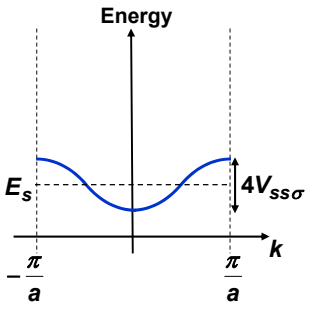
Handout 9

Application of LCAO to Energy Bands in Solids and the Tight Binding Method

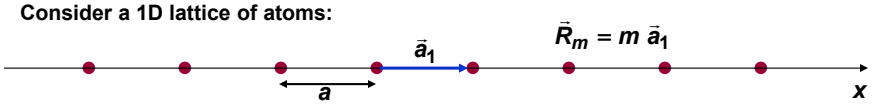
In this lecture you will learn:

- An approach to energy bands in solids using LCAO and the tight binding method

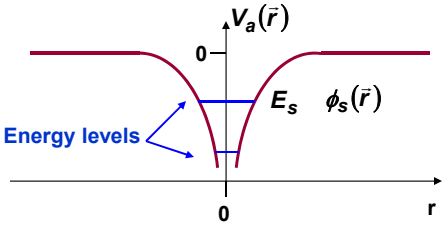


Example: A 1D Crystal with 1 Orbital per Primitive Cell

Consider a 1D lattice of atoms:



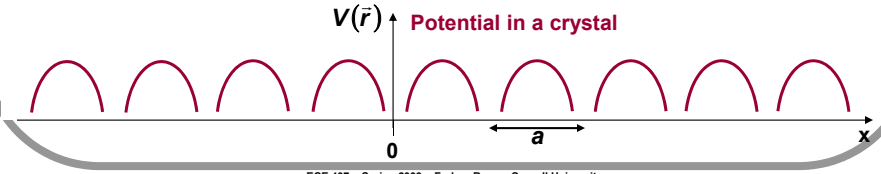
Each atom has the energy levels as shown



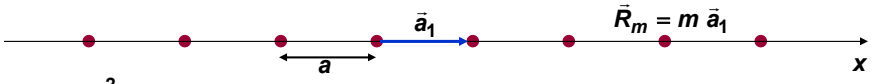
- The electrons in the lowest energy level(s) are well localized and do not take part in bonding with neighboring atoms

- The electrons in the outermost s-orbital participate in bonding

The crystal has the Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_m V_a(\vec{r} - \vec{R}_m)$



Tight Binding Approach for a 1D Crystal



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_m V_a\left(\vec{r} - \vec{R}_m\right) \longrightarrow \text{Periodic potential}$$

We assume that the solution is of the LCAO form: $\psi(\vec{r}) = \sum_m c_m\, \phi_s\left(\vec{r} - \vec{R}_m\right)$

And assume that orbitals on different atoms are approx. orthogonal:

$$\left\langle \phi_s\left(\vec{r} - \vec{R}_n\right) \middle| \phi_s\left(\vec{r} - \vec{R}_m\right) \right\rangle = \delta_{n\,m}$$

• If we have *N* atoms in the lattice, then our solution is made up of *N* different s-orbitals that are sitting on the *N* atoms

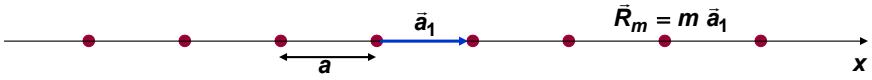
• In principle one can take the assumed solution, as written above, plug it in the Schrodinger equation, get an *N*x*N* matrix and solve it (just as we did in the case of molecules). But one can do better ……..

We know from Bloch's theorem that the solution must satisfy the following:

$$\left|\psi\left(\vec{r} + \vec{R}\right)\right|^2 = \left|\psi(\vec{r})\right|^2$$

$$\psi\left(\vec{r} + \vec{R}\right) = e^{i\,\vec{k}\,.\,\vec{R}}\psi(\vec{r})$$

Tight Binding Approach for a 1D Crystal



Consideration 1:

For the solution: $\psi(\vec{r}) = \sum_m c_m\, \phi_s\left(\vec{r} - \vec{R}_m\right)$

to satisfy:

$$\left|\psi\left(\vec{r} + \vec{R}\right)\right|^2 = \left|\psi(\vec{r})\right|^2$$

one must have the same value of $|c_m|^2$ for all *m* (i.e. all coefficients must have the same weight).

So we can write without loosing generality: $c_m = \frac{e^{i\,\theta_m}}{\sqrt{N}} \longrightarrow \int |\psi(\vec{r})|^2 d^3\vec{r} = 1$

Consideration 2:

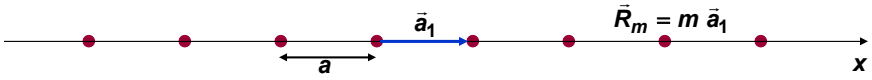
For the solution: $\psi(\vec{r}) = \sum_m \frac{e^{i\,\theta_m}}{\sqrt{N}}\, \phi_s\left(\vec{r} - \vec{R}_m\right)$

to satisfy:

$$\psi\left(\vec{r} + \vec{R}\right) = e^{i\,\vec{k}\,.\,\vec{R}}\psi(\vec{r})$$

one must have the phase value equal to: $\theta_m = \vec{k}\,.\,\vec{R}_m$

Tight Binding Approach for a 1D Crystal



Consideration 2 (contd…):

Proof:

$$\psi(\vec{r}) = \sum_m \frac{e^{i\theta_m}}{\sqrt{N}} \phi_s(\vec{r} - \vec{R}_m) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \phi_s(\vec{r} - \vec{R}_m)$$

For the Bloch condition we get:

$$\psi(\vec{r} + \vec{R}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \phi_s(\vec{r} + \vec{R} - \vec{R}_m) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \phi_s(\vec{r} - (\vec{R}_m - \vec{R}))$$

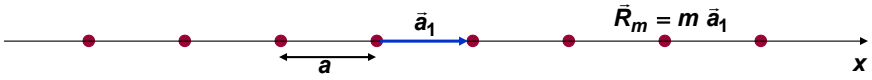
Let:

$$\vec{R}_m - \vec{R} = \vec{R}_p$$

$$\Rightarrow \psi(\vec{r} + \vec{R}) = \sum_p \frac{e^{i\,k\,.\,(\vec{R}_p + \vec{R})}}{\sqrt{N}} \phi_s(\vec{r} - \vec{R}_p) = e^{i\,\vec{k}\,.\,\vec{R}} \sum_p \frac{e^{i\,\vec{k}\,.\,\vec{R}_p}}{\sqrt{N}} \phi_s(\vec{r} - \vec{R}_p)$$

$$= e^{i\,\vec{k}\,.\,\vec{R}}\, \psi(\vec{r})$$

Tight Binding Approach for a 1D Crystal



So we can write the solution as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \phi_s(\vec{r} - \vec{R}_m)$$

And we know that it is a Bloch function because:

$$\psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}} \psi_{\vec{k}}(\vec{r})$$

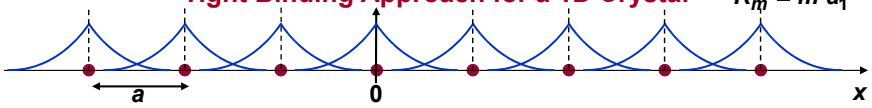
All that remains to be found is the energy of this solution – so we plug it into the Schrodinger equation:

$$\hat{H} \left| \psi_{\vec{k}}(\vec{r}) \right\rangle = E(\vec{k}) \left| \psi_{\vec{k}}(\vec{r}) \right\rangle$$

$$\Rightarrow \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \hat{H} \left| \phi_s(\vec{r} - \vec{R}_m) \right\rangle = E(\vec{k}) \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left| \phi_s(\vec{r} - \vec{R}_m) \right\rangle$$

Tight Binding Approach for a 1D Crystal

$\vec{R}_m = m\,\vec{a}_1$



$$\Rightarrow \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \hat{H} \left|\phi_s(\vec{r}-\vec{R}_m)\right\rangle = E(\vec{k}) \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left|\phi_s(\vec{r}-\vec{R}_m)\right\rangle$$

Multiply this equation with $\langle\phi_s(\vec{r})|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors and
- assume that the orbitals on different atoms are orthogonal

$$\frac{e^{i\,\vec{k}\,.\,\vec{R}_1}}{\sqrt{N}} \langle\phi_s(\vec{r})|\hat{H}\left|\phi_s(\vec{r}-\vec{R}_1)\right\rangle + \frac{1}{\sqrt{N}} \langle\phi_s(\vec{r})|\hat{H}\left|\phi_s(\vec{r})\right\rangle + \frac{e^{i\,\vec{k}\,.\,\vec{R}_{-1}}}{\sqrt{N}} \langle\phi_s(\vec{r})|\hat{H}\left|\phi_s(\vec{r}-\vec{R}_{-1})\right\rangle$$

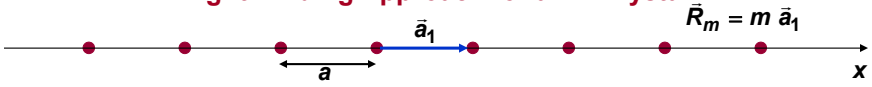
$$= E(\vec{k}) \frac{1}{\sqrt{N}} \langle\phi_s(\vec{r})|\phi_s(\vec{r})\rangle$$

$$\Rightarrow -V_{ss\sigma} \frac{e^{i\,\vec{k}\,.\,\vec{a}_1}}{\sqrt{N}} + \frac{1}{\sqrt{N}} E_s - \frac{e^{-i\,\vec{k}\,.\,\vec{a}_1}}{\sqrt{N}} V_{ss\sigma} = E(\vec{k}) \frac{1}{\sqrt{N}}$$

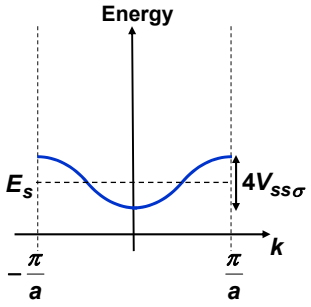
$$\Rightarrow E(\vec{k}) = E_s - 2V_{ss\sigma} \cos(\vec{k}\,.\,\vec{a}_1)$$

Tight Binding Approach for a 1D Crystal

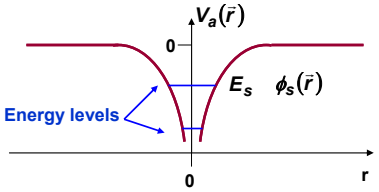
$\vec{R}_m = m\,\vec{a}_1$

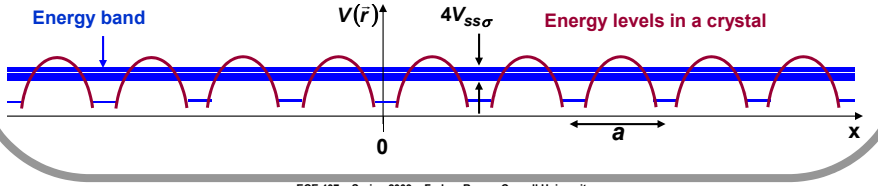


$$E(\vec{k}) = E_s - 2V_{ss\sigma} \cos(\vec{k}\,.\,\vec{a}_1)$$

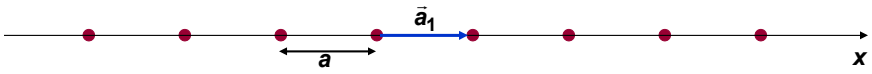


Energy levels in an isolated atom

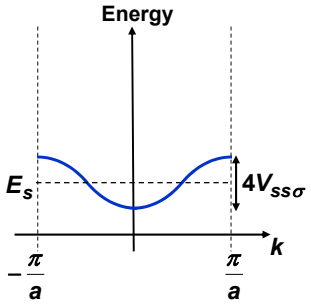




Tight Binding Approach for a 1D Crystal

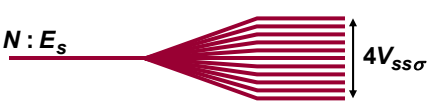


$$E(\vec{k}) = E_s - 2V_{ss\sigma}\cos(\vec{k}\,.\,\vec{a}_1)$$



- Number of quantum states at the starting point = 2 x number of orbitals used in the LCAO solution = 2*N*
- Number of quantum states at the ending point = 2 x energy levels per band for an *N* atom crystal = 2*N*

⇒ Initial number of quantum states = Final number of quantum states

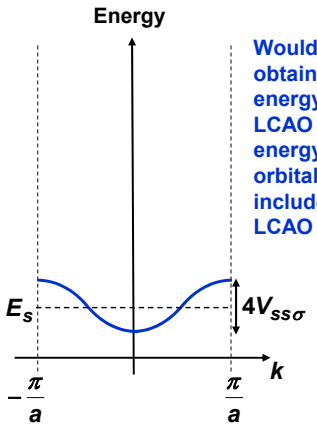


A band of *N* energy levels
2*N* quantum states

Tight Binding vs NFEA for a 1D Crystal

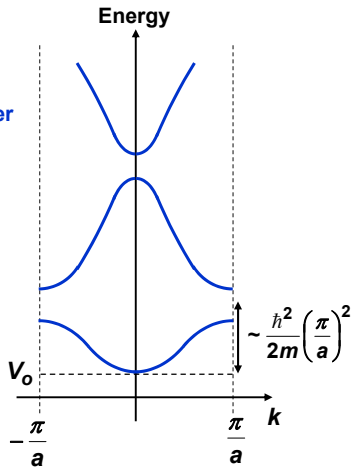
LCAO – Tight Binding

$$E(\vec{k}) = E_s - 2V_{ss\sigma}\cos(\vec{k}\,.\,\vec{a}_1)$$



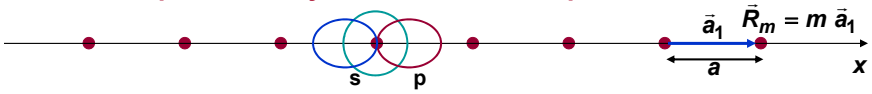
Would have also obtained the higher energy bands in LCAO if higher energy atomic orbitals were also included in the LCAO solution

Nearly Free Electron Approach (NFEA)



The energy matrix elements are of the order of: $V_{ss\sigma} \sim \frac{\hbar^2}{m}\frac{1}{a^2}$

Example: A 1D Crystal with 2 Orbitals per Primitive Cell



Each atoms now has a s-orbital and a p-orbital that contributes to energy band formation

$$\phi_s(\vec{r}) \rightarrow E_s$$
$$\phi_p(\vec{r}) \rightarrow E_p$$

We write the solution in the form:

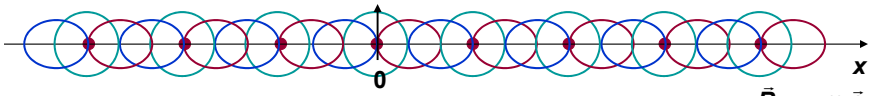
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[c_s(\vec{k})\,\phi_s(\vec{r}-\vec{R}_m) + c_p(\vec{k})\,\phi_p(\vec{r}-\vec{R}_m) \right]$$

Verify that it satisfies: $\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{\vec{k}}(\vec{r})$

And plug it into the Schrodinger equation:

$$\hat{H}\,|\psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k})\,|\psi_{\vec{k}}(\vec{r})\rangle$$

Tight Binding Approach for a 1D Crystal



$\vec{R}_m = m\,\vec{a}_1$

$$\hat{H}\,|\psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k})\,|\psi_{\vec{k}}(\vec{r})\rangle$$

Step 1:

Multiply the equation with $\langle\phi_s(\vec{r})|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors and
- assume that the orbitals on different atoms are orthogonal

$$\left[E_s - 2V_{ss\sigma}\cos(\vec{k}.\vec{a}_1) \right] c_s(\vec{k}) + 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1)\,c_p(\vec{k}) = E(\vec{k})\,c_s(\vec{k})$$

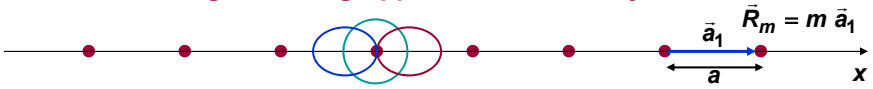
Step 2:

Multiply the equation with $\langle\phi_p(\vec{r})|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors and
- assume that the orbitals on different atoms are orthogonal

$$\left[E_p + 2V_{pp\sigma}\cos(\vec{k}.\vec{a}_1) \right] c_p(\vec{k}) - 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1)\,c_s(\vec{k}) = E(\vec{k})\,c_p(\vec{k})$$

Tight Binding Approach for a 1D Crystal



We can write the two equations in matrix form:

$$\begin{bmatrix} E_s - 2V_{ss\sigma}\cos(\vec{k}.\vec{a}_1) & 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1) \\ -2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1) & E_p + 2V_{pp\sigma}\cos(\vec{k}.\vec{a}_1) \end{bmatrix} \begin{bmatrix} c_s(\vec{k}) \\ c_p(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_s(\vec{k}) \\ c_p(\vec{k}) \end{bmatrix}$$

For each value of wavevector one obtains two eigenvalues – corresponding to two energy bands

For $\vec{k} = 0$ we get:

$$E(\vec{k}=0) = E_p + 2V_{pp\sigma}$$

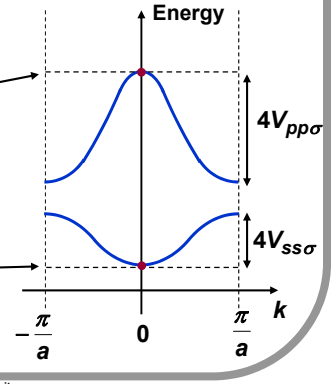
$$\begin{bmatrix} c_s(\vec{k}=0) \\ c_p(\vec{k}=0) \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Bloch function is made of only p-orbitals

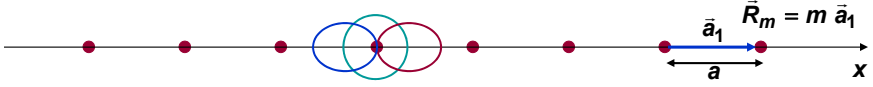
$$E(\vec{k}=0) = E_s - 2V_{ss\sigma}$$

$$\begin{bmatrix} c_s(\vec{k}=0) \\ c_p(\vec{k}=0) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Bloch function is made of only s-orbitals



Tight Binding Approach for a 1D Crystal



For $\vec{k} = \frac{\pi}{2a}\hat{x}$ we get:

$$E\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) = ?$$

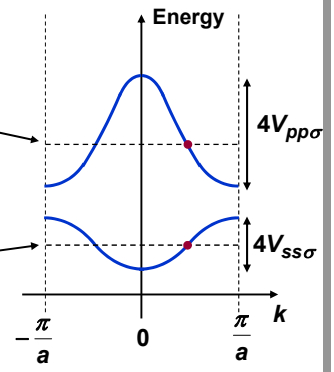
$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} ? \\ ? \end{bmatrix}$$

Bloch function is made of both s- and p-orbitals

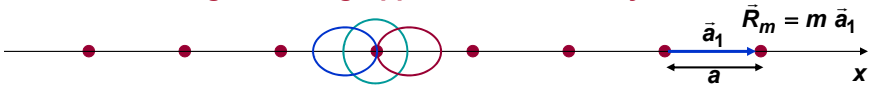
$$E\left(\vec{k} = \frac{\pi}{2a}\right) = ?$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} ? \\ ? \end{bmatrix}$$

Bloch function is made of both s- and p-orbitals



Tight Binding Approach for a 1D Crystal



For $\vec{k} = \frac{\pi}{a}\hat{x}$ we get:

$$E\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) = E_p - 2V_{pp\sigma}$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Bloch function is made of only p-orbitals

$$E\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) = E_s + 2V_{ss\sigma}$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Bloch function is made of only s-orbitals