Tight binding method (or linear combination of atomic orbitals)

- Let's generalize the LD approach:

  * Consider Bloch sum:

    atomic orbital of type i

    $$\Phi_{i\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{t}_m} e^{i\vec{k}\cdot\vec{t}_m} \phi_i(\vec{r}-\vec{t}_m)$$

  * Crystal Wavefunction: $$\psi_{\vec{k}}(\vec{r}) = \sum_i c_{i\vec{k}} \Phi_{i\vec{k}}(\vec{r})$$

  * Matrix elements: $M_{ij}(\vec{k}) = \langle \Phi_{i\vec{k}}|H|\Phi_{j\vec{k}}\rangle$

    $S_{ij}(\vec{k}) = \langle \Phi_{i\vec{k}}|\Phi_{j\vec{k}}\rangle$ ← overlaps since ϕ_i's may not be orthonormal!!

  * Secular equation: $\det\left[M_{ij}(\vec{k}) - E\,S_{ij}(\vec{k})\right] = 0$

  * If we know $V(\vec{r})$ and ϕ_i's, we could evaluate matrix elements numerically, we will consider a "semi-emperical" version

- Semi-emperical tight-binding

  * Assume very localized orbitals so overlap between sites is zero, ϕ_i's are orthonormal on the same site.

    • $\Rightarrow S_{ij}(\vec{k}) = \delta_{ij}$

  * Need to solve matrix elements: $\langle\vec{r}|\phi_{j\vec{t}_n}\rangle = \phi_j(\vec{r}-\vec{t}_n)$

    $$M_{ij\vec{k}} = \frac{1}{N} \sum_{\vec{t}_n,\vec{t}_m} e^{i\vec{k}\cdot(\vec{t}_n-\vec{t}_m)} \langle \phi_{i\vec{t}_m}|H|\phi_{j\vec{t}_n}\rangle$$

    Since H is translationally invariant, can always set $\vec{t}_m = 0$:

    $$M_{ij\vec{k}} = \sum_{\vec{t}_n} e^{i\vec{k}\cdot\vec{t}_n} \langle \phi_{i0}|H|\phi_{j\vec{t}_n}\rangle$$ ← Note, sum over $\vec{t}_m$ cancels $\frac{1}{N}$

* Express crystal potential as sum of spherically symmetric atomic-like potentials:

$$H = \frac{\vec{P}^2}{2m} + \sum_{\vec{t}_n} V_a(\vec{r} - \vec{t}_n) \equiv \frac{\vec{P}^2}{2m} + V_a^0(\vec{r}) + \overbrace{\sum_{\vec{t}_n \neq 0} V_a(\vec{r} - \vec{t}_n)}^{V'(\vec{r})}$$

So:

$$M_{ij\vec{k}} = \sum_{\vec{t}_n} e^{i\vec{k}\cdot\vec{t}_n} \int \phi_i^*(\vec{r}) \left[\frac{\vec{P}^2}{2m} + V_a^0(\vec{r}) + V'(\vec{r}) \right] \phi_j(\vec{r} - \vec{t}_n) d^3r$$
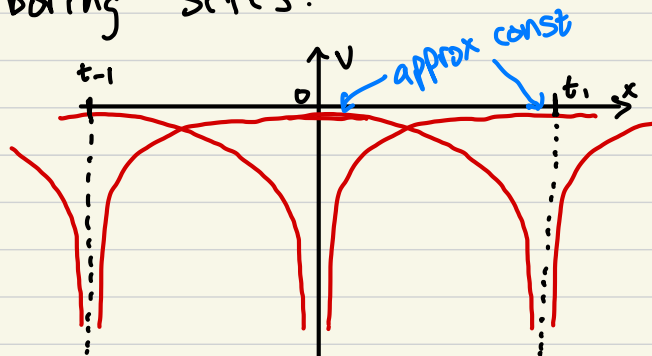
- but $\left(\frac{\vec{P}^2}{2m} + V_a^0 \right) |\phi_i\rangle = E_i |\phi_i\rangle$

So:

$$M_{ij\vec{k}} = E_i \delta_{ij} + \sum_{\vec{t}_n} e^{i\vec{k}\cdot\vec{t}_n} \int \phi_i^*(\vec{r}) V'(\vec{r}) \phi_j(\vec{r} - \vec{t}_n) d^3r$$

- The $\vec{t}_n = 0$ term in the sum is:

$$I_{ij} = \int \phi_i^*(\vec{r}) \underset{\uparrow}{V'(\vec{r})} \phi_j(\vec{r}) d\vec{r} \quad \leftarrow \text{"crystal field" integrals}$$

potential from all other sites

If we assume that $V'(\vec{r})$ decays to a constant at neighboring sites:

Then $I_{ij} = \delta_{ij} \cdot \text{Const}$ is just a rigid energy shift so we can neglect it.

* For $\vec{t}_n \neq 0$, we can consider matrix elements at increasing distances between sites (nearest neighbor, next nearest neighbor, etc.)

- Consider just nearest neighbor coupling:

$$M_{ij\vec{k}} = E_i \delta_{ij} + \sum_{\vec{t}_I} e^{i\vec{k}\cdot\vec{t}_I} \int \phi_i^*(\vec{r}) V_a(\vec{r} - \vec{t}_I) \phi_j(\vec{r} - \vec{t}_I) d^3r$$

↑ —— sum runs over nearest neighbor pairs

Note that only term in the potential that is non zero is $V_a(\vec{r} - \vec{t}_I)$, since all other terms are assumed constant at 0 and $\vec{t}_I$, and ϕ_i's assumed to be orthonormal
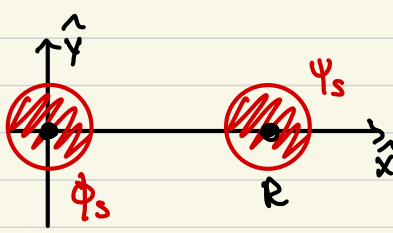
* We can describe these integrals with a small number of parameters

- Say we have s and p_x, p_y, p_z orbitals on lattice sites located at 0 and $\vec{R}$ where (l_x, l_y, l_z) are components of unit vector pointing from 0 to $\vec{R}$.

- We have 4 parameters:

$$\int \phi_s^*(\vec{r}) V_a(\vec{r} - \vec{R}) \psi_s(\vec{r} - \vec{R}) d^3r = V_{ss\sigma}$$
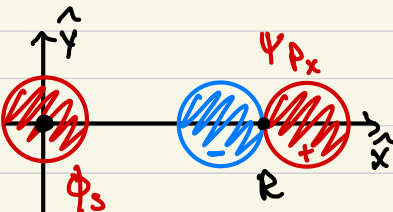
s orbital on one site

Sphereically Symmetric potential

s orbital on NN site

σ bond

$$\int \phi_s^*(\vec{r}) V_a(\vec{r} - \vec{R}) \psi_{p_x}(\vec{r} - \vec{R}) d^3r = l_x V_{sp\sigma}$$
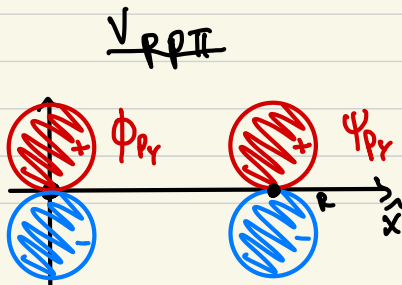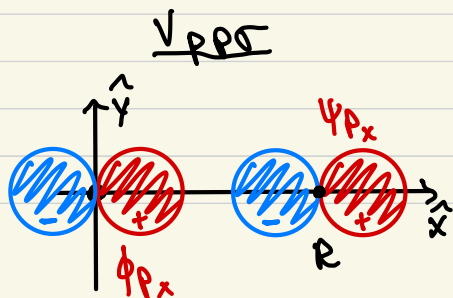
depends on sign of l_x

σ bond

$$\int \phi_{p_x}^*(\vec{r}) V_a(\vec{r} - \vec{R}) \psi_{p_x}(\vec{r} - \vec{R}) d^3r = l_x^2 V_{pp\sigma} + (1 - l_x^2) U_{pp\pi}$$

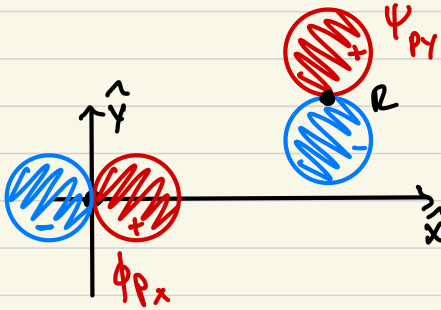component in $\hat{x}$

σ bond

component not in $\hat{x}$

π bond

$\underline{V_{pp\sigma}}$

$\underline{V_{pp\pi}}$

$$\int \phi_{P_x}^*(\vec{r}) \, V_a(\vec{r}-\vec{R}) \, \psi_{P_y}(\vec{r}-\vec{R}) \, d^3r = \ell_x \ell_y \left[V_{PP\sigma} - V_{PP\pi} \right]$$

$$\int \phi_{P_x}^*(\vec{r}) \, V_a(\vec{r}-\vec{R}) \, \psi_{P_z}(\vec{r}-\vec{R}) \, d^3r = \ell_x \ell_z \left[V_{PP\sigma} - V_{PP\pi} \right]$$

ψ_{P_y}

$\hat{y}$

R

$\hat{x}$

ϕ_{P_x}

- And so on permutating Cartesian indicies.

* Example: s and p bands in FCC crystal

- Starting with s-orbitals $\phi_s(\vec{r}-\vec{t}_m)$, Bloch sum is:

$$\Phi_{s\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{t}_m} e^{i\vec{k}\cdot\vec{t}_m} \, \phi_s(\vec{r}-\vec{t}_m)$$

- Assume that these orbitals do not interact w/ p:

$$E_{\vec{k}} = \langle \Phi_{s\vec{k}} | H | \Phi_{s\vec{k}} \rangle$$

$$= E_s + \sum_{\vec{t}_I} e^{i\vec{k}\cdot\vec{t}_I} \int \phi_s^*(\vec{r}) \, V_a(\vec{r}-\vec{t}_I) \, \phi_s(\vec{r}-\vec{t}_I) \, d^3r$$

$$= E_s + V_{ss\sigma} \sum_{\vec{t}_I} e^{i\vec{k}\cdot\vec{t}_I}$$

twelve nearest neighbors in FCC:
$$\frac{a}{2}(0, \pm1, \pm1), \qquad \frac{a}{2}(\pm1, 0, \pm1), \qquad \frac{a}{2}(\pm1, \pm1, 0)$$

So:

$$E_{\vec{k}} = E_s + 4 V_{ss\sigma} \left[\cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right) \cos\left(\frac{k_x a}{2}\right) \right]$$

- In a given direction, looks like our 1D tight binding band.

- How can we plot the dispersion? Choose "high symmetry directions" in 3D BZ, plot 1D lines along those directions.

- First, calculate reciprocal lattice vectors for FCC:

$$\vec{t_1} = \frac{a}{2}(0,1,1) \quad , \quad \vec{t_2} = \frac{a}{2}(1,0,1) \quad \vec{t_3} = \frac{a}{2}(1,1,0) \quad \leftarrow \text{Connecting face-center atoms}$$

Volume of cell: $\Omega = \vec{t_1} \cdot (\vec{t_2} \times \vec{t_3}) = \frac{a^3}{8}(0,1,1) \cdot (1,1,1)$

$$= \frac{a^3}{4}$$

$$\vec{g_1} = \frac{2\pi}{\Omega} \vec{t_2} \times \vec{t_3} = \frac{8\pi a^2}{4a^3}(-1,1,1) = \frac{2\pi}{a}(-1,1,1)$$

$$\vec{g_2} = \frac{8\pi}{a^3} \vec{t_3} \times \vec{t_1} = \frac{2\pi}{a}(1,-1,1)$$

$$\vec{g_3} = \frac{8\pi}{a^3} \vec{t_1} \times \vec{t_2} = \frac{2\pi}{a}(1,1,-1)$$

- Now choose "high symmetry points." For FCC see G and P Sec. II.5:

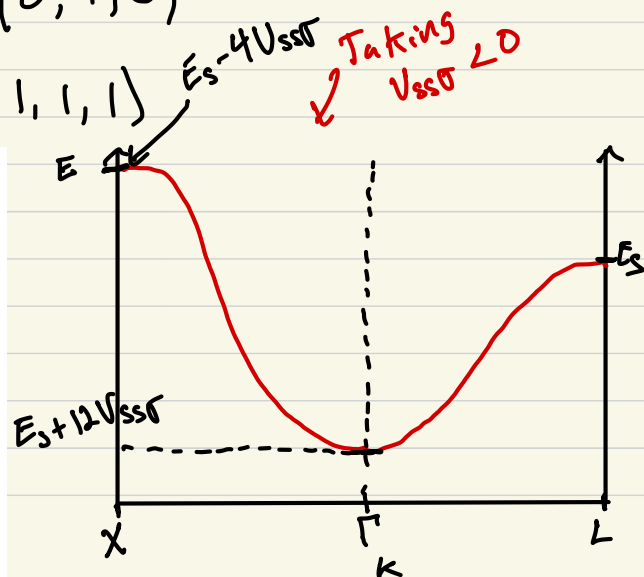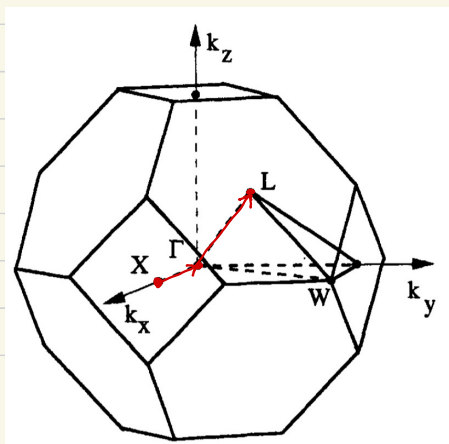$$\Gamma = 0\vec{g_1} + 0\vec{g_2} + 0\vec{g_3} \Rightarrow \vec{k} = (0,0,0)$$

$$X = \frac{1}{2}\vec{g_1} + 0\vec{g_2} + \frac{1}{2}\vec{g_3} \Rightarrow \vec{k} = \frac{2\pi}{a}(0,1,0)$$

$$L = \frac{1}{2}\vec{g_1} + \frac{1}{2}\vec{g_2} + \frac{1}{2}\vec{g_3} \Rightarrow \vec{k} = \frac{\pi}{a}(1,1,1) \quad E_s - 4U_{ss\sigma} \quad \nearrow \text{Taking } U_{ss\sigma} < 0$$

- Path through BZ:
$$X \rightarrow \Gamma \rightarrow L$$
length $\frac{2\pi}{a}$ length $\frac{\sqrt{3}\pi}{a}$

- Now let's consider the p orbitals:

$$\overline{\Phi}_{P_i \vec{k}}(\vec{r}) = \sum_{\vec{t}_m} e^{i\vec{k}\cdot\vec{t}_m} \phi_{P_i}(\vec{r} - \vec{t}_m), \quad P_i = P_x, P_y, P_z$$

- Matrix elements:

$$M_{P_i P_j \vec{k}} = E_{P_i}\delta_{ij} + \sum_{\vec{t}_I} e^{i\vec{k}\cdot\vec{t}_I} \int \phi_{P_i}^*(\vec{r}) \, U_a(\vec{r} - \vec{t}_I) \, \phi_{P_j}(\vec{r} - \vec{t}_I) \, d^3r$$

- Starting with $M_{xx\vec{k}}$ (will work out for ltw)

$$M_{xx\vec{k}} = E_{P_x P_x} + 2\cos\left(\frac{ak_x}{2}\right)\left[\cos\left(\frac{ak_y}{2}\right) + \cos\left(\frac{ak_z}{2}\right)\right]\left(U_{PP\sigma} + U_{PP\pi}\right)$$

$$+ 4\cos\left(\frac{ak_y}{2}\right)\cos\left(\frac{ak_z}{2}\right) U_{PP\pi}$$

- We can permutate indicies to get $M_{yy\vec{k}}$ and $M_{zz\vec{k}}$

- $M_{xy\vec{k}}$ is obtained in a similar way:

$$M_{xy\vec{k}} = -2\sin\left(\frac{ak_x}{2}\right)\sin\left(\frac{ak_y}{2}\right)\left[U_{PP\sigma} - U_{PP\pi}\right]$$

- So we need to solve the secular equation:

$$\det\begin{vmatrix} M_{xx\vec{k}} - E & M_{xy\vec{k}} & M_{xz\vec{k}} \\ M_{xy\vec{k}}^* & M_{yy\vec{k}} - E & M_{yz\vec{k}} \\ M_{xz\vec{k}}^* & M_{yz\vec{k}}^* & M_{zz\vec{k}} - E \end{vmatrix} = 0$$

- Take $U_{PP\sigma} > 0$, $U_{PP\pi} < 0$, $|U_{PP\sigma}| \gg |U_{PP\pi}|$, plot on the same path as s: $X \to \Gamma \to L$

Two-fold degenerate

$E_P + 4U_{PP\sigma} + 8U_{PP\pi}$

$E_P - 4U_{PP\pi}$

$E_P - 4U_{PP\sigma}$

$E_P + 2U_{PP\sigma} - 2U_{PP\pi}$

$E_P - 4U_{PP\sigma} + 4U_{PP\pi}$

X   Γ   L