Tight Binding II : LCAO

LCAO = Linear combination of atomic orbitals

→ In the previous lecture we studied the T.B model in the cases in 1D, 2D and 3D where we have only 1 atom per unit cell. The solution is a Bloch sum of the form

$$\Phi_n(r) = \frac{1}{\sqrt{N}} \sum_n e^{i k \vec{R}_n} \psi(r - \vec{R}_n)$$

1 orbital in the basis
(ex 1s orbital of H)

1 atom per unit cell

→ What if we have more than 1 atom per unit cell like in the honeycomb lattice or ZnS (Zinc blend) or diamond? Or, what if each atom contributes with more than 1 orbital (sp, sp^2, sp^3 hybridization)? Or all of the above!
(more than 1 atom per unit cell, more than 1 orbital per atom).

1- Simple case : ZnS , 2 atoms/uc , but each
with only 1 orbital (ex S orbital)

$\longrightarrow$ 2 Bloch sums :
$$\overline{\Phi}^1_\mu(r) = \frac{1}{\sqrt{N}} \sum_n e^{iKR_n} \phi_1(r - R_0 - R_n)$$

$\vec{R}_0 = (0,0,0)$

$$\overline{\Phi}^2_\mu(r) = \frac{1}{\sqrt{N}} \sum_n e^{iKR_n} \phi_2(r - R_1 - R_n)$$

$\vec{R}_1 = \frac{a}{4}(1,1,1)$

$\longrightarrow$ The crystal W.F will be a linear
combination of $\overline{\Phi}^1_K(r)$, $\Phi^2_K(r)$ (like we did in H_2^+ problem !)

$$\Psi = \alpha \Phi^1_\mu + \beta \Phi^2_\mu \quad \text{with} \begin{cases} \langle \Phi^1_n | H | \Phi^1_n \rangle = H^{11} \\ \\ \langle \Phi^2_n | H | \Phi^2_n \rangle = H^{22} \\ \\ \langle \Phi^2_n | H | \Phi^1_n \rangle = \langle \Phi^1_K | H | \Phi^2_n \rangle^* \\ \quad = H_{12} \end{cases}$$

$\longrightarrow$ Scalar eq :
$$\det \begin{bmatrix} H^{11} - E(n) & H^{12} \\ H^{21} & H^{22} - E(n) \end{bmatrix} = 0$$

$H_{11} = E_S^1$; $H_{22} = E_S^2$ $\longrightarrow$ No k dependance , No NN of same atom !

$$H_{21} = -t \left(e^{iKd_1} + e^{iKd_2} + e^{iKd_3} + e^{iKd_4} \right) = H_{12}$$

with $d_1 = \frac{a}{4}(1,1,1)$, $d_2 = \frac{a}{4}(1,\bar{1},\bar{1})$ ← Vectors T.

$d_3 = \frac{a}{4}(\bar{1},1,\bar{1})$; $d_4 = \frac{a}{4}(\bar{1}\bar{1}1)$ &N.N

· General Theory for LCAO Method in crystals.

→ In general, crystal with ℓ atoms in the basis.

$$r_{j,\ell} = R_j + R_\ell \qquad R_j \rightarrow j\text{th primitive cell}$$

$R_\ell \rightarrow$ position of atom ℓ of the basis in UC.

$h_\ell (r) \rightarrow$ Hamiltonian for isolated atom ℓ with it's nucleus at the origin.

$$h_\ell \, \phi_{m,\ell} (r - r_{j,\ell}) = E_{m\ell} \, \phi_{m,\ell} (r - r_{j\ell}) \quad \begin{cases} E_m & \text{Corresponding} \\ \phi_m & \text{to atomic} \\ & \text{orbital } m \end{cases}$$

Note : $\langle \phi_{m\ell} | \phi_{m\ell'} \rangle = \delta_{\ell,\ell'}$

$H = H_{aT} + H_{inT}$; $H_{inT} \rightarrow$ very small $\Rightarrow$ we diagonalize H using perturbation Th.

$\rightarrow$ The crystal unperturbed Hamiltonian :

$$H_o = \sum_{j,\ell} h_\ell (r - r_{j,\ell})$$

$\rightarrow$ The unperturbed WF will be Bloch sums of the atomic W.F

$$\Phi_{m,\ell,k} = \frac{1}{\sqrt{N}} \sum_j e^{ik \cdot r_j} \Phi_{m,\ell} (r - r_{j,\ell})$$

$\longrightarrow$ The eigenfunctions Ψ_k of H $\left(H = H_o + H_{int} \right)$ can be written as L.C of $\Phi_{m,k,\ell}$

$$\Rightarrow \Psi_k = \sum_{m\ell} C_{m,\ell} \, \Phi_{m,\ell,k}$$

To calculate the eigenfunctions & eigenvectors of H we solve variationally

$$\frac{\langle \Psi_n | H | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} = \langle E \rangle$$

same as usual, like H_2^+

We make use of The fact That Bloch fns are
orThogonal, and arrive aT The secular equation.

$$\sum_{m\ell} \left(H^{m\ell}_{m'\ell'} - E_k \, \delta_{mm'} \, \delta_{\ell\ell'} \right) C_{m'\ell'}(k) = 0$$

only if all overlaps are zero,
otherwise we carry overlap matrix

↓

Secular eq.

* Matrix elements $\quad H^{m\ell}_{m'\ell'} \equiv \langle \bar{\Phi}_{m,\ell,k} | H | \bar{\Phi}_{m'\ell';k} \rangle$

↓

Size of This matrix $(M \times P) \times (M \times P)$

$m = 1 \dots M$ (# of orbitals per aTom)

$\ell = 1 \dots P$ (# of aToms in The basis)

if we know $V(r)$ and $\Phi_{m,\ell}$ we could evaluate The
matrix elements numerically (inTegrals in a 3D grid)
but we will consider a "semi-empirical" version
(assume The inTegrals To be parameters, in a fiT of ex Band strucTure)

Assumptions in Semiempirical TB:

→ very localized orbitals, so overlap is zero $S_{(k)\,m'\ell'}^{m\ell} = \delta_{(k)\,m,m'}^{\ell\ell'}$

* Matrix elements:

$$H_{m'\ell'}^{m\ell}(k) = \sum_{j=1}^{N}\sum_{j'=0}^{N} \frac{1}{N} e^{i(r_{j\ell}-r_{j'\ell'})k} \langle \phi(r-r_{j\ell})|H|\phi(r-r_{j'\ell'})\rangle_{m'\ell'}$$

$$= \sum_{j=0}^{N} e^{i(R_j + r_\ell - r_{\ell'})k} \langle \phi(r-r_\ell)|H|\phi(r-r_{j,\ell'})\rangle$$
$$\underbrace{\phantom{i(R_j + r_\ell - r_{\ell'})}}_{r_{\ell\ell'}} \quad me \quad m'\ell'$$

* In This step we Have eliminated $\sum_{j'=1}^{N}$ using The TranslaTional symm of The lattice, putting $\bar{R}_{j'} = 0$ always aT The origin, This sum gives a factor N which cancels The $\frac{1}{N}$.

* The sum $\sum_{j}$ runs over first N.N only (in general)

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

$$H = \frac{-\hbar^2}{2m} \nabla^2 + \sum_j V_a(r - R_j) = h_o + \overbrace{\sum_{j \neq 0} V_a(r - r_j)}^{V'(r)}$$

So:
$$H(k)_{m'\ell'}^{m\ell} = \sum_j e^{ik(\vec{R}_j - \vec{r}_{\ell\ell'})} \int \phi_{m,\ell}(r - r_\ell) \left[h_o + V'(r) \right] \phi_{m',\ell'}(r - r_\ell - R_j)$$

$$= E_j \, \delta_{m'\ell'}^{m\ell} + \sum_j e^{ik(\vec{R}_j - \vec{r}_{\ell\ell'})} \int \overbrace{\phi_{m\ell}(r) \, V'(r) \, \phi_{m,\ell'}(r - r_\ell - R_j)}^{I_{m\ell}^{m'\ell'}(j)} \, d^3r$$

.   .   .
.   .
.   .

$$I_{m\ell}^{m'\ell'}(j) = \int \phi_{\ell m\ell}(r) \, V'(r) \, \phi_{m'\ell'}(r - r_\ell) \quad \leftarrow \text{ "crystal-field integrals"}$$

potential from all
other sites

✳ for $R_j = 0$ ⇒ interaction within the u. cell, 1ˢᵗ NN for a lattice with basis

✳ for $R_j \neq 0$ we can consider N.N, 2nd NN...
(NN only coupling here) → in a lattice with basis $R_j = 1$ iₜₒ 2nd NN

$$H^{m\,\ell}_{m'\ell'}(k) = E_m \, \delta^{\ell\ell'}_{mm'} + \sum_{r_{NN}} e^{ik\,r_{NN}} \int \phi_{m\ell}(\vec{r}-\vec{\rho}) \, V_a(r-\sigma_{nn}) \, \phi_{m'\ell'}(r-r-\sigma_m)$$

↑ sum runs over NN only

→ We can describe these integrals with a smaller number of parameters.

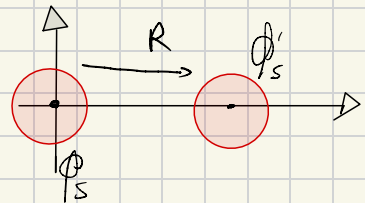- Say we have $s, p_x p_y p_z$ orbitals at $(0,0,0)$
  and $\vec{R}$

$$\vec{R} = (\ell_x, \ell_y, \ell_z) \to \text{components of unit vectors}$$
from 0 to R

- We have 4 parameters:

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

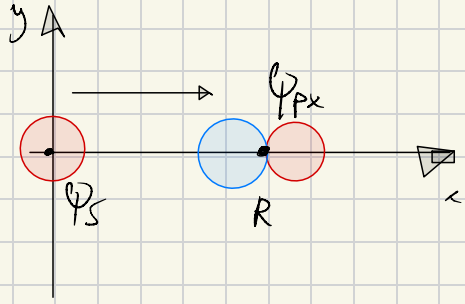s orbital on site (0,0,0)   spherically symm. potential   s orbital at $\vec{R}$

$\downarrow$
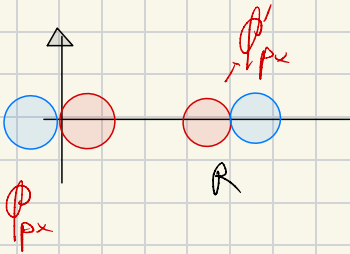
sigma bond

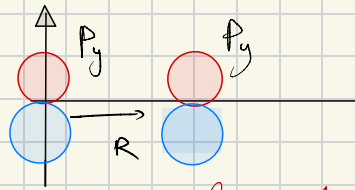$$\int \phi_s^*(r) \, V_a \, \phi_{px}(r-R) = l_x \, V_{sp\sigma}$$

depends on The
sign of l_x

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

component in $\hat{x}$ component not in $\hat{x}$ π Bond

$V_{pp\sigma}$

$V_{pp\pi}$

need both l_x, l_y to be non zero.

$$\int \phi_{px}^*(r) \, V_a \, \phi_{py}(r-R) \, d^3r = l_x \, l_y \, [V_{pp\sigma} - V_{pp\pi}]$$

$$\int \phi_{px}^*(r) \, V_a \, \phi_{pz}(r-R) = l_x \, l_z \, [V_{pp\sigma} - V_{pp\pi}]$$

• And so on permuting cartesian indices

* Example s & p orbitals in FCC crystal. (1 atom/u cell)

• Start with s orbitals, Bloch sum is:

$$\phi_{s,k} = \frac{1}{\sqrt{N}} \sum_{R_j} e^{i k R_j} \phi_s (r - R_j) \quad \left(\text{with atom at origin}\right)$$

$$E_n = \langle \phi_{k,s} | H | \phi_{k,s} \rangle = E_s + \sum_{NN} e^{i k r_{NN}} \int \phi_s (r) V_a \phi_s (r - r_{NN})$$

$$= E_s + V_{ss\sigma} \sum_{NN} e^{i k r_{NN}}$$

Twelve N.N in FCC

$$\frac{a}{2} (0, \pm 1, \pm 1) ; \quad \frac{a}{2} (\pm 1, 0, \pm 1) ; \quad \frac{a}{2} (\pm 1, \pm 1, 0)$$

So :

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

• In a given direction looks like the 1D TB band.

• How can we plot the dispersion? choose "high symmetry"
directions in 3D BZ, plot 1D lines along these directions

• First calculate R.L.V for FCC

$$a_1 = \frac{a}{2}(0,1,1) \quad ; \quad a_2 = \frac{a}{2}(1,0,1) \quad ; \quad a_3 = \frac{a}{2}(1,1,0)$$

$$\vec{R}_j = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$V_{cell} = \frac{V_{cube}}{4} = \frac{a^3}{4}$$

$$b_1 = \frac{2\pi}{a}(-1,1,1)$$

$$b_2 = " \quad (1,-1,1)$$

$$b_3 = " \quad (1,1,-1)$$

• Now choose High Sym. Points for FCC (see website
or G.P book sec II.5)

$$\Gamma = (0,0,0) \rightarrow \vec{k} = (0,0,0)$$

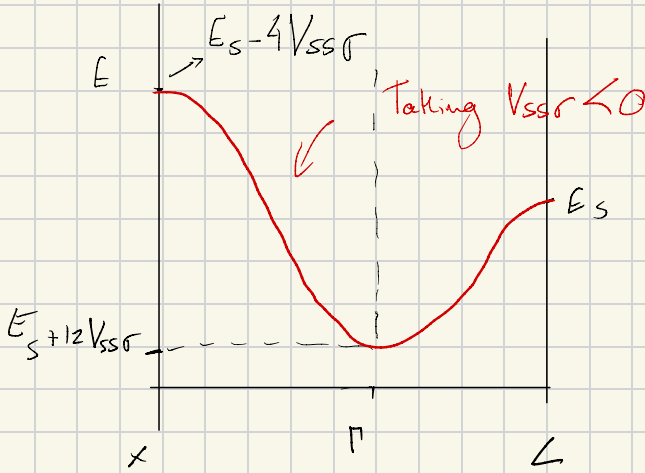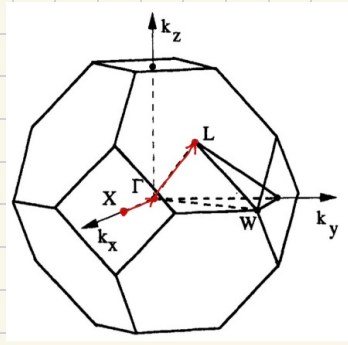$$X = \frac{1}{2}b_1 + 0b_2 + \frac{1}{2}b_3 \Rightarrow \vec{k} = \frac{2\pi}{a}(0,1,0)$$

$$L = \frac{1}{2}b_1 + \frac{1}{2}b_2 + \frac{1}{2}b_3 \Rightarrow \vec{k} = \frac{\pi}{a}(1,1,1)$$

- Path Through BZ

$$x \rightarrow \Gamma \rightarrow L$$

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

E $E_s - 4V_{ss\sigma}$

Taking $V_{ss\sigma} < 0$

E_s

$E_s + 12 V_{ss\sigma}$

X Γ L

- Now let's consider the p orbitals

$$\Phi_{p_i, n}(r) = \frac{1}{\sqrt{N}} \sum_{R_n} e^{i\vec{k}\cdot\vec{R}_n} \phi_{p_i}(r - R_n) \qquad p_i = x, y, z$$

(and only 1 atom in unit cell).

- Matrix elements:

$$H_{P_i, P_j}^{(k)} = E_p \delta_{ij} + \sum_{nn} e^{i k \vec{R}_{nn}} \int \phi_{P_i}^{\vec{*}}(r) V_a \phi_{P_j}(r - R_{nn}) d^3r$$

- Starting with $H_{xx}(k)$

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

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

- We can permutate indices to get H_{yy} and H_{33}

- H_{xy} is obtained in a similar way

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

So we need to solve the secular eq:

$$\det \begin{vmatrix} H_{xx}^k - E & H_{xy}^k & H_{x3}^k \\ H_{xy}^{*k} & H_{yy}^k - E & H_{y3}^k \\ H_{x3}^{*k} & H_{y3}^{*k} & H_{33}^k - E \end{vmatrix} = 0$$

• Take $V_{pp\sigma} > 0$, $V_{pp\pi} < 0$ $|V_{pp\sigma}| \gg |V_{pp\pi}|$

$\rightarrow$ plot on same path as S

Two fold degenerate

$E_p + 2V_{pp\sigma} - 2V_{pp\pi}$

$E_p - 4V_{pp\sigma} + 4V_{pp\pi}$

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