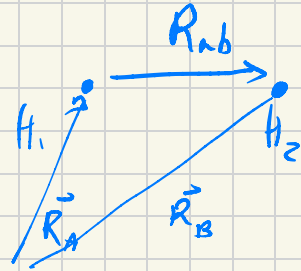



Tight Binding Model

1. Basic Recap of Molecular Tight Binding Hamiltonian:

H_2^+ molecule Hamiltonian:

$$H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R_{AB}}$$



The WF of the system is a linear combination of 2 1s orbitals

$$\begin{cases} |\phi_A\rangle = \text{s orbital of atom A} \\ |\phi_B\rangle = \text{" " " " B} \end{cases}$$

$$|\psi\rangle = C_A |\phi_A\rangle + C_B |\phi_B\rangle$$

→ Calculate C_A, C_B using the variational Th:

$$\langle E \rangle = \min_{\{C_A, C_B\}} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{C_A^2 H_{AA} + C_B^2 H_{BB} + 2 C_A C_B H_{AB}}{C_A^2 \cancel{S_{AA}} + 2 C_A C_B S_{AB} + C_B^2 \cancel{S_{BB}}}$$

with $\langle \phi_A | H | \phi_A \rangle = H_{AA}$ (and the others equally)

$$\left. \left(\frac{\partial \langle E \rangle}{\partial C_A} \right) \right|_{C_B} = 0 \rightarrow C_A (H_{AA} - \langle E \rangle) + C_B (H_{AB} - S_{AB} \langle E \rangle) = 0$$

$$\left. \left(\frac{\partial \langle E \rangle}{\partial C_B} \right) \right|_{C_A} = 0 \rightarrow C_A (H_{AB} - S_{AB} \langle E \rangle) + C_B (H_{BB} - \langle E \rangle) = 0$$

Secular equations

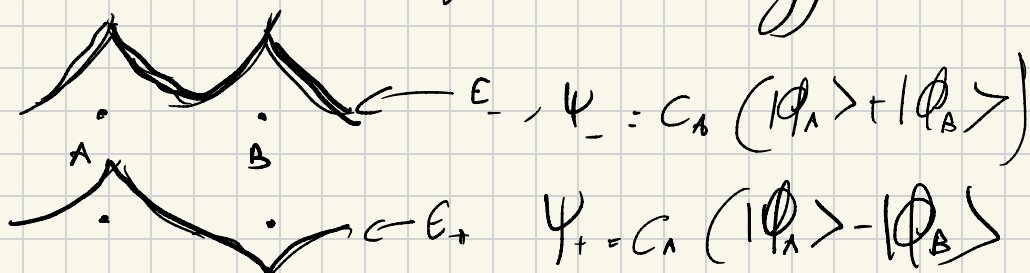
$$\det [H - ES] = 0 \Rightarrow \begin{vmatrix} H_{AA} - \langle E \rangle & H_{AB} - S_{AB} \langle E \rangle \\ H_{BA} - S_{BA} \langle E \rangle & H_{BB} - \langle E \rangle \end{vmatrix} = 0$$

$$E_{\pm} = \frac{H_{AA} + H_{BB}}{1 \pm S}$$

← with $H_{AA} = H_{BB}$ = onsite term
and S_{AB} = overlap (= 1 if orthogonal basis)

$$C_{A\pm} = \mp C_{B\pm}$$

⊕ → excited state (antibonding)
⊖ → ground state (bonding)

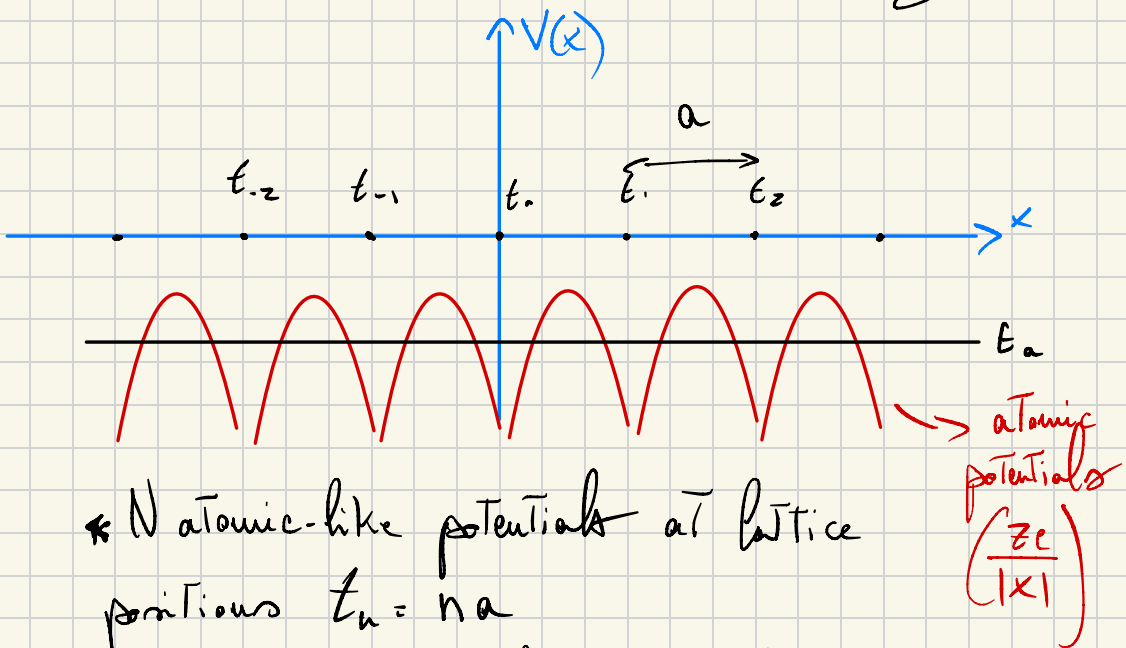


Tight Binding Model in periodic crystals

- Most simple case: 1D, identical atoms

* When a (lat. constant) is large $a \gg r_{at}$
atoms are far apart \rightarrow No interactions,
recover atomic energy levels. (all degenerate)

* Closer $a \rightarrow \neq 0 - z + r_{at} \rightarrow$ interacting \rightarrow bands



* N atomic-like potentials at lattice positions $x_n = na$

* ϕ_a is the orbital of a single atom (ex 1s orbital of H). With energy E_a (when atom isolated)
 \rightarrow We assume ϕ are real, and non degenerate.

atomic potentials
 $\left(\frac{ze}{|x|} \right)$

→ We will use the basis $\{\phi_a(x-t_n)\}$ to build the crystal w.f

→ Note this is an incomplete basis set!

→ Assume ϕ_a 's are orthonormal

$$\langle \phi_a^{t_n} | \phi_a^{t_m} \rangle = \delta_{m,n} \quad \left[\text{notation } \langle x | \phi_a^{t_n} \rangle = \phi(x-t_n) \right]$$

* Write crystal Hamiltonian in the basis of atomic orbitals

$$\langle \phi_a^{t_n} | H | \phi_a^{t_n} \rangle = E_0 \quad \leftarrow \text{on-site energy}$$

$$\langle \phi_a^{t_n} | H | \phi_a^{t_{n \pm 1}} \rangle = \gamma \quad \leftarrow \begin{array}{l} \gamma(a), \text{ depends on lattice constant} \\ \text{negative, } \gamma < 0; \\ \text{nearest neighbors hopping} \end{array}$$

$$\langle \phi_a^{t_n} | H | \phi_a^{t_m} \rangle = 0 \quad \text{if } |m-n| > 1$$

• What is H ? $H = H_{\text{at}} + \Delta U(r)$, where $\Delta U(r)$ contains all the corrections to the atomic potential necessary to recover the full periodic potential of the system.

* We know The potential is periodic. The solution has to be a Bloch state. We can build a Bloch WF in The basis of atomic orbitals:

$$\underline{\Phi}_{\vec{k}}(x) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}t_n} \phi_a(x-t_n)$$

• Let's prove These satisfy Bloch's Th.

$$\underline{\Phi}_{\vec{k}}(x+t_m) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}t_n} \phi_a(x+t_m-t_n)$$

→ multiply by $t = e^{i\vec{k}t_m} e^{-i\vec{k}t_m}$ $\tilde{t}_n = t_n - t_m$ (a L.V.)

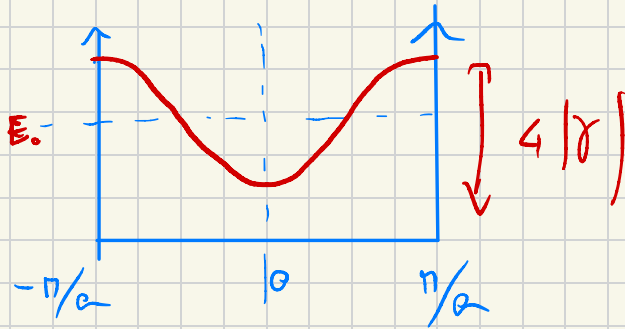
$$= \frac{1}{\sqrt{N}} e^{i\vec{k}t_m} \sum_n e^{i\vec{k}(t_n - t_m)} \phi_a(x - (t_n - t_m)) =$$

$$= \frac{1}{\sqrt{N}} e^{i\vec{k}t_m} \underline{\Phi}_{\vec{k}}(x) \quad \text{Q.E.D}$$

* Note: Bloch sums w/ different \vec{k} are orthonormal!

→ Energy dispersion of Band: $E(\vec{k}) = \langle \underline{\Phi}_{\vec{k}} | H | \underline{\Phi}_{\vec{k}} \rangle$

$$E(k) = E_0 - \gamma e^{ika} - \gamma e^{-ika} = E_0 + 2\gamma \cos(ka)$$



* Expand to 2nd order around $k=0$

$$E(k) \approx E_0 + 2\gamma - \gamma a^2 k^2 = E_0 + 2\gamma - \frac{\hbar^2 k^2}{2m^*}$$

Where effective mass $m^* = \frac{\hbar^2}{2|\gamma|a^2}$ ← larger hopping, smaller effective mass

- Tight-Binding Hamiltonian as an operator:

$$\hat{H} = E_0 \sum_n |\phi^n\rangle \langle \phi^n| + \gamma \sum_n [|\phi^n\rangle \langle \phi^{n+1}| + |\phi^{n+1}\rangle \langle \phi^n|]$$

* Using our Bloch sum $|\Phi_k\rangle = \frac{1}{\sqrt{N}} \sum_m e^{ikt_m} \phi(x-t_m)$

we can calculate the dispersion:

$$\begin{aligned} \hat{H}|\Phi_k\rangle &= \frac{1}{\sqrt{N}} \sum_m e^{ikt_m} \left[E_0 \sum_n |\phi^n\rangle \langle \phi^n | \phi^m \rangle \right. \\ &\quad \left. + \gamma \sum_n \left(|\phi^n\rangle \langle \phi^{n+1} | \phi^m \rangle + |\phi^{n+1}\rangle \langle \phi^n | \phi^m \rangle \right) \right] \\ &= \frac{1}{\sqrt{N}} \sum_m e^{ikt_m} \left(E_0 |\phi^m\rangle + \gamma [|\phi^{m-1}\rangle + |\phi^{m+1}\rangle] \right) \\ &= E_0 |\Phi_k\rangle + \gamma \left(e^{-ika} + e^{ika} \right) |\Phi_k\rangle = \\ &= [E_0 + 2\gamma \cos(ka)] |\Phi_k\rangle \end{aligned}$$

* In the $|\phi_n\rangle = |\phi(x-t_n)\rangle$ basis, we can write \hat{H} as a $N \times N$ matrix (assume γ is real).

ex : 4x4 :

$$\begin{bmatrix} E_0 & \gamma & 0 & 0 \\ \gamma & E_0 & \gamma & 0 \\ 0 & \gamma & E_0 & \gamma \\ 0 & 0 & \gamma & E_0 \end{bmatrix} \leftarrow \text{Tridiagonal matrix}$$

• many physics problems can be expressed as a Tridiagonal matrix

• most general form :

$$m = \begin{bmatrix} \alpha_0 & \beta_1 & 0 & \dots & \dots \\ \beta_1 & \alpha_1 & \beta_2 & & \\ 0 & \beta_2 & \alpha_2 & \beta & \\ \vdots & & \beta_3 & \alpha_3 & \end{bmatrix} \leftarrow \text{assume } m \text{ is large but finite}$$

* Suppose we would like to determine $\left(\frac{1}{m}\right)_{00}$ ← Top left element of m^{-1}
 (We will see why later)

$$\left(\frac{1}{m}\right)_{00} = \frac{1}{\alpha_0 - \frac{\beta_1^2}{\alpha_1 - \frac{\beta_2^2}{\alpha_2 - \frac{\beta_3^2}{\alpha_3 - \dots}}}} \leftarrow \text{(for } n \text{ in positive or negative directions)}$$

See Gross-Parav.

Sec I.4.2

"Continued fractions"

→ From 1D To 3D

* Still 1 orbital per atom.

Bloch orbital (same but now $\vec{t}_n \rightarrow \vec{R}_n$
 $x \rightarrow r$)

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

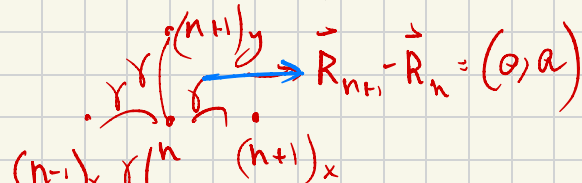
For the dispersion $E(k)$ now we have $\vec{k} = (k_x, k_y, k_z)$
 (Same as $\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$)

Ex: SC (let's do it in 2D). $\vec{R} = n_1 a \hat{i} + n_2 a \hat{j}$

$k \rightarrow (k_x, k_y)$

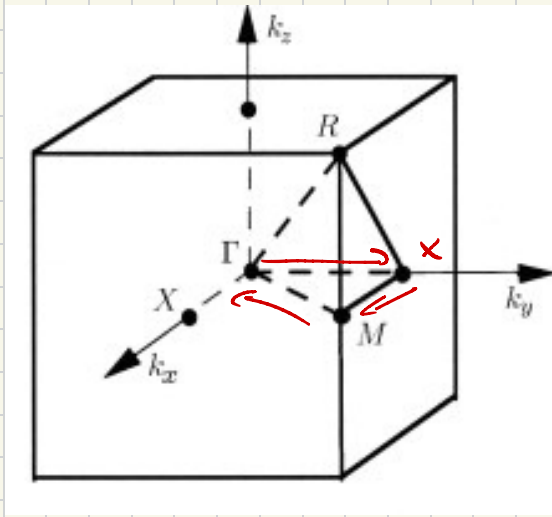
$(k_x, k_y) \quad (0, a) \quad \vec{k}(\vec{R}_{n+1} - \vec{R}_n) \dots$

$$E(k) = \langle \Phi_{\vec{k}} | H | \Phi_{\vec{k}} \rangle = E_0 + \gamma \left[e^{i k_x a} + e^{-i k_x a} + e^{i k_y a} + e^{-i k_y a} \right]$$



$$E(k) = E_0 + 2\gamma \left[\cos(k_x a) + \cos(k_y a) \right]$$

Plot along the SC BZ!



← 1st Bz of SC
With high symmetry
lines.

Path in 2D $\rightarrow \Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$

in 3D we just add an
extra $\cos(k_z a)$ term to
the sum

Path in 3D $\rightarrow \Gamma \rightarrow R \rightarrow X \rightarrow M \rightarrow \Gamma$ (for example).

\rightarrow Write a code to plot the Band.

So \rightarrow 1 orbital in 1D, 2D, 3D will result
always in a single band. But when we did
the molecule (H_2^+) example we obtained 2 energies!

\Rightarrow The # of bands = # of orbitals we use to build
our basis.

