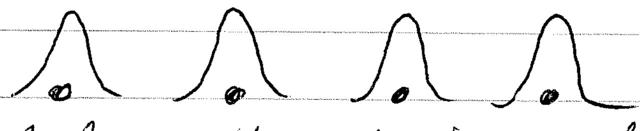
## Tight Binding Method

If ions are spaced far apart on the length scale on which the atomic bound state wavefunction decays, then expect that atomic wavefunctions will give a good approximation to the Bloch electron eigenstate in the periodic potential of all ions.



However the tails of the atomic wavefunctions will overlap allowing the electron to hop from ion to ion, behaving like a free Bloch electron.

For simplicity, assume the atomic valence electron is a single "s" ~~shell~~ orbital electron. This atomic state is non-degenerate. Let its wave function be $\varphi_0(\vec{r})$ for ion centered at origin.

We can construct a Bloch electron state out of the individual atomic states $\varphi_0(\vec{r}-\vec{R})$ by

$$\psi_k(\vec{r}) = \sum_i e^{i\vec{k}\cdot\vec{R}_i}\varphi_0(\vec{r}-\vec{R}_i)$$

Counting: We go from $N$ atomic wavefunction $\varphi_0(\vec{r}-\vec{R}_i)$, $N$ values of $\vec{R}_i$, to $N$ Bloch wavefunctions $\psi_k(\vec{r})$, $N$ values of $\vec{k}$ in 1st BZ.

(only mix atomic wavefunctions $\varphi_0(\vec{r}-\vec{R}_i)$ where electron has same spin value)

Let $H = H_{at} + \Delta U$

$H$ is Hamiltonian of entire system
$H_{at}$ is Hamiltonian of atom at origin
$\Delta U$ is potential from all atoms *except* the one at the origin

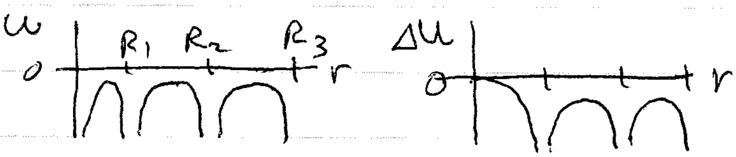
ie if total potential is $U(\vec{r}) = \sum_{R_i} v(\vec{r}-\vec{R}_i)$ ← atomic potential

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

$$H_{at} = \frac{p^2}{2m} + v(\vec{r})$$

$$\Delta U = \sum_{R_i \neq 0} v(\vec{r}-\vec{R}_i) = U(\vec{r}) - v(\vec{r})$$

choose energy scale so that $\Delta U(0) = 0$.




Now consider:

$$\langle \varphi_0 | H | \psi_k \rangle = \langle \varphi_0 | H_{at} + \Delta U | \psi_k \rangle$$

$$\varepsilon_k \langle \varphi_0 | \psi_k \rangle = E_a \langle \varphi_0 | \psi_k \rangle + \langle \varphi_0 | \Delta U | \psi_k \rangle$$

energy of Bloch state $\psi_k$

atomic energy level of $\varphi_0$

$$\varepsilon_k = E_a + \frac{\langle \varphi_0 | \Delta U | \psi_k \rangle}{\langle \varphi_0 | \psi_k \rangle}$$

$$\langle \varphi_0 | \psi_k \rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} \int d^3r\, \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)$$

$$= \underset{\uparrow \text{ from } \vec{R}_i = 0}{1} + \sum_{R_i \neq 0} e^{i\vec{k}\cdot\vec{R}_i} \underbrace{\int d^3r\, \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)}_{\text{overlap}}$$

If ions are far apart, overlap integrals are small. Only keep nearest neighbor terms, ie only sum over the smallest non-zero values of $\vec{R}$.

$$\langle \varphi_0 | \psi_k \rangle = 1 + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i} \underbrace{\int d^3r\, \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)}_{\alpha(\vec{R}_i)}$$

$$\boxed{\langle \varphi_0 | \psi_k \rangle = 1 + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\, \alpha(\vec{R}_i)}$$

$\alpha$ is small

$$\langle \varphi_0 | \Delta U | \psi_k \rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} \int d^3r\, \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi(\vec{r}-\vec{R}_i)$$

$$= \int d^3r\, \varphi_0^*(r)\, \Delta U(\vec{r})\, \varphi_0(\vec{r})$$

$$+ \sum_{R_i \neq 0} e^{i\vec{k}\cdot\vec{R}_i} \int d^3r\, \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi(\vec{r}-\vec{R}_i)$$

again, keep only terms for nearest neighbor $\vec{R}_i$.

define $\beta \equiv -\int d^3r\, \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_0(\vec{r})$

$$\gamma(\vec{R}) \equiv -\int d^3r\, \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)$$

$$\boxed{\langle \psi_0 | \Delta U | \psi_k \rangle = -\beta - \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\, \gamma(\vec{R})}$$

$$\mathcal{E}_k \simeq E_a - \left[\frac{\beta + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\gamma(\vec{R})}{1+\sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\alpha(\vec{R})}\right]$$

$$\boxed{\mathcal{E}_k \simeq E_a - \beta - \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\left(\gamma(\vec{R}) - \beta\alpha(\vec{R})\right)}$$

since $\alpha$ small, $\frac{1}{1+\alpha} \simeq 1-\alpha$
terms of order $(\gamma\alpha)$ are dropped as 2nd order

Now $\alpha(\vec{R}) = \int d^3r\, \varphi_0^*(\vec{r})\varphi_0(\vec{r}-\vec{R}) = \int d^3r\, \varphi_0^*(\vec{r}+\vec{R})\varphi_0(\vec{r})$
$= \alpha^*(-\vec{R})$

For s-orbital has real wave function $\varphi_0 \Rightarrow \alpha = \alpha^*$
so $\alpha(\vec{R}) = \alpha(-\vec{R})$

$$\gamma(\vec{R}) = -\int d^3r\, \varphi_0^*(\vec{r})\,\Delta U(\vec{r})\,\varphi_0(\vec{r}-\vec{R})$$

take $\vec{r} \to -\vec{r}$

$$= -\int d^3r\, \varphi_0^*(-\vec{r})\,\Delta U(-\vec{r})\,\varphi_0(-\vec{r}-\vec{R})$$

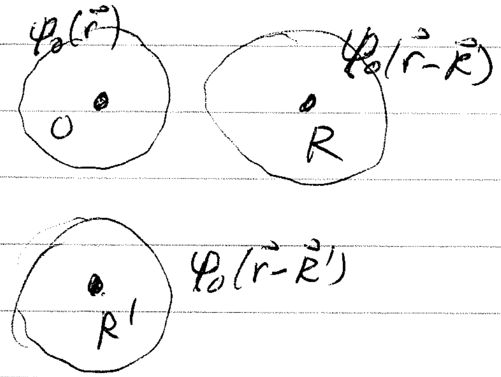
If crystal has inversion symmetry, ie $\Delta U(-\vec{r}) = \Delta U(\vec{r})$
and since s-orbital is spherically symmetric, ie
$\varphi_0(\vec{r})$ depends only on $|\vec{r}|$ so $\varphi_0(\vec{r}) = \varphi_0(-\vec{r})$, then

$$= -\int d^3r\, \varphi_0^*(\vec{r})\,\Delta U(\vec{r})\,\varphi_0(\vec{r}+\vec{R}) = \gamma(-\vec{R})$$

So $\gamma(\vec{R}) = \gamma(-\vec{R})$ and $\alpha(\vec{R}) = \alpha(-\vec{R})$

$$\boxed{\mathcal{E}_k = E_a - \beta - \sum_{nn}\left[\gamma(\vec{R}) - \beta\alpha(\vec{R})\right]\cos\vec{k}\cdot\vec{R}}$$

Moreover if the crystal has cubic symmetry, then since $\varphi_0$ is rotationally symmetric, $\gamma(\vec{R})$ and $\alpha(\vec{R})$ will be the same value for all nn $\vec{R}$




All will have cubic symmetry so $\gamma(\vec{R}) = \gamma(\vec{R}')$
$\alpha(\vec{R}) = \alpha(\vec{R}')$

$$\varepsilon_k = E_a - \beta - \tilde{\gamma} \sum_{nn} \cos(\vec{k}\cdot\vec{R}) \qquad \tilde{\gamma} = \gamma - \beta\alpha$$

See A+M for case of fcc lattice.
Here we consider the simpler sc lattice
nn $\vec{R}$ are $\pm a\hat{x}$, $\pm a\hat{y}$, $\pm a\hat{z}$

$\vec{k}\cdot\vec{R}$ are $\pm k_x a$, $\pm k_y a$, $\pm k_z a$

$$\varepsilon_k = E_a - \beta - 2\tilde{\gamma}\,(\cos k_x a + \cos k_y a + \cos k_z a)$$

band width $\varepsilon_k^{max} - \varepsilon_k^{min} = 12\tilde{\gamma}$

for small k, $\cos ka \simeq 1 - \frac{1}{2}k^2a^2$

$$\varepsilon_k \simeq E_a - \beta - 2\tilde{\gamma}\left(3 - \tfrac{1}{2}k_x^2a^2 - \tfrac{1}{2}k_y^2a^2 - \tfrac{1}{2}k_z^2a^2\right)$$

$$\simeq E_a - \beta - 6\tilde{\gamma} + \tilde{\gamma}\, k^2a^2$$

$\Rightarrow$ surfaces of constant energy $\sim k^2$
so are spherical, just like free electrons
(or in weak potential approx if $k$ is not
near any Bragg plane)

effective mass $\quad \frac{1}{2}\frac{\hbar^2 k^2}{m^*} \sim \tilde{\gamma} k^2 a^2$

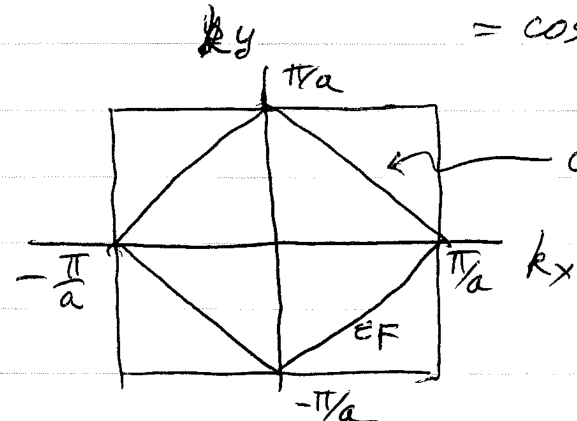
$$\Rightarrow \quad m^* \simeq \frac{\hbar^2}{2\tilde{\gamma}a^2}$$

<u>But at higher $k$</u>

<u>in 2D</u> $\quad \varepsilon_k = E_a - \beta - 2\tilde{\gamma}\,(\cos k_x a + \cos k_y a)$

the curves $k_y = \frac{\pm\pi}{a} \pm k_x$ have constant energy

$$\cos k_x a + \cos(\pm\pi \pm k_x)$$
$$= \cos k_x a + \cos(\pi \pm k_x) = 0$$




const energy surface enclosing $\frac{1}{2}$ area of $1^{st}$ BZ

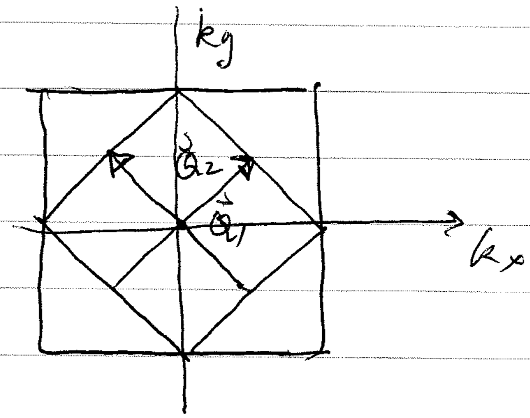
$1^{st}$ BZ

(nested Fermi surface

this will be Fermi surface for $Z=1 \Rightarrow 1$ electron per BL site, so $1^{st}$ BZ is half filled.

So Fermi surface need not be close to spherical!

<u>Nested Fermi surface</u> – when a common wavevector $\vec{Q}$ maps a section of the fermi surface onto another section.

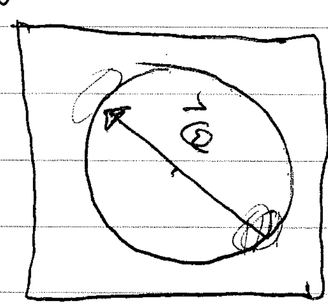



← In this example, $\vec{Q}_1$ takes $\frac{1}{4}$ fermi surface onto opposite surface

⇒ Many electrons at fermi surface can scatter by $\vec{Q}$ with little cost in energy.

system has strong susceptibility with respect to fluctuations at wavevector $\vec{Q}$.

This does <u>not</u> happen for spherical Fermi surfaces




For a fixed wave-vector $\vec{Q}$ as shown, only a small fraction of fermi surface can scatter at little energy cost.

For $\vec{k}$ near $\vec{k}_0 = \pm\frac{\pi}{a}\hat{x} \pm \frac{\pi}{a}\hat{y}$ corner of BZ

$$\vec{k} = \vec{\delta k} + \vec{k}_0$$

$$\varepsilon_k = E_a - \beta - 2\tilde{\gamma}\left(\cos(\pm\pi + \delta k_x a) + \cos(\pm\pi + \delta k_y a)\right)$$

$$= E_a - \beta + 2\tilde{\gamma}\left(\cos \delta k_x a + \cos \delta k_y a\right)$$

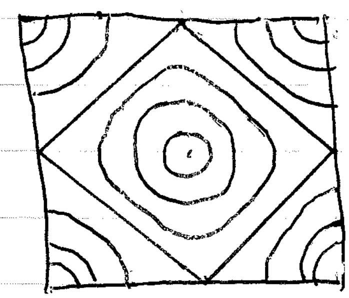
sign is now "+"

$$\simeq E_a - \beta + 2\tilde{\gamma}\left(1 - \tfrac{1}{2}(\delta k_x a)^2 + 1 - \tfrac{1}{2}(\delta k_y a^2)\right)$$

$$= E_a - \beta + 4\tilde{\gamma} - \tilde{\gamma}\,|\delta\vec{k}|^2 a^2$$

depends only on $|\delta\vec{k}|^2$

So constant energy curves are circular about $\vec{k}_0$



← constant energy surfaces

minimum energy of band is at origin $\vec{k} = 0$

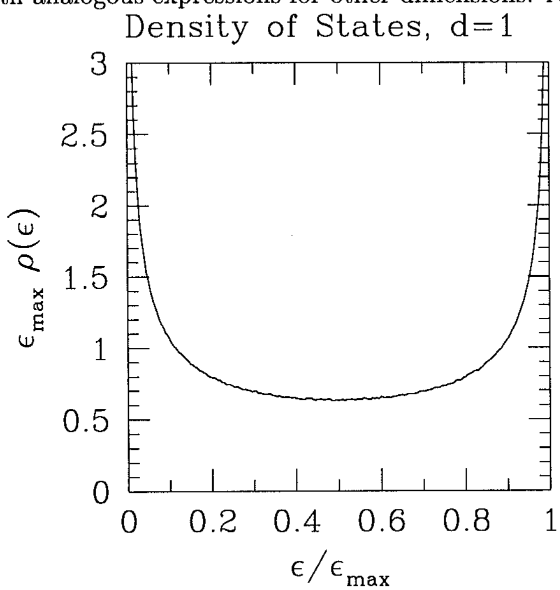
maximum energy of band is at corners $\vec{k}_0 = \pm\frac{\pi}{a}\hat{x} \pm \frac{\pi}{a}\hat{y}$

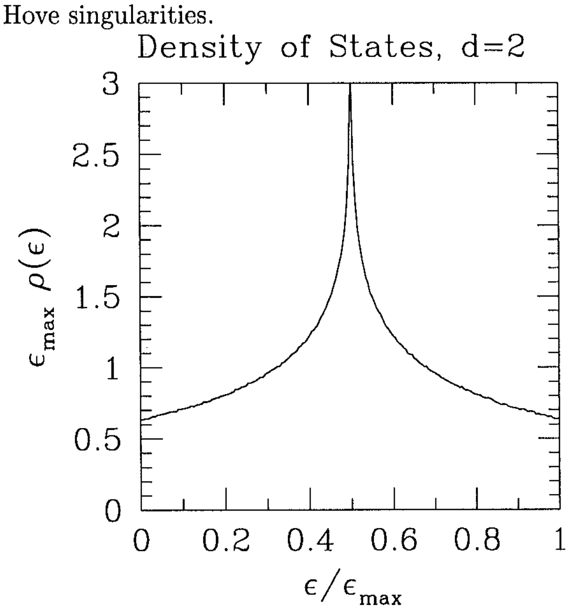
# Tight Binding Density of States

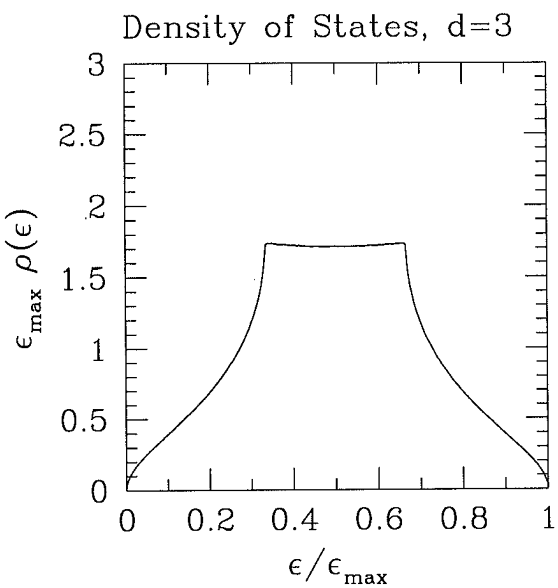
Here are plots of densities of states for the tight-binding Hamiltonian for "cubic" lattices in several dimensions. In three dimensions the energy is given by

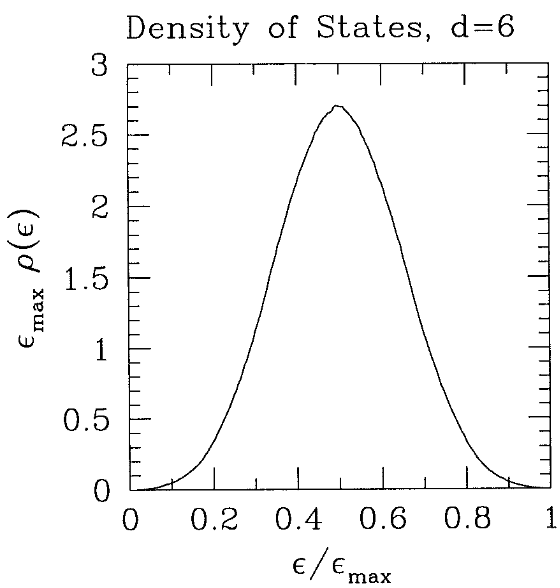
$$\epsilon(k) = t[6 - 2(\cos k_x a + \cos k_y a + \cos k_z a)], \tag{1}$$

with analogous expressions for other dimensions. Note the Van Hove singularities.



What happens in our tight binding model if each ion contributes 2 electrons, ie $Z=2$?

If the width of the s-band $\sim \tilde{\gamma}$ is sufficiently small so that the maximum energy of the s-band is well below the energy of the atomic p-orbital (actually it needs to be below the lowest energy of the p-band computed from the p-orbitals), then the $2N$ electrons will completely fill the $2N$ states of the s-band, leaving the higher p-band empty. The $\vec{k}$ of the 1st BZ of the s-band are all filled and the Fermi surface (the points in $\vec{k}$-space that have the most energetic electrons) will be the discrete points

$$\vec{k}_0 = \pm \frac{\pi}{a}\hat{x} \pm \frac{\pi}{a}\hat{y} \pm \frac{\pi}{a}\hat{z} \qquad \text{(for s.c. BL)}$$

at the corners of the 1st BZ – these are the $\vec{k}$ that gives the largest $\varepsilon(\vec{k})$ for the s-band.

The system is then an <u>insulator</u>, with a <u>finite energy gap</u> between states at the Fermi surface and the lowest unoccupied electron states (in the p-band).