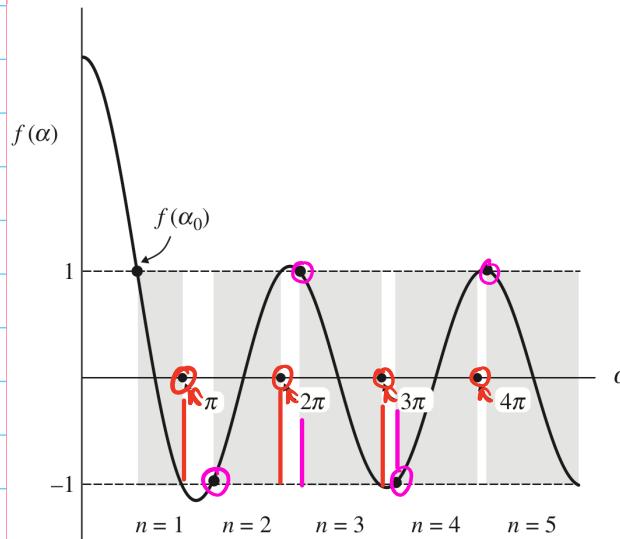
→ The 1st band has its minimum at $K=0$, and $E(K=0) = E_0$ depends on the potential.

→ At the B.Z. edge, $KA = \pi$, $a = \pi$

and $E(k) = \frac{\hbar^2 \pi^2}{2ma^2}$ which is the free electron value.

→ This model reduces to the particle in a box energies at $ka=n\pi$ at the top of a band since the potential term in Eq(4) is operative at these points.

$$\cos(n\pi) = \cos(\alpha) + \frac{P \sin(n\pi)}{n\pi}$$



→ The n^{th} gap starts at $ka=n\pi$ and $f(n\pi) = (-1)^n$

→ We can approximate the size of the gap for large n , when the potential energy is nearly negligible compared to the kinetic energy, i.e., "nearly free electron system".

Suppose the n^{th} gap starts at $\alpha=n\pi$ and ends at $\alpha=n\pi+\Delta\alpha$, where $\Delta\alpha$ is small.

Then Eq(4) becomes

$$(-1)^n = \cos(n\pi + \Delta\alpha) + \frac{P \sin(n\pi + \Delta\alpha)}{(n\pi + \Delta\alpha)}$$

Expanding we get $\Delta\alpha = \frac{2P}{n\pi}$, then the gap is

$$\Delta E = E(\pi + \Delta\alpha) - E(\pi) = \frac{2\hbar^2 P}{m a^2} = 2V.$$

We will obtain this result using perturbation theory.

Nearly-free Electron Model

In many metals, electrons can be considered as almost free, so their wavefunctions and energies are not expected to differ much from the free electron model (FEM).

Rather than using the Kronig-Penney model we are going to use perturbation theory on the FEM to obtain the results for the nearly-free electron model (NFEM).

Unlike the (K-P) model the extension of the NFEM to 3D is straight forward and with no fundamental complications.

Recall $\mathcal{H} = \left[\frac{\vec{P}^2}{8m} + V(r) \right].$

Let $V(\vec{r}) \neq 0$, but weak, then using standard perturbation to second order we get

$$E(\vec{k}) = E_0(\vec{k}) + V_{\vec{k}\vec{k}} + \sum_{\vec{k} \neq \vec{k}'} \frac{|V_{\vec{k}'\vec{k}}|^2}{E_0(\vec{k}') - E_0(\vec{k})}$$

where

$$V_{\vec{k}'\vec{k}} = \langle \Psi_{\vec{k}'}^\circ | V(\vec{r}') | \Psi_{\vec{k}}^\circ \rangle = \frac{1}{\sqrt{L^3}} \int e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}'} V(\vec{r}') d\vec{r}'$$

and

$$V_{\vec{k}'\vec{k}} = \langle \Psi_{\vec{k}'}^\circ | V(\vec{r}') | \Psi_{\vec{k}}^\circ \rangle = \frac{1}{\sqrt{L^3}} \int V(\vec{r}') d\vec{r}' = V_0$$

where $E_0(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ is the FEM energy, \sqrt{V} is the crystal volume and we set $\sqrt{V} = 1$. V_0 is the average potential and $\langle V_{\vec{k}} \rangle = \frac{\int \vec{e}^{i\vec{k} \cdot \vec{r}} V(\vec{r}) d\vec{r}}{\sqrt{V}}$.

The constant V_0 shifts all the energies irrespective of $\vec{k} \rightarrow$ we can set $V_0 = 0$.

Since $V(\vec{r})$ is periodic then

$$V(\vec{r}) = \sum_{\vec{q}} V(\vec{q}) e^{i\vec{q} \cdot \vec{r}}, \text{ and}$$

$$V(\vec{q}) = \int e^{-i\vec{q} \cdot \vec{r}} V(\vec{r}) d\vec{r} \quad (\text{we set } \sqrt{V} = 1).$$

Then

$$V_{\vec{k}, \vec{k}} = \langle \Psi_{\vec{k}} | V(\vec{r}) | \Psi_{\vec{k}} \rangle = \sum_{\vec{q}} V(\vec{q}) \int e^{i(\vec{k} - \vec{k}' + \vec{q}) \cdot \vec{r}} d\vec{r}$$

$$V_{\vec{k}, \vec{k}} = \sum_{\vec{q}} V(\vec{q}) \delta_{\vec{k}, \vec{k} + \vec{q}}.$$

Then the energy becomes

$$E(\vec{k}) = E_0(\vec{k}) + \sum_{\vec{q}} \frac{|V(\vec{q})|^2}{E_0(\vec{k}) - E_0(\vec{k} + \vec{q})}$$

The second order term is usually very small since for most \vec{k} it is the square of the potential divided by the kinetic energy.

Our perturbation scheme breaks down when $E(\vec{k}) = E(\vec{k} + \vec{q})$.

The points are $k^2 = k^2 + 2\vec{k} \cdot \vec{q} + q^2 \rightarrow 2\vec{k} \cdot \vec{q} + q^2 = 0$

which is the famous Bragg condition in X-ray scattering from crystals. This condition also determines the B.Z. zone boundary. For example, in 1D,

$$2K \left(\frac{\pm 2\pi}{a} \right) + \left(\frac{2\pi}{a} \right)^2 = 0,$$

hence $K = \pm \frac{\pi}{a}$.

Hence, the unperturbed energies are degenerate at the B.Z. zone boundaries, and degenerate perturbation theory can be used to solve the Schrödinger Eqn. for \vec{k} -near these boundaries.

Consider $|\Psi_{\vec{k}}\rangle = \alpha |\Psi_{\vec{k}}^0\rangle + \beta |\Psi_{\vec{k}+\vec{g}}^0\rangle$

$$W_{\vec{k}\vec{k}} = \langle \Psi_{\vec{k}}^0 | V(\vec{r}) | \Psi_{\vec{k}}^0 \rangle = V_0$$

$$W_{\vec{k}\vec{k}+\vec{g}} = \langle \Psi_{\vec{k}}^0 | V(\vec{r}) | \Psi_{\vec{k}+\vec{g}}^0 \rangle = \int e^{i\vec{g}\cdot\vec{r}} V(\vec{r}) d\vec{r} = V(-\vec{g})$$

$$W_{\vec{k}+\vec{g}\vec{k}} = \langle \Psi_{\vec{k}+\vec{g}}^0 | V(\vec{r}) | \Psi_{\vec{k}}^0 \rangle = \int e^{-i\vec{g}\cdot\vec{r}} V(\vec{r}) d\vec{r} = V(\vec{g})$$

$$W_{\vec{k}+\vec{g}, \vec{k}+\vec{g}} = V_0$$

$$\begin{pmatrix} V_0 - E' & V(\vec{g})^* \\ V(\vec{g}) & V_0 - E' \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

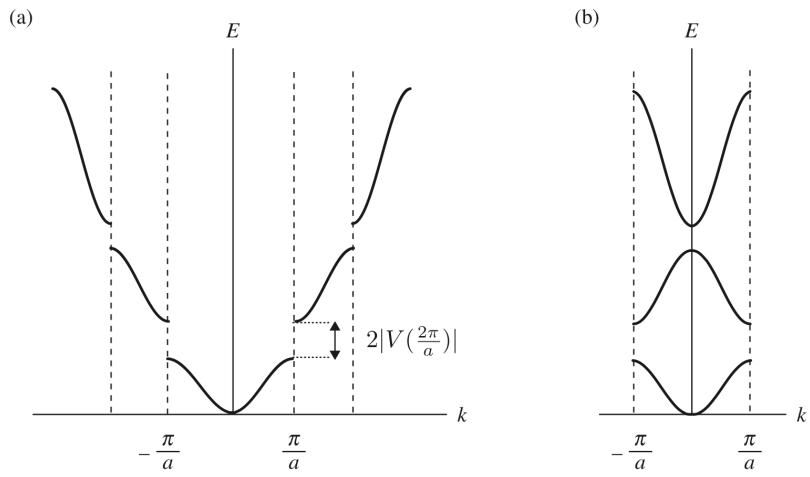
$$(V_0 - E')^2 - |V(\vec{g})|^2 = 0$$

$$E' = E_0(\vec{k}) + V_0 \pm \sqrt{|V(\vec{g})|^2} = E_0(\vec{k}) \pm |V(\vec{g})| \quad (\text{we took } V_0 = 0).$$

We can also calculate the states near these gaps, and we get

$$\alpha = \beta = \frac{1}{\sqrt{2}} \quad \text{for the lower state} \quad \text{and} \quad \alpha = -\beta = \frac{1}{\sqrt{2}} \quad \text{for the upper}$$

state. Then $|\Psi_1|^2$ is peaked at the lattice points while $|\Psi_2|^2$ is peaked between the lattice points.



Nearly-free electron model. (a) Extended zone scheme. (b) Reduced zone scheme.

The energy bands of the NFEM are almost identical to those of the FEM **except** near the zone edges.

The Tight-binding Model

At the opposite limit of the NFEM is the tight-binding model (TBM). This approximation is more appropriate for solids in which the atoms resemble slightly perturbed free atoms.

- NFEM starts with free electrons perturbed by a weak lattice potential
- TBM starts with atomic-like states and perturbs them with a potential due to the interaction with nearby atoms.
- The NFEM is good for close-packed solids in which the overlap between electrons from adjacent atoms is large. Then, metals are good for this type of description.
- The TBM is good for systems where the overlap between adjacent atoms is small and the atomic separations are large.

To get insights on the TB model, let us recall the Kronig-Penney model with attractive potentials and $E < 0$ (bound states). In this case $\alpha = i\phi$ (purely imaginary) and

$$\cos(k) = \cosh(\phi) + P \frac{\sinh(\phi)}{\phi}$$

This can be solved if we consider an attractive potential $\rightarrow P < 0$ and E can be negative.

$$\cos(\kappa) = \cosh(\phi) - \frac{|P|}{\phi} \sinh(\phi).$$

This is easy to solve if $\phi \gg 1$, where

$$\cos(\kappa) = \frac{e^\phi}{2} \left(1 - \frac{|P|}{\phi} \right).$$

Since $|\cos(\kappa)| \leq 1$ and e^ϕ is large we need $(1 - |P|/\phi) \sim 0$ (or $\phi = P + S\phi$).

$$\cos(\kappa) = \frac{e^{|P|+S\phi}}{2} \left(1 - 1 - \frac{S\phi}{\phi} \right) = \frac{e^{|P|}}{2} \frac{S\phi}{\phi} = \frac{S\phi}{2|P|} e^{|P|}$$

Then $2|P|\cos(\kappa)e^{-|P|} = S\phi$. But $E = -\frac{\hbar^2 \phi^2}{2ma^2}$, then

$$E = -\frac{\hbar^2}{2ma^2} (|P|^2 + 2|P|S\phi + S\phi^2) = -\frac{\hbar^2 |P|^2}{2ma^2} \left(1 + 2\frac{S\phi}{|P|} + \dots \right)$$

$$E = -\frac{\hbar^2}{2ma^2} |P|^2 \left(1 + 4e^{-|P|} \cos(\kappa) + \dots \right) \text{ or}$$

$$E = -\frac{\hbar^2}{2ma^2} |P|^2 \left[1 + 4 \exp\left(-\frac{|V|ma^2}{\hbar^2}\right) \cos(\kappa a) + \dots \right]$$

The first term is the ground state energy of a bound state in 1D.

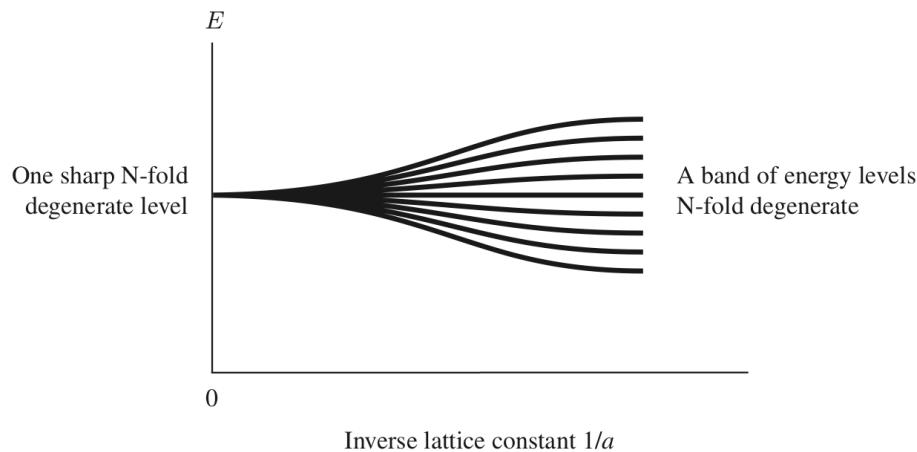
For large a the potential wells are separated and N independent potentials give rise to N -independent bound states.

When a gets smaller, the wells interact, and the levels spread. The second term captures the spread.

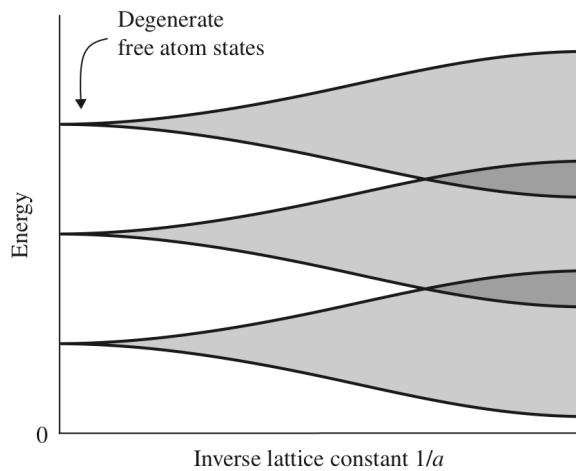
The total spread is $\Delta E = 4E_0 \bar{e}^{-a/l}$ where $E_0 = \frac{mV^2 a^2}{2\hbar^2}$ and l is the radius of the bound state, $l = \frac{\hbar^2}{4Vma}$, and the spread is small until $a \ll l$.

Then $E = E_0 + 4E_0 \bar{e}^{-a/l} \cos(ka) + \dots$

This is similar to what happens in a TB model



Spreading of one N -fold degenerate δ -function level into a band as a function of the inverse of the lattice constant using the Kronig–Penney model.



Spreading of atomic levels into bands as the lattice constant a decreases.

Before we derive the general form of a tight-binding Hamiltonian, let us recall that the one-body operator in 2nd quantization is

$$\hat{A} = \sum_{\alpha, \beta} \hat{a}_\alpha^\dagger \langle \alpha | \hat{A} | \beta \rangle a_\beta = \sum_{\alpha, \beta} \hat{a}_\alpha^\dagger a_\beta a_\beta^\dagger; \quad \text{if } \langle \alpha | \hat{A} | \beta \rangle.$$

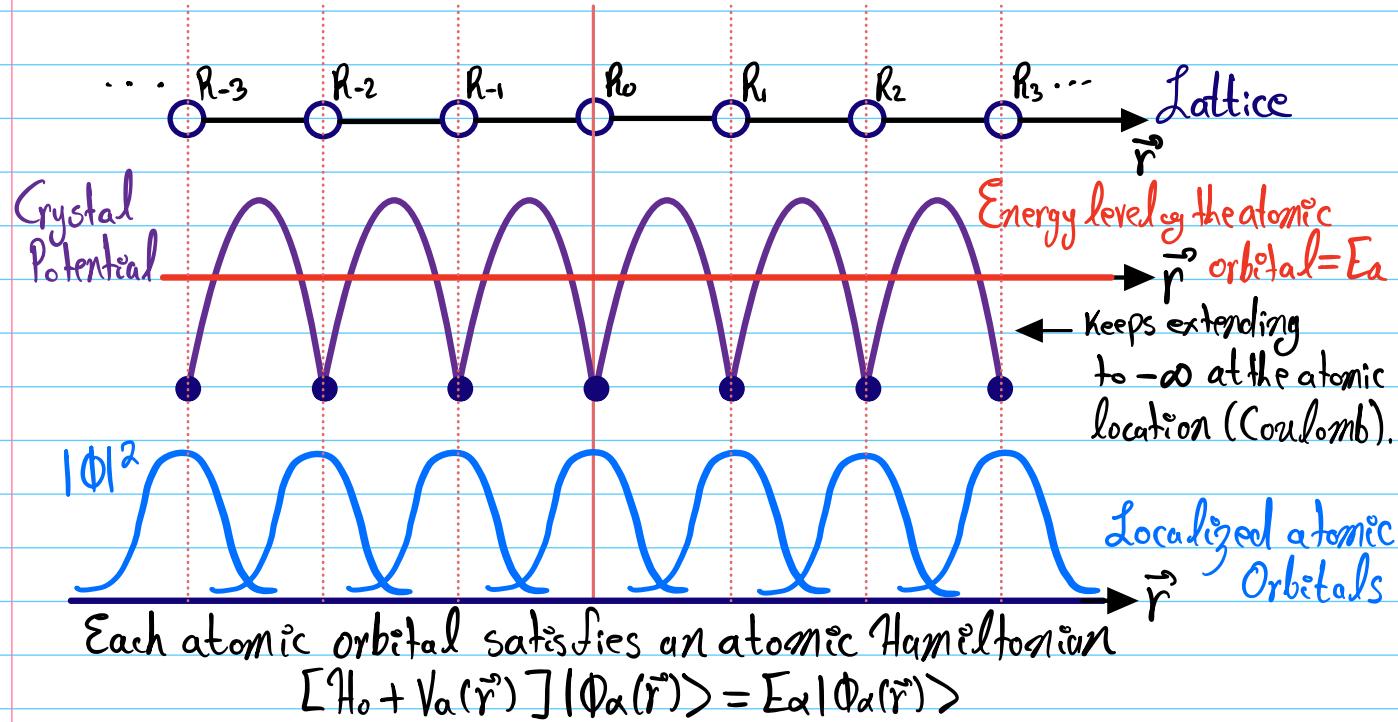
For the free particle Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m}$, then in a 2nd quantized form

$$\hat{H}_0 = \sum_{K, K'} \hat{a}_K^\dagger \left\langle K \left| \frac{\hat{p}^2}{2m} \right| K' \right\rangle \hat{a}_{K'} = \sum_{K, K'} \hat{a}_K^\dagger \left\langle K \left| \frac{k^2}{2m} \right| K' \right\rangle \hat{a}_{K'}$$

$$\hat{H}_0 = \sum_{K, K'} \hat{a}_K^\dagger \frac{k^2 \hbar^2}{2m} \hat{a}_K \left\langle K | K' \right\rangle, \text{ but } \left\langle K | K' \right\rangle = \delta_{K, K'}, \text{ then}$$

$$\hat{H}_0 = \sum_K \hat{a}_K^\dagger \frac{k^2 \hbar^2}{2m} \hat{a}_K = \sum_K \epsilon_K \hat{a}_K^\dagger \hat{a}_K = \sum_K \epsilon_K n_K, \text{ where } n_K = \hat{a}_K^\dagger \hat{a}_K.$$

What if we have a lattice?



When we have a lattice the Hamiltonian becomes

$\hat{H} = \hat{H}_0 + \sum_n \hat{V}_a(\vec{r} - \vec{R}_n)$; where $\hat{V}_a(\vec{r} - \vec{R}_n)$ are atomic-like potentials at the atomic locations.

In this problem, it is natural to chose atomic orbitals as our basis. Then in 2nd quantization, the Hamiltonian operator becomes

$$\hat{H} = \sum_{\alpha, \beta} \sum_n \hat{a}_\alpha^\dagger(\vec{r}) \langle \Phi_\alpha(\vec{r}) | \hat{H} | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle \hat{a}_\beta(\vec{r} - \vec{R}_n) + \text{H.C.}$$

Hermition conjugate.

$\hat{a}_\alpha^\dagger(\vec{r} - \vec{R}_n)$ and $\hat{a}_\alpha(\vec{r} - \vec{R}_n)$ are creation and annihilation operators that create or annihilate an electron with state $|\alpha\rangle$ at atomic location \vec{R}_n .

$|\Phi_\alpha(\vec{r})\rangle$ is the atomic orbital centered at the origin and it is an eigenstate of an atomic Hamiltonian with an energy E_α .

The atomic orbitals form an orthonormal set of bases.

What is the matrix element $\langle \Phi_\alpha(\vec{r}) | \hat{H} | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle$

$$\langle \Phi_\alpha(\vec{r}) | \hat{H}_0 + \hat{V}_a(\vec{r}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle + \langle \Phi_\alpha(\vec{r}) | \hat{H}_0 + \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle$$

$$\langle \Phi_\alpha(\vec{r}) | \hat{H}_0 + \hat{V}_a(\vec{r}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle = E_\alpha \langle \Phi_\alpha(\vec{r}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle$$

$$= E_\alpha S_{\alpha, \beta} S(\vec{r} - \vec{R}_n) \quad (\text{Onsite Energy}).$$

$$\langle \Phi_\alpha(\vec{r}) | \hat{H}_0 + \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle = \langle \Phi_\alpha(\vec{r}) | \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_\beta(\vec{r}) \rangle$$

$$+ \langle \Phi_\alpha(\vec{r}) | \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_\beta(\vec{r} - \vec{R}_n) \rangle$$

$$\langle \Phi_\alpha(\vec{r}) | \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_\beta(\vec{r}) \rangle = \int d^3r \Phi_\alpha^*(\vec{r}) \hat{V}_a(\vec{r} - \vec{R}_{n \neq 0}) \Phi_\beta(\vec{r})$$

This is called the **crystal field integral**. If the neighboring atomic potentials are almost constant in the regions where the wavefunctions are extended, then the

crystal field integral becomes a constant, i.e.,

$$\int d^3r \Phi_{\alpha}^*(\vec{r}) V_a(\vec{r} - \vec{R}_{n \neq 0}) \Phi_{\beta}(\vec{r}) \simeq \int d^3r \Phi_{\alpha}^*(\vec{r}) V_0 \Phi_{\beta}(\vec{r}) \simeq \eta \delta_{\alpha, \beta} \delta(\vec{r} - \vec{R}_n)$$

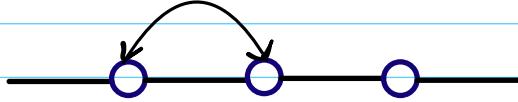
contributes to the onsite energy.

$$\langle \Phi_{\alpha}(\vec{r}) | V_a(\vec{r} - \vec{R}_{n \neq 0}) | \Phi_{\beta}(\vec{r} - \vec{R}_{n \neq 0}) \rangle = \int d^3r \Phi_{\alpha}^*(\vec{r}) V_a(\vec{r} - \vec{R}_n) \Phi_{\beta}(\vec{r} - \vec{R}_{n \neq 0})$$

This is called the orbital-overlap integral. This integral determines the different electron hoppings

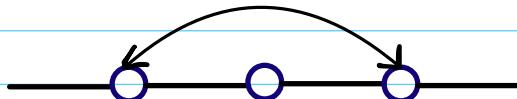
The nearest neighbor hopping (NN)

$$\langle \Phi_{\alpha}(\vec{r} - \vec{R}_m) | V(\vec{r} - \vec{R}_n = m \pm 1) | \Phi_{\beta}(\vec{r} - \vec{R}_n = m \pm 1) \rangle = t_{m,n}$$



Second nearest neighbour hopping

$$\langle \Phi_{\alpha}(\vec{r} - \vec{R}_m) | V(\vec{r} - \vec{R}_n = m \pm 2) | \Phi_{\beta}(\vec{r} - \vec{R}_n = m \pm 2) \rangle = t'_{m,n}$$



Then we have found the tight-binding Hamiltonian

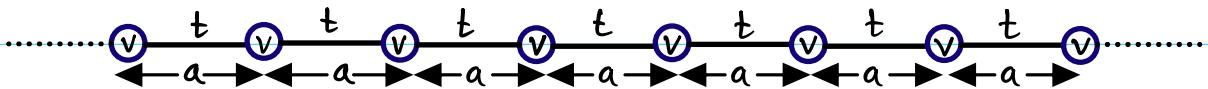
$$\hat{H} = \sum_i \hat{a}^{\dagger}(\vec{r} + \vec{R}_i) \hat{a}(\vec{r} + \vec{R}_i) + \sum_i \left(t_{i,i+1} \hat{a}^{\dagger}(\vec{r} - \vec{R}_i) \hat{a}(\vec{r} - \vec{R}_{i+1}) + t_{i+1,i} \hat{a}^{\dagger}(\vec{r} - \vec{R}_{i+1}) \hat{a}(\vec{r} - \vec{R}_i) \right) \\ + \sum_i \left(t_{i,i+2} \hat{a}^{\dagger}(\vec{r} - \vec{R}_i) \hat{a}(\vec{r} - \vec{R}_{i+2}) + t_{i+2,i} \hat{a}^{\dagger}(\vec{r} - \vec{R}_{i+2}) \hat{a}(\vec{r} - \vec{R}_i) \right)$$

$\epsilon = E_{\alpha} + \eta$ and this is the onsite energy

Note that sometimes the notation $\sum_{\langle ij \rangle}$ means NN ($i, i+1$) and $\sum_{\langle\langle i,j \rangle\rangle}$ means 2nd NN ($i, i+2$).

Now, using the tight-binding model we can find the band structure for different crystals. We can also deal with terminations.

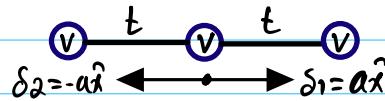
Example: The monoatomic chain of atoms.



Consider an infinite linear monoatomic chain. The NN-hopping is constant and equal to t , and the onsite energy is V .

The tight-binding Hamiltonian is

$$\hat{H}_{TB} = V \sum_{\vec{r}_A} \hat{a}^{\dagger}(\vec{r}_A) \hat{a}(\vec{r}_A) - \frac{t}{2} \sum_{\vec{r}_A} \sum_{\vec{\delta}_j} \hat{a}^{\dagger}(\vec{r}_A + \vec{\delta}_j) \hat{a}(\vec{r}_A) + \hat{a}^{\dagger}(\vec{r}_A) \hat{a}(\vec{r}_A + \vec{\delta}_j)$$



Lattice translations make the quasi-momentum a good quantum number, and we can use the Fourier transform

$$\hat{a}(\vec{r}_i) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in BZ} e^{i\vec{k} \cdot \vec{r}_i} \hat{c}(\vec{k})$$

Let us start with the onsite energy term

$$\frac{1}{N} \sum_{\vec{r}_A} \sum_{\vec{k}, \vec{k}' \in BZ} e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}_A} \hat{c}^{\dagger}(\vec{k}') \hat{c}(\vec{k})$$

Recall that $\sum_{\vec{r}} e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \sum_{\vec{r}} e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = N \delta_{\vec{k}, \vec{k}'}$ and that,

$$\sum_{\vec{k} \in BZ} e^{i\vec{k} \cdot (\vec{r} - \vec{r}')} = N \delta_{\vec{r}, \vec{r}'} , \text{ then}$$

$$V \sum_{\vec{k} \in B.Z} \hat{C}^+(\vec{k}) C(\vec{k}) = \sum_{\vec{k} \in B.Z} \hat{C}^+(\vec{k}) V \hat{C}(\vec{k}) \quad (\text{On site energy term}).$$

Next, the first part of the hopping term

$$\begin{aligned} \sum_{\vec{r}_A} \sum_{\vec{\delta}_j} \hat{a}^+(\vec{r}_A + \vec{\delta}_j) \hat{a}(\vec{r}_A) &= \frac{1}{N} \sum_{\vec{r}_A} \sum_{\vec{\delta}_1, \vec{\delta}_2} \sum_{\vec{k}, \vec{k}' \in B.Z} e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}_A} e^{i\vec{k} \cdot \vec{\delta}_j} \hat{C}^+(\vec{k}') \hat{C}(\vec{k}) \\ &= \frac{N}{N} \sum_{\vec{k} \in B.Z} \sum_{\vec{\delta}_1, \vec{\delta}_2} e^{i\vec{k} \cdot \vec{\delta}_j} \hat{C}^+(\vec{k}) \hat{C}(\vec{k}) \quad [\vec{k} = (k_x, 0, 0)] \\ &= \sum_{\vec{k} \in B.Z} (e^{ik_x a} + e^{-ik_x a}) \hat{C}^+(\vec{k}) \hat{C}(\vec{k}) \end{aligned}$$

the 2nd part of the hopping is nothing more than the Hermitian conjugate of the first

$$\sum_{\vec{r}_A} \sum_{\vec{\delta}_j} \hat{a}^+(\vec{r}_A) \hat{a}(\vec{r}_A + \vec{\delta}_j) = \sum_{\vec{k} \in B.Z} (e^{ik_x a} + e^{-ik_x a}) \hat{C}^+(\vec{k}) \hat{C}(\vec{k}).$$

Hence

$$-\frac{t}{2} \sum_{\vec{r}_A} \sum_{\vec{\delta}_j} \hat{a}^+(\vec{r}_A + \vec{\delta}_j) \hat{a}(\vec{r}_A) + \hat{a}^+(\vec{r}_A) \hat{a}(\vec{r}_A + \vec{\delta}_j) = \sum_{\vec{k} \in B.Z} \hat{C}^+(\vec{k}) [-2t \cos(k_x a)] \hat{C}(\vec{k})$$

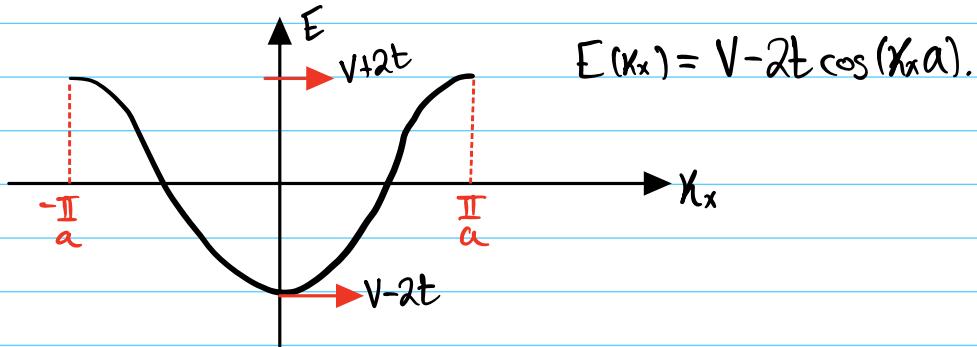
and

$$\hat{H}_{TB} = \sum_{\vec{k} \in B.Z} \hat{C}^+(\vec{k}) [V - 2t \cos(k_x a)] \hat{C}(\vec{k})$$

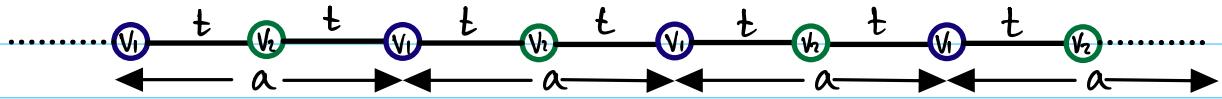
Note : $h(\vec{k})$ is called the Kernel of the Hamiltonian, it gives us the

eigenenergies, and it can be made into a Bloch Hamiltonian by requiring $h(\vec{k}') = h(\vec{k} + \vec{q})$. This is done by utilizing the gauge invariance of the \hat{H}_{TB} , i.e., changing $\hat{a} \rightarrow e^{i\phi}\hat{a}$.

Then we have found the energy dispersion of a linear chain



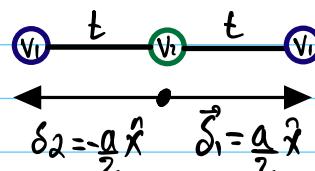
Example: Linear chain with bases. (Diatomeric Chain).



Consider a linear chain of length N with two different atoms (A and B), as shown above. The lattice constant is a and the distance between the A and B atoms is $a/2$. The hopping constant between the different atoms is t and the onsite energy of atoms A is V_A and for B is V_B .

The tight binding Hamiltonian for this system is

$$\hat{H}_{TB} = -t \sum_{\vec{r}_A} \sum_j \hat{a}_B^\dagger(\vec{r}_A + \vec{\delta}_j) \hat{a}_A(\vec{r}_A) + h.c. + V_A \sum_{\vec{r}_A} \hat{a}_A^\dagger(\vec{r}_A) \hat{a}_A(\vec{r}_A) + V_B \sum_{\vec{r}_B} \hat{a}_B^\dagger(\vec{r}_B) \hat{a}_B(\vec{r}_B).$$



$$\hat{a}_\alpha(\vec{r}_i) = \frac{1}{\sqrt{N}} \sum_{\vec{K} \in BZ} e^{i\vec{K} \cdot \vec{r}_i} \hat{C}_\alpha(\vec{K})$$

Using the formula above and

$$\sum_{\vec{r}} e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} = \sum_i e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_i} = N \delta_{\vec{k}, \vec{k}'}, \text{ after some math we get}$$

$$\hat{H}_{TB} = \sum_{\vec{k} \in BZ} (\hat{c}_A^{\dagger}(\vec{k}) \quad \hat{c}_B^{\dagger}(\vec{k})) \begin{pmatrix} V_A & -2t \cos(k_x a/2) \\ -2t \cos(k_x a/2) & V_B \end{pmatrix} \begin{pmatrix} c_A(\vec{k}) \\ c_B(\vec{k}) \end{pmatrix}$$

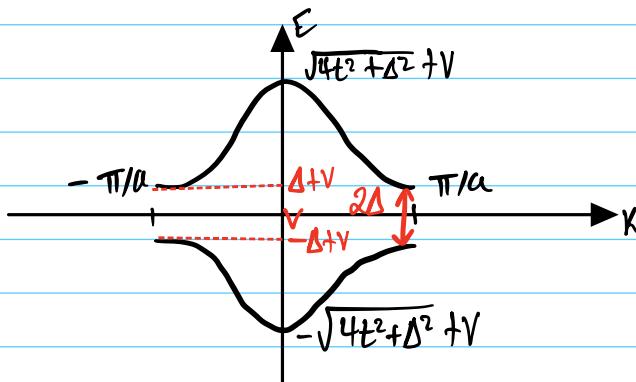
$h(\vec{k})$

Expressing $\begin{pmatrix} V_A & 0 \\ 0 & V_B \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \begin{pmatrix} V & 0 \\ 0 & V \end{pmatrix}$, we can write $h(\vec{k})$ as

$$h(\vec{k}) = -2t \cos(k_x a/2) \sigma_x + \Delta \sigma_z + \Delta \sigma_0 \quad (\sigma_x, \sigma_y, \sigma_z \text{ are the Pauli matrices and } \sigma_0 \text{ is the identity matrix})$$

With some math we can find the eigenvectors of $h(\vec{k})$, such that

$$E(\vec{k}) = V \pm \sqrt{4t^2 \cos(k_x a/2) + \Delta^2} = V \pm \sqrt{2t^2(1 + \cos(k_x a))^2 + \Delta^2}$$



(Recall that the lattice constant is a and $G = 2\pi/a$)

Tight-binding Method for Finite Systems with Periodic Boundary Conditions.

When we have a finite system, the TB Hamiltonian becomes a finite matrix and its diagonalization is usually a numerical task.

Before we proceed let us go in more depth about the properties and effects of

Periodic Boundary Conditions (PBC):

PBC can be imposed to account for finite crystal size.

In 1D PBCs imply that for a crystal of N cells and lattice constant a

$\Psi(x+Na) = \Psi(x)$. If we use the Bloch condition, we have

$$\Psi(x+Na) = e^{iK_x Na} \Psi(x), \text{ which implies that}$$

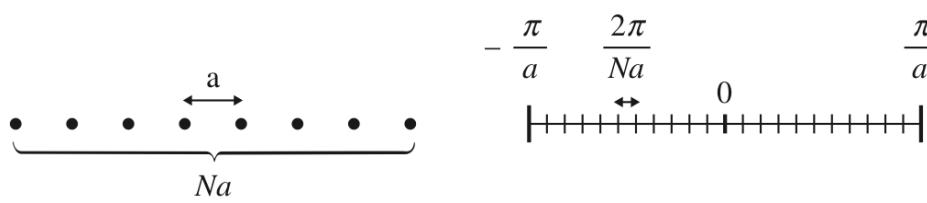
$$e^{iK_x Na} = 1 \rightarrow K_x Na = 2n\pi \rightarrow K_x = \frac{2n\pi}{Na} \quad (n=0, \pm 1, \pm 2, \dots)$$

For a 1D, the B.Z. is defined as $-\frac{\pi}{2} < K_x \leq \frac{\pi}{2}$, where $\frac{\pi}{a} = \frac{2\pi}{\lambda}$ and the allowed states are constrained by

$$-\frac{N}{2} < n \leq \frac{N}{2}.$$

Then we have N K -states in the B.Z. spaced $\frac{2\pi}{Na}$ apart.

(a) Real space (b) Reciprocal space



In 3D we have $\Psi(\vec{r} + N_i \vec{a}_i) = \Psi(\vec{r})$ ($i=1, 2, 3$), and using the Bloch condition we have

$$\exp(i\vec{K} \cdot N_i \vec{a}_i) = 1 \quad \text{and}$$

$$\vec{K} \cdot N_i \vec{a}_i = 2\pi m_i \quad (m_i = 0, \pm 1, \pm 2, \pm 3, \dots)$$

Expressing \vec{k} in terms of the basis vectors in reciprocal space

$$\vec{k} = l_1 \vec{g}_1 + l_2 \vec{g}_2 + l_3 \vec{g}_3 \quad (l_i's \text{ are not integers})$$

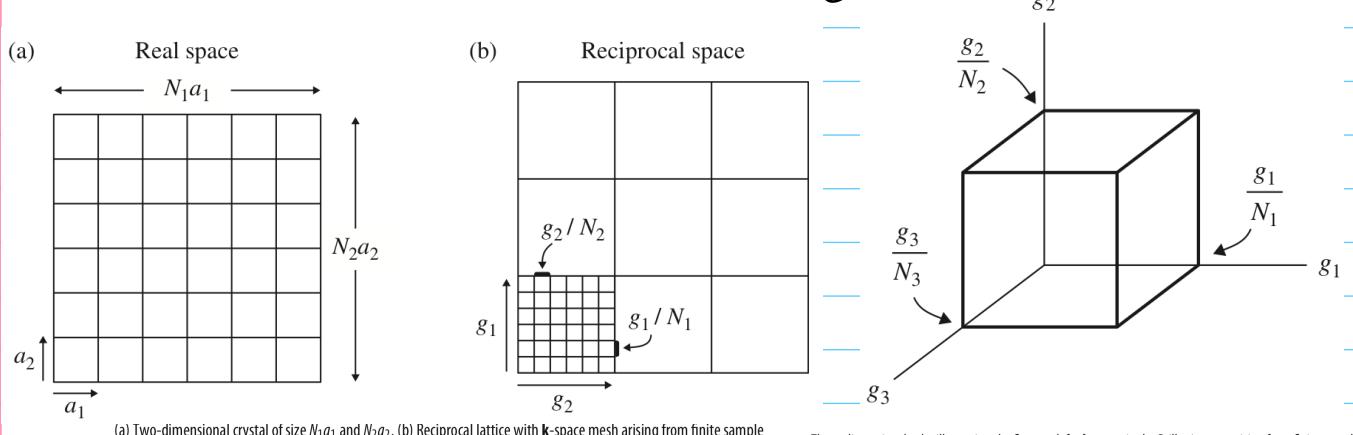
and using

$$\vec{g}_i \cdot \vec{a}_i = 2\pi N_i, \text{ we find}$$

$$\vec{k} \cdot \vec{N} \vec{a}_i = 2\pi N_i l_i = 2\pi m_i, \text{ hence } l_i = \frac{m_i}{N_i} \text{ and}$$

$$\vec{k} = \sum_{i=1}^3 l_i \vec{g}_i = \sum_{i=1}^3 m_i \left(\frac{\vec{g}_i}{N_i} \right).$$

The mesh is very fine and depends on the # of unit cells.



(a) Two-dimensional crystal of size $N_1 a_1$ and $N_2 a_2$. (b) Reciprocal lattice with \mathbf{k} -space mesh arising from finite sample size.

Three-dimensional cube illustrating the fine mesh for \mathbf{k} -states in the Brillouin zone arising from finite sample size.

The number of \mathbf{k} -states in the B.Z. is given by the volume of the B.Z. divided by the cell containing only one state

$$\frac{\vec{g}_1 \cdot (\vec{g}_2 \times \vec{g}_3)}{N_1 \cdot (N_2 N_3)} = N_1 N_2 N_3 = N$$

Hence, the total # of \mathbf{k} -states is equal to the total # of unit cells in the crystal.

In solid-state sometimes we need to sum a function $f(\vec{k})$ over the wavevector \vec{k} . If the sample is large and the states are close together, we can take the sum

as an integral, i.e.,

$$\sum_{\vec{k}} f(\vec{k}) = \frac{V_x}{(2\pi)^3} \int f(\vec{k}') d^3 k'$$

where V_x is the crystal volume $= N V_c$ (V_c is the cell volume).

To answer the question of how many states are there in the B.Z. we set $f(\vec{k})=1$ and

$$\frac{V_x}{(2\pi)^3} \int_{BZ} d^3 k = \frac{V_x V_{BZ}}{(2\pi)^3} = \frac{V_x}{V_c} = N.$$

Now, going back to the TB model of a finite system with PBC.

Let us consider a linear chain of atoms with N -cells and PBCs. For this system the TB Hamiltonian is

$$H_{TB} = (\hat{a}_0^\dagger \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_N^\dagger) \begin{bmatrix} V & -t & 0 & 0 & \dots & -t \\ -t & V & -t & 0 & \dots & \vdots \\ 0 & -t & V & -t & 0 & \vdots \\ \vdots & 0 & -t & V & -t & \vdots \\ \vdots & \vdots & 0 & -t & V & \vdots \\ -t & \vdots & \vdots & 0 & \vdots & \ddots \end{bmatrix}_{N \times N} \begin{pmatrix} \hat{a}_0 \\ \hat{a}_1 \\ \hat{a}_2 \\ \vdots \\ \vdots \\ \hat{a}_N \end{pmatrix}$$

This is the kernel and we need to diagonalize it to find the dispersion relation.

Electron (or hole) Velocity in a Band and the f-sum Rule

Now that we can evaluate the band structure and compute $E_n(\vec{k})$ we can ask what is the velocity and the effective mass (m^*) characterizing the electron or the hole in a band state.

Let us consider non-degenerate energy levels. If we know the energy levels at a particular \vec{k} -point, i.e., we know $E_n(\vec{k}_0)$ for all n . from this information we can determine the energy at a neighbouring \vec{k} -point \vec{k}' , where $\vec{k}' = \vec{k}_0 + \vec{k}$.

Consider the wave equation for the periodic part of the Bloch state at \vec{k}'

$$\left[\frac{(\vec{p} + \hbar\vec{k}')^2}{2m} + V(\vec{r}) \right] |\psi_{n,\vec{k}'}(\vec{r})\rangle = E_n(\vec{k}') |\psi_{n,\vec{k}'}(\vec{r})\rangle$$

then

$$\left[\frac{(\vec{p} + \hbar\vec{k}_0)^2}{2m} + V(\vec{r}) + \hbar\vec{k} \cdot (\vec{p} + \hbar\vec{k}_0) + \frac{\hbar^2\vec{k}^2}{2m} \right] |\psi_{n,\vec{k}'}(\vec{r})\rangle = E_n(\vec{k}') |\psi_{n,\vec{k}'}(\vec{r})\rangle$$

Gave the energy levels
at \vec{k}_0 .

We call this
term H'

This is a number
that is 2nd order in \vec{k}

We use the term H' as a perturbation if \vec{k} is small. When H' is a perturbation this method is called " \vec{k}, \vec{p} perturbation theory".

To second order in \vec{k} we have

$$E_n(\vec{k}_0 + \vec{k}) = \frac{\hbar^2 k^2}{2m} + E_n(\vec{k}_0) + \langle \psi_{n,\vec{k}_0} | H' | \psi_{n,\vec{k}_0} \rangle + \sum_{n \neq n'} \frac{|\langle \psi_{n',\vec{k}_0} | H' | \psi_{n,\vec{k}_0} \rangle|^2}{E_n(\vec{k}_0) - E_{n'}(\vec{k}_0)}$$

notice that $\{|\psi_{n,\vec{k}_0}\rangle\}$ is an orthonormal set since they are solutions to $H(\vec{k}_0)$.

Another way to obtain $E_n(\vec{k}')$ to second order is to expand around \vec{k}_0 in a Taylor series

$$E(\vec{k}_0 + \vec{k}) = E_n(\vec{k}_0) + \sum_{i=1}^3 \frac{\partial E(\vec{k}_0)}{\partial k_i} k_i + \frac{1}{2} \sum_{i,j=1}^3 \frac{\partial^2 E_n(\vec{k}_0)}{\partial k_i \partial k_j} k_i k_j.$$

Then we can equate terms order by order.

The first term is

$$\frac{\partial E_n(\vec{k}_0)}{\partial k_{0i}} = \frac{\hbar}{m} \langle u_{n\vec{k}_0} | p_i + \hbar k_{0i} | u_{n\vec{k}_0} \rangle$$

$$\frac{\partial E_n(\vec{k}_0)}{\partial k_{0i}} = \frac{\hbar}{m} \langle u_{n\vec{k}_0} | p_i | u_{n\vec{k}_0} \rangle$$

This result allows us to evaluate the velocity in the i th direction for an electron in the state (n, \vec{k}_0) , using

$$v_{i,n,\vec{k}_0} = \frac{1}{\hbar} \frac{\partial E_n(\vec{k}_0)}{\partial k_{0i}}$$

Next we equate the 2nd order term and find the f-sum rule

$$\frac{m}{(m_n)_{ij}} = \delta_{ij} + \sum_{n' \neq n} f_{nn'}^{ij},$$

where the effective mass is defined as

$$\frac{1}{(m_n)_{ij}} \equiv \frac{1}{\hbar^2} \frac{\partial^2 E_n(\vec{k}_0)}{\partial \vec{k}_{0i} \partial \vec{k}_{0j}},$$

and $f_{nn'}^{ij}$ is the oscillator strength which is related to matrix elements between Bloch states of the momentum operator

$$f_{nn'}^{ij} = \frac{1}{m} \frac{\langle n' \vec{k}_0 | p_i | n \vec{k}_0 \rangle \langle n \vec{k}_0 | p_j | n' \vec{k}_0 \rangle + \langle n' \vec{k}_0 | p_j | n \vec{k}_0 \rangle \langle n \vec{k}_0 | p_i | n' \vec{k}_0 \rangle}{E_n(\vec{k}_0) - E_{n'}(\vec{k}_0)}$$