## Methods for describing bands in 3D (G and P Chapter V)

- We consider now one electron in a 3D periodic potential:

$$\left[\frac{\vec{p}^2}{2m} + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \quad , \quad V(\vec{r}+\vec{t}_n) = V(\vec{r})$$

* We will focus mainly on simple lattices (no basis)
* We will usually assume we have a given, fixed, local crystal potential
* We will consider several methodologies to get electronic structure of crystals, many are generalizations of 1D ☺

# Tight binding method (or linear combination of atomic orbitals)

- Let's generalize the 1D approach:

  * Consider Bloch sum:

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

($\phi_i$: atomic orbital of type $i$)

  * 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 $\phi_i$'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 $\phi_i$'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, $\phi_i$'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 alway 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:

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

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:

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

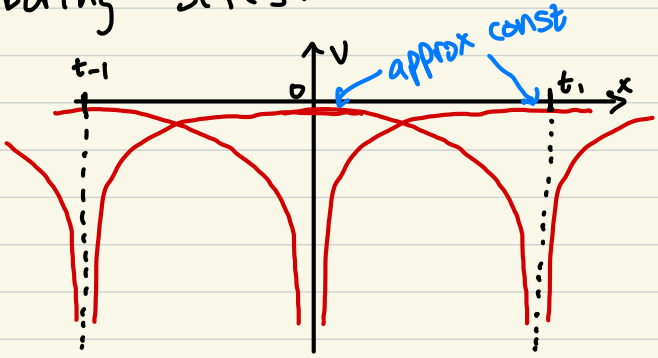
- The $\vec{t}_n = 0$ term in the sum is:

$$I_{ij} = \int \phi_i^*(\vec{r}) \, V'(\vec{r}) \, \phi_j(\vec{r}) \, d\vec{r}$$

← "crystal field" integrals

↑ potential from all other sites

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




Then $I_{ij} = \delta_{ij} * \text{Const}$ 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 nonzero is $V_a(\vec{r}-\vec{t}_I)$, since all other terms are assumed constant at 0 and $\vec{t}_I$, and $\phi_i$'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 $\vec{R}$.

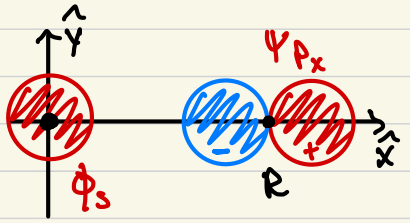
- We have 4 parameters:

$$\int \phi_s^*(\vec{r})\, V_a(\vec{r}-\vec{R})\, \psi_s(\vec{r}-\vec{R})\, d^3r = V_{ss\sigma}$$

↑ s orbital on one site; ↑ spherically symmetric potential; ↑ s orbital on NN site; ↑ σ bond


$$\int \phi_s^*(\vec{r})\, V_a(\vec{r}-\vec{R})\, \psi_{px}(\vec{r}-\vec{R})\, d^3r = l_x V_{sp\sigma}$$

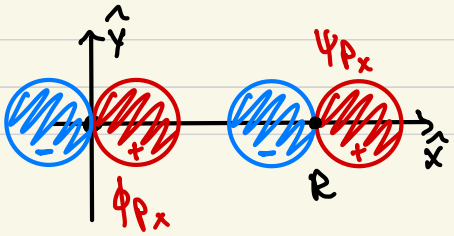
σ bond ↓; ↑ depends on sign of $l_x$



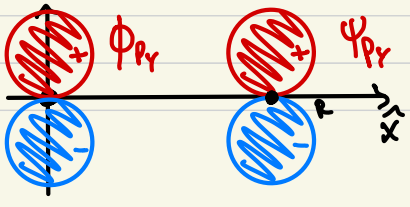

$$\int \phi_{p_x}^*(\vec{r})\, V_a(\vec{r}-\vec{R})\, \psi_{px}(\vec{r}-\vec{R})\, d^3r = l_x^2 V_{pp\sigma} + (1-l_x^2) V_{pp\pi}$$

↑ component in $\hat{x}$; ↑ σ bond; ↑ component not in $\hat{x}$; ↑ π bond

$V_{pp\sigma}$



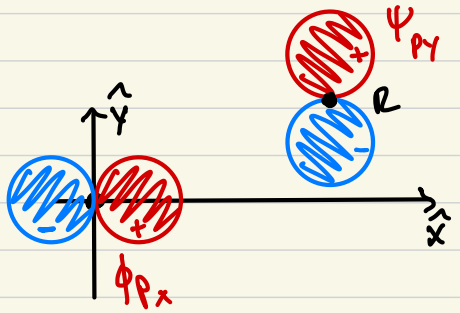

$V_{pp\pi}$



need both $l_x$ and $l_y$ to be nonzero

$$\int \phi_{p_x}^*(\vec{r})\, V_a(\vec{r}-\vec{R})\, \psi_{p_y}(\vec{r}-\vec{R})\, d^3r = l_x l_y \left[V_{pp\sigma} - V_{pp\pi}\right]$$

$$\int \phi_{p_x}^*(\vec{r})\, V_a(\vec{r}-\vec{R})\, \psi_{p_z}(\vec{r}-\vec{R})\, d^3r = l_x l_z \left[V_{pp\sigma} - V_{pp\pi}\right]$$




- And so on permutating Cartesian indices.

* 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:

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

$$= E_s + \sum_{\vec{t}_I}{}' e^{ik\cdot\vec{t}_I} \int \phi_s^*(\vec{r})\, V_a(\vec{r}-\vec{t}_I)\, \phi_s(\vec{r}-\vec{t}_I)\, d^3r$$

$$= E_s + V_{ss\sigma} \sum_{\vec{t}_I}{}' e^{ik\cdot\vec{t}_I}$$

twelve nearest neighbors in FCC:

$$\frac{a}{2}(0,\pm1,\pm1), \quad \frac{a}{2}(\pm1,0,\pm1), \quad \frac{a}{2}(\pm1,\pm1,0)$$

So:

will work out for HW

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

- 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:

$\vec{t}_1 = \frac{a}{2}(0,1,1)$, $\vec{t}_2 = \frac{a}{2}(1,0,1)$ $\vec{t}_3 = \frac{a}{2}(1,1,0)$ ← 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:

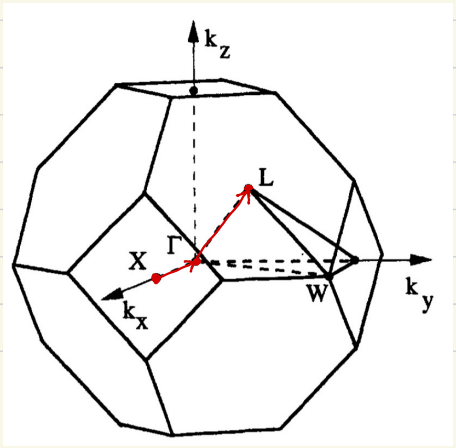
$\Gamma = 0\vec{g}_1 + 0\vec{g}_2 + 0\vec{g}_3 \Rightarrow \vec{k} = (0,0,0)$

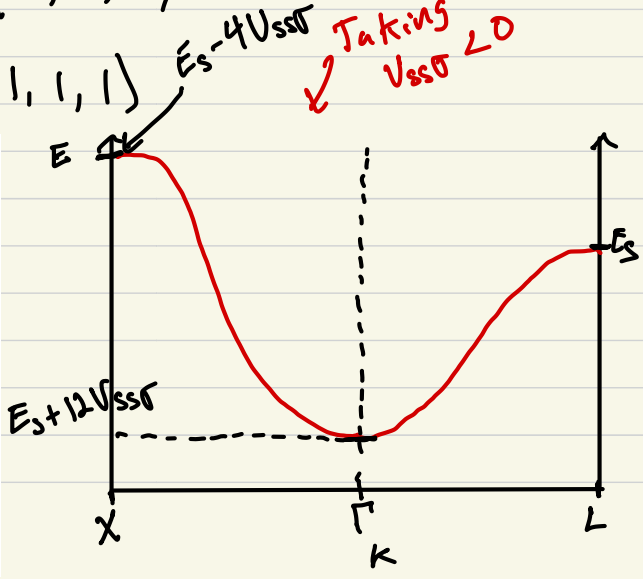
$X = \frac{1}{2}\vec{g}_1 + 0\vec{g}_2 + \frac{1}{2}\vec{g}_3 \Rightarrow \vec{k} = \frac{2\pi}{a}(0,1,0)$

$L = \frac{1}{2}\vec{g}_1 + \frac{1}{2}\vec{g}_2 + \frac{1}{2}\vec{g}_3 \Rightarrow \vec{k} = \frac{\pi}{a}(1,1,1)$

- Path through BZ: $X \rightarrow \Gamma \rightarrow L$

length $\frac{2\pi}{a}$ ↑ length $\frac{\sqrt{3}\pi}{a}$ ↑



- Now lets consider the p orbitals:

$$\Phi_{p_i \vec{k}}(\vec{r}) = \sum_{\vec{t}_m} e^{i\vec{k}\cdot\vec{t}_m}\, \phi_{p_i}(\vec{r} - \vec{t}_m), \quad p_i = p_x, p_y, p_z$$

- Matrix elements:

$$M_{p_i p_j \vec{k}} = E_p \delta_{ij} + \sum_{\vec{t}_I} e^{i\vec{k}\cdot\vec{t}_I} \int \phi^*_{p_i}(\vec{r})\, U_a(\vec{r} - \vec{t}_I)\, \phi_{p_j}(\vec{r} - \vec{t}_I)\, d^3r$$

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

$$M_{xx\vec{k}} = E_p + 2\cos\left(\frac{ak_x}{2}\right)\left[\cos\left(\frac{ak_y}{2}\right) + \cos\left(\frac{ak_z}{2}\right)\right](V_{pp\sigma} + V_{pp\pi}) + 4\cos\left(\frac{ak_y}{2}\right)\cos\left(\frac{ak_z}{2}\right)V_{pp\pi}$$

- 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:

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

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