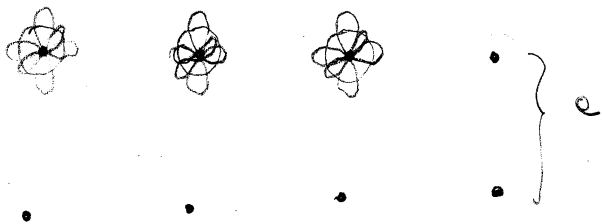


Example (previous problem) 2d monatomic square lattice with four orbitals



Once again we neglect the overlap between the electronic orbitals on different ions

$H_{\nu\nu'}(\vec{k}) \equiv \sum_{\nu} \delta_{\nu\nu'} + K_{\nu\nu'}(\vec{k})$ we obtain by symmetry that $c_{\nu\nu'} = 0$ if $\nu \neq \nu'$

	$ s\rangle$	$ p_x\rangle$	$ p_y\rangle$	$ p_z\rangle$
$\langle s $	$\tilde{\epsilon}_s + V_{sss} g_0$	$V_{sp\sigma} g_1$	$V_{sp\sigma} g_2$	0
$\langle p_x $	$V_{sp\sigma} g_1^*$	$\tilde{\epsilon}_{p_x} + V_{pp\sigma} g_4 + V_{pp\pi} g_3$	0	0
$\langle p_y $	$V_{sp\sigma} g_2^*$	0	$\tilde{\epsilon}_{p_y} + V_{pp\sigma} g_3 + V_{pp\pi} g_4$	0
$\langle p_z $	0	0	0	$\tilde{\epsilon}_{p_z} + V_{pp\pi} g_0$

where

$$g_0 = e^{-ik_x a} + e^{ik_x a} + e^{-ik_y a} + e^{ik_y a}$$

$$g_1 = e^{-ik_x a} - e^{ik_x a} \quad ; \quad g_2 = e^{-ik_y a} - e^{ik_y a}$$

$$g_3 = e^{-ik_y a} + e^{ik_y a} \quad ; \quad g_4 = e^{-ik_x a} + e^{ik_x a}$$

Note:

○	○	V_{sss}	○	∞	$V_{sp\sigma}$	∞	∞	$V_{pp\sigma}$
∞	∞	$V_{pp\pi}$						

The nomenclature for the hopping integrals is

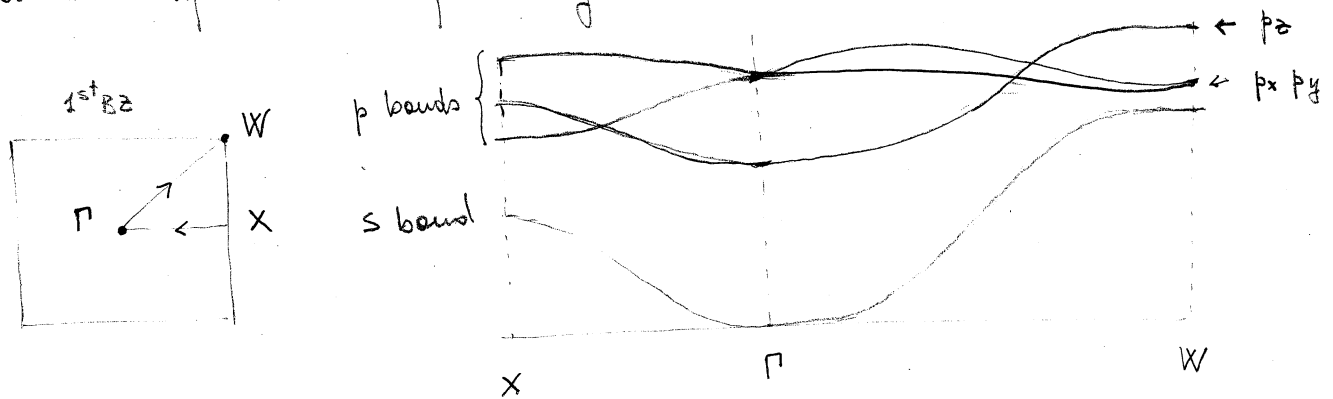
$\frac{V_{ab}}{l}$ \times
 l of atoms \times symmetry of the bond

σ	0	nodal planes intersecting the bond axis
π	1	" " " "
δ	2	" " " "

• Since we consider 4 orbitals within a unit cell we expect to obtain 4 bands

• The bands would become flat if $a \rightarrow \infty$ since all hopping parameters decay with the atomic distance.

• $\tilde{\epsilon}_{p\perp} > \tilde{\epsilon}_{p\parallel}$ since p_x and p_y extend more towards the attractive potentials of the neighboring ions



At the high symmetry points one can identify the degeneracies:

$$\Gamma \quad g_0 = 4 \quad g_1 = g_2 = 0 \quad g_3 = g_4 = 2 \quad \Rightarrow \quad p_x \text{ and } p_y \text{ bands coincide}$$

$$X = \left[\frac{\pi}{a}, 0 \right] \quad g_0 = 2 \quad g_1 = -2i \quad g_2 = 0 \quad g_3 = 2 \quad g_4 = 0$$

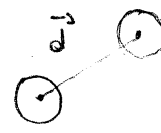
no degeneracies are expected since p_x and s hybridize while p_y and p_z are decoupled

W again the degeneracy between p_y and p_x bands is expected, since $g_1 = g_2 = 0 \quad g_3 = g_4$

In general, for 3D crystal structures one has to consider hopping integrals and overlaps between orbitals arbitrarily distributed in space.

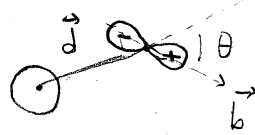
Orbital overlap / hopping integrals for 3D crystals

i) $\langle s_1 | \hat{V}_{at} | s_2 \rangle = V_{ss\sigma}$ (2.42)

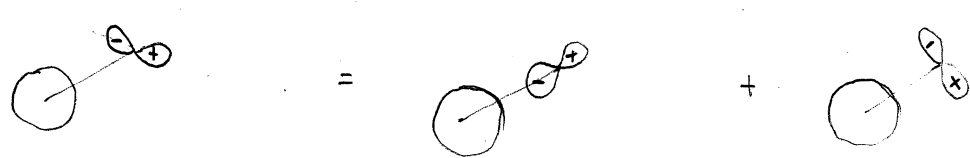


it is independent from the orientation of the bond axis \hat{d} , due to the rotational symmetry of the s orbital as well as of the atomic potential

ii) $\langle s_1 | \hat{V}_{at} | p \rangle_2 = V_{sp\sigma} \hat{d} \cdot \hat{b} = V_{sp\sigma} \cos\theta$ (2.43)



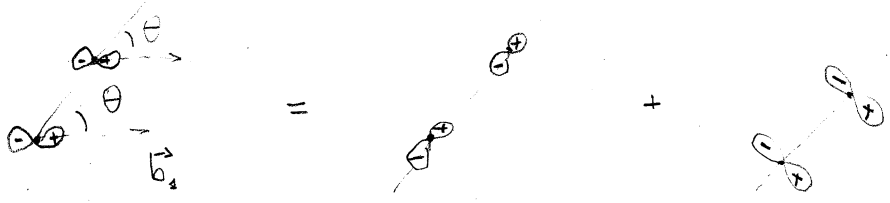
In fact we can decompose



$$\langle s_1 | \hat{V}_{at} | p \rangle_2 = V_{sp\sigma} \cos\theta + 0$$

iii) $\langle p_1 | \hat{V}_{at} | p_2 \rangle = (\hat{d} \cdot \hat{b}_1)(\hat{d} \cdot \hat{b}_2) V_{pp\sigma} + [\hat{b}_1 - \hat{d}(\hat{b}_1 \cdot \hat{d})][\hat{b}_2 - \hat{d}(\hat{b}_2 \cdot \hat{d})] V_{pp\pi}$

For example, if \hat{b}_1, \hat{b}_2 and \hat{d} belong to the same plane and $\hat{b}_1 \parallel \hat{b}_2$



$$\langle p_x | \hat{V}_{at} | p_x \rangle = V_{pp\sigma} \cos^2\theta + V_{pp\pi} \sin^2\theta$$

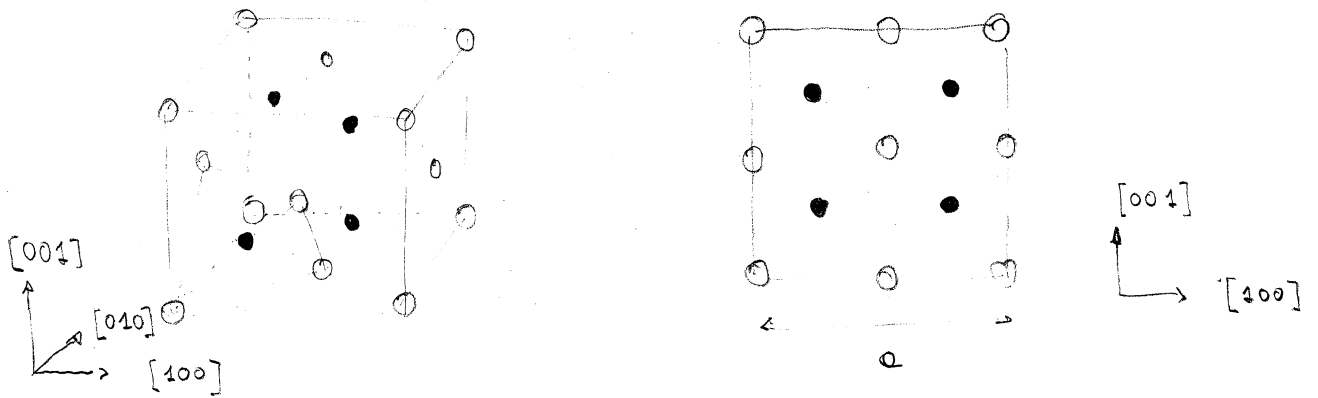
Similar argument can be pushed forward also for the d orbitals.

For a review see Slater and Koster Phys. Rev. 94, 1498 (1954)

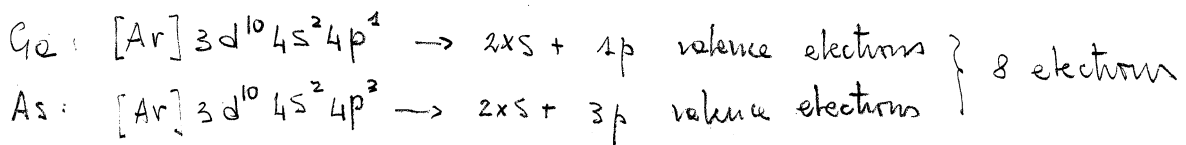
The Zincblende and diamond structures

Zincblende and diamond structures: two interpenetrating fcc. They can be viewed as an fcc with a two-point basis $\{\vec{r}\} = \{\vec{0}, \frac{a}{4}(\hat{x} + \hat{y} + \hat{z})\}$

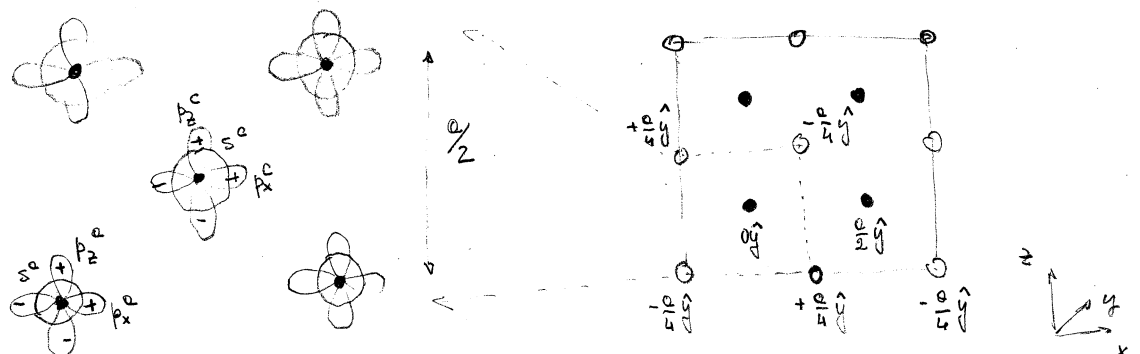
- Zincblende structure: solid composed by $A_{III}B_{IV}$ or $A_{II}B_{VI}$ atoms as for example GeAs, ZnS
- Diamond structure: for example C, Ge or Si, all belonging to the group IV.



Now, if for example concentrate on GeAs



In the elementary cell: 1 Ge (cation) + 1 As (anion)
 The basis which is used is $s^c, s^a, p_x^c, p_x^a, p_y^c, p_y^a, p_z^c, p_z^a$



one has to consider in the LCAO both s and p orbitals.

We recall the secular equation in the tight binding approximation

$$\left\| \epsilon_V \delta_{V'V} \delta_{\vec{r}'\vec{r}} + C_{V'V} \delta_{\vec{r}'\vec{r}} + \sum_{n.n.} e^{-i\vec{k}\cdot\vec{R}} \gamma_{V'V}(\vec{R}+\vec{r}'-\vec{r}) \right\| = 0$$

If the definition of the extended states is modified in the one

$$|V\vec{r}\vec{k}\rangle = \frac{1}{\sqrt{N_{\text{cell}}}} e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |V\vec{r}\vec{R}\rangle$$

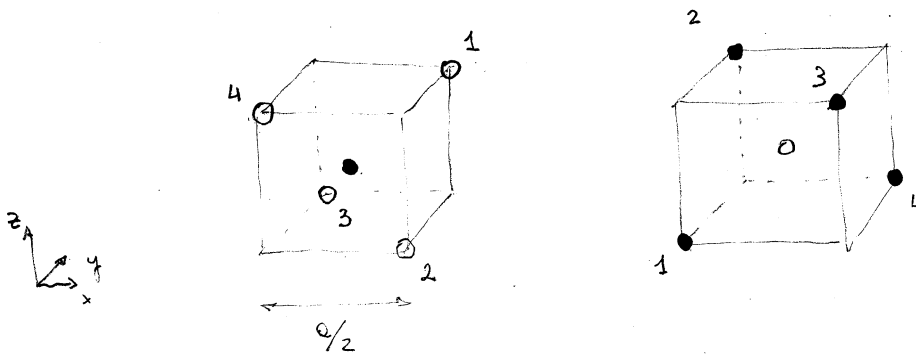
overall phase factor \Rightarrow legitimate change

The secular equation becomes:

$$\left\| \epsilon_V \delta_{V'V} \delta_{\vec{r}'\vec{r}} + C_{V'V} \delta_{\vec{r}'\vec{r}} + \sum_{n.n.} e^{-i\vec{k}\cdot(\vec{R}+\vec{r}'-\vec{r})} \gamma_{V'V}(\vec{R}+\vec{r}'-\vec{r}) \right\| = 0$$

The new definition makes the formula more symmetric in the sense that the phase $e^{-i\vec{k}\cdot(\vec{R}+\vec{r}'-\vec{r})}$ also contains the ATOMIC distance, exactly as the hopping integral $\gamma_{V'V}(\vec{R}+\vec{r}'-\vec{r})$.

The nearest neighbours for the anion and the cation can be more clearly visualized in tetrahedral structures:



Thus the phase factors

$$\begin{aligned} e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4} &= g_0 \\ e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4} &= g_1 \\ e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} - e^{i\vec{k}\cdot\vec{d}_4} &= g_2 \\ e^{i\vec{k}\cdot\vec{d}_1} - e^{i\vec{k}\cdot\vec{d}_2} - e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4} &= g_3 \end{aligned}$$

$$\vec{d}_1 = [111] \frac{a}{4}$$

$$\vec{d}_2 = [1\bar{1}\bar{1}] \frac{a}{4}$$

$$\vec{d}_3 = [\bar{1}1\bar{1}] \frac{a}{4}$$

$$\vec{d}_4 = [\bar{1}\bar{1}1] \frac{a}{4}$$

neighbors
to the cation

the neighbors to
the anion are obtained
by inversion operation

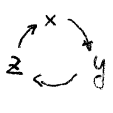
$$\vec{d}_i \rightarrow -\vec{d}_i$$

For what concerns the hopping integrals it is possible to reduce them to only 4 by using the symmetry operations of a tetrahedron

$$s^c s_1^a \rightarrow \boxed{\chi_{ss}} \text{ and the same holds for } s_i^a$$

$$s^c p_{x1}^a = s^c p_{y1}^a = s^c p_{z1}^a \rightarrow \boxed{\chi_{sp}} \text{ use the } C_3 \text{ rotation}$$

$$p_x^c s_1^a = p_y^c s_1^a = p_z^c s_1^a \Rightarrow -\chi_{sp} \text{ inversion symmetry}$$



$$p_x^c p_x^a = p_y^c p_y^a = p_z^c p_z^a \rightarrow \boxed{\chi_{xx}}$$

$$p_x^c p_y^a = p_y^c p_z^a = p_z^c p_x^a \rightarrow \boxed{\chi_{xy}}$$

$$p_y^c p_x^a = p_z^c p_y^a = p_x^c p_z^a \rightarrow \chi_{xy} \text{ inversion symmetry.}$$

All together the LCAO matrix for zincblende thus reads

	s^c	s^a	p_x^c	p_y^c	p_z^c	p_x^a	p_y^a	p_z^a
s^c	\sum_s^c	$\chi_{ss} g_0$	0	0	0	$\chi_{sp} g_1$	$\chi_{sp} g_2$	$\chi_{sp} g_3$
s^a	$\chi_{ss} g_0^*$	\sum_s^a	$-\chi_{sp} g_1^*$	$-\chi_{sp} g_2^*$	$-\chi_{sp} g_3^*$	0	0	0
p_x^c	0	$-\chi_{sp} g_1$	\sum_p^c	0	0	$\chi_{xx} g_0$	$\chi_{xy} g_3$	$\chi_{xy} g_2$
p_y^c	0	$-\chi_{sp} g_2$	0	\sum_p^c	0	$\chi_{xy} g_3$	$\chi_{xx} g_0$	$\chi_{xy} g_1$
p_z^c	0	$-\chi_{sp} g_3$	0	0	\sum_p^c	$\chi_{xy} g_2$	$\chi_{xy} g_1$	$\chi_{xx} g_0$
p_x^a	$\chi_{sp} g_1^*$	0	$\chi_{xx} g_0^*$	$\chi_{xy} g_3^*$	$\chi_{xy} g_2^*$	\sum_p^a	0	0
p_y^a	$\chi_{sp} g_2^*$	0	$\chi_{xy} g_3^*$	$\chi_{xx} g_0^*$	$\chi_{xy} g_1^*$	0	\sum_p^a	0
p_z^a	$\chi_{sp} g_3^*$	0	$\chi_{xy} g_2^*$	$\chi_{xy} g_1^*$	$\chi_{xx} g_0^*$	0	0	\sum_p^a

Eventually we can relate the hopping integral to the 3 fundamental

ones $V_{ss\sigma}$ $V_{sp\sigma}$ $V_{pp\pi}$

$$\chi_{ss} = V_{ss\sigma} \quad \chi_{sp} = + V_{sp\sigma} / \sqrt{3} \quad \chi_{pp} = \frac{V_{pp\sigma}}{3} + \frac{2}{3} V_{pp\pi} \quad \chi_{xy} = \frac{V_{pp\sigma}}{3} - \frac{V_{pp\pi}}{3}$$

proof: $\chi_{ss} = V_{ss\sigma}$ in formula (2.42). For the other cases we consider

$$\vec{d}_1 = \frac{a}{4} [1, 1, 1] \Rightarrow \hat{d} = \frac{1}{\sqrt{3}} [1, 1, 1]$$

$$\chi_{sp} = \langle s^c | \hat{v}_{et} | p_{1x}^a \rangle = V_{sp\sigma} \hat{d} \cdot \hat{b}^a = V_{sp\sigma} \hat{d} \cdot \hat{x} = V_{sp\sigma} \frac{1}{\sqrt{3}}$$

$$\begin{aligned} \chi_{xx} &= \langle p_x^c | \hat{v}_{et} | p_{1x}^a \rangle = (\hat{d} \cdot \hat{b}^c) (\hat{d} \cdot \hat{b}_1^a) V_{pp\sigma} + [\hat{b}^c - \hat{d} (\hat{d} \cdot \hat{b}^c)] \cdot [\hat{b}_1^a - \hat{d} (\hat{d} \cdot \hat{b}_1^a)] V_{pp\pi} \\ &= (\hat{d} \cdot \hat{x}) (\hat{d} \cdot \hat{x}) V_{pp\sigma} + [\hat{x} - \hat{d} (\hat{d} \cdot \hat{x})] \cdot [\hat{x} - \hat{d} (\hat{d} \cdot \hat{x})] V_{pp\pi} \\ &= \frac{1}{3} V_{pp\sigma} + [\hat{x} \cdot \hat{x} - (\hat{x} \cdot \hat{d})^2] V_{pp\pi} = \frac{1}{3} V_{pp\sigma} + \frac{2}{3} V_{pp\pi} \end{aligned}$$

$$\begin{aligned} \chi_{xy} &= (\hat{d} \cdot \hat{x}) (\hat{d} \cdot \hat{y}) V_{pp\sigma} + [\hat{x} - \hat{d} (\hat{d} \cdot \hat{x})] \cdot [\hat{y} - \hat{d} (\hat{d} \cdot \hat{y})] V_{pp\pi} = \\ &= (\hat{d} \cdot \hat{x}) (\hat{d} \cdot \hat{y}) V_{pp\sigma} - (\hat{x} \cdot \hat{d}) (\hat{y} \cdot \hat{d}) V_{pp\pi} = \frac{1}{3} V_{pp\sigma} - \frac{1}{3} V_{pp\pi} \end{aligned}$$

There are no general analytic solutions to the LCAO secular equation for the zincblende and diamond structures. At the Γ point though one can state e.g.

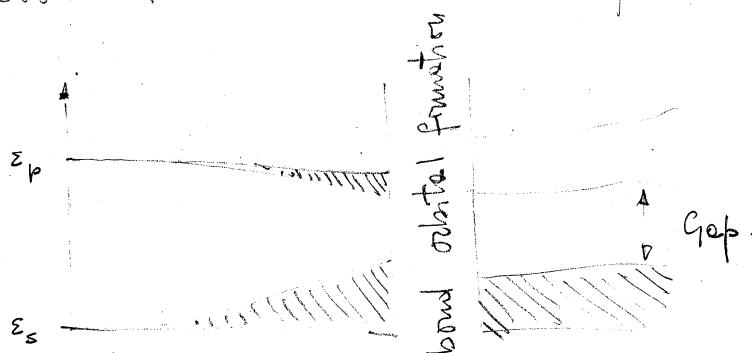
$$E_s = \frac{\tilde{\Sigma}_s^c + \tilde{\Sigma}_s^a}{2} \pm \sqrt{\left(\frac{\tilde{\Sigma}_s^c - \tilde{\Sigma}_s^a}{2} \right)^2 + (4\chi_{ss})^2}$$

$$E_p = \frac{\tilde{\Sigma}_p^c + \tilde{\Sigma}_p^a}{2} \pm \sqrt{\left(\frac{\tilde{\Sigma}_p^c - \tilde{\Sigma}_p^a}{2} \right)^2 + (4\chi_{xx})^2} \quad \text{sx dependent}$$

since $g_1 = g_2 = g_3 = 0$ and $g_0 = 4$ at the Γ point.

As a summary of all previous examples we can remain with the ideas.

- The bands of continuous energy arise in solids by the hybridization of the atomic levels.
- The width of the bands is characterized by the hopping integral $\gamma(\vec{R})$.
- A qualitative difference distinguishes the solids in which the atomic energy level separation is larger or smaller than the band width. In the second case band orbital formation leads to the band structure of covalent solids.



metal

covalent solid
(semiconductor or
insulator)

$\frac{1}{d} \leftarrow d$ is the "typical distance between 2 atoms in the crystal structure.

The denomination metal and semiconductor/insulator is referring to the transport properties of the system close to its equilibrium configuration and will be analyzed later in this chapter and in chapter 4. Here it is enough to mention that in covalent solids the bands cannot any more be associated to a specific atomic level.

2.5 | Almost free electrons

The point of view complementary to the LCAO one, is to consider the periodic potential as a small perturbation.

In this situation it is convenient to express the Bloch waves as linear combination of (DELOCALIZED) PLANE WAVES.

Using the completeness of the plane waves basis $|\vec{k}\rangle$ (where, for simplicity, we keep neglecting the spin quantum number associated to an electron) and expand:

$$|\psi\rangle = \sum_{\vec{k}} c_{\vec{k}} |\vec{k}\rangle \quad \text{or} \quad \psi(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}} \langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{V}} \sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

By projecting the SE for the electrons in a solid (2.7) on the state $|\vec{k}'\rangle$

$$\begin{aligned} \langle \vec{k}' | \hat{h} | \psi \rangle &= \sum_{\vec{k}} c_{\vec{k}} \langle \vec{k}' | -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) | \vec{k} \rangle = \\ &= \sum_{\vec{k}} \left(c_{\vec{k}} \varepsilon_{\vec{k}}^0 \delta_{\vec{k}'\vec{k}} + c_{\vec{k}} \sum_{\vec{G}} \tilde{V}(\vec{G}) \delta_{\vec{k}', \vec{k}+\vec{G}} \right) \end{aligned}$$

In the last equality we have used $V(\vec{r}) = \sum_{\vec{G}} \tilde{V}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$ with $\tilde{V}(\vec{G}) = \int_{\text{cell}} d\vec{r} e^{-i\vec{G}\cdot\vec{r}} V(\vec{r})$
 $\langle \vec{r} | e^{i\vec{G}\cdot\vec{r}} | \vec{k} \rangle = \langle \vec{r} | \vec{k} + \vec{G} \rangle$ and $\langle \vec{k}' | \vec{k} \rangle = \delta_{\vec{k}'\vec{k}}$.

If $|\psi\rangle$ is an eigenstate of $\hat{h} \Rightarrow \hat{h}|\psi\rangle = \varepsilon|\psi\rangle$ and consequently

$$\sum_{\vec{k}} |\vec{k}\rangle \left(c_{\vec{k}} \frac{\hbar^2 k^2}{2m} + \sum_{\vec{G}} \tilde{V}(\vec{G}) c_{\vec{k}-\vec{G}} \right) = \varepsilon \sum_{\vec{k}} c_{\vec{k}} |\vec{k}\rangle$$

or, by exploiting the orthogonality of $|\vec{k}\rangle$

$$\left[c_{\vec{k}} \frac{\hbar^2 k^2}{2m} + \sum_{\vec{G}} \tilde{V}(\vec{G}) c_{\vec{k}-\vec{G}} \right] = \varepsilon c_{\vec{k}} \quad (2.45)$$

- Since \vec{k} only couples to $\vec{k}-\vec{G}$ one can consider only $\vec{k} \in \frac{1}{2}\text{BZ}$.

Moreover

$$\varepsilon(\vec{k} + \vec{G}) = \varepsilon(\vec{k})$$

- For a given \vec{k} there are as many solutions as vectors \vec{G} (i.e. infinite)
 \Rightarrow we have to introduce a (band) index n .

- Specifically, for a given $\vec{k} \in 1^{st} BZ$ the eigenfunctions have the form

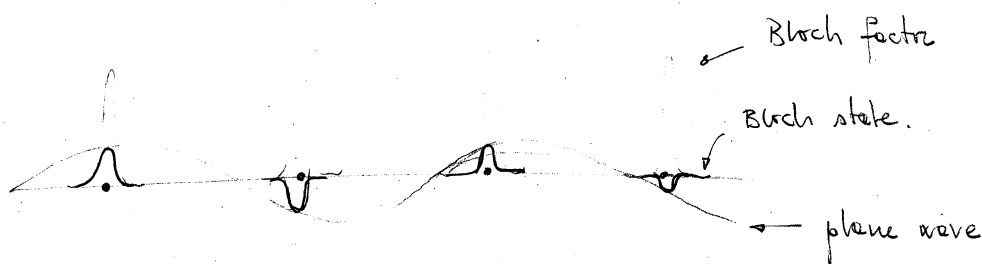
$$\begin{cases} \hat{h} |n\vec{k}\rangle = \varepsilon_n(\vec{k}) |n\vec{k}\rangle \\ \psi_{n\vec{k}}(\vec{r}) = \langle \vec{r} | n\vec{k} \rangle = \frac{1}{\sqrt{V}} \sum_{\vec{G}} c_{\vec{k}+\vec{G}}^{(n)} e^{i(\vec{k}+\vec{G})\vec{r}} \end{cases}$$

The eigenfunctions have the Bloch form $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$

since

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}+\vec{G}}^{(n)} e^{i\vec{G}\cdot\vec{r}} \quad (2.45)$$

is periodic $u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r} + \vec{R})$ and $\vec{R} \in BL$.



The eigenvalue equation is obtained from (2.45). By shifting it of \vec{G}'

$$c_{\vec{k}-\vec{G}'} \varepsilon_{\vec{k}-\vec{G}'}^0 + \sum_{\vec{G}} \tilde{V}(\vec{G}) c_{\vec{k}-\vec{G}-\vec{G}'} = \varepsilon_n(\vec{k}) c_{\vec{k}-\vec{G}'}$$

But, renaming the summing variable \vec{G}

$$\sum_{\vec{G}} \left[\varepsilon_{\vec{k}-\vec{G}}^0 \delta_{\vec{G}\vec{G}'} + \tilde{V}(\vec{G}-\vec{G}') \right] c_{\vec{k}-\vec{G}} = \sum_{\vec{G}} \varepsilon_n(\vec{k}) \delta_{\vec{G}\vec{G}'} c_{\vec{k}-\vec{G}}$$

The eigenvalue equation reads:

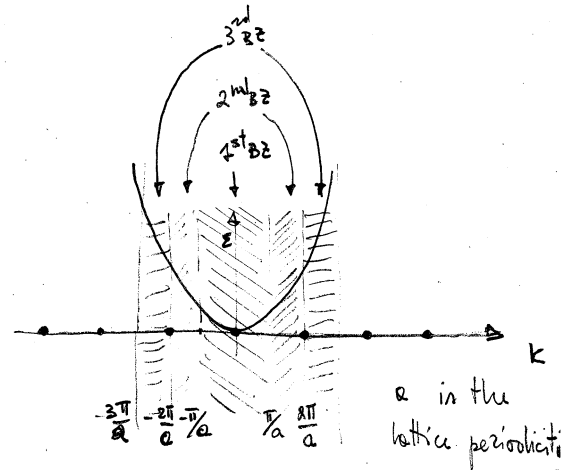
$$\left\| \left(\varepsilon_{\vec{k}-\vec{G}'}^0 - \varepsilon_n(\vec{k}) \right) \delta_{\vec{G}\vec{G}'} + \tilde{V}(\vec{G}-\vec{G}') \right\| = 0 \quad (2.47)$$

The eq. (2.47) is exact. The efficiency of the approach, though, depends crucially on the convergence of the plane wave expansion, i.e. on the strength of the periodic potential. The kinetic term should dominate.

Let us consider the case in which the free electron picture is only slightly perturbed. For simplicity, consider the 1D case

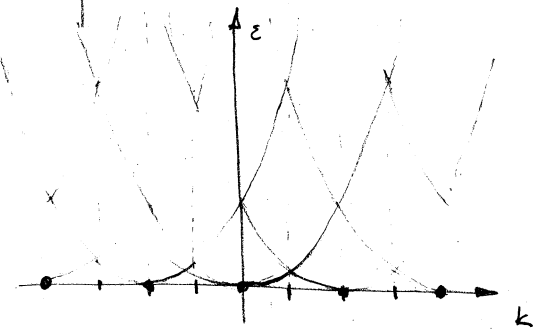
■ Step 1: No electron-ion interaction

i) Draw the free electron parabola and identify Brillouin zones

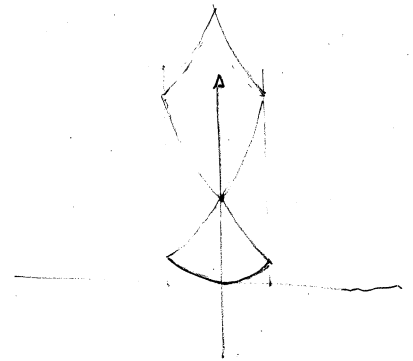


Note: the first Brillouin zone is obtained by identifying the D-1 surface (here a point) \perp to the vectors connecting the Γ point to the nearest neighbours and bisecting this vectors. The next zones are obtained by repeating the operations with further neighbours

ii) Take into account the periodicity of the dispersion relation to obtain a repeated zone scheme i.e. repeat the parabolas centered in \vec{G} .



iii) Fold the dispersion relation into the 1st BZ to obtain the reduced zone scheme



■ Step 2: Include the interaction

i) Fix \vec{k} and \vec{G}_1 and check for the degeneracy of $\epsilon_{\vec{k}-\vec{G}_1}^0$ with $\vec{G} \neq \vec{G}_1$

If $|\epsilon_{\vec{k}-\vec{G}_1}^0 - \epsilon_{\vec{k}-\vec{G}_j}^0| \gg |\tilde{V}_{e1}|$ we apply ordinary perturbation theory

$$\epsilon = \epsilon_{\vec{k}-\vec{G}_1}^0 + \sum_{\vec{G} \neq \vec{G}_1} \frac{|\tilde{V}(\vec{G}-\vec{G}_1)|^2}{\epsilon_{\vec{k}-\vec{G}_1}^0 - \epsilon_{\vec{k}-\vec{G}}^0} + O(\tilde{V}^3) \quad (2.48)$$