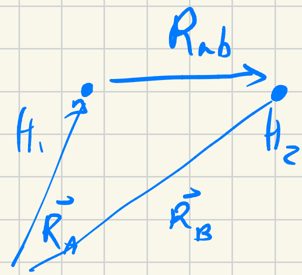
# Tight Binding Model

## 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

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

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

$\rightarrow$ Calculate $C_A, C_B$ using the variational Th:

$$\langle E\rangle = \min_{\{C_A, C_B\}} \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_AC_B H_{AB}}{C_A^2 \cancel{S_{AA}}^{\,1} + 2C_AC_B S_{AB} + C_B^2 \cancel{S_{BB}}_{\,1}}$$

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

$\mathcal{L}(C,E) = \sum_{ij} C_i H_{ij} C_j - E \sum_{ij} C_i S_{ij} C_j$ → Lagrangian, $E$ are Lagrangian multipliers.

$$\frac{\partial \mathcal{L}}{\partial c_i} = \sum_j c_j (H_{ij} - E S_{ij}) \longrightarrow C_A\left(H_{AA} - \langle E \rangle\right) + C_B\left(H_{AB} - S_{AB}\langle E \rangle\right) = 0$$

$$(\hat{H} - E\hat{S})\cdot\hat{C} = 0 \qquad H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}$$ rows of matrix equation

$$S = \begin{pmatrix} S & 1 \\ 1 & S \end{pmatrix} \quad C = \begin{pmatrix} C_A \\ C_B \end{pmatrix} \longrightarrow C_A\left(H_{AB} - S_{AB}\langle E \rangle\right) + C_B\left(H_{BB} - \langle E \rangle\right) = 0$$

Secular equations

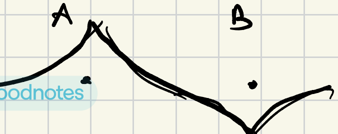
$$\det\left[H - ES\right] = 0 \Rightarrow \begin{vmatrix} H_{AA} - \langle E \rangle & H_{AB} - S_{AB}\langle E \rangle \\ H_{BA} - S_{BA}\langle E \rangle & H_{BB} - \langle E \rangle \end{vmatrix} = 0$$

$$E_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$ ← 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)

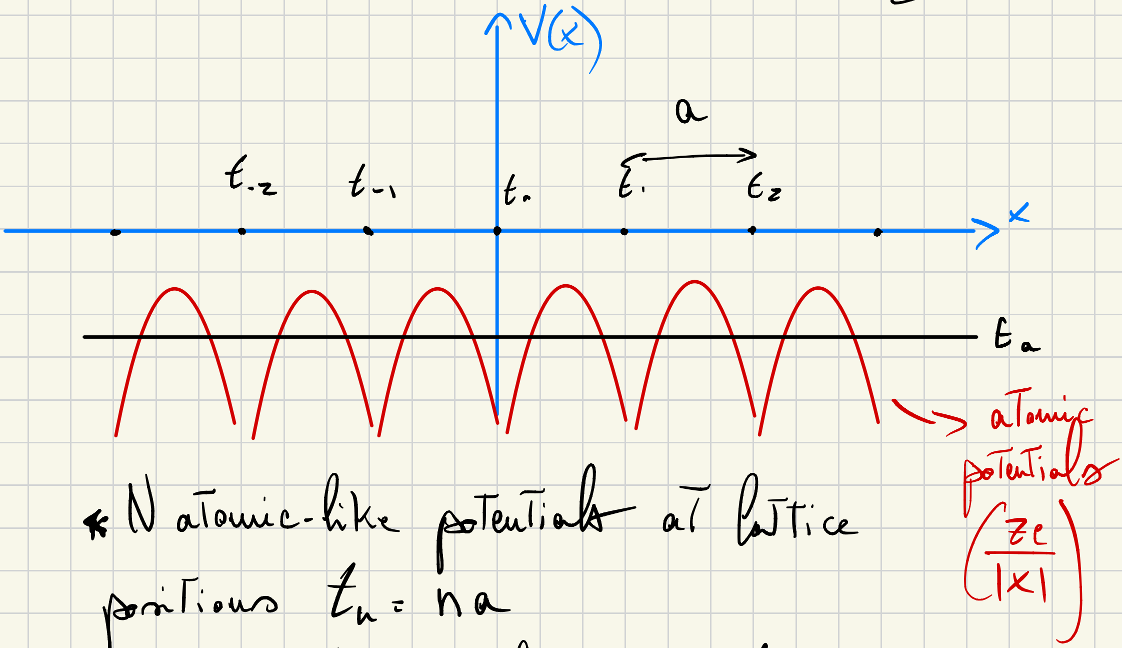

← $E_-$, $\psi_- = C_A\left(|\phi_A\rangle + |\phi_B\rangle\right)$



← $E_+$ $\psi_+ = C_A\left(|\phi_A\rangle - |\phi_B\rangle\right)$

# 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 appart $\Longrightarrow$ No interactions, recover atomic energy levels. (all degenerate)
  * Closer $a \to 10-2 * r_{at} \to$ interacting $\to$ <u>bands</u>




* $N$ atomic-like potentials at lattice positions $t_n = na$
* $\phi_a$ is the orbital of a single atom (ex 1S orbital of H). With energy $E_a$ (when atom isolated)
  $\to$ We assume $\phi$ are real, and non degenerate.

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

→ Note this is an incomplete basis set!

• Assume $\phi_a$'s are orthonormal

$$\langle \phi_a^{t_n} | \phi_a^{t_m} \rangle = \delta_{m,n}$$

[notation $\langle x | \phi_a^{t_n} \rangle = \phi(x-t_n)$]

* Write crystal Hamiltonian in the basis of atomic orbitals

$$\langle \phi_a^{t_n} | H | \phi_a^{t_n} \rangle = E_0 \leftarrow \text{onsite energy}$$

$\gamma(a)$, depends on lattice constant

$$\langle \phi_a^{t_n} | H | \phi_a^{t_{n\pm1}} \rangle = \gamma \leftarrow \text{negative, } \gamma<0;$$

nearest neighbors hopping

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

• What is $H$? $H = H_{at} + \Delta U(r)$, 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:

$$\underline{\Phi}_k(x) = \frac{1}{\sqrt{N}} \sum_n e^{ikt_n} \phi_a(x - t_n)$$

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

$$\underline{\Phi}_k(x + t_m) = \frac{1}{\sqrt{N}} \sum_n e^{ikt_n} \phi_a(x + t_m - t_n)$$

→ multiply by $1 = e^{ikt_m} e^{-ikt_m}$

$\tilde{t}_n = t_n - t_m$ (a L.V)

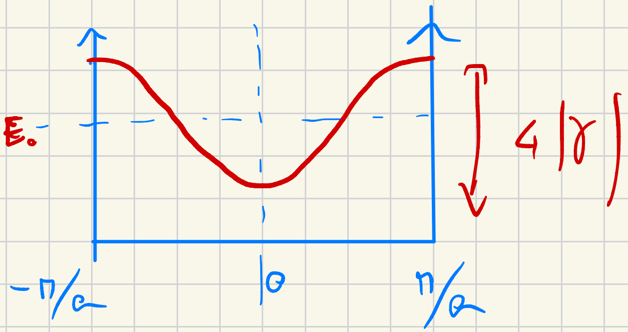
$$= \frac{1}{\sqrt{N}} e^{ikt_m} \sum_n e^{ik\underbrace{(t_n - t_m)}_{\tilde{t}_n}} \phi_a(x - \underbrace{(t_n - t_m)}_{\tilde{t}_n}) =$$

$$= \frac{1}{\sqrt{N}} e^{ikt_m} \underline{\Phi}_k(x) \quad \text{Q.E.D}$$

* Note: Bloch sums w/ different k are orthonormal!

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

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




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

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

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

— Tight-Binding Hamiltonian as an operator:

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

* 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:

$$\hat{H}|\Phi_k\rangle = \frac{1}{\sqrt{N}} \sum_m e^{ikt_m} \Big[ E_0 \sum_n |\phi^n\rangle \underbrace{\langle \phi^n | \phi^m \rangle}_{\delta_{nm}}$$

$$+ \gamma \sum_n \Big( |\phi^n\rangle\langle\phi^{n+1}|\phi^m\rangle + |\phi^{n+1}\rangle \underbrace{\langle\phi^n|\phi^m\rangle}_{\delta_{nm}} \Big) \Big]$$

$$= \frac{1}{\sqrt{N}} \sum_m e^{ikt_m} \Big( E_0 |\phi^m\rangle + \gamma \big[ |\phi^{m-1}\rangle + |\phi^{m+1}\rangle \big] \Big)$$

$$= E_0 |\Phi_k\rangle + \gamma \left( e^{-ika} + e^{ika} \right) |\Phi_k\rangle =$$

$$= \left[ E_0 + 2\gamma \cos(ka) \right] |\Phi_k\rangle$$

* In the $|\phi_n\rangle = |\phi(x - t_n)\rangle$ basis, we can write $H$ as a $N \times N$ matrix (assume $\gamma$ 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 :

$$m = \begin{bmatrix} \alpha_0 & \beta_1 & 0 & \cdots \\ \beta_1 & \alpha_1 & \beta_2 & \\ 0 & \beta_2 & \alpha_2 & \beta \\ \vdots & & \beta_3 & \alpha_3 & \ddots \end{bmatrix}$$

← assume m 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)

$$\left(\frac{1}{m}\right)_{00} = \frac{1}{a_0 - \underbrace{\frac{\beta_1^2}{\alpha_1 - \frac{\beta_2^2}{\cdots}}}_{} - \underbrace{\frac{\beta_0^2}{\alpha_{-1} - \frac{\beta_{-1}^2}{\cdots}}}_{}}$$

"Continued fractions"

← (for n in positive or negative directions)

See Grosso-Parrav. Sec I.4.2

→ From 1D To 3D

* Still 1 orbital per atom.

Bloch orbital (same but now $t_n \to \vec{R}_n$, $x \to r$)

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

For the dispersion $E(k)$ now we have $\vec{k} = (k_x, k_y, k_z)$

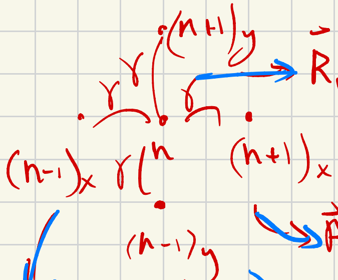
(Same as $\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$)

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

$k \to (k_x, k_y)$

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

$$E(k) = \langle \Phi_k | H | \Phi_k \rangle = E_0 + \gamma \left[ e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} \right]$$




$\vec{R}_{n+1} - \vec{R}_n = (0, a)$

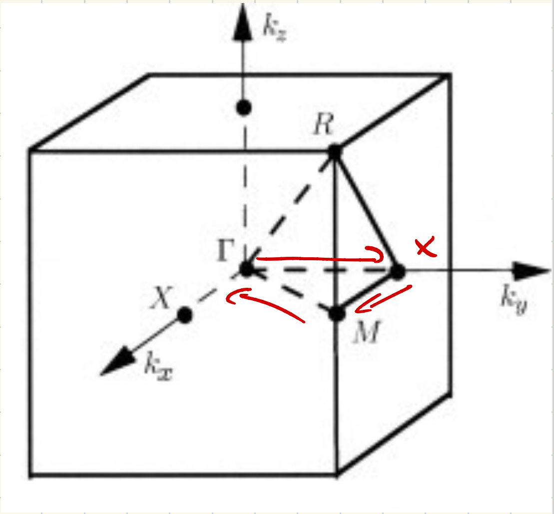
$\vec{R}_{n+1} - \vec{R}_n = (a, 0)$

$\vec{R}_{n-1} - \vec{R}_n = (-a, 0)$

$\vec{R}_{n-1} - \vec{R}_n = (0, -a)$

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

Plot along the SC BZ!




← 1st BZ of SC

With high symmetry lines.

Path in 2D → Γ → X → M → Γ

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

Path in 3D → Γ → R → X → M → Γ (for example).

→ Write a code to plot the Band.

So ~~…~~ 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!

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