

Continuity of $E_n(\vec{k})$ and meaning of its first and second derivatives

$$\hbar \rho_{n,\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\vec{r}) \right) \rho_{n,\vec{k}}(\vec{r})$$

$$\rho_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} \cdot U_{n,\vec{k}}(\vec{r})$$

$$\hbar \rho_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} \left[-\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\vec{r}) + \frac{\hbar^2}{2m} k^2 - \frac{\hbar^2}{2m} i\vec{k}\nabla \right] \cdot U_{n,\vec{k}}(\vec{r})$$

$$= E_n(\vec{k}) e^{i\vec{k}\vec{r}} U_{n,\vec{k}}(\vec{r})$$

$$\text{Thus, } E_n(\vec{k}) = \int U_{n,\vec{k}}^*(\vec{r}) \tilde{h} U_{n,\vec{k}}(\vec{r}) d^3r$$

$$\tilde{h} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\vec{r}) + \frac{\hbar^2}{2m} k^2 - \frac{\hbar^2}{2m} i\vec{k}\nabla \right]$$

$$\tilde{h}(\vec{k}) U_{n,\vec{k}}$$

↓

$$\boxed{\tilde{h}(\vec{k}) U_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) U_{n,\vec{k}}(\vec{r})}$$

(let's) look at the neighborhood

of $\epsilon_n(\vec{k})$:

$$\epsilon_n(\vec{k} + \vec{x}) = \int u_{n, \vec{k} + \vec{x}}^*(\vec{r}) \tilde{h}(\vec{k} + \vec{x}) u_{n, \vec{k} + \vec{x}}(\vec{r}) d^3r$$

$$\tilde{h}(\vec{k} + \vec{x}) - \tilde{h}(\vec{k}) = \frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{k}\vec{x}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \nabla$$

Use perturbation theory, to expand wrt $u_{n, \vec{k}}(\vec{r})$: ψ -order

$$\begin{aligned} \epsilon_n(\vec{k} + \vec{x}) &= \int u_{n, \vec{k}}^*(\vec{r}) \tilde{h}(\vec{k}) u_{n, \vec{k}}(\vec{r}) d^3r + \\ &+ \int u_{n, \vec{k}}^*(\vec{r}) \left\{ \frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{x}\vec{k}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \nabla \right\} u_{n, \vec{k}}(\vec{r}) d^3r \\ &+ \sum_m \frac{\left| \int u_{n, \vec{k}}^*(\vec{r}) \left\{ \frac{\hbar^2}{2m} (\vec{x}^2 + 2\vec{x}\vec{k}) - \frac{\hbar^2}{2m} 2i\vec{x} \cdot \nabla \right\} u_{m, \vec{k}}(\vec{r}) d^3r \right|^2}{\epsilon_n(\vec{k}) - \epsilon_m(\vec{k})} \end{aligned}$$

1st-order
2nd-order

$$+ O(\vec{x}^3)$$

Introduce momentum operator:

$$\vec{P}_{n,n} = \langle u_{n, \vec{k}}(\vec{r}) | \frac{\hbar}{i} \nabla | u_{n, \vec{k}}(\vec{r}) \rangle$$

$$= \langle u_{n, \vec{k}}(\vec{r}) | \hbar \vec{k} + \frac{\hbar}{i} \nabla | u_{n, \vec{k}}(\vec{r}) \rangle$$

↖ Bloch theorem

Substitute in $\epsilon_n(\vec{k} + \vec{x})$:

$$\epsilon_n(\vec{k} + \vec{x}) - \epsilon_n(\vec{k}) = \frac{\hbar}{m} \vec{x} \cdot \vec{P}_{n,n} + \frac{\hbar^2}{2m} \vec{x}^2 +$$

$$+ \frac{\hbar^2}{2m} \sum_{n \neq n} \frac{|\vec{x} \cdot \vec{P}_{n,n}|^2}{\epsilon_n(\vec{k}) - \epsilon_n(\vec{k})} + O(x^3)$$

The limit $|\vec{x}| = 0$:

$\Rightarrow E_n(\vec{k})$ is continuous

First derivative :

$$\nabla_{\vec{k}} E_n(\vec{k}) = \frac{\hbar}{m} \vec{p}_{nn}$$

In the case of free electrons :

$\vec{p}_{nn} \sim \vec{k}$, in reality it is $\sim \nabla_{\vec{k}} E_n(\vec{k})$

Second derivative :

$$\frac{\partial^2}{\partial k_\alpha \partial k_\beta} E_n(\vec{k}) = \frac{\hbar}{m} \text{ for free electrons}$$

In reality, we can only take the second derivative at certain points of BZ:

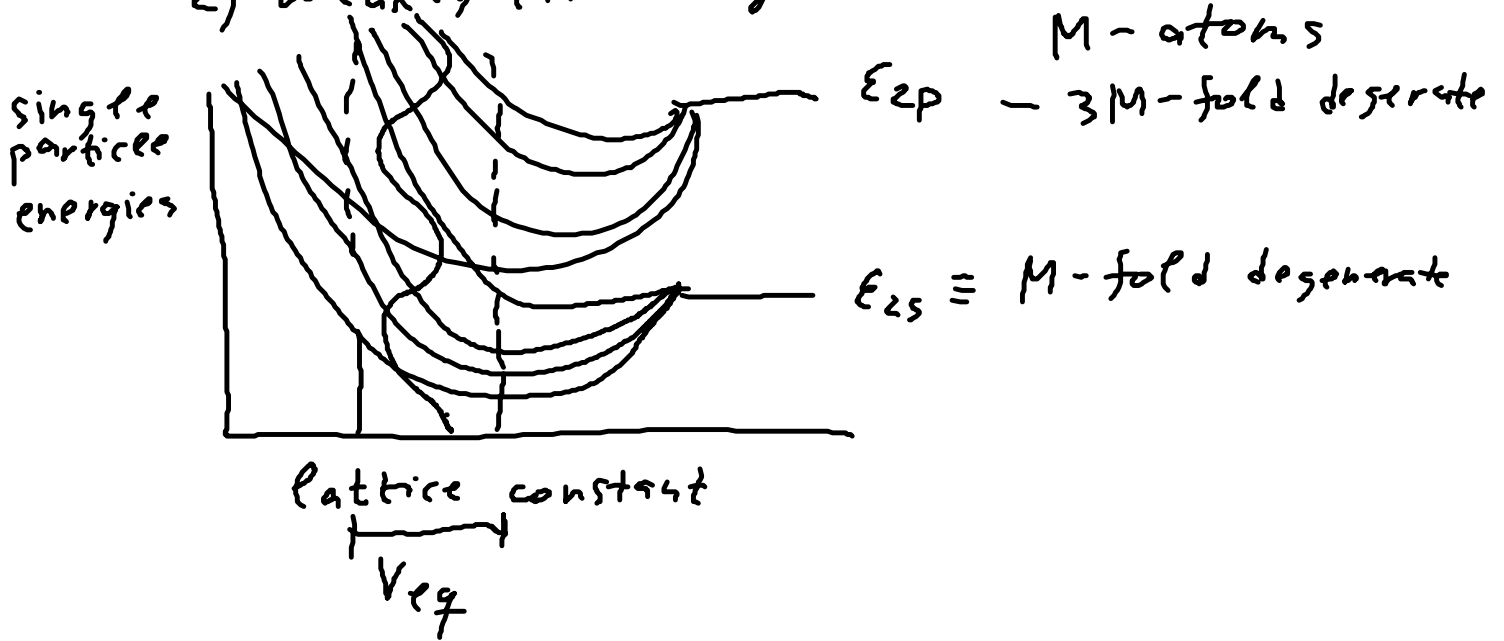
$$\frac{\partial^2}{\partial k_\alpha \partial k_\beta} E_n(\vec{k}) = \frac{\hbar}{m^*}$$

The LCAO method \equiv tight-binding

Two limits for the description of solids :

1) Plane waves

2) Weakly interacting atoms



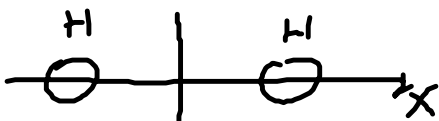
Accurate methods combine the two concepts, and these methods are:

1) Pseudopotential method

2) LMO (Linear muffin-tin orbital method)

3) Augmented plane waves

Reminder of H_2



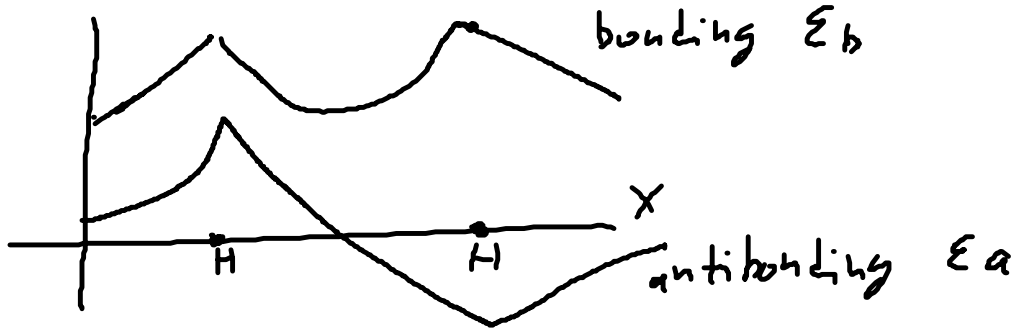
Start with H^{1s} orbital:

$$\psi_{2s}^b(\vec{r}) = \frac{1}{\sqrt{2}} \left(\hat{P}_{2s}(\vec{r} - \vec{R}_1) + \hat{P}_{2s}(\vec{r} - \vec{R}_2) \right)$$

$$\psi_{2s}^a(\vec{r}) = \frac{1}{\sqrt{2}} \left(\hat{P}_{2s}(\vec{r} - \vec{R}_1) - \hat{P}_{2s}(\vec{r} - \vec{R}_2) \right)$$

↑ antibonding

↑ bonding

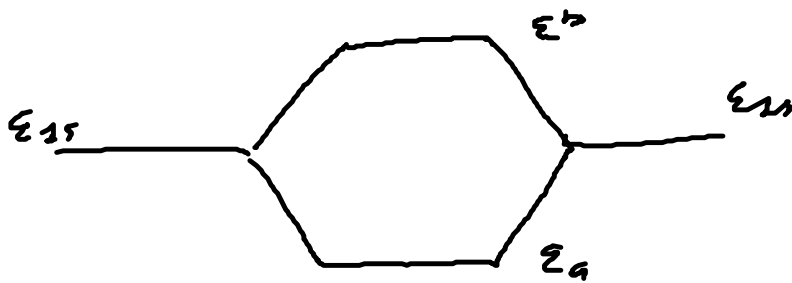


$\epsilon_b \rightarrow$ lower energy

$\psi^b: \oplus \oplus$ $|\psi^b|^2$ has a maximum between the nuclei

$\epsilon_a \rightarrow$ higher energy

$\psi^a: \oplus \ominus$ $|\psi^a|^2$ is zero between the nuclei



Now let's use this concept for a crystal.

$$\chi_d(\vec{k}, \vec{r}) = \frac{1}{\sqrt{A}} \sum_{\vec{R}_I}^M \delta_I(\vec{k}) \hat{f}_d(\vec{r} - \vec{R}_I)$$

$M \equiv$ number of atoms

From Bloch theorem $\delta_I(\vec{k}) = e^{i\vec{k} \cdot \vec{R}_I}$

$$\hat{f}_d \equiv 1s, 2s, 2p, \dots$$

\Rightarrow There is an infinite number of phases

$$e^{i\vec{k} \cdot \vec{R}_I} = +1, \dots, -1$$

$$\text{For } \vec{k} = \Gamma \rightarrow +1$$

$$\text{For } \vec{k} = \frac{1}{2}\vec{G} \rightarrow -1$$

For normalisation, we choose:

$$\langle \hat{f}_\alpha(\vec{r}) | \hat{f}_\beta(\vec{r}) \rangle = \delta_{\alpha\beta}$$

and $A = M = \text{number of atoms}$

$$\Rightarrow \langle \chi_\alpha(\vec{k}, \vec{r}) | \chi_\beta(\vec{k}, \vec{r}) \rangle \neq \delta_{\alpha\beta}$$

The eigenfunctions of h :

$$f_n(\vec{k}, \vec{r}) = \sum_{\beta} C_{n,\beta}(\vec{k}) \chi_{\beta}(\vec{k}, \vec{r})$$

The secular Kohn-Sham equation:

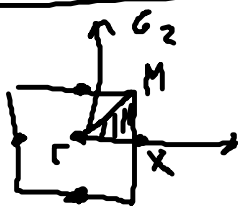
$$\sum_{\beta} [h_{\alpha\beta} - S_{\alpha\beta} E_n(\vec{k})] C_{n\beta}(\vec{k}) = 0$$

where

$$\begin{aligned} h_{\alpha\beta} &= \langle \chi_\alpha(\vec{k}, \vec{r}) | h | \chi_\beta(\vec{k}, \vec{r}) \rangle \\ &= \frac{1}{M} \sum_{\vec{R}_I, \vec{R}_J} e^{i\vec{k}(\vec{R}_I - \vec{R}_J)} \langle \hat{f}_\alpha(\vec{r} - \vec{R}_I) | h | \hat{f}_\beta(\vec{r} - \vec{R}_J) \rangle \\ &= \sum_{\vec{R}_I} e^{i\vec{k}\vec{R}_I} \underbrace{\langle \hat{f}_\alpha(\vec{r} - \vec{R}_I) | h | \hat{f}_\beta(\vec{r}) \rangle}_{E_{\alpha\beta}(\vec{R}_I)} \end{aligned}$$

$$\begin{aligned} S_{\alpha\beta} &= \langle \chi_\alpha(\vec{k}, \vec{r}) | \chi_\beta(\vec{k}, \vec{r}) \rangle \\ &= \sum_{\vec{R}_I} e^{i\vec{k}\vec{R}_I} \underbrace{\langle \hat{f}_\alpha(\vec{r} - \vec{R}_I) | \hat{f}_\beta(\vec{r}) \rangle}_{S_{\alpha\beta}(\vec{R}_I)} \end{aligned}$$

LCAO bandstructure for 2D square lattice



One s orbital per atom

\vec{k}	$\rho_s(\vec{k}, \vec{r})$	energy
Γ	$\begin{array}{c} \oplus \\ \oplus \oplus \oplus \\ \oplus \\ \oplus \end{array}$	fully bonding (lowest energy)
$(\frac{\pi}{2}, \frac{\pi}{2})$ X	$\begin{array}{c} \oplus \\ \ominus \oplus \ominus \\ \oplus \\ \ominus \end{array}$	half-half mid-value energy
$(\frac{\pi}{2}, \frac{\pi}{2})$ M	$\begin{array}{c} \ominus \\ \ominus \oplus \ominus \\ \ominus \\ \ominus \end{array}$	anti-bonding maximum energy

