

Equation (2.28) can be used to prove the Kramers' theorem for a crystalline solid.

Let  $\Delta$  be a symmetry operation which leaves the crystal structure invariant. Moreover let's ensure that such a symmetry operation preserves the scalar product, i.e. it is a combination of rotation and inversion operations.

$$\Delta \{ \vec{R}_i \} = \{ \vec{R}_i \} \quad \text{in particular} \quad \Delta(\{ \vec{R} \}) = \{ \vec{R} \}$$

It follows that:

$$\begin{aligned} \varepsilon_n(\vec{k}) &= E_n + \sum_{\vec{R} \neq 0} \chi_n(\vec{R}) e^{-i\vec{k} \cdot \vec{R}} = && \Delta \text{ conserves the scalar product} \\ &= E_n + \sum_{\vec{R} \neq 0} \chi_n(\vec{R}) e^{-i\Delta(\vec{k}) \cdot \Delta(\vec{R})} = && \Delta \text{ is invertible} \\ &= E_n + \sum_{\vec{R} \neq 0} \chi_n(\Delta^{-1} \Delta \vec{R}) e^{-i\Delta(\vec{k}) \cdot \Delta(\vec{R})} = && \Delta \text{ is linear and invertible} \\ &&& \Rightarrow \Delta(\vec{R}) \neq 0 \Leftrightarrow \vec{R} \neq 0. \\ &= E_n + \sum_{\vec{R} \neq 0} \chi_n(\Delta^{-1}(\vec{R})) e^{-i\Delta(\vec{k}) \cdot \vec{R}} = && \chi_n(\Delta^{-1} \vec{R}) = \chi_n(\vec{R}) \\ &= E_n + \sum_{\vec{R} \neq 0} \chi_n(\vec{R}) e^{-i\Delta(\vec{k}) \cdot \vec{R}} = \varepsilon_n(\Delta(\vec{k})) \end{aligned}$$

$$\begin{aligned} \chi_n(\Delta^{-1} \vec{R}) &= \langle n, \Delta^{-1} \vec{R} | \hat{h} | n, \vec{0} \rangle = \langle n, \vec{R} | \hat{\Delta}^\dagger \hat{h} | n, \vec{0} \rangle = \langle n, \vec{R} | \hat{h} \hat{\Delta} | n, \vec{0} \rangle \\ &= \langle n, \vec{R} | \hat{h} | n, \vec{0} \rangle = \chi_n(\vec{R}) \end{aligned}$$

$$\hat{\Delta} \phi(\vec{r}) = \phi(\Delta^{-1}(\vec{r}))$$

Both  $E_n$  and  $\chi_n(\vec{R})$  can be evaluated at different levels of approximation. In the tight binding approximation one

- neglects 3 centers integrals
- considers only nearest neighbours (n.n.)

In practice

$$E_n \approx \int d\vec{r} W_n^*(\vec{r}) \left[ \frac{\hat{p}^2}{2m} + \sum_{\vec{R}' \in \text{n.n.}} \nabla_{\vec{r}} \cdot (\vec{r} - \vec{R}') \right] W_n(\vec{r})$$

$$\chi_n(\vec{R} - \vec{R}') \approx \int d\vec{r} W_n^*(\vec{r} - \vec{R}) \sum_{\vec{r}} \left[ \nabla_{\vec{r}} \cdot (\vec{r} - \vec{R}) + \nabla_{\vec{r}} \cdot (\vec{r} - \vec{R}') \right] W_n(\vec{r} - \vec{R}')$$

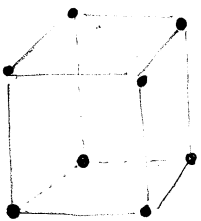
and  $\vec{R}, \vec{R}'$  are n.n.

Example: 1D chain in tight binding

$$\begin{array}{c} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \leftarrow a \quad \rightarrow \\ \cdot \quad \cdot \quad \cdot \\ -1 \quad 0 \quad 1 \end{array} \Rightarrow \Sigma(k) = E + \chi(a) e^{-ika} + \chi(-a) e^{ika}$$

$$\chi(a) = \chi(-a) \leftarrow \text{Kramers theorem} \quad = E + 2\gamma \cos ka$$

Example: simple cubic lattice



6 nearest neighbours  $\chi = \chi(\pm a\hat{x}) = \chi(\pm a\hat{y}) = \chi(\pm a\hat{z})$

$$\Rightarrow \Sigma(\vec{k}) = E + 2\gamma (\cos k_x a + \cos k_y a + \cos k_z a)$$

In practice the Wannier functions are not known for a general system since to obtain them one has first to solve the eigenvalue problem and hence determine the Bloch functions. A useful approximation of the Wannier functions can be obtained in terms of Linear Combination of Atomic Orbitals (LCAO)

#### 2.4 The LCAO construction

i) Starting point of the LCAO construction is the idea that the eigenvalues and eigenfunctions of the isolated atom are known. We can thus introduce the atomic wave function

$$\langle \vec{r} | \nu \vec{R} \rangle \equiv \phi_{\text{at}, \nu}(\vec{r} - \vec{R} - \vec{c}) \quad (2.29)$$

characterized by the Bravais lattice point  $\vec{R}$ , the position  $\vec{c}$  of the basis atom in the primitive cell and  $\nu$ , a collective name for the

the atomic quantum numbers  $n, m, l$ .  $\phi_{\text{at}, \nu}(\vec{r})$  solves the SE

$$\hat{h}_{\text{at}} \phi_{\text{at}, \nu}(\vec{r}) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{at}}(\vec{r}) \right] \phi_{\text{at}, \nu}(\vec{r}) = \epsilon_{\nu} \phi_{\text{at}, \nu}(\vec{r}) \quad (2.30)$$

with eigenvalue  $\epsilon_{\nu}$ .

ii) Consider the effect of the crystal, i.e. all the ionic potential and divide the single electron hamiltonian  $\hat{h}$  into 2 parts

$$\hat{h} = \hat{h}_{\text{at}, \vec{R}, \vec{c}} + \Delta V_{\vec{R}, \vec{c}}(\vec{r}) \quad (2.31)$$

where

$$\hat{h}_{\text{at}, \vec{R}, \vec{c}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{at}}(\vec{r} - \vec{R} - \vec{c})$$

$$\Delta V_{\vec{R}, \vec{c}}(\vec{r}) = \sum_{\vec{c}' \neq \vec{c}} V_{\text{at}}(\vec{r} - \vec{R} - \vec{c}') + \sum_{\substack{\vec{R}' \neq \vec{R} \\ \vec{c}' \neq \vec{c}}} V_{\text{at}}(\vec{r} - \vec{R}' - \vec{c}') \quad (2.32)$$

iii) Construct the extended states out of the atomic ones with the periodicity of the Bravais lattice  $\{\vec{R}_n = \sum_{i=1}^3 n_i \vec{a}_i\}$ .

$$\left\{ \begin{aligned} \Psi_{\nu\vec{t}\vec{k}}(\vec{r}) &= \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_{\text{at},\nu}(\vec{r}-\vec{R}-\vec{t}) \\ |\nu\vec{t}\vec{k}\rangle &= \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\nu\vec{t}\vec{R}\rangle \end{aligned} \right. \quad (2.33)$$

The extended states satisfy the Bloch theorem  $\Psi_{\nu\vec{t}\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \Psi_{\nu\vec{t}\vec{k}}$  but are not (in general) Bloch functions. The extended states form a complete basis.

proof:

$$\begin{aligned} \sum_{\nu\vec{t}\vec{k}} \Psi_{\nu\vec{t}\vec{k}}^*(\vec{r}) \Psi_{\nu\vec{t}\vec{k}}(\vec{r}') &= \frac{1}{N_{\text{cell}}} \sum_{\vec{k}\vec{R}\vec{R}'} e^{-i\vec{k}\cdot(\vec{R}-\vec{R}')} \sum_{\vec{t}\vec{v}} \phi_{\text{at},\nu}^*(\vec{r}-\vec{R}-\vec{t}) \phi_{\text{at},\nu}(\vec{r}'-\vec{R}'-\vec{t}) \\ &= \sum_{\vec{R}\vec{t}} \sum_{\nu} \phi_{\text{at},\nu}^*(\vec{r}-\vec{R}-\vec{t}) \phi_{\text{at},\nu}(\vec{r}'-\vec{R}-\vec{t}) = N_{\text{atoms}} \delta(\vec{r}-\vec{r}') \quad \blacksquare \end{aligned}$$

iv) Use the complete set  $|\nu\vec{t}\vec{k}\rangle$  for the expansion of the Bloch function associated to the eigenvalue  $\varepsilon_n(\vec{k})$

$$|n\vec{k}\rangle = \sum_{\nu\vec{t}} C_{n,\nu\vec{t}}(\vec{k}) |\nu\vec{t}\vec{k}\rangle \quad (2.34)$$

Notice that the expansion involve the same  $\vec{k}$  in the Bloch and extended states.

v) The eigenvalue  $\varepsilon_n(\vec{k})$  and the coefficients  $C_{n,\nu\vec{t}}(\vec{k})$  result from the solution of the secular equation

$$\left\| \left[ \varepsilon_{\nu} - \varepsilon_n(\vec{k}) \right] S_{\nu\vec{t}',\nu\vec{t}}(\vec{k}) + K_{\nu\vec{t}',\nu\vec{t}}(\vec{k}) \right\| = 0 \quad (2.35)$$

and

$$\sum_{\nu\vec{c}} \left\{ \left[ \varepsilon_{\nu} - \varepsilon_n(\vec{k}) \right] S_{\nu\vec{c}',\nu\vec{c}}(\vec{k}) + K_{\nu\vec{c}',\nu\vec{c}}(\vec{k}) \right\} C_{n,\nu\vec{c}}(\vec{k}) = 0 \quad (2.36)$$

where

$\varepsilon_{\nu}$  is the energy of the atomic level  $\nu$ .

$$\left\{ \begin{aligned} S_{\nu\vec{c}',\nu\vec{c}}(\vec{k}) &= \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \int_V d\vec{r} \phi_{\text{at},\nu'}^*(\vec{r}-\vec{R}-\vec{c}') \phi_{\text{at},\nu}(\vec{r}-\vec{c}) \\ K_{\nu\vec{c}',\nu\vec{c}}(\vec{k}) &= \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \int_V d\vec{r} \phi_{\text{at},\nu'}^*(\vec{r}-\vec{R}-\vec{c}') \Delta V_{\vec{c},\vec{c}'}(\vec{r}) \phi_{\text{at},\nu}(\vec{r}-\vec{c}) \end{aligned} \right. \quad (2.37)$$

proof:

$$\hat{h} |n\vec{k}\rangle = \varepsilon_n(\vec{k}) |n\vec{k}\rangle$$

In other terms, using (2.34)

$$\sum_{\nu\vec{c}} \hat{h} C_{n,\nu\vec{c}}(\vec{k}) |\nu\vec{c}\vec{k}\rangle = \varepsilon_n(\vec{k}) \sum_{\nu\vec{c}} C_{n,\nu\vec{c}}(\vec{k}) |\nu\vec{c}\vec{k}\rangle$$

Finally, projecting onto  $|\nu\vec{c}\vec{k}\rangle$

$$\sum_{\nu\vec{c}} \left[ \langle \nu\vec{c}\vec{k} | \hat{h} | \nu\vec{c}\vec{k} \rangle - \varepsilon_n(\vec{k}) \langle \nu\vec{c}\vec{k} | \nu\vec{c}\vec{k} \rangle \right] C_{n,\nu\vec{c}}(\vec{k}) = 0$$

We can evaluate now the matrix elements:

$$\begin{aligned} \langle \nu\vec{c}\vec{k} | \nu\vec{c}\vec{k} \rangle &= \frac{1}{N_{\text{cell}}} \sum_{\vec{R}\vec{R}'} e^{-i\vec{k}\cdot(\vec{R}'-\vec{R})} \langle \nu\vec{c}\vec{R}' | \nu\vec{c}\vec{R} \rangle = \\ &= \frac{1}{N_{\text{cell}}} \sum_{\vec{R}\vec{R}'} e^{-i\vec{k}\cdot(\vec{R}'-\vec{R})} \int_V d\vec{r} \phi_{\text{at},\nu'}^*(\vec{r}-\vec{R}'-\vec{c}') \phi_{\text{at},\nu}(\vec{r}-\vec{R}-\vec{c}) \\ &= \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \int_V d\vec{r} \phi_{\text{at},\nu'}^*(\vec{r}-\vec{R}-\vec{c}') \phi_{\text{at},\nu}(\vec{r}-\vec{c}) = S_{\nu\vec{c}',\nu\vec{c}}(\vec{k}) \end{aligned}$$

$$\begin{aligned}
\langle \nu \vec{t}' \vec{R}' | \hat{h} | \nu \vec{t} \vec{R} \rangle &= \frac{1}{N_{\text{cell}}} \sum_{\vec{R}' \vec{R}} e^{-i\vec{k} \cdot (\vec{R}' - \vec{R})} \langle \nu \vec{t}' \vec{R}' | \hat{h}_{\text{at}, \vec{R}, \vec{t}} + \Delta \mathcal{N}_{\vec{R}, \vec{t}} | \nu \vec{t} \vec{R} \rangle \\
&= \sum_{\nu} S_{\nu \vec{t}', \nu \vec{t}}(\vec{k}) + \frac{1}{N_{\text{cell}}} \sum_{\vec{R}' \vec{R}} e^{-i\vec{k} \cdot (\vec{R}' - \vec{R})} \int_V d\vec{r} \phi_{\text{at}, \nu'}^*(\vec{r} - \vec{R}' - \vec{t}') \Delta \mathcal{N}_{\vec{R}, \vec{t}}(\vec{r}) \phi_{\text{at}, \nu}(\vec{r} - \vec{R} - \vec{t}) \\
&= \sum_{\nu} S_{\nu \vec{t}', \nu \vec{t}}(\vec{k}) + \frac{1}{N_{\text{cell}}} \sum_{\vec{R}' \vec{R}} e^{-i\vec{k} \cdot (\vec{R}' - \vec{R})} \int_V d\vec{s} \phi_{\text{at}, \nu'}^*(\vec{s} + \vec{R}' - \vec{R}' - \vec{t}') \Delta \mathcal{N}_{\vec{R}, \vec{t}}(\vec{s} + \vec{R}) \phi_{\text{at}, \nu}(\vec{s} - \vec{t}) \\
&= \sum_{\nu} S_{\nu \vec{t}', \nu \vec{t}}(\vec{k}) + \underbrace{\sum_{\vec{R}} e^{-i\vec{k} \cdot \vec{R}} \int_V d\vec{r} \phi_{\text{at}, \nu'}^*(\vec{r} - \vec{R} - \vec{t}') \Delta \mathcal{N}_{\vec{0}, \vec{t}} \phi_{\text{at}, \nu}(\vec{r} - \vec{t})}_{= K_{\nu \vec{t}', \nu \vec{t}}(\vec{k})}
\end{aligned}$$

Notice that:

- If the distance among the atoms is much larger than the extension of the atomic wave function  $\phi_{\text{at}, \nu}(\vec{r})$

$$S_{\nu \vec{t}', \nu \vec{t}}(\vec{k}) \longrightarrow \delta_{\vec{t}' \vec{t}} \delta_{\nu' \nu}$$

$$K_{\nu \vec{t}', \nu \vec{t}}(\vec{k}) \longrightarrow 0$$

Equations (2.35) and (2.36) are easily solved:  $\epsilon_n(\vec{k}) = \epsilon_{\nu}$ : i.e. the electronic bands are dispersionless and the band index  $n$  is the atomic index supplemented by the atomic basis index  $\vec{t}$ . This is the situation of the core electrons.

- The Wannier functions are expressed using known orbitals  $\phi_{\text{at}, \nu}(\vec{r})$  to which known atomic energies  $\epsilon_{\nu}$  are associated.

$$\begin{aligned}
\psi_{n\vec{k}}(\vec{r}) &= \frac{1}{\sqrt{N_{\text{cell}}}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \sum_{\nu \vec{t}} C_{n, \nu \vec{t}}(\vec{k}) \phi_{\text{at}, \nu}(\vec{r} - \vec{R} - \vec{t}) \\
\Rightarrow \mathcal{W}_n(\vec{r} - \vec{R}) &= \frac{1}{N_{\text{cell}}} \sum_{\vec{R}'} e^{-i\vec{k} \cdot (\vec{R} - \vec{R}')} \sum_{\nu \vec{t}} C_{n, \nu \vec{t}}(\vec{k}) \phi_{\text{at}, \nu}(\vec{r} - \vec{R}' - \vec{t}) \quad (2.38)
\end{aligned}$$

- Also the LCAO approach can be considered in the tight binding approximation: i.e.

$$i) \quad S_{\nu\vec{t}', \nu\vec{t}} \approx \delta_{\nu\nu} \delta_{\vec{t}'\vec{t}}$$

ii)  $K_{\nu\vec{t}', \nu\vec{t}}$  is calculated neglecting 3 centers integrals and keeping only nearest neighbours

$$\vec{t}' = \vec{t}$$

$$\begin{aligned}
 K_{\nu\vec{t}', \nu\vec{t}}(\vec{k}) &\approx \int_V d\vec{r} \phi_{\text{at}, \nu'}(\vec{r} - \vec{t}) \sum_{\substack{\vec{R} \in \text{n.n.} \\ \vec{t}'}} N_{\text{at}}(\vec{r} - \vec{R} - \vec{t}') \phi_{\text{at}, \nu}(\vec{r} - \vec{t}) \\
 &+ \sum_{\vec{R} \in \text{n.n.}} e^{-i\vec{k} \cdot \vec{R}} \int_V d\vec{r} \phi_{\text{at}, \nu'}^*(\vec{r} - \vec{R} - \vec{t}) N_{\text{at}}(\vec{r} - \vec{R} - \vec{t}) \phi_{\text{at}, \nu}(\vec{r} - \vec{t}) \\
 &= \underbrace{C_{\nu\nu}^{\vec{t}}}_{\text{crystal field}} + \underbrace{\sum_{\vec{R}} e^{-i\vec{k} \cdot \vec{R}} \chi_{\nu\nu}(\vec{R})}_{\text{hopping term} \approx \text{overlap integral}} \quad (2.39)
 \end{aligned}$$

$$\vec{t}' \neq \vec{t}$$

$$\begin{aligned}
 K_{\nu\vec{t}', \nu\vec{t}}(\vec{k}) &\approx \int_V d\vec{r} \phi_{\text{at}, \nu'}^*(\vec{r} - \vec{t}') N_{\text{at}}(\vec{r} - \vec{t}') \phi_{\text{at}, \nu}(\vec{r} - \vec{t}) \\
 &= \chi_{\nu\nu'}(\vec{t}' - \vec{t}) \quad (2.40)
 \end{aligned}$$

By combining (2.39) and (2.40) we obtain

$$K_{\nu\vec{t}', \nu\vec{t}}(\vec{k}) = C_{\nu\nu}^{\vec{t}} \delta_{\vec{t}'\vec{t}} + \sum_{\vec{R} = \vec{0}, \text{n.n.}} e^{-i\vec{k} \cdot \vec{R}} \chi_{\nu\nu}(\vec{R} + \vec{t}' - \vec{t}) \quad (2.41)$$

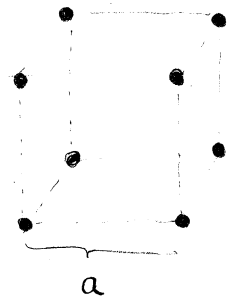
In order to illustrate the method we consider some examples.

Example: s-band on a simple cubic lattice (E.g. 3s electrons of Na on a simple cubic lattice)

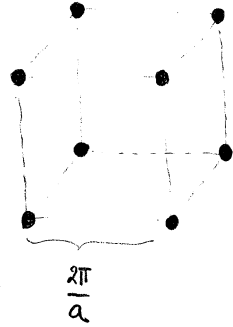
$$\varepsilon(\vec{k}) = \varepsilon_s + \sum_{\text{n.n.}} e^{-i\vec{k} \cdot \vec{R}} \gamma_{ss}(\vec{R}) + C_{ss}$$

with  $\gamma_{ss} = V_{SS\sigma}$  hopping integral  
 $\gamma_{ss} < 0$

direct lattice spanned by  $a\hat{x}, a\hat{y}, a\hat{z}$

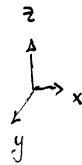
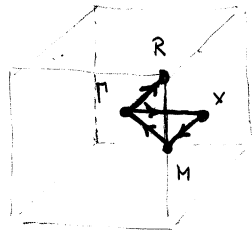


reciprocal lattice spanned by  $\frac{2\pi}{a}\hat{x}, \frac{2\pi}{a}\hat{y}, \frac{2\pi}{a}\hat{z}$



The 1<sup>st</sup> BZ with the special symmetry points

$\vec{\Gamma}, \vec{X}, \vec{M}, \vec{R}$



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

$$\vec{X} = \frac{\pi}{a}(1, 0, 0)$$

$$\vec{M} = \frac{\pi}{a}(1, 1, 0)$$

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

$$\varepsilon(\vec{k}) = \tilde{\varepsilon}_s + 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$$

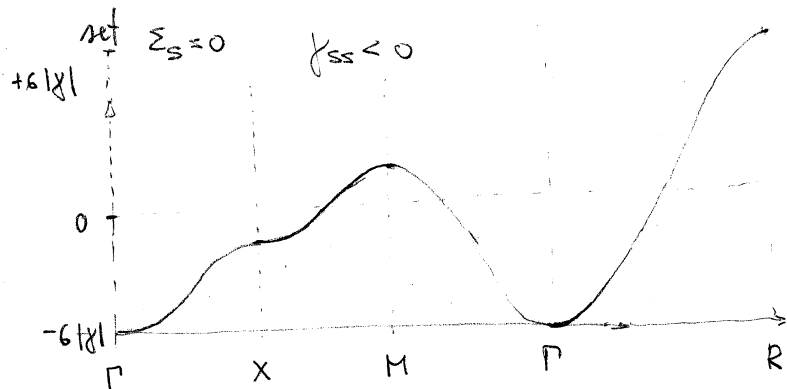
$$\tilde{\varepsilon} = \varepsilon_s + C_{ss}$$

$$\varepsilon(\vec{\Gamma}) = \tilde{\varepsilon}_s + 6\gamma$$

$$\varepsilon(\vec{X}) = \tilde{\varepsilon}_s + 2\gamma(2-1) = \tilde{\varepsilon}_s + 2\gamma$$

$$\varepsilon(\vec{M}) = \tilde{\varepsilon}_s + 2\gamma(1-2) = \tilde{\varepsilon}_s - 2\gamma$$

$$\varepsilon(\vec{R}) = \tilde{\varepsilon}_s + 2\gamma(-3) = \tilde{\varepsilon}_s - 6\gamma$$



Note: parabolic dispersion, as for free electrons around the  $\Gamma$  point

$$|\vec{R}|a \ll 1 \quad \varepsilon(\vec{k}) = \tilde{\varepsilon}_s + 2\gamma \left[ 3 - \frac{1}{2} (k_x^2 + k_y^2 + k_z^2) a^2 \right] = \tilde{\varepsilon}_s + 6\gamma - \gamma k^2 a^2$$

One can describe these states as free electrons with an effective mass

$$m^* = -\frac{\hbar^2}{2a^2\gamma} \quad \gamma \rightarrow 0 \quad m^* \rightarrow \infty \Rightarrow \text{the electrons cannot move}$$



Example: Two atomic orbitals and a simple 1D Bravais lattice

$v = s, p_x$  and 1 dimensional lattice with lattice constant  $a$ :



$\vec{\tau} = 0$  For simplicity we restrict ourselves to the tight binding approximation. The secular equation reads:

$$0 = \det \begin{vmatrix} \epsilon_s + C_{ss} + \gamma_{ss}(a)e^{-ika} + \gamma_{ss}(-a)e^{ika} - \epsilon_n & \gamma_{sp}(a)e^{-ika} + \gamma_{sp}(-a)e^{ika} \\ \gamma_{ps}(a)e^{-ika} + \gamma_{ps}(-a)e^{ika} & \epsilon_p + C_{pp} + \gamma_{pp}(a)e^{-ika} + \gamma_{pp}(-a)e^{ika} - \epsilon_n \end{vmatrix}$$

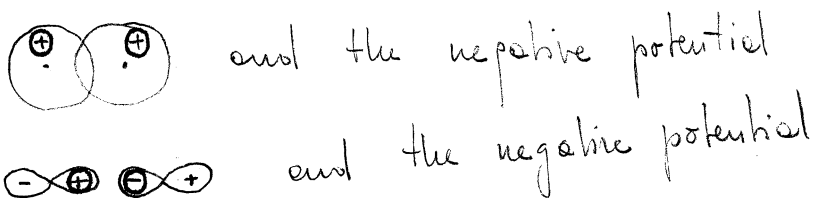
$$= \det \begin{vmatrix} \epsilon_s + C_{ss} + 2\gamma_{ss} \cos(ka) - \epsilon_n & -2i\gamma_{sp} \sin(ka) \\ 2i\gamma_{sp} \sin(ka) & \epsilon_p + C_{pp} + 2\gamma_{pp} \cos(ka) - \epsilon_n \end{vmatrix}$$

Where we have used the fact that  $\phi_{s,p_x}$  are real functions and

$$\gamma_{ss}(a) \equiv \int_V d\vec{r} s(\vec{r} - a\hat{x}) N_{\text{tot}}(\vec{r} - a\hat{x}) s(\vec{r}) = \int_V d\vec{r} s(-\vec{r} - a\hat{x}) N_{\text{tot}}(-\vec{r} - a\hat{x}) s(-\vec{r})$$

$$= \int_V d\vec{r} s(\vec{r} + a\hat{x}) N_{\text{tot}}(\vec{r} + a\hat{x}) s(\vec{r}) \equiv \gamma_{ss}(-a)$$

and analogously for  $\gamma_{pp}$ . Interestingly, though  $\gamma_{ss} > 0$  and  $\gamma_{pp} < 0$ .



Instead:

$$\begin{aligned} \chi_{sp}(a) &= \int_V d\vec{r} \, s(\vec{r}-a\hat{x}) \sqrt{a} \phi_p(\vec{r}-a\hat{x}) \phi_s(\vec{r}) = \\ &= \int_V d\vec{r} \, s(-\vec{r}-a\hat{x}) \sqrt{a} \phi_p(-\vec{r}-a\hat{x}) \phi_s(-\vec{r}) = \\ &= - \int_V d\vec{r} \, s(\vec{r}+a\hat{x}) \sqrt{a} \phi_p(\vec{r}+a\hat{x}) \phi_s(\vec{r}) = -\chi_{sp}(-a) \end{aligned}$$

Moreover one can easily prove that  $c_{sp} = c_{ps} = 0$

$$\begin{aligned} c_{sp} &= \int_V d\vec{r} \, s(\vec{r}) \left[ \sqrt{a} \phi_p(\vec{r}-a\hat{x}) + \sqrt{a} \phi_p(\vec{r}+a\hat{x}) \right] \phi_s(\vec{r}) \\ &= \int_V d\vec{r} \, s(-\vec{r}) \left[ \sqrt{a} \phi_p(-\vec{r}-a\hat{x}) + \sqrt{a} \phi_p(-\vec{r}+a\hat{x}) \right] \phi_s(-\vec{r}) \\ &= \int_V d\vec{r} \, s(\vec{r}) \left[ \sqrt{a} \phi_p(\vec{r}+a\hat{x}) + \sqrt{a} \phi_p(\vec{r}-a\hat{x}) \right] (-1) \phi_s(\vec{r}) = -c_{sp} = 0 \end{aligned}$$

The band structure of the system reads:

$$\varepsilon_{\pm}(k) = \frac{\tilde{\varepsilon}_p + \tilde{\varepsilon}_s}{2} + (\chi_{pp} + \chi_{ss}) \cos ka \pm \sqrt{\left[ \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_s}{2} + (\chi_{pp} - \chi_{ss}) \cos ka \right]^2 + 4\chi_{sp}^2 \sin^2 ka}$$

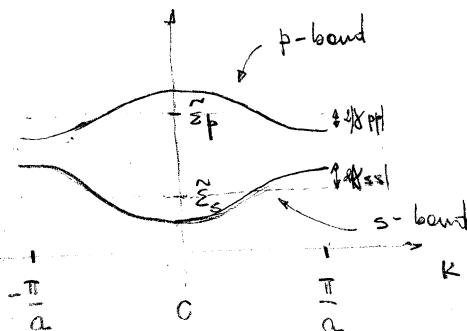
where  $\tilde{\varepsilon}_s = \varepsilon_s + c_{ss}$  and  $\tilde{\varepsilon}_p = \varepsilon_p + c_{pp}$ . If  $\tilde{\varepsilon}_p - \tilde{\varepsilon}_s \gg |\chi_{sp}|$ , the second term in the square root can be neglected and

$$\varepsilon_- = \varepsilon_s + 2\chi_{ss} \cos ka$$

$$\varepsilon_+ = \varepsilon_p + 2\chi_{pp} \cos ka$$

$$C_{-s}(k) = 1 \quad C_{-p}(k) = 0$$

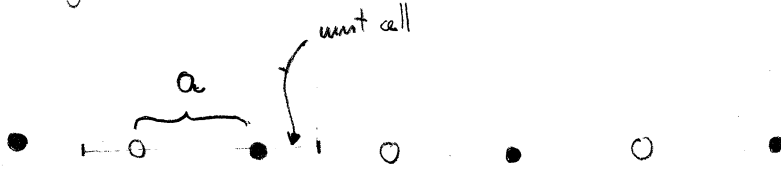
$$C_{+s}(k) = 0 \quad C_{+p}(k) = 1 \quad \forall k$$



$\Rightarrow$  the Wannier and the atomic function coincide (see eq. 2.38)

In the case in which  $|k_{sp}| \approx \tilde{\epsilon}_p - \tilde{\epsilon}_s$  one obtains instead bands which hybridize the s and  $p_x$  atomic orbitals.

Example: 1D crystal structure with biatomic basis



We assume a tight binding Hamiltonian of the form

$$\hat{h} = \sum_{\vec{R}} \left\{ \epsilon_s |\vec{R} + \vec{t}_s\rangle \langle \vec{R} + \vec{t}_s| + \epsilon_0 |\vec{R} + \vec{t}_0\rangle \langle \vec{R} + \vec{t}_0| + t \left( |\vec{R} + \vec{t}_0\rangle \langle \vec{R} + \vec{t}_s| + |\vec{R} + \vec{t}_s\rangle \langle \vec{R} + \vec{t}_0| \right) + t \left( |\vec{R} + 2a\hat{x} + \vec{t}_0\rangle \langle \vec{R} + \vec{t}_s| + |\vec{R} + \vec{t}_s\rangle \langle \vec{R} + 2a\hat{x} + \vec{t}_0| \right) \right.$$

The extended states can be written as:

$$|\bullet, k\rangle = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_j e^{ikja} |ja\hat{x} + \vec{t}_s\rangle$$

$$|0, k\rangle = \frac{1}{\sqrt{N_{\text{cell}}}} \sum_j e^{ikja} |ja\hat{x} + \vec{t}_0\rangle$$

which corresponds to a secular equation

$$\det \begin{pmatrix} \epsilon_s - \epsilon(k) & t(1 + e^{2ika}) \\ t(1 + e^{-2ika}) & \epsilon_0 - \epsilon(k) \end{pmatrix} = 0 \quad k \in \left[ -\frac{\pi}{2a}, \frac{\pi}{2a} \right]$$

$$\epsilon_{\pm}(k) = \frac{\epsilon_s + \epsilon_0}{2} \pm \sqrt{\frac{(\epsilon_s - \epsilon_0)^2}{4} + 4t^2 \cos^2 ka}$$

The hybridization is strongest at the  $\Gamma$  point.