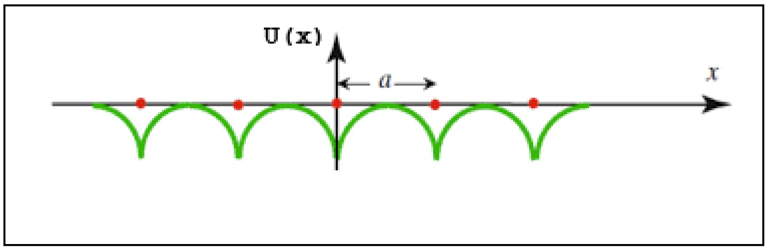
Chapter 8 : The nearly free electron model and the tight binding model

The electronic structure of solids is usually described by two different approaches, the nearly free electron model and the tight binding model. Their primary differences are as follows:

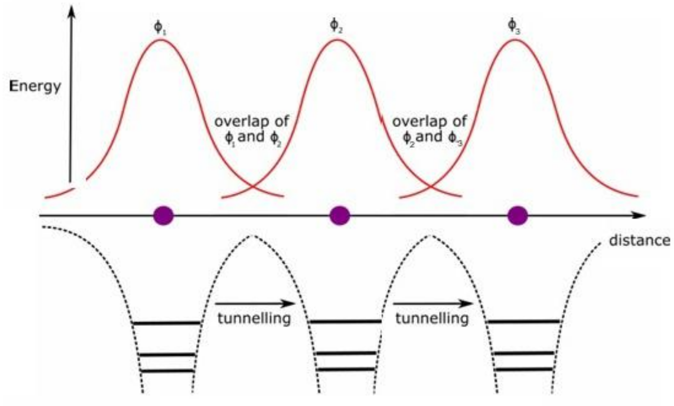
1- Nearly Free Electron Model (NFEM)



This model considers that electrons in a solid are nearly free, which means they move in a weak periodic potential caused by ions in the crystal lattice. The potential is treated as a small perturbation to the free electron gas, and the electrons are delocalized over the whole crystal. The model is particularly useful for metals and simple metals where the potential is relatively weak. The mathematical approach is based on solving Schrödinger equation for a free electron gas with a weak periodic potential treated as a perturbation, resulting in forming nearly parabolic energy bands with small deviations due to the weak periodic potential. In conclusion, the model focuses on the delocalized nature of electrons and the influence of weak periodic potential on their motion.

2- Tight Binding Model (TBM)

This model assumes that electrons are tightly bound to their respective atoms, and the wavefunctions of neighboring atoms overlap only slightly. This model is more appropriate for describing insulators and semiconductors where electrons are more localized. The mathematical approach is based on the idea that wavefunction is constructed as a linear combination of atomic orbitals (LCAO) from neighboring atoms. The overlap between LCAOs leads to the formation of energy bands that can have non-parabolic shapes, reflecting the atomic orbitals from which they originated.



$$\psi = c_1\,\phi_1 + c_2\phi_2 + c_3\phi_3$$

① Nearly free electron model:

again, this model assumes that electrons in a solid are nearly free, meaning they move in a weak periodic potential that can be treated as a small perturbation

so $H = H_0 + U(r)$; H_0: unperturbed Hamiltonian

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

weak compared to the kinetic energy term $\left(-\frac{\hbar^2\nabla^2}{2m}\right)$, such that the potential $U(\vec{r})$ can be treated as a perturbation on top of the completely solved problem of free electron $\left(H_0 = -\frac{\hbar^2\nabla^2}{2m}\right)$.

with $H_0|k\rangle = \varepsilon_k^{(0)}|k\rangle$

$\downarrow$

plane waves and

$\varepsilon_k^{(0)} = \frac{\hbar^2k^2}{2m}$; $|k\rangle = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$

$|k\rangle$ form a complete set of orthogonal states $\langle k'|k\rangle = \delta_{k,k'}$

- in this chapter we are using the bra ket notation to represent wave functions in reciprocal space ($|k\rangle$). in coordinate representation, we have

$$\underset{\substack{\downarrow \\ \text{projection} \\ \text{of } |k\rangle \text{ on } \langle\vec{r}|}}{\langle\vec{r}|k\rangle} = \underset{\substack{\searrow \\ \text{wave function}}}{\psi_k(\vec{r})} = \sum_{\vec{K}} \underbrace{\psi(\vec{k}+\vec{K})}_{\hookrightarrow\ \text{coefficients not wave function}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}}$$

$$= e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_{\vec{K}} \psi(\vec{k}+\vec{K}) e^{i\vec{K}\cdot\vec{r}}}_{\text{Block's theorem}} = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

from scattering theory, the periodic potential $U(\vec{r})$ can scatter electron from state $\vec{k} \to \vec{k}'$ and the matrix elements of the potential can be written as

$$\langle \vec{k}' | U | \vec{k} \rangle = FT[U]_{\vec{k}-\vec{k}'}$$, fourier transform of $U(\vec{r})$ evaluated at $\vec{k}-\vec{k}'$

$\downarrow$

transition amplitude from initial state $|k\rangle$ to final state $\langle k'|$

$$= \begin{cases} 0, & \text{if } \vec{k}-\vec{k}' \neq \vec{K} \to \text{reciprocal lattice vector} \\ U_K, & \text{if } \vec{k}-\vec{k}' = \vec{K} \end{cases}$$

so scattering occurs only if the difference between initial and final wavevectors is a reciprocal lattice vector.

U_K can be evaluated using

$$U_K = \frac{1}{\Omega} \int_{\Omega} d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}}$$

$\Omega \to$ unit cell

now according to perturbation theory, the zeroth, first, and second corrections to energy ε_k in the state $|k\rangle$ is given by

$$\varepsilon_{\vec{k}} = \varepsilon^{(0)}_{\vec{k}} + \langle \vec{k} | U | \vec{k} \rangle + \sum_{\vec{k}' \neq \vec{k}} \frac{|\langle k' | U | k \rangle|^2}{\varepsilon^{(0)}_{\vec{k}} - \varepsilon^{(0)}_{\vec{k}'}} \quad \text{---(1)}$$

$\downarrow$ zeroth (bare energy)

$$\varepsilon^{(0)}_{k} = \frac{\hbar^2 k^2}{2m}$$

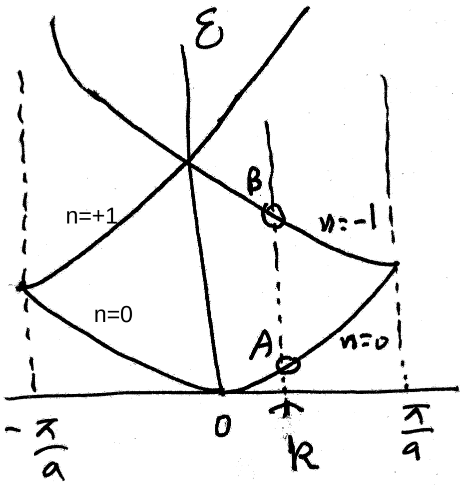
$\downarrow$ 1st

$\downarrow$ 2nd ; $\vec{k}' = \vec{k} - \vec{K}$

taking $\vec{k} - \vec{k}' = \vec{K} \to \varepsilon^{(0)}_{\vec{k}'} = \varepsilon_{\vec{k}-\vec{K}} = \frac{\hbar^2}{2m} |\vec{k} - \vec{K}|^2$

or " $k' - k = K \to \varepsilon^{(0)}_{\vec{k}'} = \varepsilon^{(0)}_{\vec{k}+\vec{K}} = \frac{\hbar^2}{2m} |\vec{k} + \vec{K}|^2$

$\varepsilon_k^{(0)} = \varepsilon_{k-K}^{(0)} = \varepsilon_{k+K}^{(0)}$ only equal at zone edges (degenerate points) the first-order correction is the expectation value (average) of the potential calculated using the unperturbed states, i.e $\langle \vec{k}|U|\vec{k}\rangle$. for a specific k as shown in figure, where there is no degeneracy at k, we can apply the non-degenerate perturbation theory. let us see how energy at point A is affected when switching on the weak periodic potential $U(\vec{r})$.



at point A, we have $|\vec{k}+\vec{K}\rangle = \frac{1}{\sqrt{\Omega}} e^{i\vec{K}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}$, now for 1D solid, we have

$\vec{K} = \frac{2\pi}{a} n$, $n=0 \Rightarrow \vec{K}=0$

$$\Rightarrow |k\rangle = \frac{1}{\sqrt{a}} e^{i\vec{k}\cdot\vec{r}}, \text{ so}$$

$$\langle \vec{k}|U(\vec{r})|\vec{k}\rangle = \langle \vec{k}|U(x)|\vec{k}\rangle = \frac{1}{a}\int_0^a e^{-i\vec{k}\cdot\vec{r}} U(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d^3\vec{r}$$

$$= \frac{1}{a}\int_0^a d^3\vec{r}\, U(\vec{r}) = \frac{1}{a}\int_0^a dx\, U(x) = \text{constant} = U_0$$

similarly at point B, we have

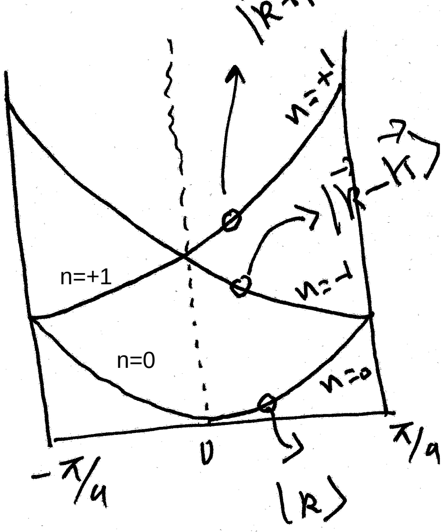
$$|k-\vec{K}\rangle = \frac{1}{\sqrt{a}} e^{-i\vec{K}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} \Rightarrow$$

$$\langle \vec{k}-\vec{K}|U(\vec{r})|\vec{k}-\vec{K}\rangle = \frac{1}{a}\int_0^a e^{i\vec{K}\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{r}} U(\vec{r}) e^{-i\vec{K}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} d^3\vec{r}$$

$$= \frac{1}{a}\int_0^a d^3\vec{r}\, U(\vec{r}) = \frac{1}{a}\int_0^a dx\, U(x) \equiv U_0$$

so, simply, the 1st order correction $\varepsilon_k^{(1)}$ is just a constant that represents the average potential. its effec is just to shift all energy levels by same amount U_0. Note that in some cases U_0 is either zero or constant. for example, if $U(x) \propto \cos\frac{2\pi}{a}x$ or $U(x) \propto \sin\frac{2\pi}{a}x$, then $\langle \vec{k}|U(x)|\vec{k}\rangle =$ zero. on the other hand if $U(x) \propto \cos^2\frac{\pi}{a}x$, than $\langle \vec{k}|U(x)|k\rangle = 1/2$.

Now let us find the second order correction of $\mathcal{E}_k$ of the state $|k\rangle$ at Point A. Now we consider that the bare state $|k\rangle$ $(n=0)$ is affected by only the closest states $|\vec{k}-\vec{K}\rangle$ $(n=-1)$ and $|\vec{k}+\vec{K}\rangle$ $(n=+1)$ as shown in figure, so



$$\mathcal{E}_k^{(2)} = \sum_{\vec{k}' \neq \vec{k}} \frac{|\langle \vec{k}'|U|\vec{k}\rangle|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{k'}^{(0)}}$$

$$= \frac{|\langle \vec{k}+\vec{K}|U|k\rangle|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{k+K}^{(0)}} + \frac{|\langle \vec{k}-\vec{K}|U|k\rangle|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{\vec{k}-\vec{K}}^{(0)}} \quad \ldots (2)$$

$$= \frac{|U_K|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{\vec{k}+\vec{K}}^{(0)}} + \frac{|U_{-K}|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{\vec{k}-\vec{K}}^{(0)}} \quad ; \text{ where } \langle k'|U|k\rangle = U_{k'-k}$$

when $\mathcal{E}_k^{(0)} = \frac{\hbar^2 k^2}{2m}$, $\mathcal{E}_{k+K}^{(0)} = \frac{\hbar^2}{2m}|\vec{k}+\vec{K}|^2$; $\mathcal{E}_{k-K}^{(0)} = \frac{\hbar^2}{2m}|\vec{k}-\vec{K}|^2$

Now since, the potential is very weak, than $|U_K|^2$ is very small w.r.t/ the energy differences in the denominators, i.e $|U_K|^2 = |U_{-K}|^2 << |\mathcal{E}_k^{(0)} - \mathcal{E}_{k+K}^{(0)}|$ or $|\mathcal{E}_k^{(0)} - \mathcal{E}_{k-K}^{(0)}|$, so $\mathcal{E}_k^{(2)}$ is so small. In conclusion, far away from the edges of the 1st B.Z ($k=0, \pm\pi/a$), energy states are not affected by the periodic potential.

Now let us see the effect of the periodic potential at points very close or at zone edge i.e at $k = \pm\pi/a$. according to Laue condition ($\vec{k}' - \vec{k} = \vec{K}$ or equivalently $\vec{k} - \vec{k}' = \vec{K}$), and in order for $\langle k'|U|k\rangle$ to be non-zero, we must have $\vec{k}' - \vec{k} = \vec{K}$, so

$$\vec{k}' = \vec{k} + \vec{K}$$

$$\Rightarrow \vec{k}'^2 = (\vec{k}+\vec{K})^2 = (\vec{k}+\vec{K})\cdot(\vec{k}+\vec{K}) = k^2 + K^2 + 2\vec{k}\cdot\vec{K}, \text{ so}$$

$\cancel{k'^2 = k^2} + K^2 + 2\vec{k}\cdot\vec{K}$, but for elastic scattering $k'^2 = k^2$

$$\boxed{0 = K^2 + 2\vec{k}\cdot\vec{K}}$$

When $|\vec{k}+\vec{K}|^2 = (\vec{k}+\vec{K})\cdot(\vec{k}+\vec{K}) = k^2 + \underbrace{K^2 + 2\vec{k}\cdot\vec{K}}_{0} = k^2$

$\Rightarrow \mathcal{E}_{k+K}^{(0)} = \frac{\hbar^2}{2m}|\vec{k}+\vec{K}|^2 = \frac{\hbar^2 k^2}{2m} = \mathcal{E}_k^{(0)}$, so $\mathcal{E}_k^{(0)}$ and $\mathcal{E}_{k+K}^{(0)}$ are degenerate at zone edge, and hence $\mathcal{E}_k^{(2)}$ diverges.

|k> and |k+K> are degenerate at k = -pi/a, as |k> and |k-K> are also degenerate at k= +pi/a

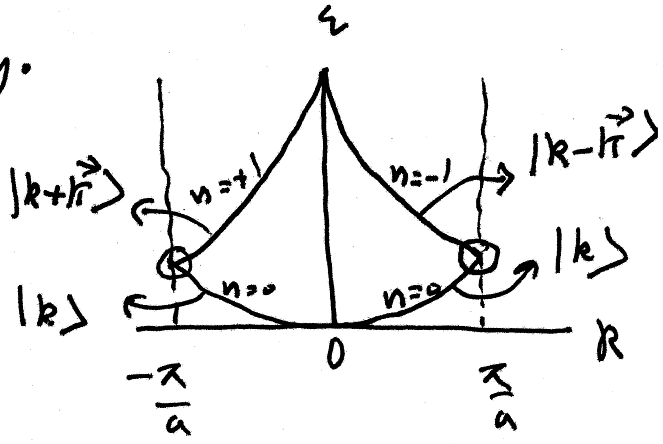
$$\mathcal{E}_k^{(2)} = \sum_{k'\neq k} \frac{|\langle k'|U|k\rangle|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{k'}^{(0)}} = \sum_{K} \frac{|U_{\vec{K}}|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{k+K}^{(0)}},$$

equivalently, if one defines $\vec{k} - \vec{k}' = \vec{K} \Rightarrow \vec{k}' = \vec{k} - \vec{K}$, $\Rightarrow |\vec{k}-\vec{K}|^2 = k^2$

$\Rightarrow \mathcal{E}_{k-K}^{(0)} = \frac{\hbar^2}{2m}|\vec{k}-\vec{K}|^2 = \frac{\hbar^2 k^2}{2m} = \mathcal{E}_k$ and $\mathcal{E}_k^{(2)} = \sum_{K} \frac{|U_K|^2}{\mathcal{E}_k^{(0)} - \mathcal{E}_{k-K}^{(0)}}$

Now when $\varepsilon_k^{(0)} \approx \varepsilon^{(0)}_{\vec{k}+\vec{K}}$, the non-deg pert theory will not work any more. However, this case can be treated by the degenerate per. theory. so at zone boundary, we have $\varepsilon_k^{(0)} = \varepsilon^{(0)}_{\vec{k}+\vec{K}}$ and this happens when $|\vec{k}| = |\vec{k}+\vec{K}|$.

to fix this problem, we diagonalize H in the space of the states that causes the degeneracy.



the $k = \pm \frac{\pi}{a}$ are symmetric, so let us work out the problem at $k = -\pi/a$; i.e using the states $|k\rangle$ and $|k+\vec{K}\rangle$

here we have a 2x2 matrix for H

$$H = \begin{pmatrix} \langle k|H|k\rangle & \langle \vec{k}|H|\vec{k}+\vec{K}\rangle \\ \langle \vec{k}+\vec{K}|H|\vec{k}\rangle & \langle \vec{k}+\vec{K}|H|\vec{k}+\vec{K}\rangle \end{pmatrix}$$

$$\langle k|H|k\rangle = \langle \vec{k}|H_0|\vec{k}\rangle + \langle \vec{k}|U|\vec{k}\rangle = \varepsilon_k^{(0)} + U_0$$

$$\langle \vec{k}+\vec{K}|H|k+\vec{K}\rangle = \langle \vec{k}+\vec{K}|H_0|\vec{k}+\vec{K}\rangle + \langle \vec{k}+\vec{K}|U|\vec{k}+\vec{K}\rangle$$

$$= \varepsilon^{(0)}_{\vec{k}+\vec{K}} + U_0$$

$$\langle \vec{k}+\vec{K}|H|\vec{k}\rangle = \underbrace{\langle \vec{k}+\vec{K}|H_0|\vec{k}\rangle}_{\varepsilon_k^{(0)}|k\rangle} + \langle \vec{k}+\vec{K}|U|\vec{k}\rangle$$

$$= \varepsilon_k^{(0)} \langle \vec{k}+\vec{K}|\vec{k}\rangle + \underline{\underline{U_K}}$$

$\langle k'|U|k\rangle = U_{k'-k}$

Now $\langle \vec{k}+\vec{K} | \vec{k} \rangle = 0$ as they are orthogonal, so

$$\langle \vec{k}+\vec{K} | H | k \rangle = U_K$$

and finally, $\langle \vec{k} | H | \vec{k}+\vec{K} \rangle = \langle \vec{k}+\vec{K} | U | \vec{k} \rangle^* = U_K^*$

so $H = \begin{pmatrix} \varepsilon_k^{(0)} + U_0 & U_K^* \\ U_K & \varepsilon^{(0)}_{\vec{k}+\vec{K}} + U_0 \end{pmatrix}$; Now right on the edge of B.Z, $\varepsilon_k^{(0)} = \varepsilon^{(0)}_{\vec{k}+\vec{K}}$

$$= \begin{pmatrix} \varepsilon_k^{(0)} + U_0 & U_K^* \\ U_K & \varepsilon_k^{(0)} + U_0 \end{pmatrix}, \text{ so } H\psi = \varepsilon\psi$$

$$\Rightarrow \begin{pmatrix} \varepsilon_k^{(0)} + U_0 & U_K^\dagger \\ U_K & \varepsilon_k^{(0)} + U_0 \end{pmatrix} \begin{pmatrix} |k\rangle \\ |k+\vec{K}\rangle \end{pmatrix} = \varepsilon \begin{pmatrix} |k\rangle \\ |k+\vec{K}\rangle \end{pmatrix}$$

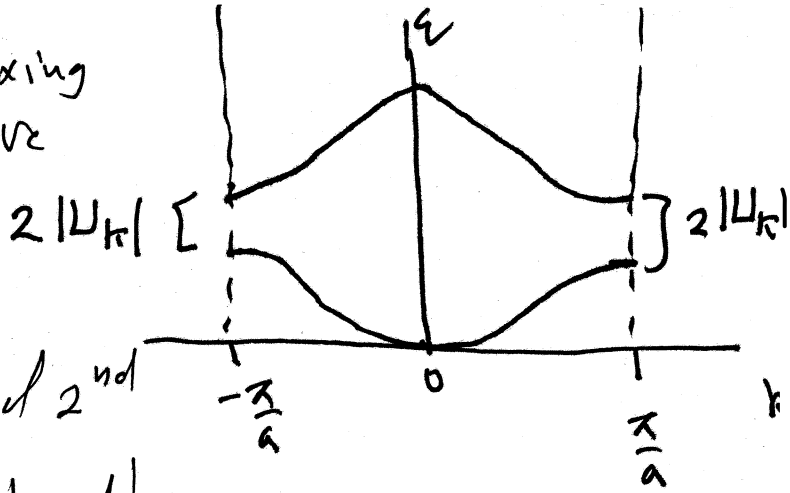
$$\Rightarrow \begin{vmatrix} \varepsilon_k^{(0)} + U_0 - \varepsilon & U_K^\dagger \\ U_K & \varepsilon_k^{(0)} + U_0 - \varepsilon \end{vmatrix} = 0 \Rightarrow \left(\varepsilon_k^{(0)} + U_0 - \varepsilon\right)^2 = |U_K|^2$$

$$\varepsilon_k^{(0)} + U_0 - \varepsilon = \pm |U_K|$$

$$\Rightarrow \varepsilon = \underset{\substack{\uparrow \\ \text{zeroth}}}{\varepsilon_k^{(0)}} \underset{\substack{\downarrow \\ \text{first}}}{+ U_0} \underset{\searrow \text{second}}{\pm |U_K|} \text{ corrections}$$

so due to the Periodic weak Potential, the two states $|k\rangle$ and $|k+K\rangle$ repele each others ; i.e $|k\rangle$ is pushed down $\varepsilon_- = \varepsilon_k^{(0)} + U_0 - |U_K|$, and the state $|\vec{k}+\vec{K}\rangle$ is pushed up with $\varepsilon_+ = \varepsilon_k^{(0)} + U_0 + |U_K|$, so creating a gap of size $\Delta\varepsilon = 2|U_K|$

similarly at $k = +\pi/a$, mixing $|k\rangle$ with $|\vec{k}-\vec{K}\rangle$ would give the same result.



Example 1: Find the 1st and 2nd corrections to energy due to the constant potential $U(x) = W_0$; $W_0 > 0$

$$\varepsilon_k^{(1)} = \langle k | U(x) | k \rangle = \langle k | W_0 | k \rangle = W_0 \langle k | k \rangle = W_0$$

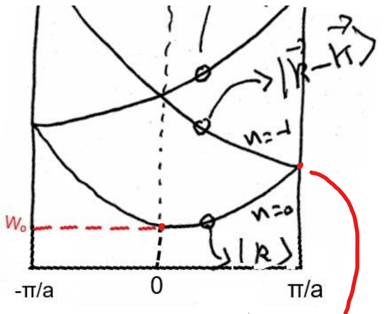
$$\varepsilon_k^{(2)} = \sum_{k' \neq k} \frac{|\langle k' | U(x) | k \rangle|^2}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}} ;$$

Now $\langle k' | U(x) | k \rangle = W_0 \langle k' | k \rangle = W_0 \, \delta_{k,k'}$

$$\Rightarrow \varepsilon_k^{(2)} = W_0 \sum_{k' \neq k} \frac{\delta_{k,k'}}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}} = 0 \text{ as } k' \neq k$$

so the constant potential uniformly shifts all energy levels by W_0 at first order. There is no 2nd order correction because the constant potential does not mix different k states. Hence, no energy gaps are created by this constant potential.

the energy for any state $|k\rangle$ is



$$\varepsilon_k = \varepsilon_k^{(0)} + \varepsilon_k^{(1)} = \frac{\hbar^2 k^2}{2m} + W_0$$

at $k = 0 \Rightarrow \varepsilon_k = W_0$

at $k = \pm\pi/a \Rightarrow \varepsilon_k = \frac{\hbar^2}{2m}\left(\pm\frac{\pi}{a}\right)^2 + W_0 = \frac{\hbar^2\pi^2}{2ma^2} + W_0$

Example 2: consider the Periodic Potential $U(x) = 2V_0 \cos\left(\frac{2\pi}{a}x\right)$ of 1D solid with lattice spacing. Find $\varepsilon_k^{(1)}$, $\varepsilon_k^{(2)}$, and the energy gap created at $k = \pm\pi/a$.

Now let $|k\rangle = \frac{1}{\sqrt{a}} e^{ikx} \Rightarrow \langle k| = \frac{1}{\sqrt{a}} e^{-ikx}$, so

$$\varepsilon_k^{(1)} = \langle k|U(x)|k\rangle = \frac{1}{a}\int_0^a e^{-ikx}\, 2V_0 \cos\frac{2\pi}{a}x \; e^{ikx}\, dx$$

$$= \frac{2V_0}{a}\int_0^a dx \cos\left(\frac{2\pi}{a}x\right) = 0$$, as we integrate the cos over its Period $\frac{2\pi}{2\pi/a} = a$

$$\varepsilon_k^{(2)} = \sum_{k'\neq k} \frac{|\langle k'|U(x)|k\rangle|^2}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}}$$; where $|k'\rangle = \frac{1}{\sqrt{a}} e^{ik'x}$

Now $$\langle k'|U(x)|k\rangle = \frac{2V_0}{a}\int_0^a e^{-ik'x} \cos\frac{2\pi}{a}x \; e^{ikx}\, dx$$

$$= \frac{2V_0}{a}\int_0^a e^{-ik'x}\left[\frac{e^{i\frac{2\pi}{a}x} + e^{-i\frac{2\pi}{a}x}}{2}\right] e^{ikx}\, dx$$

$$= \frac{V_0}{a}\int_0^a e^{-ik'x}\left[e^{i(k+\frac{2\pi}{a})x} + e^{i(k-\frac{2\pi}{a})x}\right] dx$$

$$= \frac{V_0}{a}\left[\int_0^a e^{-i(k'-(k+\frac{2\pi}{a}))x}\, dx + \int_0^a e^{-i(k'-(k-\frac{2\pi}{a}))x}\, dx\right]$$

$$= \frac{V_0}{a}\left[a\,\delta_{k',k+\frac{2\pi}{a}} + a\,\delta_{k',k-\frac{2\pi}{a}}\right]$$ only two terms contribute from $k' = k + \frac{2\pi}{a}$ and $k' = k - \frac{2\pi}{a}$

$$\Rightarrow \langle k'|U(x)|k\rangle = V_0\left[\delta_{k',k+\frac{2\pi}{a}} + \delta_{k',k-\frac{2\pi}{a}}\right]$$

$$\Rightarrow \varepsilon_k^{(2)} = \frac{|V_0|^2}{\varepsilon_k^{(0)} - \varepsilon^{(0)}_{k+\frac{2\pi}{a}}} + \frac{|V_0|^2}{\varepsilon_k^{(0)} - \varepsilon^{(0)}_{k-\frac{2\pi}{a}}} ,$$

Now $\varepsilon_k^{(0)} - \varepsilon^{(0)}_{k+\frac{2\pi}{a}} = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}\right)^2 = \frac{\hbar^2}{2m}\left(-\frac{4\pi^2}{a^2} - \frac{4\pi k}{a}\right)$

and $\varepsilon_k^{(0)} - \varepsilon^{(0)}_{k-\frac{2\pi}{a}} = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}\left(k-\frac{2\pi}{a}\right)^2 = \frac{\hbar^2}{2m}\left(-\frac{4\pi^2}{a^2} + \frac{4\pi k}{a}\right)$

$$\Rightarrow \varepsilon_k^{(2)} = \frac{2mV_0^2}{\hbar^2}\left[\frac{1}{-\frac{4\pi^2}{a^2} - \frac{4\pi k}{a}} + \frac{1}{-\frac{4\pi^2}{a^2} + \frac{4\pi k}{a}}\right]$$

$$= -\frac{mV_0^2}{\hbar^2}\left[\frac{1}{\frac{2\pi^2}{a^2} + \frac{2\pi k}{a}} + \frac{1}{\frac{2\pi^2}{a^2} - \frac{2\pi k}{a}}\right]$$

$$= -\frac{mV_0^2}{\hbar^2}\left[\frac{4\pi^2/a^2}{4\pi^2/a^2\left(\frac{\pi}{a}+k\right)\left(\frac{\pi}{a}-k\right)}\right]$$

$$= -\frac{mV_0^2}{\hbar^2}\,\frac{1}{\left(\frac{\pi}{a}\right)^2 - k^2} ,$$ which diverges at $k = \pm \pi/a$

- to find the energy gap at $k = \pm\pi/a$, let us work on $k = +\pi/a$, so need to mix $|k\rangle$ with $|k-\pi\rangle$, and Hence H becomes

$$H = \begin{pmatrix} \langle k|H|k\rangle & \langle k|H|k-\pi\rangle \\ \langle k-\pi|H|k\rangle & \langle k-\pi|H|k-\pi\rangle \end{pmatrix}$$

Now $\underline{\langle k|H|k\rangle} = \langle k|H_0+U(x)|k\rangle$

$$= \langle k|\underbrace{H_0|k\rangle}_{\varepsilon_k^{(0)}|k\rangle} + \underbrace{\langle k|U|k\rangle}_{\text{zero as found earlier}}$$

$$= \varepsilon_k^{(0)}\underbrace{\langle k|k\rangle}_{1} = \varepsilon_k^{(0)}$$

and

$\underline{\langle k-K|H|k-K\rangle} = \langle k-K|H_0+U|k-K\rangle$

$$= \langle k-K|\underbrace{H_0|k-K\rangle}_{\varepsilon^{(0)}_{k-K}|k-K\rangle} + \underbrace{\langle k-K|U|k-K\rangle}_{\text{zero}}$$

$$= \varepsilon^{(0)}_{k-K}\underbrace{\langle k-K|k-K\rangle}_{1} + 0 = \varepsilon^{(0)}_{k-K} = \varepsilon^{(0)}_{k}$$

as $\varepsilon^{(0)}_{k-K} = \varepsilon^{(0)}_{k}$ at $k = +\pi/a$
(degenerate)

Now

$\underline{\langle k-K|H|k\rangle} = \langle k-K|H_0+U|k\rangle$

$$= \langle k-K|\underbrace{H_0|k\rangle}_{\varepsilon_k^{(0)}|k\rangle} + \underbrace{\langle k-K|U|k\rangle}_{U_K}$$

$$= \varepsilon_k^{(0)}\underbrace{\langle k-K|k\rangle}_{\text{zero}} + U_K = U_K$$, where $K = -\frac{2\pi}{a}$

as $|k\rangle$ and $|k-K\rangle$ are orthogonal

$$U_K = \frac{1}{a}\int_0^a dx\, U(x)\, e^{-iKx} = \frac{1}{a}\int_0^a dx\; 2V_0 \cos\frac{2\pi}{a}x \;\; e^{i\frac{2\pi}{a}x}$$

$$= \frac{2V_0}{a}\int_0^a dx\; e^{i\frac{2\pi}{a}x}\left[\frac{e^{i\frac{2\pi}{a}x} + e^{-i\frac{2\pi}{a}x}}{2}\right]$$

$$\Rightarrow U_K = \frac{V_0}{a}\left[\int_0^a e^{i\frac{4\pi}{a}x}\,dx + \int_0^a dx\right] = \frac{V_0}{a}\left[\frac{a}{i4\pi}e^{i\frac{4\pi}{a}x}\Big|_0^a + a\right]$$

$$= \frac{V_0}{a}\left[\frac{a}{i4\pi}(\underset{=1}{\underset{\downarrow}{e^{i4\pi}}} - 1) + a\right] = \frac{V_0}{a}a = V_0$$

Note that $\langle k-K|U|k\rangle$ can be calculated directly, knowing that $|k\rangle = \frac{1}{\sqrt{a}}e^{ikx}$ and $|k-K\rangle = \frac{1}{\sqrt{a}}e^{-i\frac{2\pi}{a}x}e^{ikx}$, so

$$\langle k-K|U|k\rangle = \int_0^a dx\,\frac{1}{\sqrt{a}}e^{+i\frac{2\pi}{a}x}e^{-ikx}\,2V_0\cos\frac{2\pi}{a}x\,\frac{1}{\sqrt{a}}e^{ikx}$$

$$= \frac{V_0}{a}\left[\int_0^a dx\,e^{i\frac{4\pi}{a}x} + \int_0^a dx\right] = V_0$$

Now $\underline{\langle k|H|k-K\rangle} = \langle k-K|H|k\rangle^* = V_0^* = V_0$ as V_0 is real

$$\Rightarrow H = \begin{pmatrix}\varepsilon_k^{(0)} & V_0 \\ V_0 & \varepsilon_k^{(0)}\end{pmatrix} \Rightarrow H\psi = \varepsilon\psi \Rightarrow \begin{pmatrix}\varepsilon_k^{(0)} & V_0 \\ V_0 & \varepsilon_k^{(0)}\end{pmatrix}\begin{pmatrix}|k\rangle \\ |k-K\rangle\end{pmatrix} = \varepsilon\begin{pmatrix}|k\rangle \\ |k-K\rangle\end{pmatrix}$$

$$\Rightarrow \begin{vmatrix}\varepsilon_k^{(0)} - \varepsilon & V_0 \\ V_0 & \varepsilon_k^{(0)} - \varepsilon\end{vmatrix} = 0 \Rightarrow (\varepsilon_k^{(0)} - \varepsilon)^2 = V_0^2 \Rightarrow \varepsilon_k^0 - \varepsilon = \pm V_0$$

$$\Rightarrow \varepsilon = \varepsilon_k^{(0)} \pm V_0$$

$$\Rightarrow \varepsilon = \varepsilon_k^{(0)} + \underbrace{\varepsilon_k^{(1)}}_{\text{zero}} + \varepsilon_k^{(2)} = \varepsilon_k^{(0)} \pm V_0$$

$$\Rightarrow \varepsilon^+ = \varepsilon_k^{(0)} + V_0, \quad \varepsilon^+ = \varepsilon_k^{(0)} - V_0$$

$$\Delta\varepsilon = \varepsilon^+ - \varepsilon^- = 2V_0 \equiv \text{band gap}$$

Let us find the eigenstates: the eigenvalue equation reads

$$H \begin{pmatrix} |k\rangle \\ |k-K\rangle \end{pmatrix} = \varepsilon \begin{pmatrix} |k\rangle \\ |k-K\rangle \end{pmatrix} \Rightarrow (H-\varepsilon)\begin{pmatrix} |k\rangle \\ |k-K\rangle \end{pmatrix} = 0$$

↳ called eigenvector

$$\Rightarrow \begin{pmatrix} \varepsilon_k^{(0)} - \varepsilon & V_0 \\ V_0 & \varepsilon_k^{(0)} - \varepsilon \end{pmatrix} \begin{pmatrix} |k\rangle \\ |k-K\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

for $\varepsilon_+ = \varepsilon_k^{(0)} + V_0 \Rightarrow \begin{pmatrix} \varepsilon_k^{(0)} - \varepsilon_k^{(0)} - V_0 & V_0 \\ V_0 & \varepsilon_k^{(0)} - \varepsilon_k^{(0)} - V_0 \end{pmatrix} \begin{pmatrix} |k\rangle^+ \\ |k-K\rangle^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

$$\Rightarrow \begin{pmatrix} -V_0 & V_0 \\ V_0 & -V_0 \end{pmatrix} \begin{pmatrix} |k\rangle^+ \\ |k-K\rangle^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow -V_0 |k\rangle^+ + V_0 |k-K\rangle^+ = 0$$

$$\Rightarrow |k-K\rangle^+ = |k\rangle^+$$

$\Rightarrow$ both arbitrary

$$\Rightarrow \begin{pmatrix} |k\rangle^+ \\ |k-K\rangle^+ \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \Rightarrow |k\rangle^+ = 1 \text{ and } |k-K\rangle^+ = 1$$

now the eigenstate can be written in terms of the eigenvectors

as $|\psi\rangle = \sum_K |k+K\rangle e^{i(\vec{k}+\vec{K})\cdot\vec{r}} = \sum_K |k+K\rangle e^{i(k+K)x}$ in 1D

$$= \sum_{n=0,-1} |k + \tfrac{2\pi}{a} n\rangle e^{i(k+\frac{2\pi}{a}n)x}$$

$$= |k\rangle e^{ikx} + |k-K\rangle e^{-ikx}$$

at $k = \pi/a$, we have

$|\psi\rangle = |k\rangle e^{i\frac{\pi}{a}x} + |k-K\rangle e^{-i\pi/a\, x}$, so for ε_+, we have

$$|\psi\rangle^+ = \underbrace{|k\rangle^+}_{1} e^{i\pi/a\, x} + \underbrace{|k-K\rangle^+}_{1} e^{-i\pi/a\, x} = e^{i\pi/a\, x} + e^{-i\pi/a\, x} = 2\cos\frac{\pi}{a}x$$

let us normalize $|\psi\rangle^+$ using $\langle\psi^+|\psi^+\rangle = 1$

let $|\psi\rangle^+ = 2A\cos\frac{\pi}{a}x$; A is normalization constant

$$\Rightarrow \langle\psi^+|\psi^+\rangle = 1 \Rightarrow 4A^2 \underbrace{\int_0^L \cos^2\frac{\pi}{a}x\,dx}_{L/2} = 1 \Rightarrow 2A^2L = 1$$

$$\Rightarrow A = \frac{1}{\sqrt{2L}}$$

$$\Rightarrow |\psi\rangle^+ = \frac{2}{\sqrt{2L}}\cos\frac{\pi}{a}x = \sqrt{\frac{2}{L}}\cos\frac{\pi}{a}x$$

similarly for $\mathcal{E}_- = \mathcal{E}_k^{(0)} - V_0$, one finds

$\begin{pmatrix}|k\rangle^- \\ |k-K\rangle^-\end{pmatrix} = \begin{pmatrix}1 \\ -1\end{pmatrix} \Rightarrow |k\rangle^- = 1$ and $|k-K\rangle^- = -1$, so

$$|\psi\rangle^- = |k\rangle^- e^{i\pi/a\,x} + |k-K\rangle^- e^{-i\pi/a\,x} = e^{i\pi/a\,x} - e^{-i\pi/a\,x}$$

$$= 2i\sin\pi/a\,x$$

so $\langle\psi^-| = -2i\sin\frac{\pi}{a}x$

normalize $\langle\psi^-|\psi^-\rangle = 1 \Rightarrow \underbrace{4A^2\int_0^L \sin^2\frac{\pi}{a}x\,dx = 1}$, where $|\psi\rangle^- = 2iA\sin\frac{\pi}{a}x$

$\Rightarrow A = \frac{1}{\sqrt{2L}}$

$\Rightarrow A = \frac{1}{\sqrt{2L}} \Rightarrow |\psi\rangle^- = i\sqrt{\frac{2}{L}}\sin\frac{\pi}{a}x$

see that the two eigenvectors are orthogonal $(1 \quad 1)\begin{pmatrix}1 \\ -1\end{pmatrix} = [1-1] = 0$ and the two eigenstates are orthogonal as well

$$\langle\psi^+|\psi^-\rangle = \frac{2i}{L}\int_0^L \cos\frac{\pi}{a}x\,\sin\frac{\pi}{a}x\,dx = \frac{-2ia}{2\pi L}\left[\cos^2\left(\frac{\pi L}{a}\right) - 1\right]$$

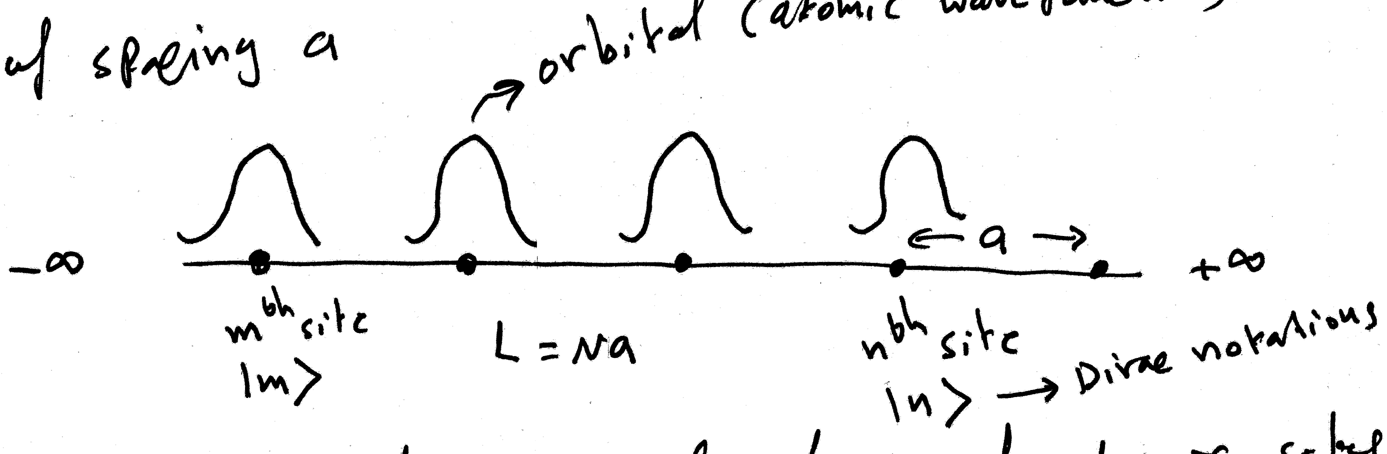
but $L = Na$ $\quad = \frac{-ia}{\pi L}\left[(\cos N\pi)^2 - 1\right] = \frac{-ia}{\pi L}\left[\underbrace{(\cos(N\pi))^2}_{1} - 1\right]$; N is integer

$= \text{Zero}$

Tightly Bound electrons and The tight Binding model

in general, there are several methods of band structure calculations, such as Perturbation method, tight-binding method, Pseudo Potential method; and others. in the last section, , we discussed the Perturbation method, where we assumed that electrons are delocalized and move around the sample under a Periodic Potential. in this section, we discuss the tight-binding method. this method is also called linear combination of atomic orbitals (LCAO). here, we will solve the single particle schrodinger equation for the states in a crystal by expanding Bloch states in term of a linear combination of atomic orbitals.

- here we consider a 1D tight-Binding chain of atoms of spacing a



atomic orbitals are localized around atomic sites

with $\langle \vec{r} | m \rangle = \phi(\vec{r} - \vec{R}_m)$; $\vec{R}_m$ Position of nucleus m

$\langle \vec{r} | n \rangle = \phi(\vec{r} - \vec{R}_n)$; $\vec{R}_n$ " " " n

we see that these orbitals are hardly overlap, so

$$\langle m|n\rangle = \int_V \phi^*(\vec r-\vec R_m)\,\phi(\vec r-\vec R_n)\,d^3r \approx 0$$ almost zero for $m \neq n$

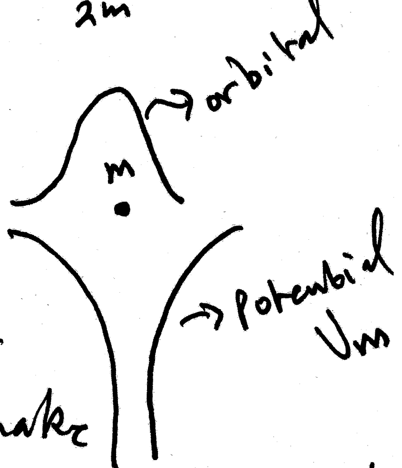
and for $m=n$, $\langle m|m\rangle = \int_V |\phi(\vec r-\vec R_m)|^2\, d^3\vec r = 1$

so $\langle m|n\rangle = \delta_{mn}$, i.e these orbitals are orthonormal

- Now for an isolated atom (labeled m), the atomic hamiltonian H_{at} is $H_{at} = K + V_m = \frac{p^2}{2m} + V_m$

$$H_{at}|m\rangle = \mathcal{E}_{at}|m\rangle$$

$$(K+V_m)|m\rangle = \mathcal{E}_{at}|m\rangle$$



Clearly, a single atomic orbital does not satisfy Bloch's theorem. However, if we make a linear combination of atomic orbitals, then the resultant Tight binding wavefunction does satisfy Bloch's theor.

$$\psi_{n\vec k}(\vec r) = \underbrace{\frac{1}{\sqrt N}}_{\text{for normalization}} \sum_{\vec R} e^{i\vec k\cdot\vec R}\,\phi_n(\vec r-\vec R) \quad \text{---(1)}$$

; note that $\phi_n(\vec r-\vec R) = \phi(\vec r-\vec R_n)$ just symbols

let us check first the normalization

$$I = \langle \psi_{n\vec k}(\vec r)|\psi_{n\vec k}(\vec r)\rangle = \int \psi^*_{nk}\,\psi_{nk}\, d^3\vec r$$

$$= \frac{1}{N}\sum_R \sum_{R'} \int e^{-i\vec k\cdot\vec R}\,\phi_n^*(\vec r-\vec R)\, e^{i\vec k\cdot\vec R'}\,\phi_n(\vec r-\vec R')\,d^3\vec r$$

$$= \frac{1}{N} \sum_{R} \sum_{R'} e^{i\vec{k}\cdot(\vec{R}'-\vec{R})} \int \phi_n^*(\vec{r}-\vec{R})\, \phi_n(\vec{r}-\vec{R}')\, d^3\vec{r}$$

where R, R' sums over all translation vectors
$0 \rightarrow N-1$ or $1 \rightarrow N$

Now using

$$\int \phi_m^*(\vec{r}-\vec{R})\, \phi_n(\vec{r}-\vec{R}')\, d^3r = 1 \text{, when } m=n \text{ and } \vec{R}=\vec{R}'$$

$= 0$, otherwise

or $= \delta_{nm,\, RR'}$

$$\Rightarrow \frac{1}{N} \sum_{R} \sum_{R'} e^{i\vec{k}\cdot(\vec{R}'-\vec{R})}\, \delta_{R',R}$$

$$= \frac{1}{N} \sum_{R} e^{0} = \frac{1}{N} \sum_{R} 1 = \frac{1}{N}\left(\sum_{R} 1\right) = \frac{N}{N} = 1$$

so eq^n (1) is correctly normalized. let us also check that eq$^{(1)}$ does satisfy Bloch's theorem

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

$$\Rightarrow \psi_{nk}(\vec{r}+\vec{R}') = \frac{1}{\sqrt{N}} \sum_{R} e^{i\vec{k}\cdot\vec{R}}\, \phi_n(\vec{r}-\vec{R}+\vec{R}') = \frac{1}{\sqrt{N}} \sum_{R} e^{i\vec{k}\cdot\vec{R}}\, \phi_n(\vec{r}-(\vec{R}-\vec{R}'))$$

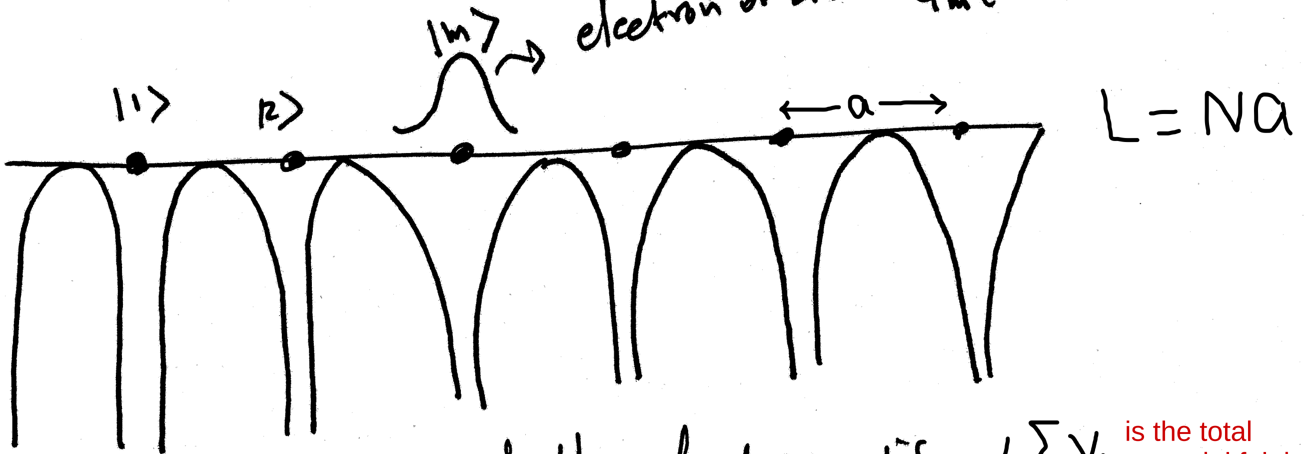
let $R'' = R - R'$

$$= \frac{1}{\sqrt{N}} \sum_{R''} e^{i\vec{k}\cdot(\vec{R}'+\vec{R}'')}\, \phi_n(\vec{r}-\vec{R}'') = e^{i\vec{k}\cdot\vec{R}'} \frac{1}{\sqrt{N}} \sum_{R''} e^{i\vec{k}\cdot\vec{R}''}\, \phi_n(\vec{r}-\vec{R}'')$$

$$= e^{i\vec{k}\cdot\vec{R}'}\, \psi_{nk}(\vec{r});$$

↳ R'' is dummy
let $R'' \rightarrow R$

Now again, let us consider one dimensional lattice with one atom/cell and let us first have one electron in the chain. i.e, there is one electron localized on atom (m), and let us imagine that it can hop between these nuclei.



So the total hamiltonian of the electron is

$$H=\frac{\vec p^{\,2}}{2m}+\sum_j V(\vec r-\vec R_j) \rightarrow \text{Position of nucleus } j$$

$\sum_j V_j$ is the total potential felt by the electron on site |m> that is produced by all other atoms including the atom at site |m>

$$= K+\sum_j V_j \quad ; \text{ just abbreviation}$$

it is usefull first to consider, the electron interacts with a single nuclies (m) and isolate this from the sum, so

i.e $$(K+V_m)|m\rangle=\varepsilon_{at}|m\rangle \quad ; \text{ this is for an isolated atom}$$

Now recall that the condition $\langle m|n\rangle=\delta_{mn}$ is good only when nuclei are far from each other. for simplicity we will go with this assumption. Now Recall that eq^n (1) can be written into Dirac notation as

$$|\psi\rangle=\sum_{n=0}^{N-1}C_n|n\rangle \quad ; \quad C_n=\frac{1}{\sqrt N}e^{i\vec k\cdot\vec R}\equiv\frac{1}{\sqrt N}e^{ikna} \text{ in 1D}$$

with $\vec R=n\vec a$

N: # of atoms or lattice sites

Now schrodinger eq^n reads $H|\Psi\rangle = \mathcal{E}|\Psi\rangle$

in matrix form and using $|\Psi\rangle = \sum_m C_m|m\rangle$, we get

$\sum_m H\, C_m|m\rangle = \mathcal{E}\sum_m C_m|m\rangle$; multiply by $\langle n|$ to find the matrix elements H_{nm}

$$\sum_m \langle n|H|m\rangle C_m = \mathcal{E}\sum_m C_m \underbrace{\langle n|m\rangle}_{\delta_{nm}}$$

$$\boxed{\sum_m H_{nm} C_m = \mathcal{E}\, C_n} \quad ---- \ (2)$$

now need to find the matrix elements H_{nm}. now the full hamiltonian.

$H = KT + V_m + \sum_{j\neq m} V_j$; where I removed the atom m from the sum

Now

$$H|m\rangle = \underbrace{(KT+V_m)|m\rangle}_{\mathcal{E}_{at}|m\rangle} + \sum_{j\neq m} V_j|m\rangle$$; now take the inner product with $\langle n|$

$$\langle n|H|m\rangle = \mathcal{E}_{at}\langle n|m\rangle + \langle n|\sum_{j\neq m} V_j|m\rangle$$

$$\langle n|H|m\rangle = \underset{\substack{\downarrow \\ \text{on site} \\ \text{energy}}}{\mathcal{E}_{at}\,\delta_{nm}} + \underbrace{\langle n|\sum_{j\neq m} V_j|m\rangle}_{\text{interaction with all other nuclei}}$$

$\langle n|\sum_{j\neq m} V_j|m\rangle = \Big\{$ V_0 ; if $n=m$; effect of potential of all other nuclei at the position of the mth ion (ion m is excluded). this is constant and the same for all other sites and $\langle n | \sum_{j\neq m} V_j | m\rangle = \begin{cases} V_0, & \text{--- as indicated before} \\ -t; & \text{if } n\neq m \\ 0 & ;\ \text{otherwise} \end{cases}$

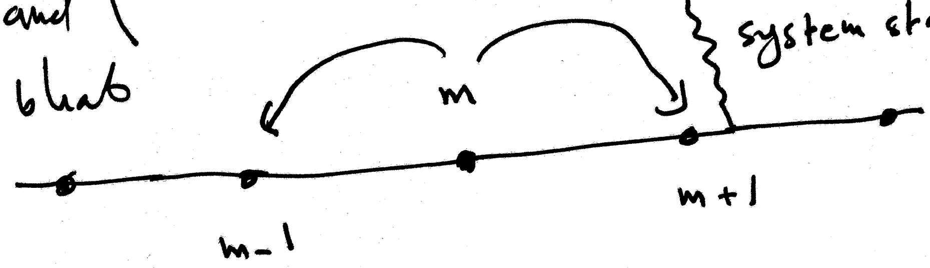
Hopping, it represe the transition amplitude for an electron to hop from initial state $|m\rangle$ to final state $|n\rangle$

- Now, to a good approximation we can assume nearest neighbor hopping; i.e if $|n-m| > 1 \Rightarrow$ No hopping

So $\langle n | \sum_{j\neq m} V_j | m\rangle = \begin{cases} V_0 & ;\ \text{if } n=m \\ -t & ;\ \text{if } n=m\pm 1 \\ 0 & ;\ \text{otherwise} \end{cases}$

Note that t is negative. This is due to that when atoms get close the potential barrier is reduced in order to minimize energy and make the system stabl

i.e it is hard for an electron to hopp back and forth between sites that are far away.



$$\text{So } H_{nm} = \underbrace{(\varepsilon_{ab} + V_0)}_{\varepsilon_0}\delta_{nm} - t\,(\underset{\substack{\downarrow \\ \text{hopp one step to right}}}{\delta_{n,m+1}} + \underset{\substack{\downarrow \\ \text{hopp one step to left}}}{\delta_{n,m-1}}) \quad \text{--}(3)$$

let us assume that there is N unit, so H is NxN matrix, then

$$H = \begin{pmatrix} \varepsilon_0 & -t & 0 & 0 & \cdots & \\ -t & \varepsilon_0 & -t & 0 & 0 & 0 \cdots \\ 0 & -t & \varepsilon_0 & -t & & 0 \\ 0 & & & \ddots & & 0 \\ 0 & 0 & -t & & \varepsilon_0 & -t \\ \vdots & \vdots & 0 & 0 & -t & \varepsilon_0 \end{pmatrix}$$

ε_o is called on – site energy

Now plugging eq^n (3) into (2) and using $c_n = \frac{1}{\sqrt{N}} e^{ikan}$, we ge

or $c_n = u\, e^{ikan}$
↳ constant of normalization

$$\sum_m H_{nm} c_m = \varepsilon c_n$$

$$\sum_m \left[\varepsilon_0 \delta_{nm} - t\left(\delta_{n,m+1} + \delta_{n,m-1}\right)\right] c_m = \varepsilon c_n$$

$$\varepsilon_0 c_n - t\left(c_{n-1} + c_{n+1}\right) = \varepsilon c_n$$

$$\frac{1}{\sqrt{N}} \varepsilon_0 e^{ikan} - t\left(\frac{1}{\sqrt{N}} e^{ika(n-1)} + \frac{1}{\sqrt{N}} e^{ika(n+1)}\right) = \varepsilon \frac{1}{\sqrt{N}} e^{ikan}$$

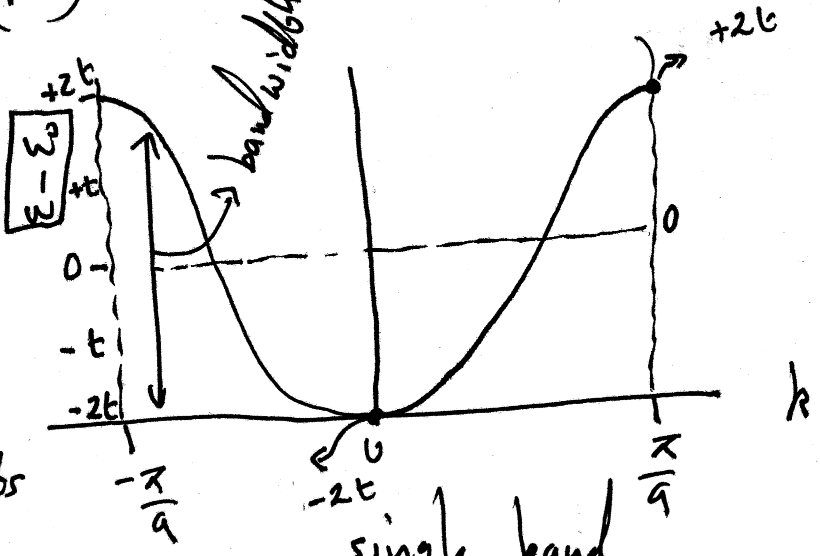
$$\varepsilon_0 \cancel{e^{ikan}} - t\cancel{e^{ikan}}\left(e^{-ika} + e^{ika}\right) = \varepsilon \cancel{e^{ikan}}$$

$$\varepsilon_0 - 2t\cos(ka) = \varepsilon$$

$$\therefore \boxed{\varepsilon = \varepsilon_0 - 2t\cos(ka)}$$ dispersion relation ---(4)

Note that there is one energy eigenvalue for each k, so there is only one band. let us plot $\varepsilon - \varepsilon_0$ vs k in the 1st B.Z

$$\varepsilon - \varepsilon_0 = -2t\cos(ka)$$

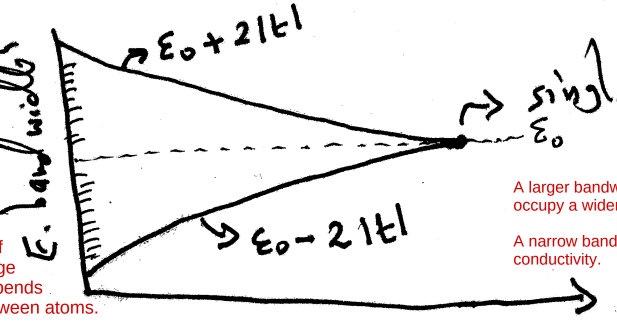


single band

bandwidth $= 2t - (2t)$
$= 4t$ for large enough 1D lattice

bandwidth: the difference in energy between the highest and lowest allowed levels within a given band

meaning, starting with a single atom, we get zero bandwidth, now by adding more atoms to the lattice, the bandwidth gets bigger i.e



No gaps; only one continuous band.

In a 1D lattice, bandwidth is independent of the number of atoms once the system is large enough to form a band. It depends on the hopping strength t between atoms.

A larger bandwidth implies greater electron mobility, as electrons can occupy a wider range of energies.

A narrow bandwidth often indicates localized electrons and less conductivity.

let us look at the shape of the band near $k=0$.

Now using $\cos x = 1 - \frac{x^2}{2}$, for $x \ll 1$, we get

$$\cos(ka) \approx 1 - (ka)^2/2$$

So $\varepsilon = \varepsilon_0 - 2t\left(1 - \frac{(ka)^2}{2}\right) = \varepsilon_0 - 2t + ta^2k^2$

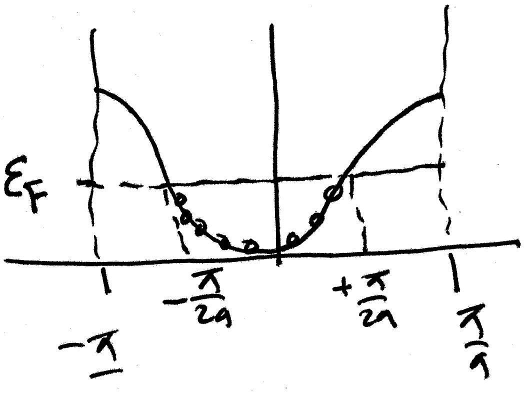
so it is quadratic in k i.e $\varepsilon \propto k^2$ (parabolic)

so the electron near the bottom of the band moves like free electron with an effective mass m^* defined as

$$\frac{\hbar^2 k^2}{2m^*} = ta^2k^2 \quad \Rightarrow \quad m^* = \frac{\hbar^2}{2ta^2}$$

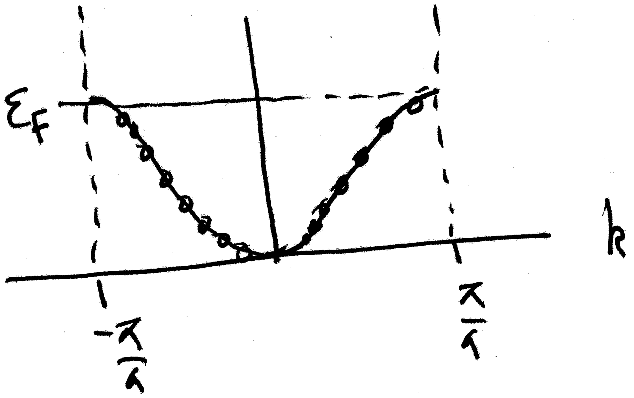
now each allowed $|k\rangle$ state can have 2 electrons with opposite spins. so having one electron/atom means, there are N electrons that at $T=0$ fill only half of the band. so the fermi surface here is composed of two points

$$k = \pm\frac{\pi}{2a}$$

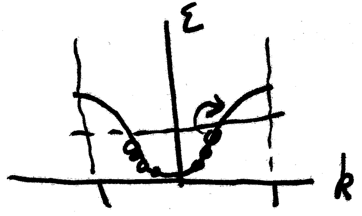


Recall that the # of available states in the band is N, which can accommodate up to 2N electrons

If the atoms are divalent, then there will be $2N$ electrons that can completely fill the band. so fermi surface is bounded by $k = \pm\frac{\pi}{a}$



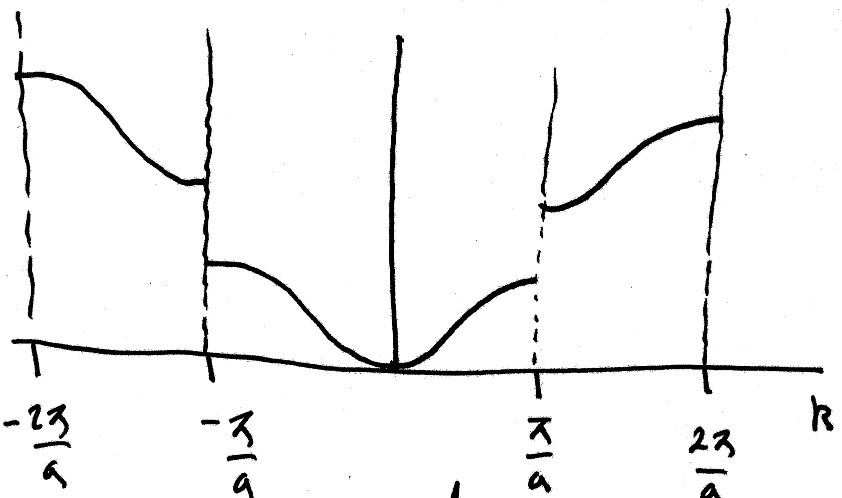
So for monovalent atoms, where there is only one valence electron for each atom, we have a half-filled band with an empty states available above ε_F. Hence electrons can easly be moved accross ε_F by an applied electric field and produce accurent. these materials are called metals; with heat capacity $C \propto T$.



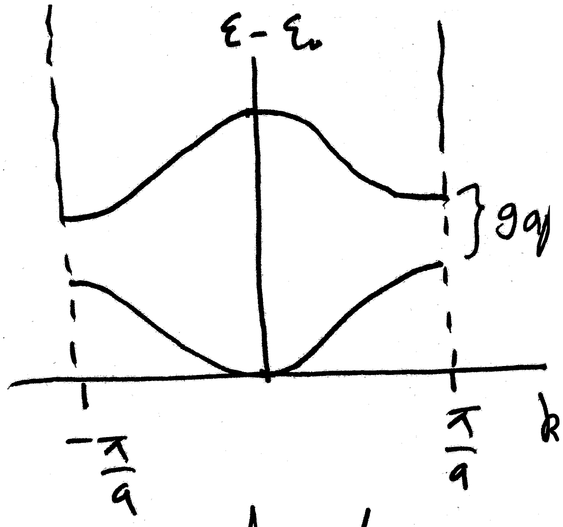
- for divalent atoms, where there are 2 valence electrons/atom, we will have a completely filled band, so there are no empty states available above ε_F for conductio These materials are called insulators with zero heat capacity $(C=0)$.

This is theoretical prediction of the TBM based on non-overleaping bands. However, in realty, most divalent solids (like Ca and Mg) are metals due to band overlap

- now so far we assumed that there was one orbital/or atom and hence we got one band. Now there are some situations, where there are more than one orbital/or atom; like for example having two different atoms/unit cell or having two different orbitals on the same atom (1s and 2p for example).
- for 2 orbitals/unit cell; and without solving this problem, the spectrum is like as follows where there are two energy bands, separated by a gap



extended



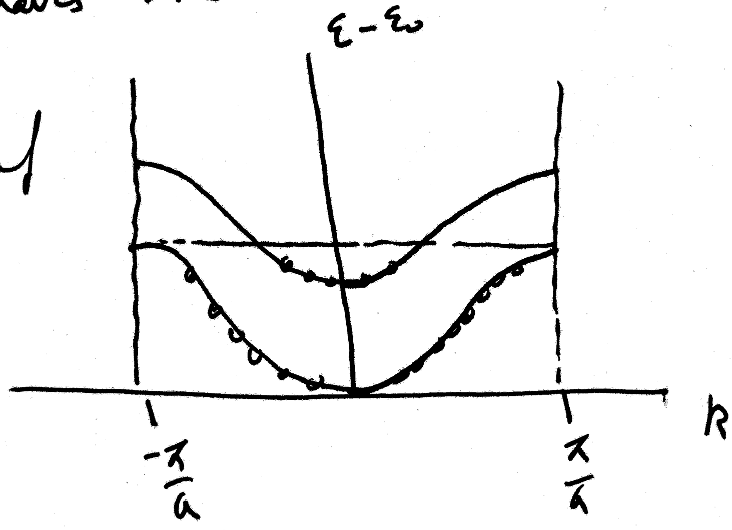
reduced

Now suppose that the unit cell has $3e^-$, so here the lower band will be filled and the upper band will be half-filled. we can call the lower band as the valence band and higher band as conduction band.

so generally; odd # of e^- / unit cell => metal
even # " / " " => insulators

however, there are many exceptions, for example Ca^{+2} has $2e^-$/ unit cell, yet it behaves like metals.

here we have partially filled bands. because the bottom of the upper band is lower than the top of the first band



The general expression for the tight-binding dispersion of a monoatomic lattice is given by

$$\varepsilon(k) = \varepsilon_0 - \sum_j t_{ij}\, e^{i\vec{k}\cdot(\vec{R}_j - \vec{R}_i)}$$

Now considering only nearest-neighbor hopping yields

$$\boxed{\varepsilon(k) = \varepsilon_0 - t \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}}$$

; where $\vec{R}$ is a vetor connecting a given lattice site to one of its nearest neighbors.

- for a square lattice, $\vec{R} = \pm a\hat{i}$; and $\vec{R} = \pm a\hat{j}$

$$\Rightarrow \varepsilon(k) = \varepsilon_0 - t\left(e^{ik_xa} + e^{-ik_xa} + e^{ik_ya} + e^{-ik_ya}\right)$$

$$= \varepsilon_0 - 2t(\cos k_xa + \cos k_ya)$$

- for a simple-cubic lattice, it yields

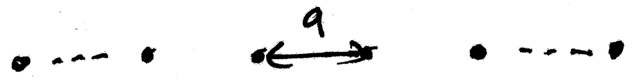
$$\varepsilon(k) = \varepsilon_0 - 2t(\cos k_xa + \cos k_ya + \cos k_za)$$

- in Homework #6, we discuss formation of bandgaps in diatomic chain ABABAB---- and diatomic square lattice with on-site energies ε_A and ε_B, respectively.

I need to go over problem 4 in HW#6 to make sure you understand how the bandgap forms and how to determine its magnitude for the 1D diatomic chain of atoms ABABAB.....

Tight Binding Density of states:

we already found that the DOS of all bands for a solid in d-dimensions was



$$D(\varepsilon) = \frac{2L^d}{(2\pi)^d}\,\frac{2\pi^{d/2}}{\Gamma(d/2)}\,k^{d-1}\,\frac{1}{|\nabla\varepsilon_k|}$$

$L = Na$

for 1D solid of spacing a, $\varepsilon = \varepsilon_0 - 2t\cos(ka)$; $t>0$

so $D_1(\varepsilon) = \frac{2L}{2\pi}\,\frac{2\sqrt{\pi}}{\sqrt{\pi}}\,\frac{1}{|\nabla_k\varepsilon|} = \frac{2L}{\pi}\,\frac{1}{|\nabla_k\varepsilon|}$

Now $\nabla_k\varepsilon(k) = \frac{\partial\varepsilon}{\partial k} = +2t\sin(ka)\cdot a = 2at\sin(ka)$

$\Rightarrow D_1(\varepsilon) = \frac{\cancel{2}L}{\pi}\,\frac{1}{\cancel{2}at\sin(ka)} = \frac{L}{\pi a t}\,\frac{1}{\sqrt{1-\cos^2(ka)}}$; where $\sin(ka) = \sqrt{1-\cos^2(ka)}$

Now using $\cos ka = \frac{\varepsilon_0-\varepsilon}{2t}$ $\Rightarrow D_1(\varepsilon) = \frac{L}{\pi a t}\,\frac{1}{\sqrt{1-\frac{(\varepsilon_0-\varepsilon)^2}{4t^2}}}$

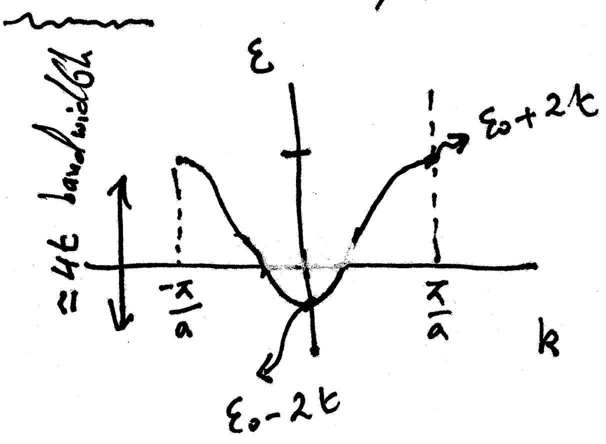
$\Rightarrow D_1(\varepsilon) = \frac{L}{\pi a t}\,\frac{1}{\sqrt{1-\left(\frac{\varepsilon_0-\varepsilon}{2t}\right)^2}}$

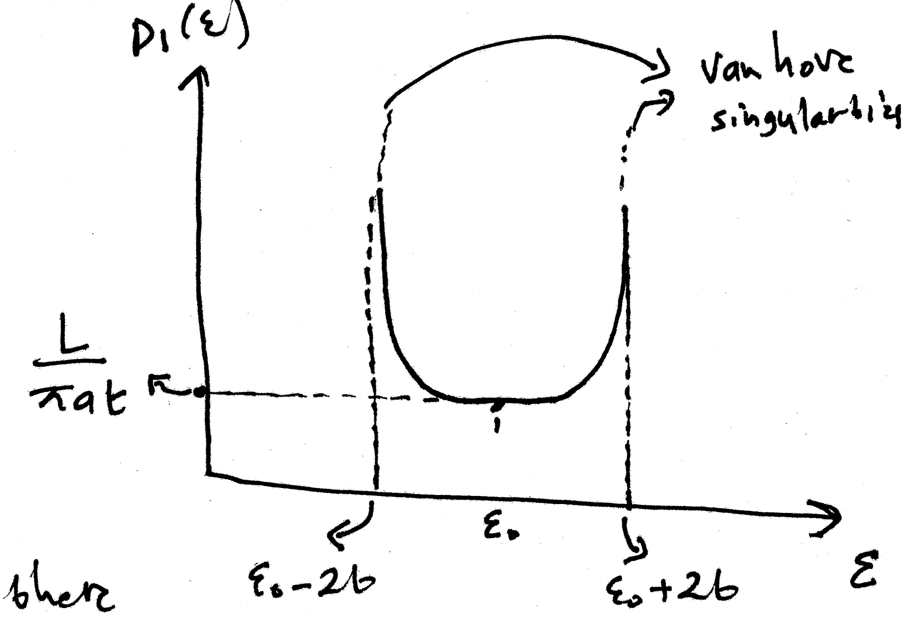
Note that $D_1(\varepsilon)$ is singular (∞), when $\left(\frac{\varepsilon_0-\varepsilon}{2t}\right)^2 = 1$

$\Rightarrow \frac{\varepsilon_0-\varepsilon}{2t} = \pm 1 \Rightarrow \varepsilon_0-\varepsilon = \pm 2t \Rightarrow \varepsilon = \varepsilon_0 \pm 2t$

i.e $\varepsilon^- = \varepsilon_0 - 2t$ and $\varepsilon^+ = \varepsilon_0 + 2t$ are the singular points where DOS diverges also note that $D_1(\varepsilon)$ is minimum when $\frac{\varepsilon_0-\varepsilon}{2t}=0$

$\Rightarrow \varepsilon=\varepsilon_0$, so





Now how many states are there between ε_0-2t and ε_0+2t

$$\int D_1(\varepsilon)\,d\varepsilon = \frac{L}{\pi a t}\int_{\varepsilon_0-2t}^{\varepsilon_0+2t}\frac{d\varepsilon}{\sqrt{1-\left(\frac{\varepsilon_0-\varepsilon}{2t}\right)^2}}$$

; let $\varepsilon_0-\varepsilon = 2t\sin\theta$

$-d\varepsilon = 2t\cos\theta\,d\theta$

$$= -\frac{L}{\pi a t}\int_{\pi/2}^{-\pi/2}\frac{2t\cos\theta\,d\theta}{\sqrt{1-\sin^2\theta}}$$

;

when $\varepsilon=\varepsilon_0-2t \Rightarrow \sin\theta=1$
$\Rightarrow \theta=\pi/2$

when $\varepsilon=\varepsilon_0+2t \Rightarrow \sin\theta=-1$
$\Rightarrow \theta=-\pi/2$

$$= -\frac{2L}{\pi a}\int_{\pi/2}^{-\pi/2}d\theta = \frac{2L}{\pi a}\int_{-\pi/2}^{\pi/2}d\theta$$

$$= \frac{2L}{\pi a}\left\{\pi/2-(-\pi/2)\right\} = \frac{2L}{\cancel{\pi}a}\cancel{\pi} = \frac{2L}{a}$$

; where $L=Na$

$$= 2N$$ as expected.

Please go over problem 6 in HW#6 to find out how to calculate DOS of 1D diatomic solid with two different atoms per unit cell ABABAB....

Bloch and Wannier representations: (optional)

we have seen that a bloch electron is conventionally labeled by an index n and a wave vector $\vec{k}$. now in the tight-binding model, the TB wave function was expanded in terms of atomic orbitals $\phi_n(\vec{r}-\vec{R})$ as

$$\psi_{nk}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_n(\vec{r}-\vec{R}) \; ; \quad ---(5)$$

there, we have made a bad assumption that the atomic orbitals, $\phi_n(\vec{r}-\vec{R})$ are orthogonal i.e $\int \phi_m^*(\vec{r}-\vec{R}_m)\phi_n(\vec{r}-\vec{R}_n) = 0$

However, this assumption is satisfactory when atoms are far away from each other, that thier orbitals are not overlaped. However, in 1937, Gregory wannier proposed a new set of functions that are perfectly localized at atomic sites and orthogonal. These set of functions are called wannier functions $W_n(\vec{r},\vec{R})$. so that the tight-binding wave function is now

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} W_n(\vec{r},\vec{R})$$

, Note that $W_n(\vec{r},\vec{R})$ is the Fourier transform of Bloch wave functions;

$$W_n(\vec{r},\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \quad --(6)$$

Now using bloch theorem for $\psi_{nk}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r})$, tha

eqⁿ (6) reads $W_n(\vec{r},\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r})$

$$= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}-\vec{R})} u_{nk}(\vec{r})$$

thus, taking into account the periodicity of $u_{nk}(\vec{r})$, we see that $W_n(\vec{r},\vec{R})$ depends on the difference $\vec{r}-\vec{R}$, so

$W_n(\vec{r},\vec{R}) = W_n(\vec{r}-\vec{R})$, so

$$\psi_{nk}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} W_n(\vec{r}-\vec{R}) \quad ---- (7)$$

$$W_n(\vec{r}-\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \quad --- (8)$$

The wannier functions form an orthonormal set, i.e

$$\int_{\Omega} d^3\vec{r}\, W_n(\vec{r},\vec{R}) W_m^*(\vec{r},\vec{R}')$$

$$= \int d^3\vec{r} \sum_{R}\sum_{R'} \frac{1}{N} e^{-i\vec{k}\cdot\vec{R}+i\vec{k}'\cdot\vec{R}'} \psi_{nk}(r)\psi^*_{mk'}(r)$$

$$= \frac{1}{N} \sum_{R}\sum_{k'} e^{-i\vec{k}\cdot\vec{R}+i\vec{k}'\cdot\vec{R}'} \underbrace{\int d^3\vec{r}\, \psi_{nk}(r)\psi^*_{mk'}(r)}_{\delta_{nm}\delta_{kk'}}$$

$$= \frac{1}{N} \sum_{R} e^{i\vec{k}\cdot(\vec{R}'-\vec{R})} \delta_{nm}$$

$$= \frac{1}{N} \Big(\underbrace{\sum_{R} \delta_{RR'}}_{N\,\delta_{RR'}}\Big) \delta_{nm} = \delta_{RR'}\delta_{nm}$$

Recall that, when $R = R'$
$\sum_{R} 1 = N$

let us switch to Dirac notations with

$\langle \vec{r} | \vec{k} \rangle = \psi_{nk}(\vec{r}) \Rightarrow |\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\vec{R}\rangle$ eq^n (7) in Dirac not

$\langle \vec{r} | \vec{R} \rangle = W_n(\vec{r}-\vec{R}) \Rightarrow |\vec{R}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} |\vec{k}\rangle$ eq^n (8) in Dirac not

Note that both $|k\rangle$ and $|R\rangle$ are orthonormal

$$\langle k'|k\rangle = \frac{1}{N} \sum_{R'} \sum_{R} e^{-i\vec{k}'\cdot\vec{R}'} e^{i\vec{k}\cdot\vec{R}} \langle R'|R\rangle$$

$$= \frac{1}{N} \sum_{R} \sum_{R'} e^{-ik'\cdot R' + ik\cdot R} \underbrace{\langle R'|R\rangle}_{\delta_{RR'}} = \frac{1}{N} \sum_{R} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}$$

$$= \delta_{kk'}$$

and similarly

$$\langle R'|R\rangle = \frac{1}{N} \sum_{k'} \sum_{k} e^{-ik'\cdot R' + ik\cdot R} \underbrace{\langle k'|k\rangle}_{\delta_{kk'}}$$

$$= \frac{1}{N} \sum_{k} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} = \delta_{RR'}$$

Now as mentioned early, the electron wave function can be expanded in terms of wannier functions; i.e

$\psi(r) = \sum_{R} C(R)\, W(\vec{r}-\vec{R})$ or $|\psi\rangle = \sum_{R} C(R) |\vec{R}\rangle$ in Dirac notations

so $H|\psi\rangle = \varepsilon|\psi\rangle \Rightarrow H \sum_{R'} C(R') |\vec{R}'\rangle = \varepsilon \sum_{R'} C(R') |R'\rangle$

multiply by $\langle \vec{R}|$

$$\sum_{R'} C(R') \langle \vec{R}|H|\vec{R}'\rangle = \varepsilon \sum_{R'} C(R') \underbrace{\langle R|R'\rangle}_{\delta_{RR'}}$$

$$\Rightarrow \sum_{R'} C(R')\, H_{RR'} = \varepsilon\, C(R) \quad \text{---} \ (9)$$

Now using the completnce of wannier functions

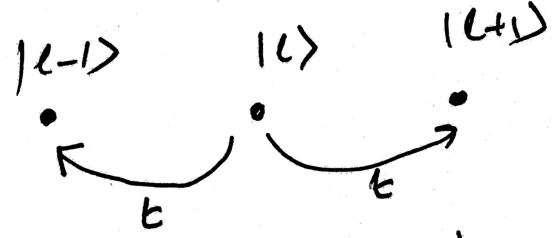
$\sum_{R} |\vec{R}\rangle\langle\vec{R}| = 1$, the hamiltonian H can be written

as $H = \sum_{R} |R\rangle\langle R| \; H \; \sum_{R'} |R'\rangle\langle R' = \sum_{R}\sum_{R'} \langle R|H|R'\rangle\, |R\rangle\langle$

$$H = \sum_{R,R'} H_{RR'}\, |R\rangle\langle R'|$$

again the 1D atoms chain can be solved using this H.

let us call or label the wannier functions by $|l\rangle \equiv |R\rangle$



so $H = \sum_{l l'} H_{ll'}\, |l\rangle\langle l'|$

Now using the TB hamiltonian in matrix form (eq 3), we get $H = \varepsilon_0 \sum_{l} |l\rangle\langle l| + t \sum_{l} |l\rangle\langle l+1| + |l\rangle\langle l-1|$

Now plugging this H into $H|\psi\rangle = \varepsilon|\psi\rangle$ and using $|\psi\rangle = \sum_{l'} c_{l'}|l'\rangle$, we get

$$\varepsilon_0 \sum_{l}\sum_{l'} |l\rangle \underbrace{\langle l|l'\rangle}_{\delta_{ll'}} c_{l'} + t \sum_{l,l'} |l\rangle\langle l+1|l'\rangle c_{l'} + |l\rangle\langle l-1|l'\rangle c_{l'} = \varepsilon \sum_{l'} c_{l'}|l'\rangle$$

↓ just relabe $l' \to l$

$$\varepsilon_0 \sum_{l} c_l |l\rangle + t \sum_{l} \left[c_{l+1}|l\rangle + c_{l-1}|l\rangle\right] = \varepsilon \sum_{l} c_l |l\rangle$$

$$\Rightarrow \sum_{l} \left[\varepsilon_0 c_l + t(c_{l+1} + c_{l-1}) - \varepsilon c_l\right] |l\rangle = 0$$

$$\Rightarrow \varepsilon_0 c_l + t(c_{l+1} + c_{l-1}) - \varepsilon c_l = 0$$

$\Rightarrow \quad \varepsilon_0 C_l + t\left(C_{l+1} + C_{l-1}\right) = \varepsilon C_l$; Now using $C_l = \frac{1}{\sqrt{N}} e^{ik}$

$$\frac{\varepsilon_0}{\sqrt{N}} e^{ikla} + \frac{t}{\sqrt{N}}\left(e^{ik(l+1)a} + e^{ik(l-1)a}\right) = \frac{\varepsilon}{\sqrt{N}} e^{ikla}$$

$$\varepsilon_0 \cancel{e^{ikla}} + b\cancel{e^{ikla}}\left(e^{ika} + e^{-ika}\right) = \varepsilon \cancel{e^{ika}}$$

$$\varepsilon_0 + t\ 2\cos(ka) = \varepsilon$$

$\Rightarrow \varepsilon = \varepsilon_0 + 2t\cos(ka)$; but t is negative

so $\varepsilon = \varepsilon_0 - 2|b|\cos(ka)$ as obtained before.