Nitride band structure

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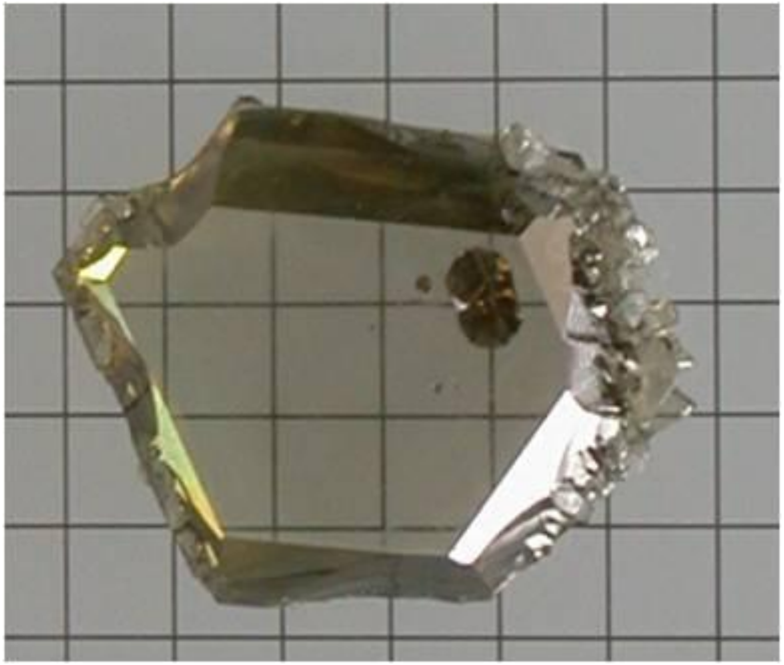
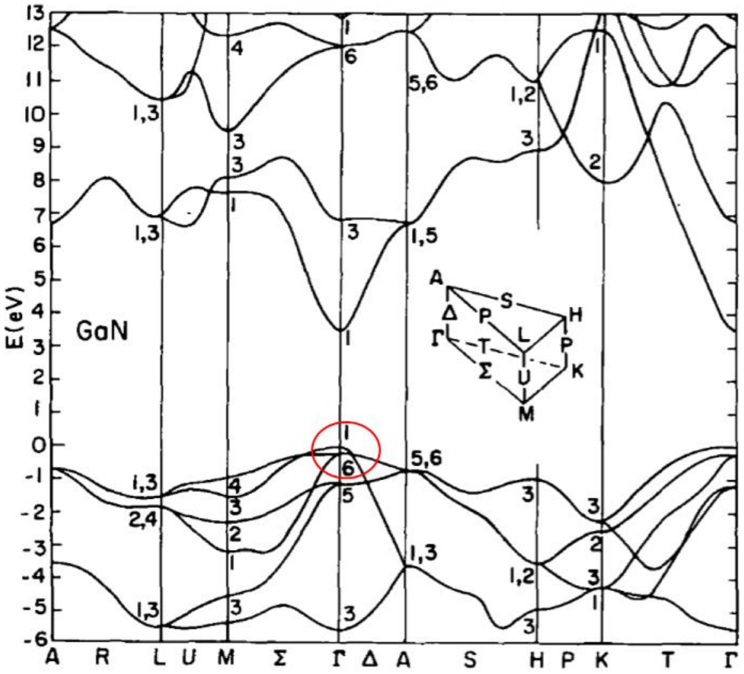
OUTLINE

From the crystal to its electronic band structure



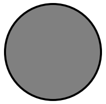


- LCAO-2 atoms
- LCAO-linear chain
- Bloch functions
- Crystal
- Cubic GaN
- Wurzite GaN and AlN

LCAO-2 atoms

Linear Combination of Atomic Orbitals

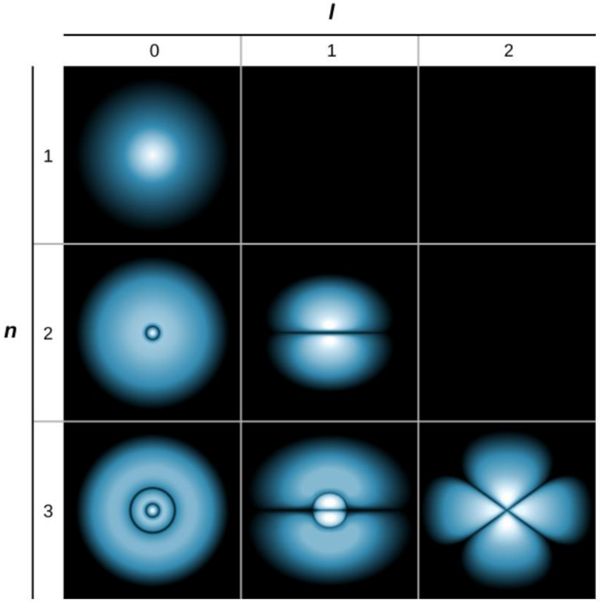
Atom i



One electron in the potential of an isolated atom:

$$H_i\varphi_i = \frac{p^2}{2m}\varphi_i + V_i\varphi_i = E_i\varphi_i$$

One finds levels with principal quantum number **n**, and with sub levels **s,p,d**… defined by the angular momentum number **l**,…



$$H_1\varphi_1 = E_{01}\varphi_1 \qquad H_2\varphi_2 = E_{02}\varphi_2$$

When atoms come close to each other, the electron wavefunction is delocalized on atoms 1 and 2 :

$$\psi = \left(c_1\varphi_1 + c_2\varphi_2\right)$$ Linear combination of atomic orbitals

$$\frac{p^2}{2m}\psi + \left(V_1 + V_2\right)\psi = E\psi$$

Develop and project on φ_1 and φ_2

$$c_1E_{01} + c_2E_{02}\langle\varphi_1|\varphi_2\rangle + c_2\langle\varphi_1|V_1|\varphi_2\rangle + c_1\langle\varphi_1|V_2|\varphi_1\rangle = Ec_1 + c_2E\langle\varphi_1|\varphi_2\rangle$$

$$c_1E_{01}\langle\varphi_2|\varphi_1\rangle + c_2E_{02} + c_2\langle\varphi_2|V_1|\varphi_2\rangle + c_1\langle\varphi_2|V_2|\varphi_1\rangle = Ec_2 + c_1E\langle\varphi_2|\varphi_1\rangle$$

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\varphi_1|V_1|\varphi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_1\rangle+\langle\varphi_2|V_2|\varphi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix} = 0$$

- Can be solved as it is ☺
- But it can be simplified by introducing assumptions which are done in the real semiconductor band structure calculations based on this approach (Tight Binding) ☺ ☺

Tight binding works well for directional bonds typical for semiconductors

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\phi_1|V_1|\phi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_2\rangle+\langle\phi_2|V_2|\phi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix}=0$$

$\langle\varphi_1|\varphi_2\rangle = 0$ Not strictly true. In addition E_{02}-E is expected to be small

$\langle\varphi_1|V_2|\varphi_1\rangle = \langle\varphi_2|V_1|\varphi_2\rangle$ by symmetry

Describes the effect of the potential of atom 2 on the energy in atom 1, and vice versa. It is a shift of the energy, with no important effect.

(when atoms are different or with less trivial symmetries, it has an effect).

Let us renormalize the energies :

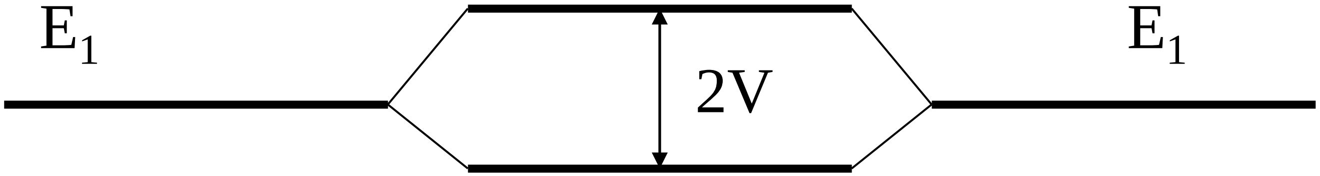
$$E_1 = E_{01} + \langle\varphi_1|V_2|\varphi_1\rangle$$
$$E_2 = E_{02} + \langle\varphi_2|V_1|\varphi_2\rangle$$

$$\begin{vmatrix} (E_1 - E) & \langle \varphi_1 | V_1 | \varphi_2 \rangle \\ \langle \varphi_2 | V_2 | \varphi_1 \rangle & (E_2 - E) \end{vmatrix} = 0$$

We introduce : $\langle \varphi_1 | V_1 | \varphi_2 \rangle \times \langle \varphi_2 | V_2 | \varphi_1 \rangle = V^2$

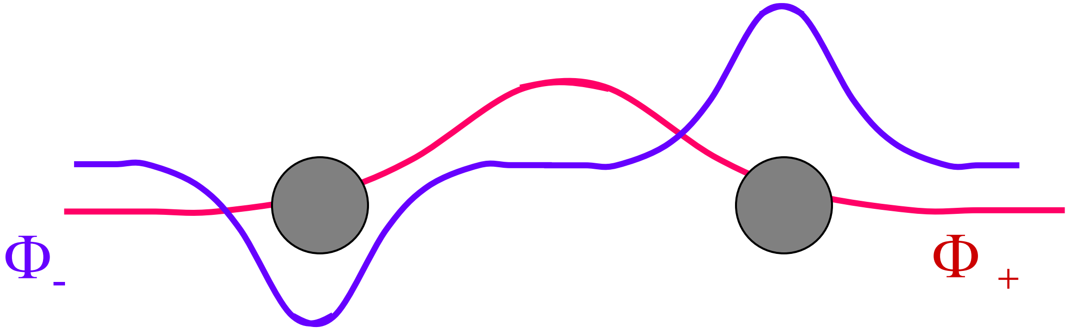
$$E = \frac{(E_1 + E_2)}{2} \pm \sqrt{(\frac{E_1 - E_2}{2})^2 + V^2}$$

If atoms are identical: $E_1=E_2$ $E = E_1 \pm |V|$



2 new energy eigenvalues

2 new eigen states



$$\boxed{\Phi_+ = \frac{1}{\sqrt{2}}\left(\varphi_1 + \varphi_2\right)}$$

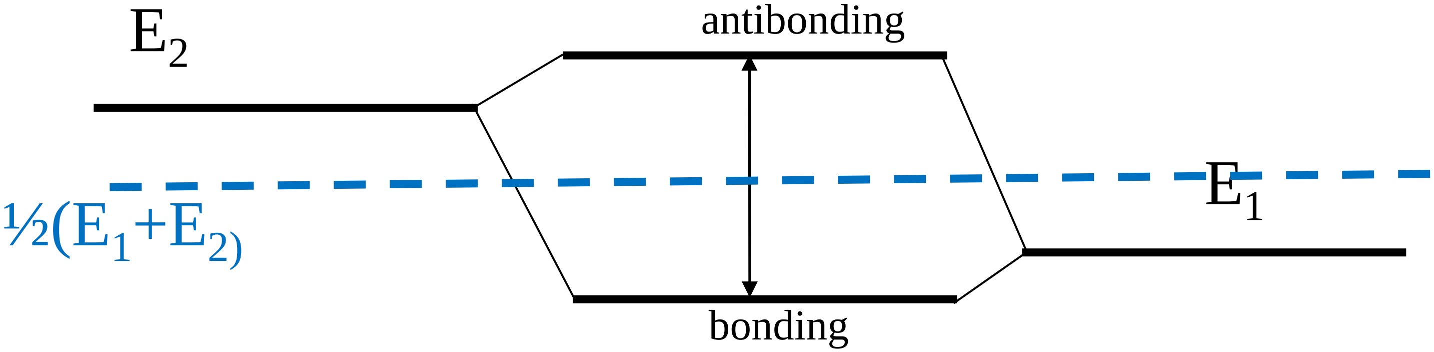
Lowest energy: bonding state

$$\boxed{\Phi_- = \frac{1}{\sqrt{2}}\left(\varphi_1 - \varphi_2\right)}$$

Highest energy: anti-bonding state

Not identical atoms

We still have $E = \frac{(E_1 + E_2)}{2} \pm \sqrt{(\frac{E_1 - E_2}{2})^2 + V^2}$



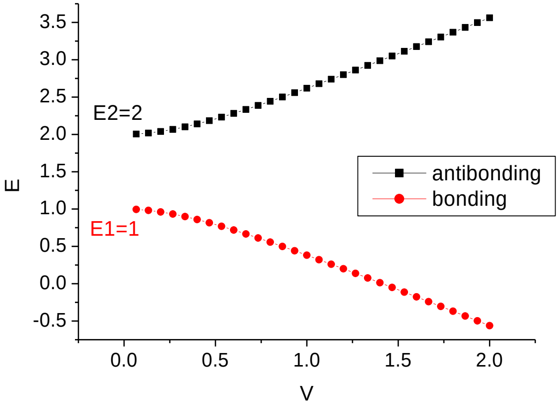
E_2

antibonding

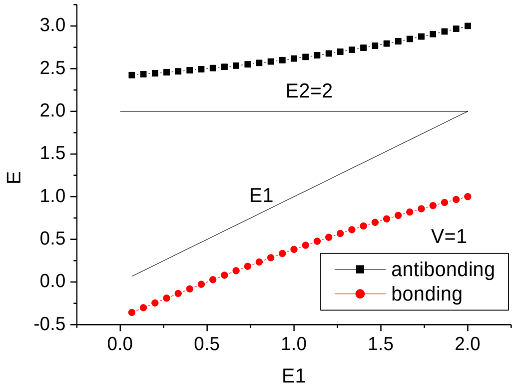
E_1

½(E_1+E_2)

bonding

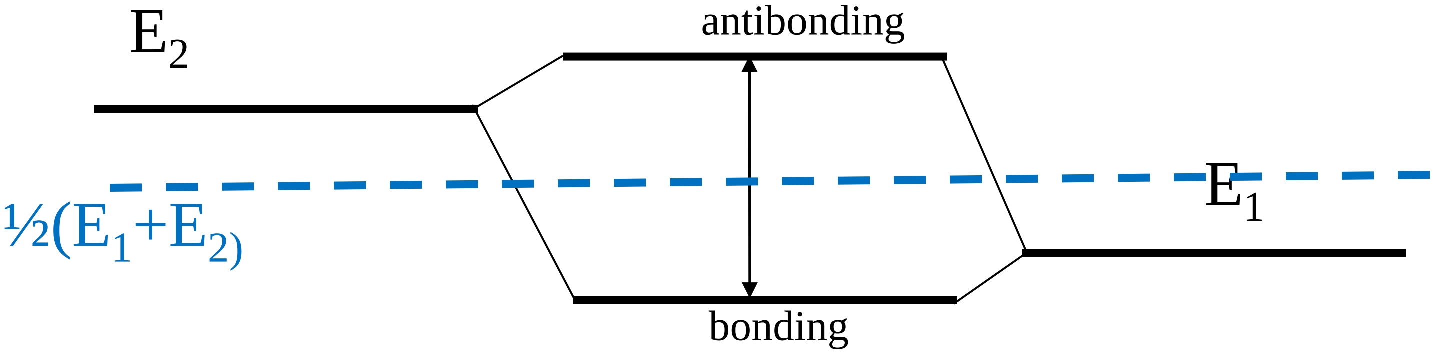


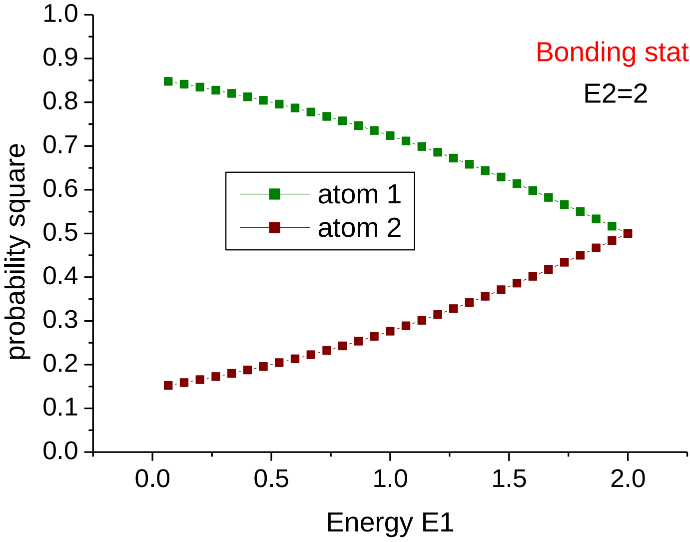
Levels split from the mean energy as V increases

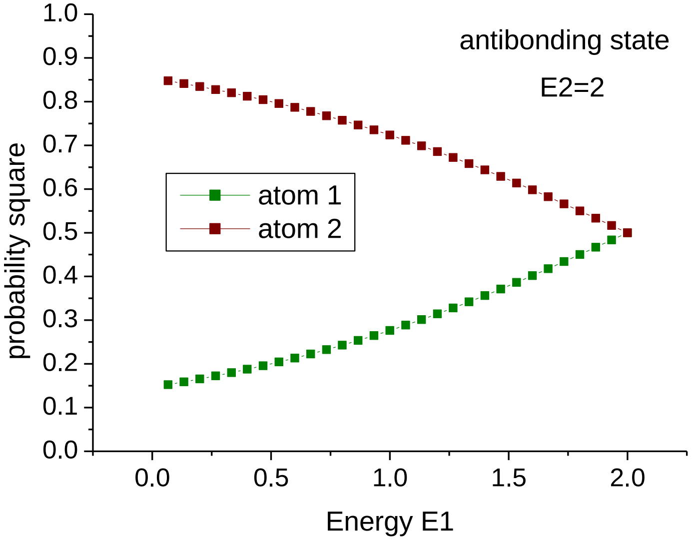


When E1-E2 increase, the bonding state gets closer to the lower energy level (E1) and the antibonding state closer to the higher level (E2)

Not identical atoms







The bonding states concentrates on atom 1 which has the lower energy

The antibonding states concentrates on atom 2 which has the higher energy

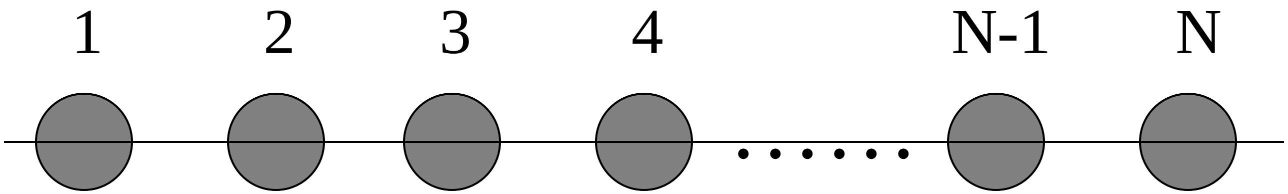
Remember that !

3 things to remember:

- 2 initial orbitals ⇒ 2 levels
- shift of the energies+ splitting
- bonding and antibonding states

LCAO-linear chain

N atoms
in a chain



$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + c_4\varphi_4 + \ldots + c_N\varphi_N$$

One keeps nearest neighbours interactions only:

$$\left\langle \varphi_n \middle| V_n \middle| \varphi_m \right\rangle = \left\langle \varphi_m \middle| V_m \middle| \varphi_n \right\rangle = \delta_{n,m\pm 1} \times V$$

V<0

Again, we use:

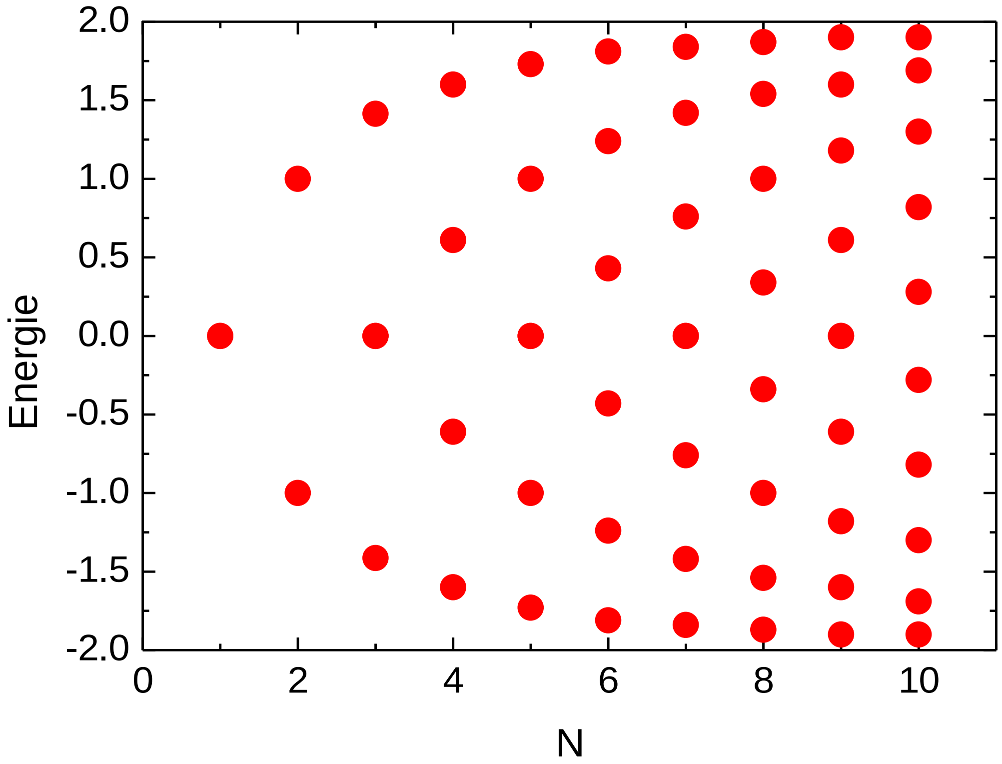
orthogonality $\left\langle \varphi_n \middle| \varphi_m \right\rangle = \delta_{nm}$

renormalization $E_n = E_{n0} + \sum_m \left\langle \varphi_n \middle| V_m \middle| \varphi_n \right\rangle$

Identical atoms, $E_n = E_0$

$$\begin{vmatrix} E_0 - E & V & 0 & 0 \\ V & E_0 - E & V & 0 \\ 0 & V & E_0 - E & V \\ 0 & 0 & V & E_0 - E \end{vmatrix} = 0$$

Energy levels as a function of the number of atoms



Levels are distributed over an energy band of width ± 2V

This behavior appears as soon as N >5

Bloch functions

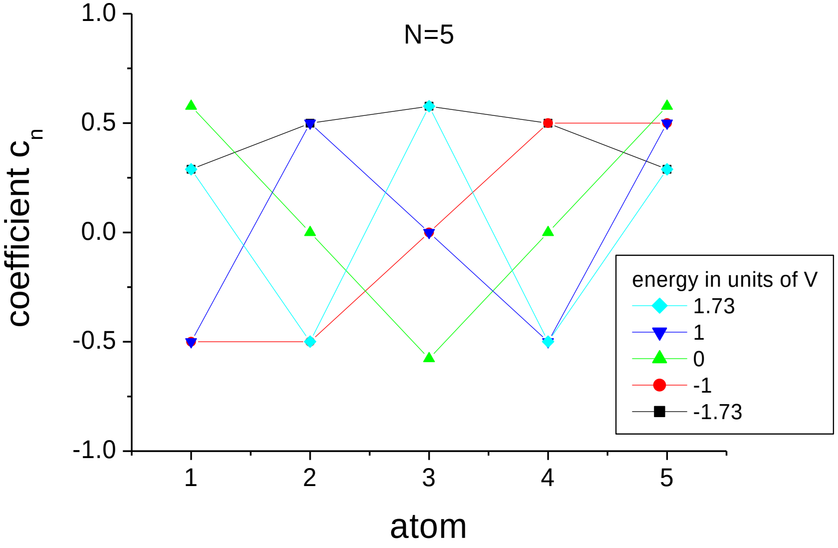
Open chain

what are the new eigen states associated with the energy eigenvalues ?

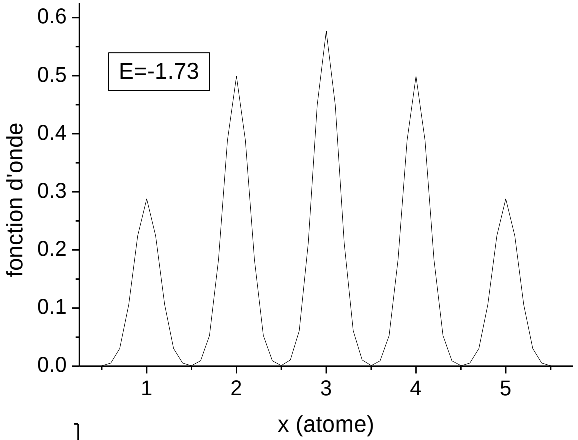
$$\Phi = \sum c_n \varphi_n$$

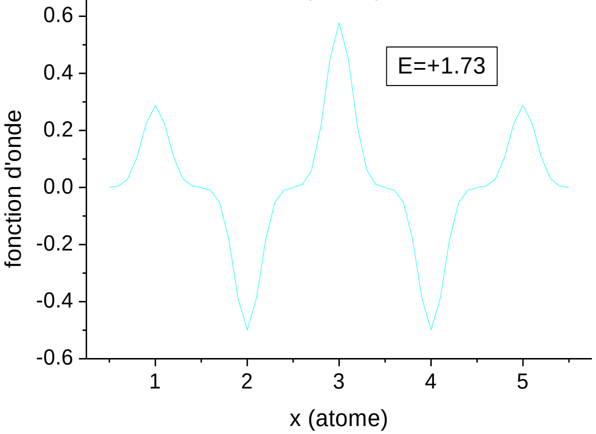
For each energy, one calculates the c_n coefficient and the wavefunction :

we take φ_n=gaussian centered on each atom n



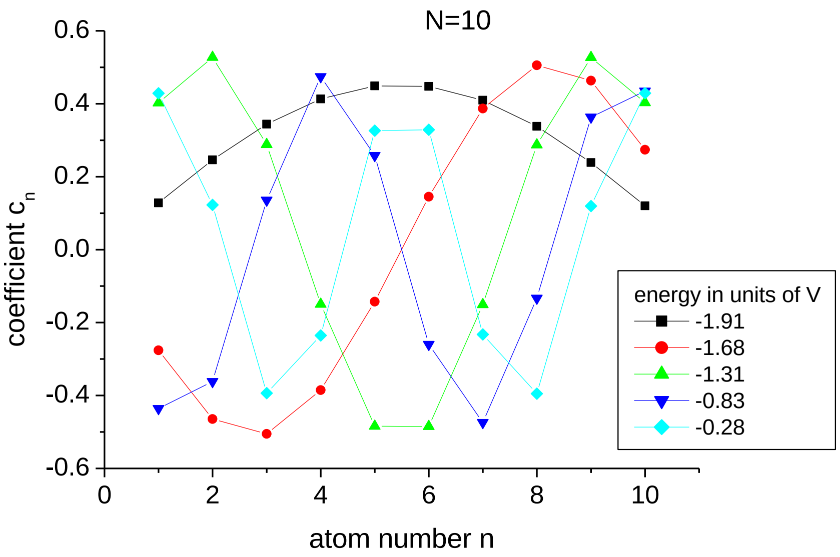
The wavefunction spacially oscillates more when energy increases

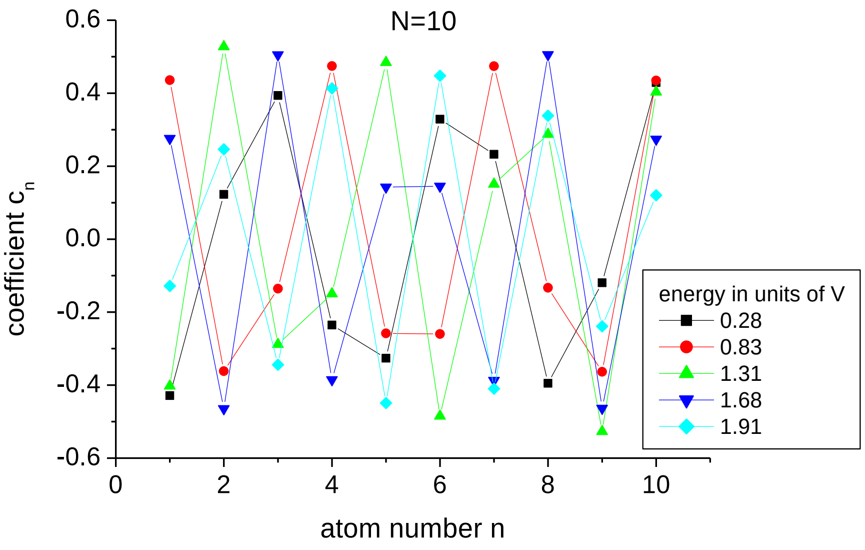


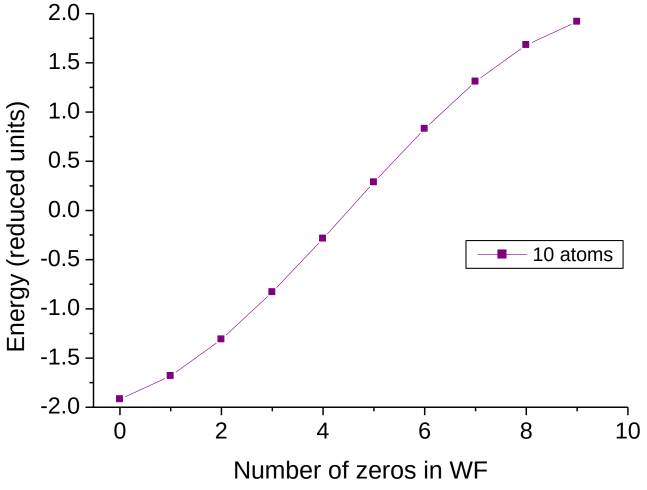


eigen states :

$$\Phi = \sum c_n \varphi_n$$







WF amplitude becomes more and more uniform (singular extremities are less visible)

Wavefunction oscillates more in space when energy increases eigen states : $\Phi = \sum c_n \varphi_n$

For large N, the system is periodic (all atoms identical), **period = a**

$$c_{n-2}V + c_{n-1}(E_0 - E) + c_n V = 0$$
$$c_{n-1}V + c_n(E_0 - E) + c_{n+1}V = 0$$

General solution : $c_n = Ae^{in\theta} = Ae^{inka}$

$\Rightarrow \quad e^{-ika}V + (E_0 - E) + e^{ika}V = 0 \quad \Rightarrow \quad E = E_0 + 2V\cos(ka)$

V<0

NB: one initial level per atom ⇒ one band

M levels ⇒ M bands

$$\boxed{E = E_0 + 2V\cos(ka)}$$

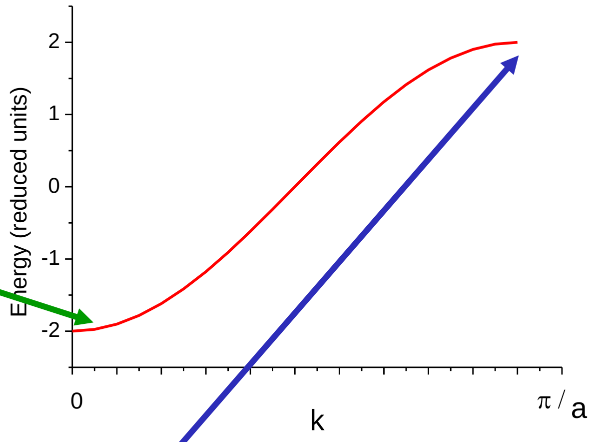
V<0

What is the variation range for k ?

Lowest energy: $E - E_0 = -2|V|$ $\Rightarrow$ k=0

$$c_n = Ae^{inka} = A$$

Constant wavefunction



Highest energy $E - E_0 = +2|V|$ $\Rightarrow$ k=π/a

$$c_n = Ae^{inka} = Ae^{in\pi}$$

WF oscillates at each atom (N zeros)

Each eigen state can be indexed by k and E(k):

$$\Phi_k = \sum_n c_n \varphi_n = \sum_n e^{ikna} \varphi_n = \sum_n e^{ikx_n} \varphi(x - x_n)$$

Bloch function in a chain

1D chain with a single atomic level → 3D crystal with **m** levels and **j** atoms per unit cell

$$\varphi(x - x_n) \longrightarrow \varphi_{jm}(r - r_{jn})$$

$$e^{ikx_n} \longrightarrow e^{ikr_{jn}}$$

$$\Phi_k \longrightarrow \Phi_{kjm}$$

$$\Phi_{kjm} = \sum_n e^{ikr_{jn}} \varphi_{jm}(r - r_{jn})$$

Bloch function in a crystal

Sum over the crystal cells, period $\mathbf{r}_{jn}$

We build the wavefunction on this complete set of Bloch functions :

$$\Psi_k = \sum_{m,j} a_{jm} \Phi_{kjm}$$

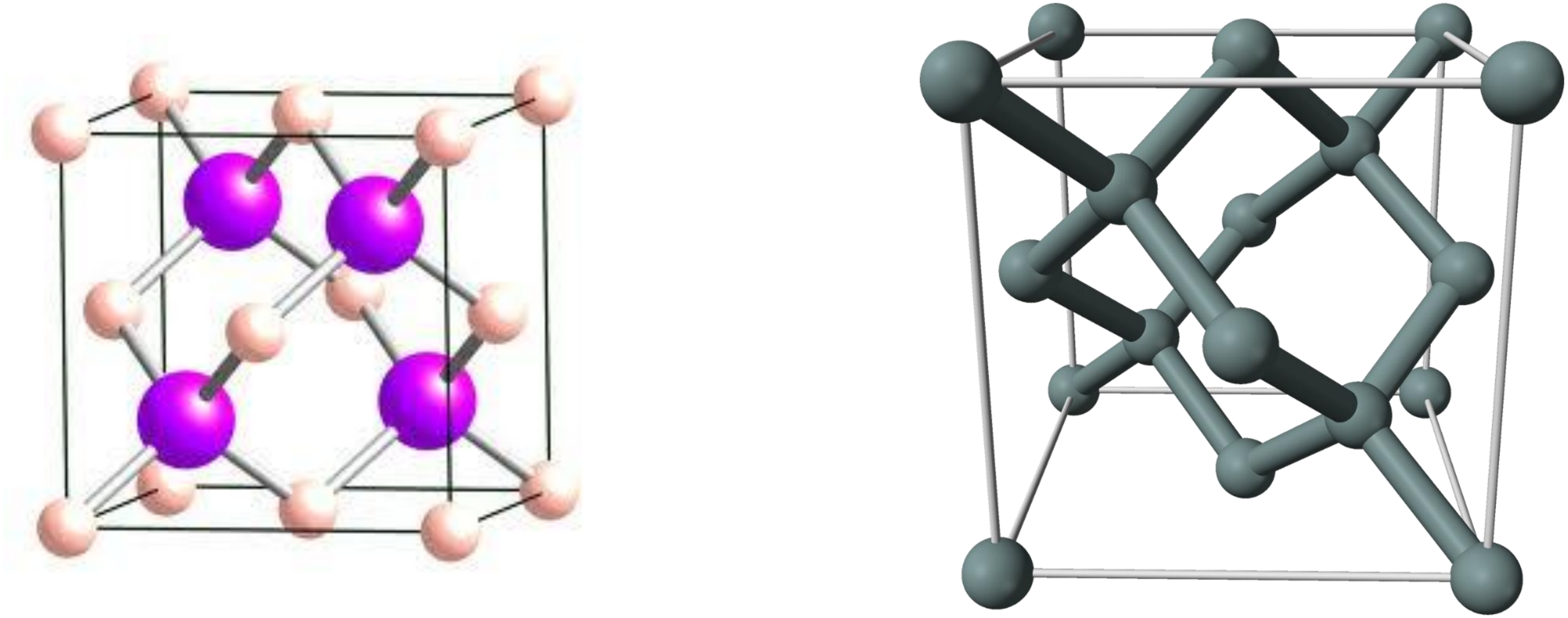
The total system is described by :

$$H\Psi_k = E_k \Psi_k$$

Crystal with cubic symmetry

Crystal structure

Easy case: Zinc blende or diamond (same atom) structure



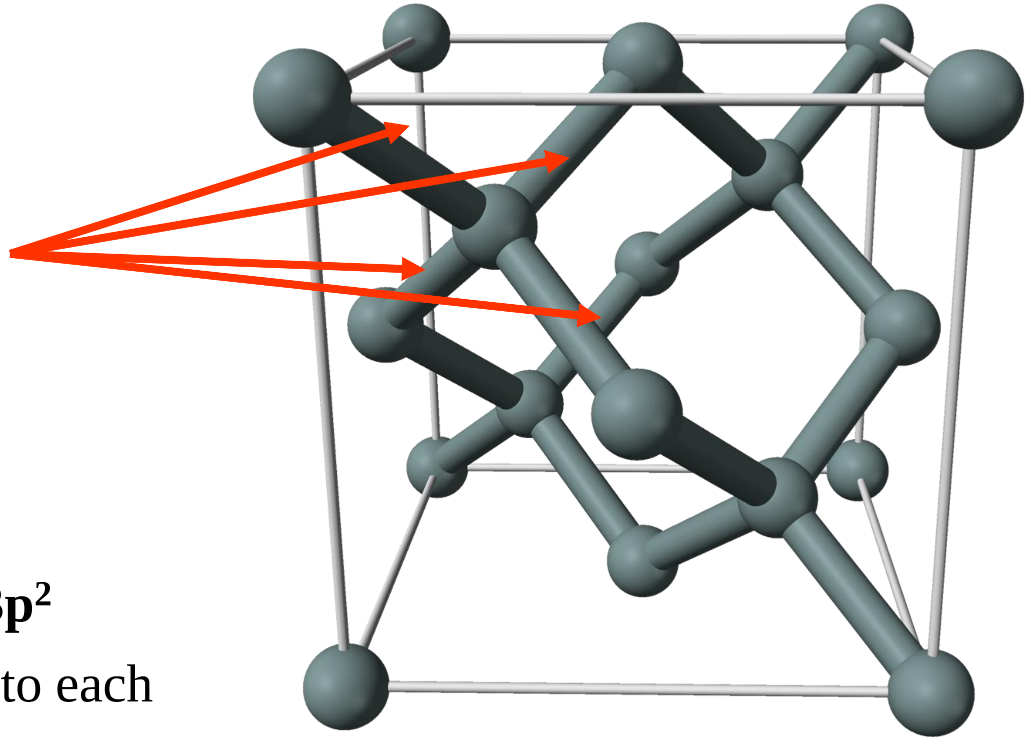
2 FCC shifted by 1/4 of diagonal

1 FCC with 2 atoms per lattice point: no inversion symmetry !

4+4 atoms per FCC cell but FCC cell = 4 primitive cells* ⇒ **2 atoms per cell (j=2)**

*with unit vectors between a corner and center of adjacent faces of the cube

sp3

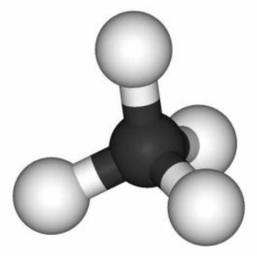


4 bonds for each atom with 109° angle: sp3 hybridization

C: $1s^2$ $\mathbf{2s^2}$ $\mathbf{2p^2}$ and Si: $1s^2$ $2s^2$ $2p^6$ $\mathbf{3s^2}$ $\mathbf{3p^2}$

The electronic orbitals which couple to each other are the most external: s and p.

Methane



C: $1s^2$ $\mathbf{2s^2}$ $\mathbf{2p^2}$ ⇨ C: $1s^2$ $4\times\mathbf{sp^3}$

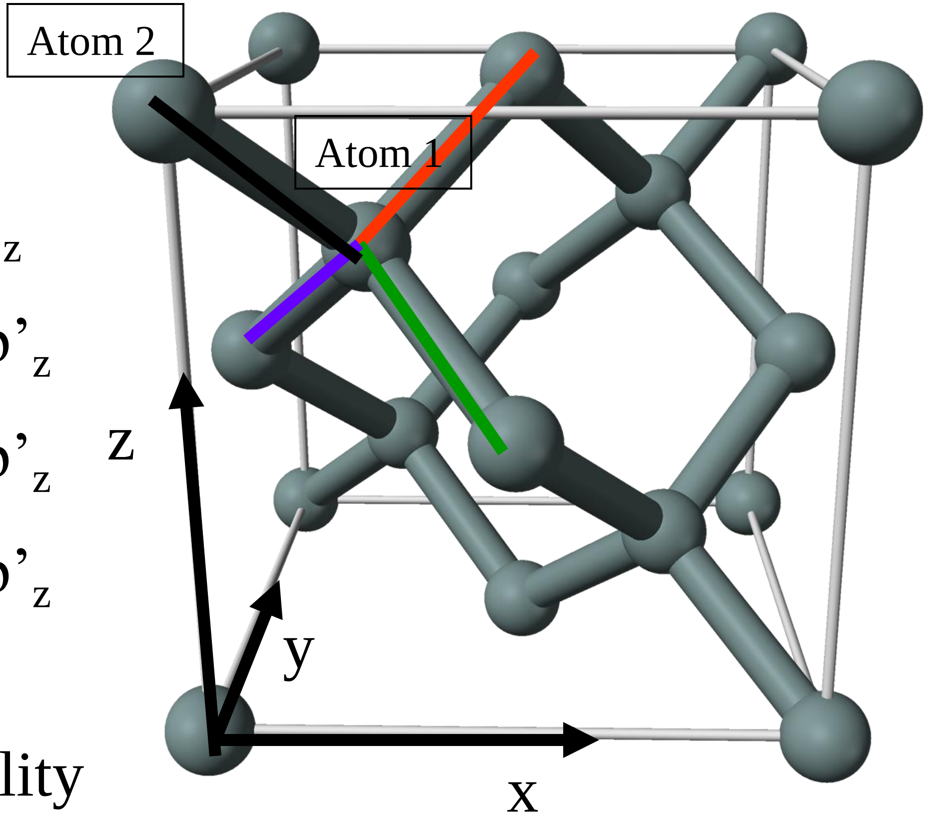
With 109° bonds to maximize the distance between H

4 levels per atom are needed in the calculation **(m=4)**

Crystal structure

Hybrid functions sp^3

atom 1	atom 2
$\varphi_1=s+p_x+p_y+p_z$	$\varphi_{1'}=s'-p'_x-p'_y-p'_z$
$\varphi_2=s+p_x-p_y-p_z$	$\varphi_{2'}=s'-p'_x+p'_y+p'_z$
$\varphi_3=s-p_x+p_y-p_z$	$\varphi_{3'}=s'+p'_x-p'_y+p'_z$
$\varphi_4=s-p_x-p_y+p_z$	$\varphi_{4'}=s'+p'_x+p'_y-p'_z$



$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$ orthogonality

$$\langle \varphi_i | V_i | \varphi_j ' \rangle = -A\delta_{ij}$$

For i and j orbital pointing towards each other and interaction restricted to nearest neighbor

[*Leman and Friedel 1962*]

Band structure calculation

$$(H-E)\Psi_k = (H-E)\sum_{m,j} a_{jm} \sum_{n} e^{ikr_{jn}} \varphi_{jm}(r-r_{jn}) = 0$$

level: 1,2,3,4

1,2 : atom

All atomic cells of the crystal

The sum over all cells (Σ_n) leads to the contribution of the 4 nearest neighbours

Projection on the 8 $\varphi_{j,m}$ functions,

$\Rightarrow$ 8 linear relations $\Rightarrow$ Determinant $D_8=0$ $\Rightarrow$ 8 solutions = 8 bands

Band structure calculation

Case of diamond

The basis is the hybrid orbitals $\varphi_{1,2,3,4}$ and $\varphi'_{1,2,3,4}$

$$\begin{array}{c}
\begin{array}{cccccccc}
\varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \varphi'_1 & \varphi'_2 & \varphi'_3 & \varphi'_4
\end{array} \\
\left|\begin{array}{cccccccc}
E-E_m & \delta/2 & \delta/2 & \delta/2 & A\alpha_0 & 0 & 0 & 0 \\
\delta/2 & E-E_m & \delta/2 & \delta/2 & 0 & A\alpha_1 & 0 & 0 \\
\delta/2 & \delta/2 & E-E_m & \delta/2 & 0 & 0 & A\alpha_2 & 0 \\
\delta/2 & \delta/2 & \delta/2 & E-E_m & 0 & 0 & 0 & A\alpha_3 \\
A\alpha_0{}^* & 0 & 0 & 0 & E-E_m & \delta/2 & \delta/2 & \delta/2 \\
0 & A\alpha_1{}^* & 0 & 0 & \delta/2 & E-E_m & \delta/2 & \delta/2 \\
0 & 0 & A\alpha_2{}^* & 0 & \delta/2 & \delta/2 & E-E_m & \delta/2 \\
0 & 0 & 0 & A\alpha_3{}^* & \delta/2 & \delta/2 & \delta/2 & E-E_m
\end{array}\right| = 0
\end{array}$$

with

Mean energy

$$E_m = (E_s + 3E_p)/4$$

$$\delta = (E_p - E_s)/2$$

$$\alpha_0 = e^{ikr_0} \qquad r_0=(0,0,0)$$

$$\alpha_1 = e^{ikr_1} \qquad r_1=(1/2,1/2,0)$$

$$\alpha_2 = e^{ikr_2} \qquad r_2=(1/2,0,1/2)$$

$$\alpha_3 = e^{ikr_3} \qquad r_3=(0,1/2,1/2)$$

Crystal structure, symmetry is involved here only, between atom 1 and atom 2

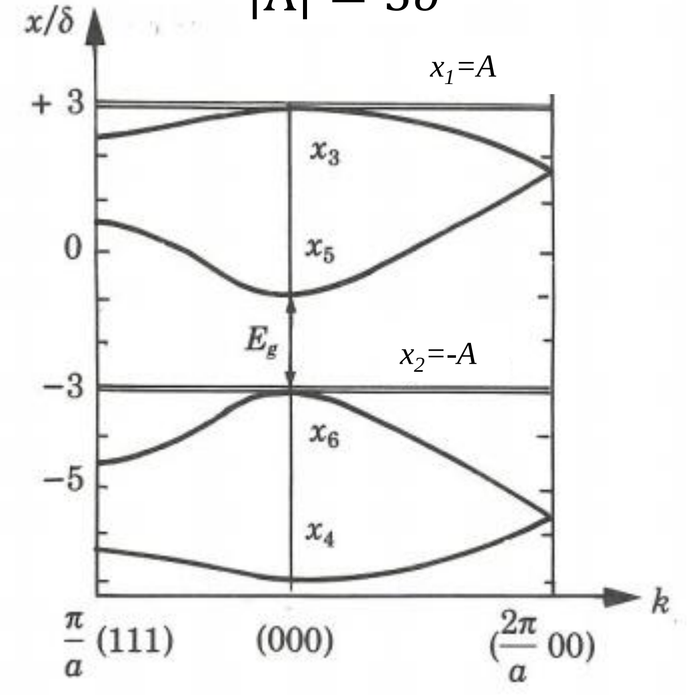
$x = E - E_p$; $\phi = 1/4 \sum \alpha_n$ $\delta = \frac{(E_p - E_s)}{2}$

$$\boxed{(x^2 - A^2)^2 (x^2 + 2\delta x - A^2 + 2\delta A\phi)(x^2 + 2\delta x - A^2 - 2\delta A\phi) = 0}$$

8 bands:

- $x = E - E_p = \pm$ A, flat bands, doubly degenerate
- 4 non degenerate bands

$|A| = 3\delta$



Complicated ! Let us focus at k=0 (Γ)

Sapoval & Hermann, cours Polytechnique 1988

Cubic case at k=0

$$\left.\begin{aligned}\alpha_0 &= e^{ikr_0}\\ \alpha_1 &= e^{ikr_1}\\ \alpha_2 &= e^{ikr_2}\\ \alpha_3 &= e^{ikr_3}\end{aligned}\right\} = 1 \quad \Rightarrow \quad \phi = 1/4\sum\alpha_n = 1$$

$$\Rightarrow \quad (x^2 - A^2)^2(x^2 + 2\delta x - A^2 + 2\delta A)(x^2 + 2\delta x - A^2 - 2\delta A) = 0$$

$$\Rightarrow \quad (x^2 - A^2)^2(x + A)(x + 2\delta - A)\ (x - A)(x + 2\delta + A) \ = 0$$

$x = E - Ep$ $\qquad$ $\delta = \frac{(E_p - E_s)}{2}$

$$x = A\ (\times 3) \Rightarrow E = E_p + A$$

$$\Rightarrow x = A - 2\delta\ (\times 1) \Rightarrow E = E_s + A$$

$$x = -A\ (\times 3) \Rightarrow E = E_p - A$$

$$x = -A - 2\delta\ (\times 1) \Rightarrow E = E_s - A$$

Cubic case at k=0

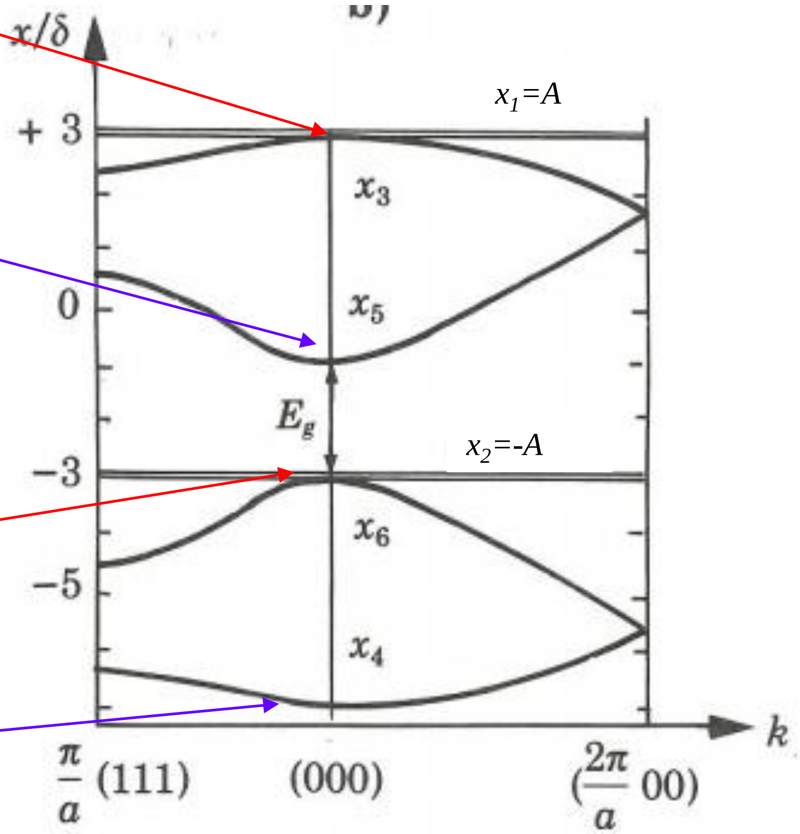
$E = E_p + A$ (×3)

$E = E_s + A$ (×1)

$E_g = 2(A-\delta) = 2A - (E_p - E_s)$

$E = E_p - A$ (×3)

$E = E_s - A$ (×1)



We focus on the eigen value $E=E_p - A$, we have 3 degenerate bands (valence bands) and we try to find the 3 eigen vectors

Cubic case $k=0$ and $E=E_p - A$

$$\begin{array}{cccccccc} \varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \varphi'_1 & \varphi'_2 & \varphi'_3 & \varphi'_4 \end{array}$$

$$\begin{pmatrix} -A+\delta/2 & \delta/2 & \delta/2 & \delta/2 & A & 0 & 0 & 0 \\ \delta/2 & -A+\delta/2 & \delta/2 & \delta/2 & \delta/2 & A & 0 & 0 \\ \delta/2 & \delta/2 & -A+\delta/2 & \delta/2 & \delta/2 & 0 & A & 0 \\ \delta/2 & \delta/2 & \delta/2 & -A+\delta/2 & \delta/2 & 0 & 0 & A \\ A & 0 & 0 & 0 & -A+\delta/2 & \delta/2 & \delta/2 & \delta/2 \\ 0 & A & 0 & 0 & \delta/2 & -A+\delta/2 & \delta/2 & \delta/2 \\ 0 & 0 & A & 0 & \delta/2 & \delta/2 & -A+\delta/2 & \delta/2 \\ 0 & 0 & 0 & A & \delta/2 & \delta/2 & \delta/2 & -A+\delta/2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_1' \\ c_2' \\ c_3' \\ c_4' \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Solve the system to find the c_i coefficients…

Cubic case at k=0 and $E=E_p - A$

One finds :

$WF_1 = \varphi_1 + \varphi_2 - \varphi_3 - \varphi_4 + \varphi'_1 + \varphi'_2 - \varphi'_3 - \varphi'_4 \sim p_x - p'_x$

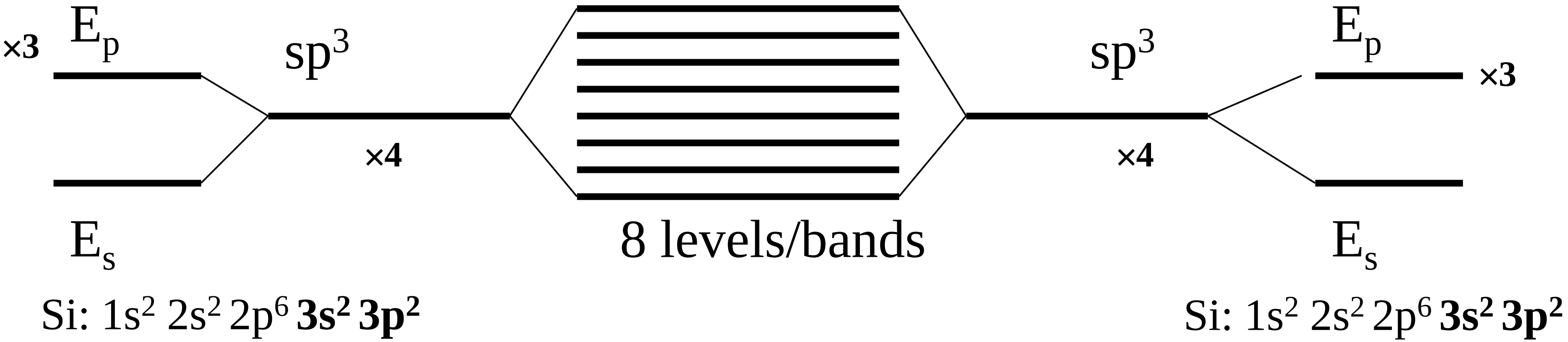
$WF_2 \sim p_y - p'_y$

$WF_3 \sim p_z - p'_z$

The 3 eigen vectors corresponding to the 3 fold degenerate bands at Γ in a cubic crystal are p_x, p_y, p_z orbitals ! Not a real surprise !

In this basis, the Hamiltonian of a cubic crystal for the valence band at Γ is

$$H = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{pmatrix}$$



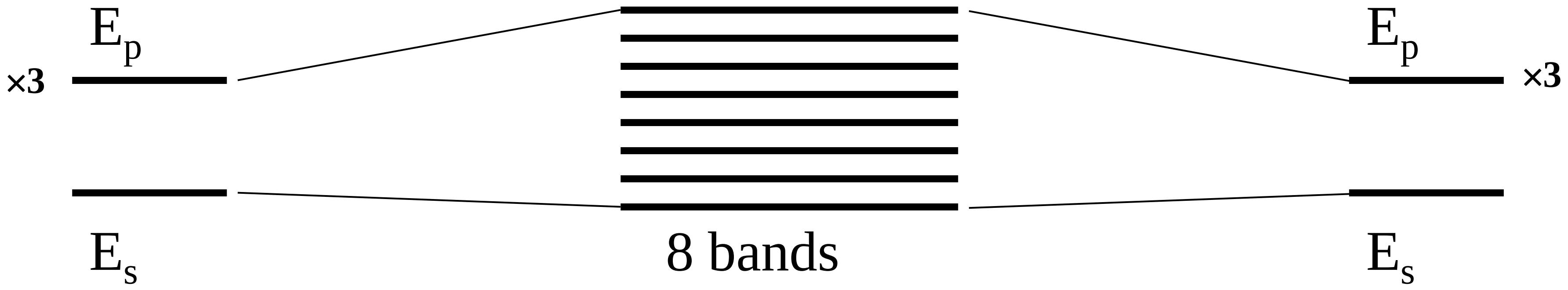
- Some levels might be degenerated for some values of k
- In particular, at k=0, ×3 degeneracy with p_x,p_y,p_z wavefunctions
- Could it be expected ?

Alternatively, on can keep the s and p orbitals for the basis and obtain a similar determinant (through a change of basis) and the same energies (Chadi and Cohen)

$$\left|\begin{array}{ccccccccc}
 & S1 & X1 & Y1 & Z1 & S2 & X2 & Y2 & Z2 \\
S1 & E_s-E_k & 0 & 0 & 0 & V_{ss}g_1 & V_{sp}g_2 & V_{sp}g_3 & V_{sp}g_4 \\
X1 & 0 & E_p-E_k & 0 & 0 & -V_{sp}g_2 & V_{xx}g_1 & V_{xy}g_4 & V_{xy}g_3 \\
Y1 & 0 & 0 & E_p-E_k & 0 & -V_{sp}g_3 & V_{xy}g_4 & V_{xx}g_1 & V_{xy}g_2 \\
Z1 & 0 & 0 & 0 & E_p-E_k & -V_{sp}g_4 & V_{xy}g_3 & V_{xy}g_2 & V_{xx}g_1 \\
S2 & V_{ss}g_1{}^* & -V_{sp}g_2{}^* & -V_{sp}g_3{}^* & -V_{sp}g_4{}^* & E_s-E_k & 0 & 0 & 0 \\
X2 & V_{sp}g_2{}^* & V_{xx}g_1{}^* & V_{xy}g_4{}^* & V_{xy}g_3{}^* & 0 & E_p-E_k & 0 & 0 \\
Y2 & V_{sp}g_3{}^* & V_{xy}g_4{}^* & V_{xx}g_1{}^* & V_{xy}g_2{}^* & 0 & 0 & E_p-E_k & 0 \\
Z2 & V_{sp}g_4{}^* & V_{xy}g_3{}^* & V_{xy}g_2{}^* & V_{xx}g_1{}^* & 0 & 0 & 0 & E_p-E_k
\end{array}\right| = 0$$

with

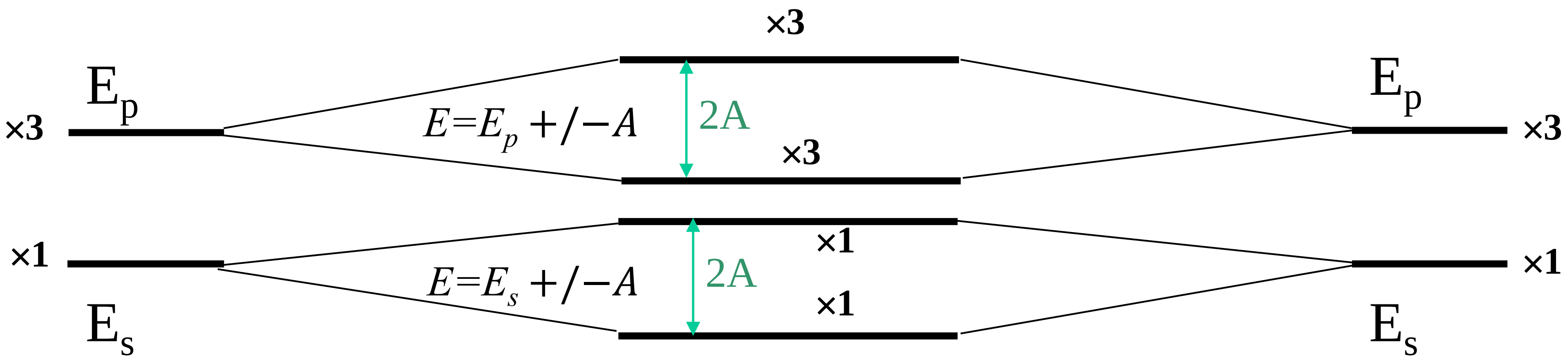
$$\begin{cases}
g_1(\mathbf{k}) = \left[e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3} + e^{i\mathbf{k}\cdot\mathbf{d}_4}\right] \\
g_2(\mathbf{k}) = \left[e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} - e^{i\mathbf{k}\cdot\mathbf{d}_3} - e^{i\mathbf{k}\cdot\mathbf{d}_4}\right] \\
g_3(\mathbf{k}) = \left[e^{i\mathbf{k}\cdot\mathbf{d}_1} - e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3} - e^{i\mathbf{k}\cdot\mathbf{d}_4}\right] \\
g_4(\mathbf{k}) = \left[e^{i\mathbf{k}\cdot\mathbf{d}_1} - e^{i\mathbf{k}\cdot\mathbf{d}_2} - e^{i\mathbf{k}\cdot\mathbf{d}_3} + e^{i\mathbf{k}\cdot\mathbf{d}_4}\right]
\end{cases}$$



[*Slater and Koster, 1954;Chadi and Cohen, 1975*]

At k=0, the picture is simple: the symmetry of the system (crystal+electron wavefunction) becomes the symmetry of the crystal (e^{ikr}=1=constant in the crystal)

$\Rightarrow$ We can expect that the electronic levels at **k=0** keep the cubic symmetry *(the symmetry group of the k=0 vector is the crystal symmetry group)*



2+6 levels at k=0

Question: ordering of the singulets and triplets ? What is the important parameter for the ordering ?

Metal versus semiconductor

k=0

$$2|A| < 2\delta = E_p - E_s$$

We have to fill the bands (the level here at k=0) with all electrons

C: $1s^2$ **$2s^2$ $2p^2$**

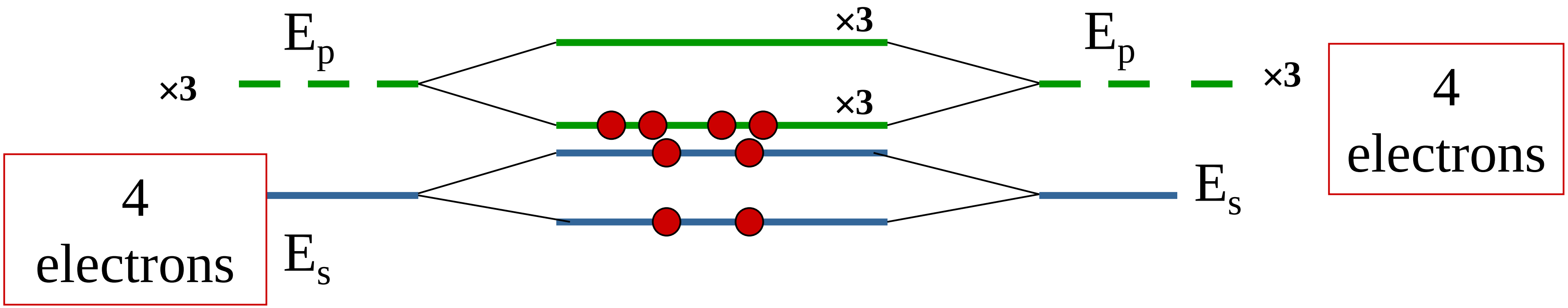
Si: $1s^2$ $2s^2$ $2p^6$ **$3s^2$ $3p^2$**

How many ?

Metal versus semiconductor

k=0

$$2|A| < 2\delta = E_p - E_s$$



C: $1s^2$ **$2s^2$ $2p^2$**

Si: $1s^2$ $2s^2$ $2p^6$ **$3s^2$ $3p^2$**

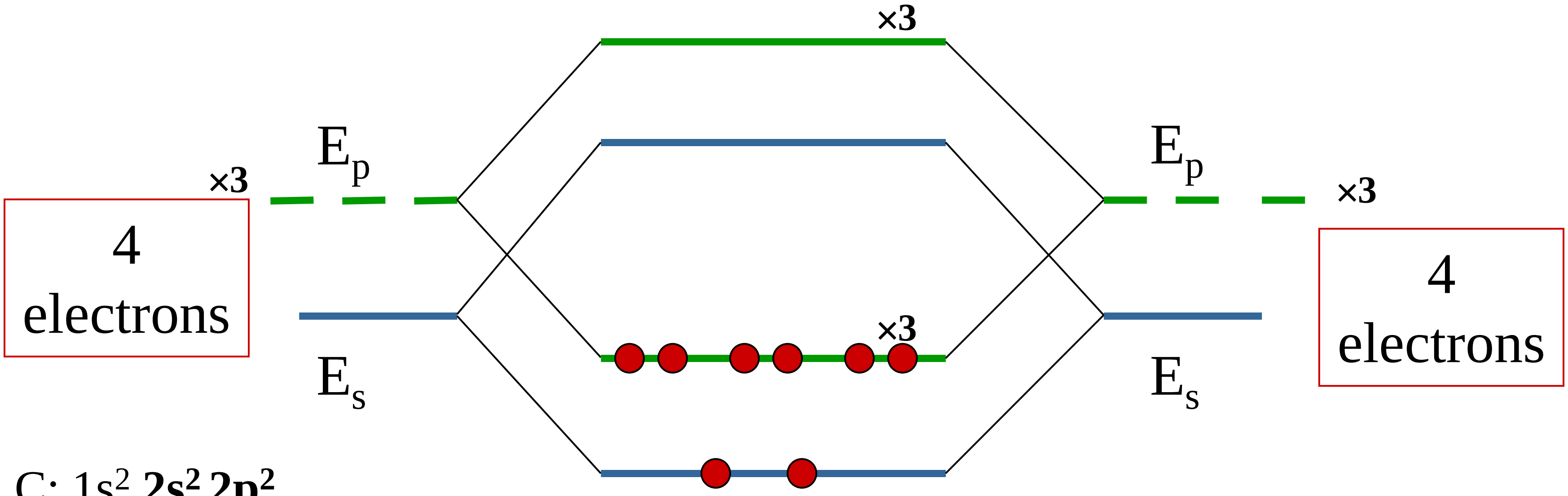
2 electrons per level (spin)

The Fermi level is in a band: metal

Metal versus semiconductor

k=0

$$2|A| > 2\delta = E_p - E_s$$



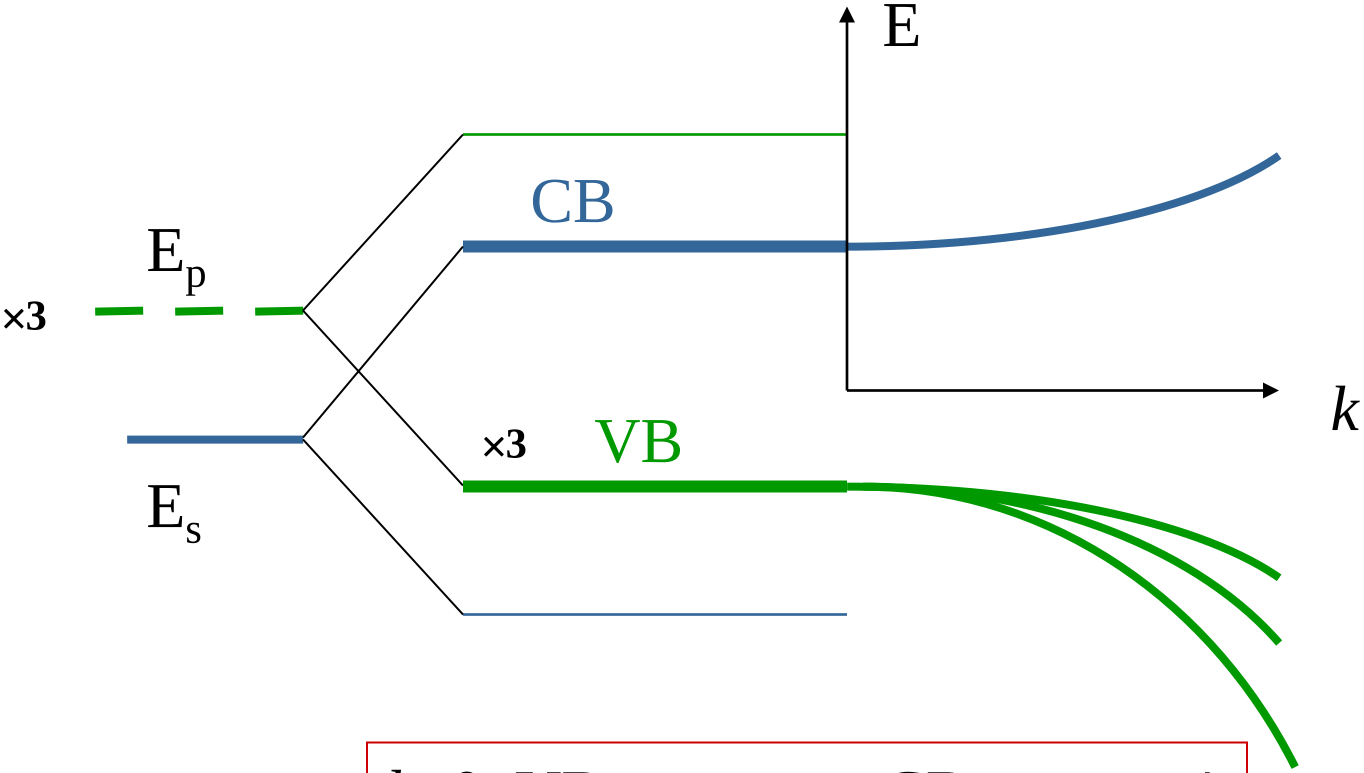
C: $1s^2$ **$2s^2$ $2p^2$**

Si: $1s^2$ $2s^2$ $2p^6$ **$3s^2$ $3p^2$**

2 electrons per level (spin)

The Fermi level is between two bands: insulator or semiconductor with a gap between valence and conduction bands, equal to $E_g=E_s+A-(E_p-A)=E_s-E_p+2A$

Band structure calculation

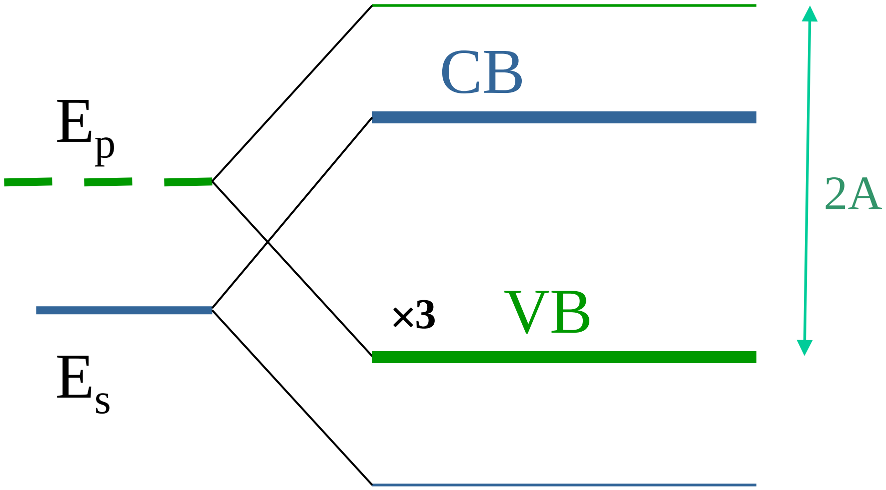


k=0: VB = pure p ; CB= pure s *

k≠0 : CB and VB mixt s and p

* within this model

Band structure calculation



$E_g = 2(A - \delta)$

CB-VB ≡Gap

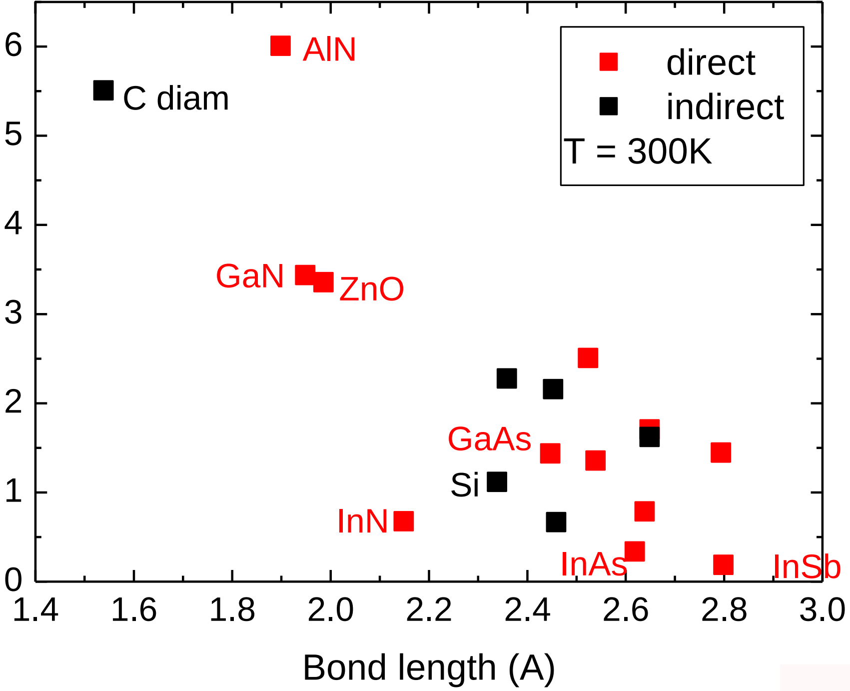
E_{gap} increases with A : $\langle \varphi_i | V_i | \varphi_j \rangle = -A$ increases for short bonds

$E_p - E_s \approx$ cte for usual atoms :

	C	Si	Ge
E_p-E_s (eV)	7.4	7.2	8.41

Prediction: Gap larger with shorter bonds

Bang gap versus bond



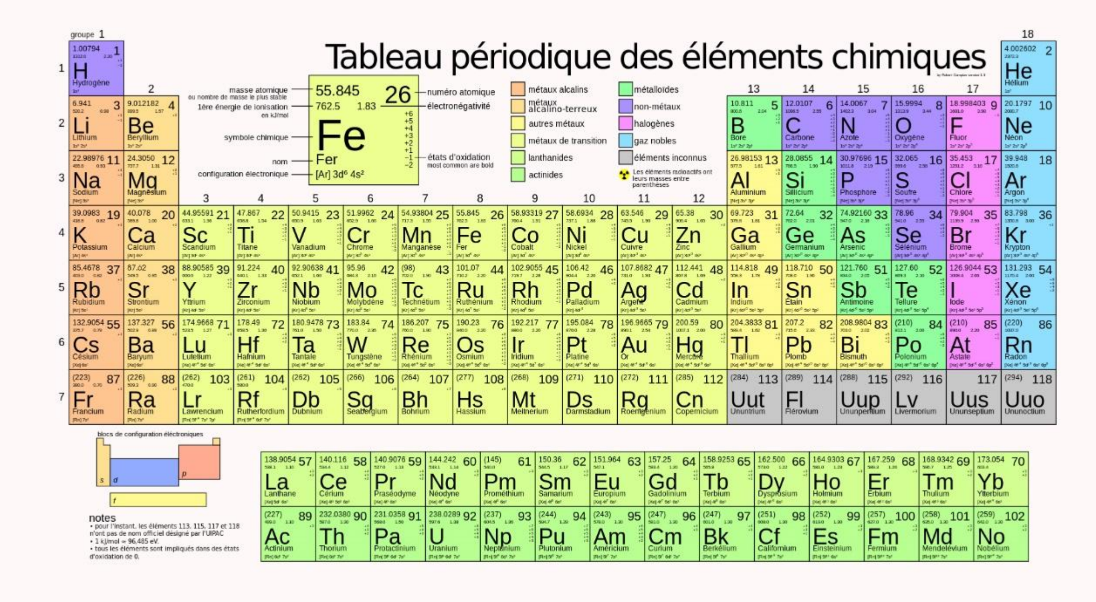


Tableau périodique des éléments chimiques

masse atomique ou nombre de masse le plus stable — 55.845
numéro atomique — 26
1ère énergie de ionisation en kJ/mol — 762.5
électronégativité — 1.83
symbole chimique — Fe
états d'oxidation most common are bold — +6 +5 +4 +3 +2 +1 −1 −2
nom — Fer
configuration électronique — [Ar] 3d⁶ 4s²

🟧	métaux alcalins
🟧	métaux alcalino-terreux
🟨	autres métaux
🟨	métaux de transition
🟩	lanthanides
🟩	actinides
🟩	métalloïdes
🟪	non-métaux
🟪	halogènes
🟦	gaz nobles
⬜	éléments inconnus

Les éléments radioactifs ont leurs masses entre parenthèses

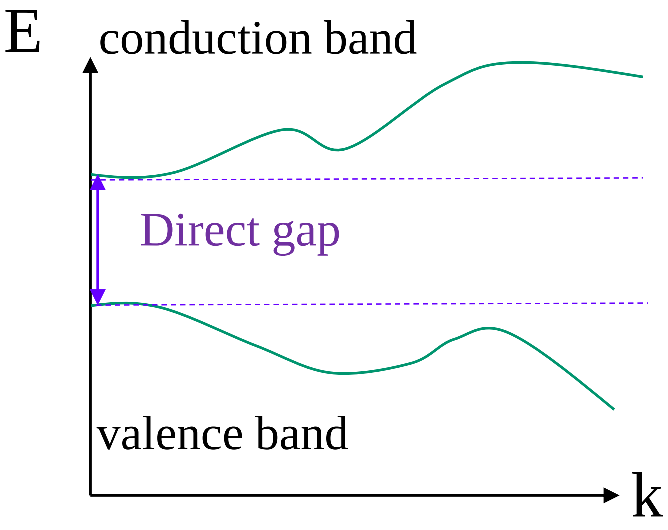
groupe	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogène 1.00794																	2 He Hélium 4.002602
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Bore 10.811	6 C Carbone 12.0107	7 N Azote 14.0067	8 O Oxygène 15.9994	9 F Fluor 18.998403	10 Ne Néon 20.1797
3	11 Na Sodium 22.98976	12 Mg Magnésium 24.3050											13 Al Aluminium 26.98153	14 Si Sillicium 28.0855	15 P Phosphore 30.97696	16 S Soufre 32.065	17 Cl Chlore 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titane 47.867	23 V Vanadium 50.9415	24 Cr Chrome 51.9962	25 Mn Manganèse 54.93804	26 Fe Fer 55.845	27 Co Cobalt 58.93319	28 Ni Nickel 58.6934	29 Cu Cuivre 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Sélénium 78.96	35 Br Brome 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdène 95.96	43 Tc Technétium (98)	44 Ru Ruthénium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Argent 107.8682	48 Cd Cadmium 112.441	49 In Indium 114.818	50 Sn Étain 118.710	51 Sb Antimoine 121.760	52 Te Tellure 127.60	53 I Iode 126.9044	54 Xe Xénon 131.293
6	55 Cs Césium 132.9054	56 Ba Baryum 137.327	71 Lu Lutetium 174.9668	72 Hf Hafnium 178.49	73 Ta Tantale 180.9478	74 W Tungstène 183.84	75 Re Rhénium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platine 195.084	79 Au Or 196.9665	80 Hg Mercure 200.59	81 Tl Thallium 204.3833	82 Pb Plomb 207.2	83 Bi Bismuth 208.9804	84 Po Polonium (210)	85 At Astate (210)	86 Rn Radon (220)
7	87 Fr Francium (223)	88 Ra Radium (226)	103 Lr Lawrencium (262)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadium (271)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut Ununtrium (284)	114 Fl Flérovium (289)	115 Uup Ununpentium (288)	116 Lv Livermorium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)

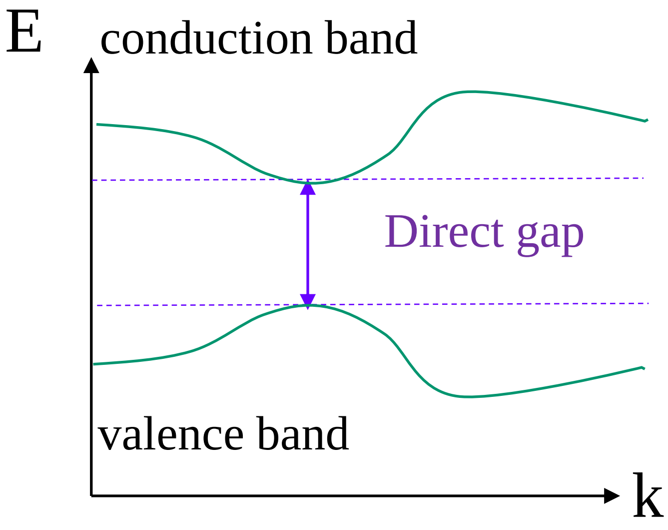
57 La Lanthane 138.9054	58 Ce Cérium 140.116	59 Pr Praséodyme 140.9076	60 Nd Néodyne 144.242	61 Pm Prométhium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.9253	66 Dy Dysprosium 162.500	67 Ho Holmium 164.9303	68 Er Erbium 167.259	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.054
89 Ac Actinium (227)	90 Th Thorium 232.0380	91 Pa Protactinium 231.0358	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Américium (243)	96 Cm Curium (247)	97 Bk Berkélium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelévium (258)	102 No Nobélium (259)

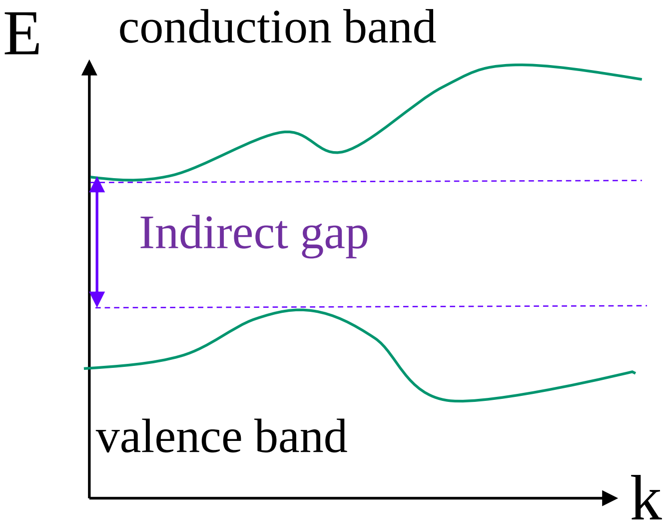
blocs de configuration éléctroniques: s d p f

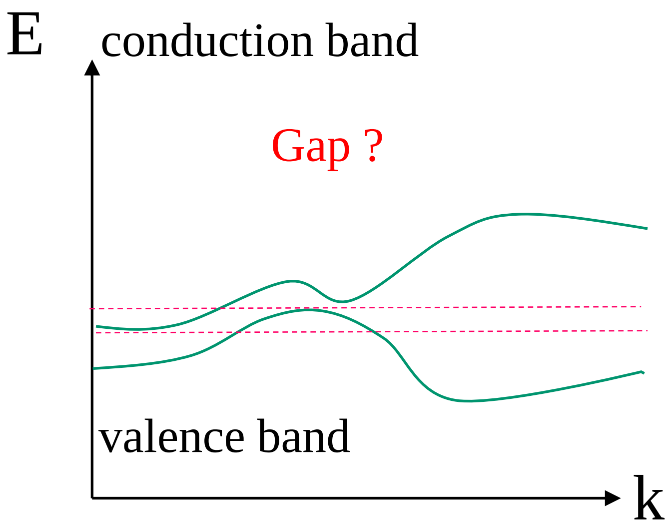
notes
- pour l'instant, les éléments 113, 115, 117 et 118 n'ont pas de nom officiel désigné par l'UIPAC
- 1 kJ/mol = 96,485 eV.
- tous les éléments sont impliqués dans des états d'oxidation de 0.

direct or indirect bandgap

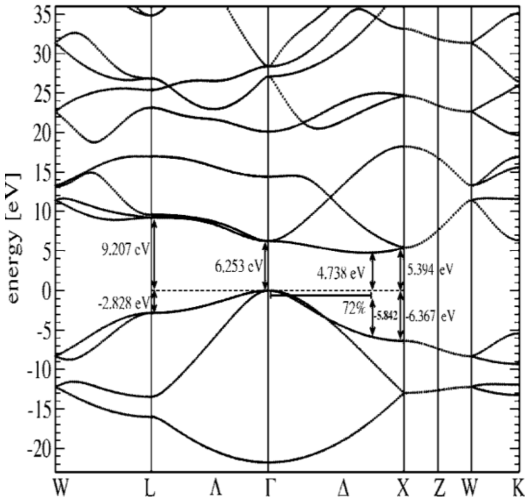






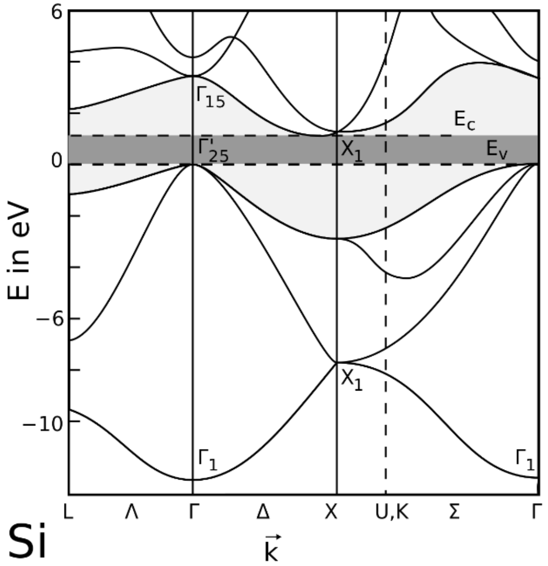


Group IV semiconductors



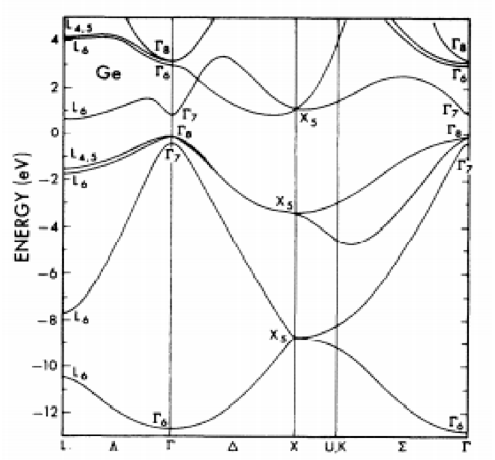
Diamant (C)

E_g=5.5 eV



E_g=1.12 eV
(SO négligé. En fait E_{so}=44 meV)

6 minima de BC
en X= (100)



8 minima de BC
en L= (111)

E_g=0.67 eV

All indirect gap SC: but can become direct under pressure. This cannot be simply predicted

When Z increases:

- Gap decreases ☺
- VB splitting (2+1) at k=0 ☹?

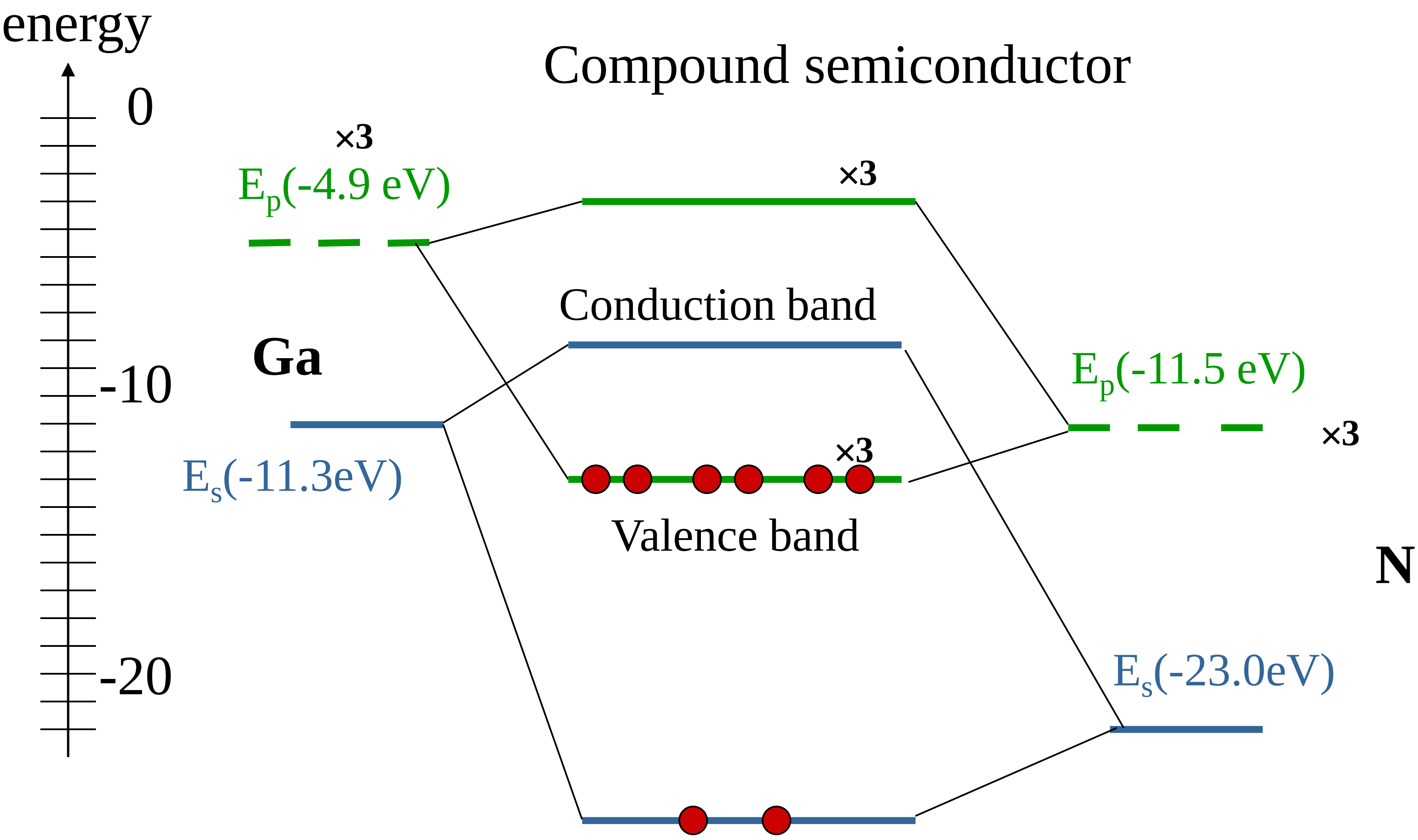
From Si to III-V

We obtained the band structure of a column IV diamond crystal with no spin

- To get cubic GaN with no spin: introduce atom 1 ≠ atome 2

Cubic GaN

Band structure calculation



Remember remark in slide 16 on the wavefunction probability in the molecule with 2 different atoms

Valence band is more element V (N)

Conduction band is more element III (Ga)

Cubic materials

$$
\begin{array}{cccccccc}
\varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \varphi'_1 & \varphi'_2 & \varphi'_3 & \varphi'_4 \\
\end{array}
$$

$$
\begin{vmatrix}
E-E_m & \delta/2 & \delta/2 & \delta/2 & A\alpha_0 & 0 & 0 & 0 \\
\delta/2 & E-E_m & \delta/2 & \delta/2 & 0 & A\alpha_1 & 0 & 0 \\
\delta/2 & \delta/2 & E-E_m & \delta/2 & 0 & 0 & A\alpha_2 & 0 \\
\delta/2 & \delta/2 & \delta/2 & E-E_m & 0 & 0 & 0 & A\alpha_3 \\
A\alpha_0{}^* & 0 & 0 & 0 & E-E_m & \delta/2 & \delta/2 & \delta/2 \\
0 & A\alpha_1{}^* & 0 & 0 & \delta/2 & E-E_m & \delta/2 & \delta/2 \\
0 & 0 & A\alpha_2{}^* & 0 & \delta/2 & \delta/2 & E-E_m & \delta/2 \\
0 & 0 & 0 & A\alpha_3{}^* & \delta/2 & \delta/2 & \delta/2 & E-E_m
\end{vmatrix} = 0
$$

$$\underbrace{\varphi_1 \quad \varphi_2 \quad \varphi_3 \quad \varphi_4}_{\text{Ga}} \qquad \underbrace{\varphi'_1 \quad \varphi'_2 \quad \varphi'_3 \quad \varphi'_4}_{\text{N}}$$

Ga

$$E_m^{Ga} = (E_s^{Ga} + 3E_p^{Ga})/4$$

$$\delta^{Ga} = (E_p^{Ga} - E_s^{Ga})/2$$

N

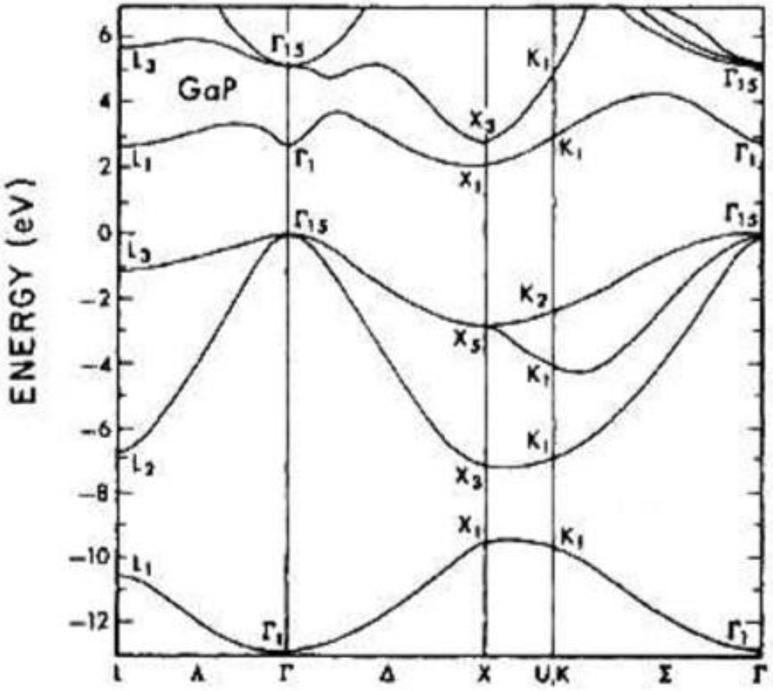
$$E_m^{N} = (E_s^{N} + 3E_p^{N})/4$$

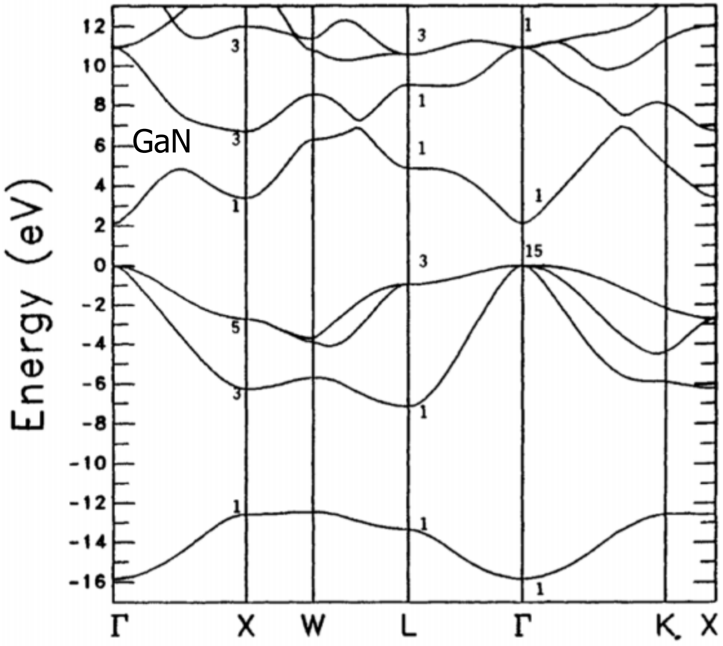
$$\delta^{N} = (E_p^{N} - E_s^{N})/2$$

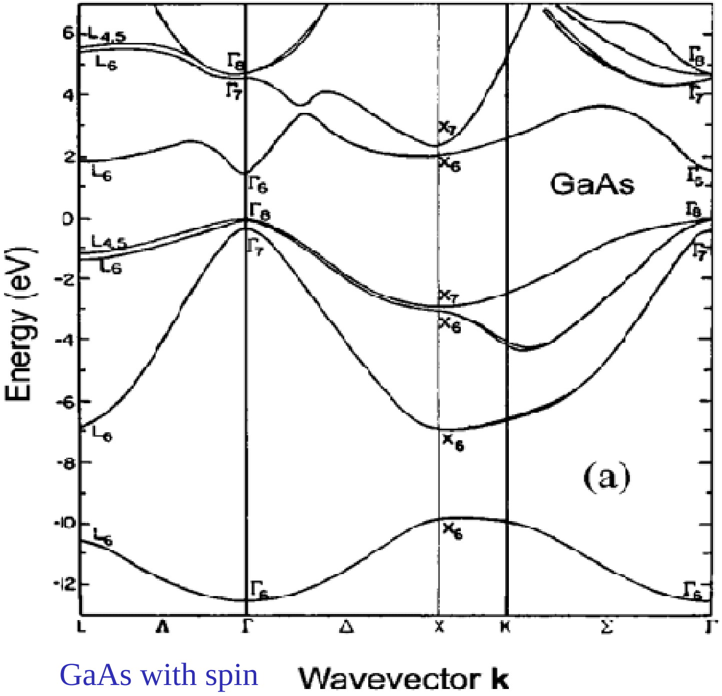
$$-A = \langle \varphi_{Ga,m} | V_{Ga} | \varphi'_{N,m} \rangle = \langle \varphi_{Ga,m} | V'_{N} | \varphi'_{N,m} \rangle$$

Remember slide 14, remark on hermitian Hamiltonian

Cubic GaN, GaAs, GaP







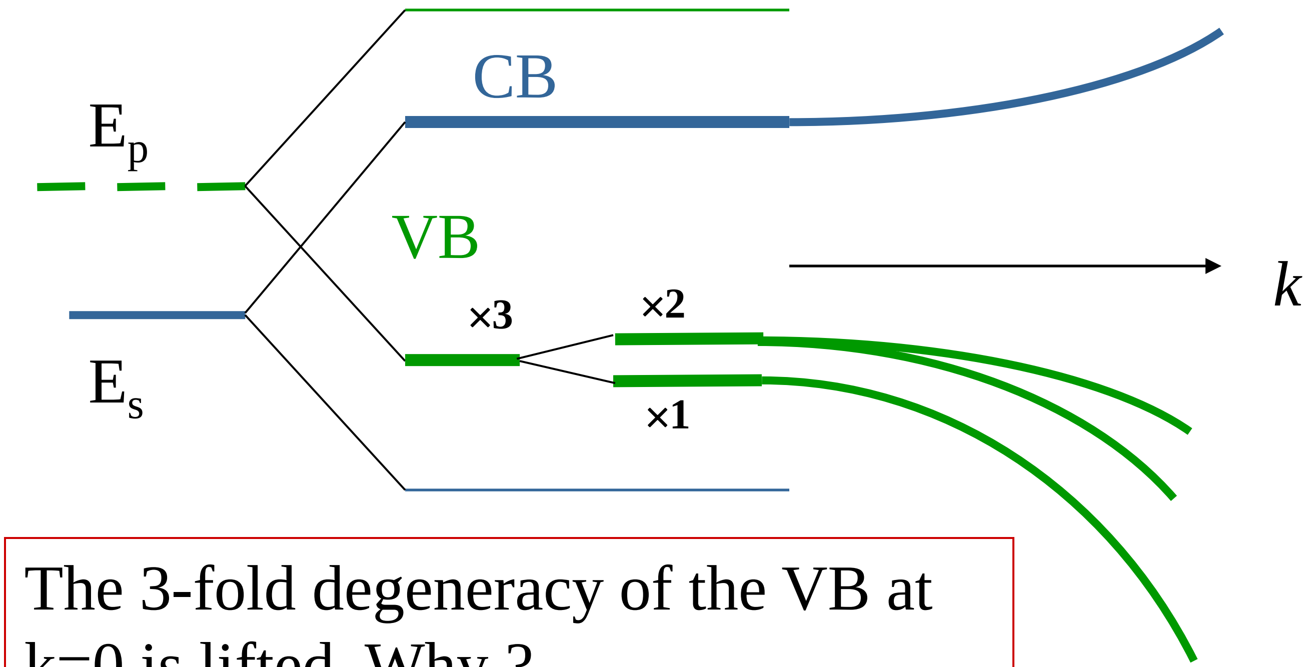
GaAs with spin

Same features for all : cubic symmetry

Valence band 3x degenerate (we exclude spin for the moment !)

NB: GaP has an indirect gap: cannot be easily predicted

Band structure calculation

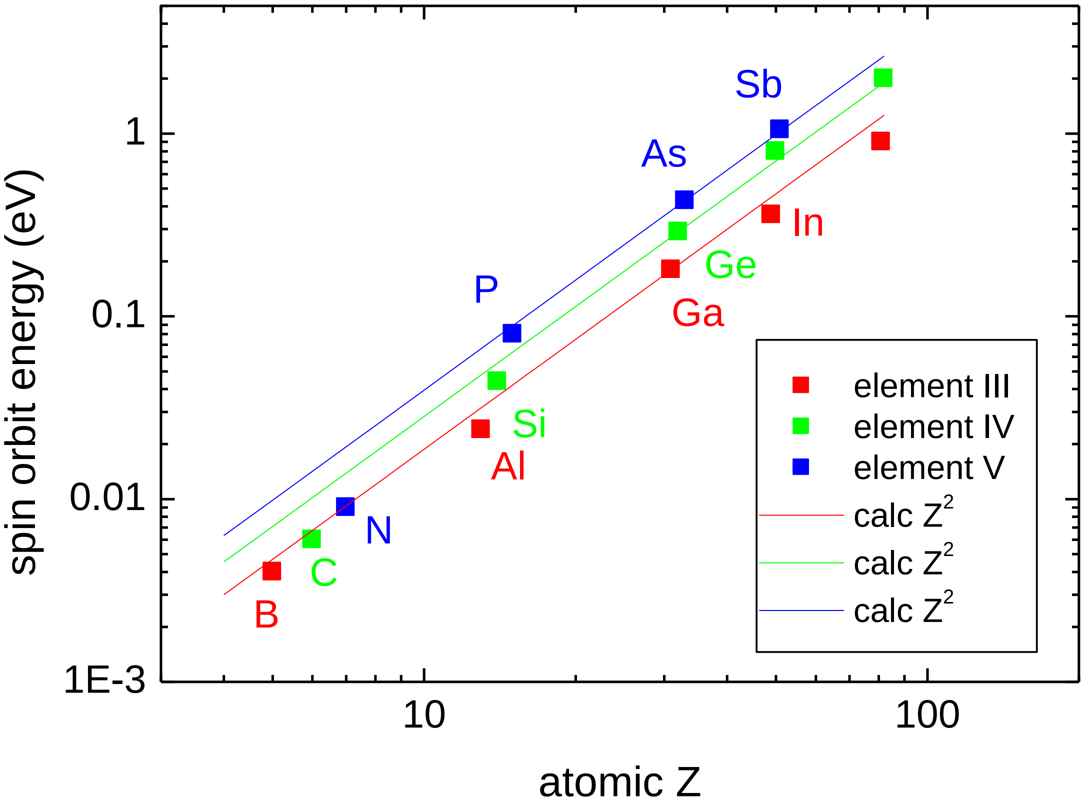


The 3-fold degeneracy of the VB at k=0 is lifted. Why ?

Spin orbit interaction splits the levels with different J ⇒2+1

Band structure

Spin orbit coupling in **atoms**: $H = \mu B_{rel} = \frac{e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L}.\vec{S}$



Relativistic effect

Depends on electron orbit (weak for external layer) and cinetic moment

Depends on atom size (dV/dr) as Z^2

Weak for light atoms in particular for N

Spin orbit splitting in **semiconductors** :

$$H = \frac{e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L}.\vec{S}$$

⇒ separates levels with different orbital moments.

In direct semiconductors, and in particular close to the Γ point, the conduction band is made of s states (l=0, j=1/2) and the valence band is made of p states (l=1, j=1/2 or 3/2)

⇒ No effect on conduction band

⇒ Splitting of the valence band Δ_{so}

$$2\vec{L}.\vec{S} = (\vec{L}+\vec{S})^2 - \vec{L}^2 - \vec{S}^2 = \vec{J}^2 - \vec{L}^2 - \vec{S}^2 = J(J+1)-L(L+1)-S(S+1)$$

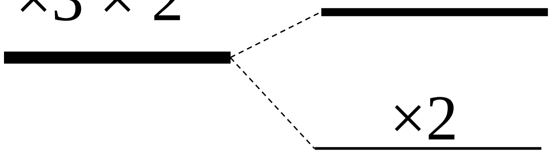
$$J=3/2 \;\Rightarrow\; \vec{L}.\vec{S} = 1/2[3/2(3/2+1)-1(1+1)-1/2(1/2+1)]=1/2$$

$$J=1/2 \;\Rightarrow\; \vec{L}.\vec{S} = 1/2[1/2(1/2+1)-1(1+1)-1/2(1/2+1)]=-1$$

valence band :

L=1,S=1/2

L_z=-1,0,1, S_z=-1/2,1/2



SOC

×3 × 2

×4

J=3/2, J_z=-3/2,-1/2,1/2,3/2

×2

J=1/2, J_z=-1/2,1/2

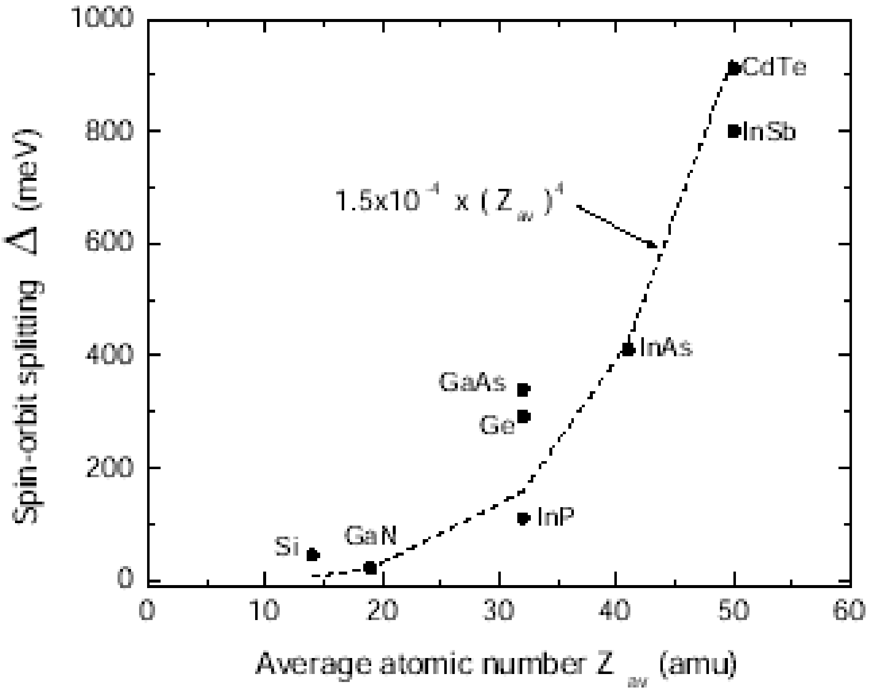
NB: we do not have E(k,↑)=E(k,↓) any more but we still have E(k,↑)=E(-k,↓) (Kramers degeneracy, time symmetry)

Band structure

Spin orbit splitting in **semiconductors** : $H = \frac{e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L}.\vec{S}$

As for atoms, SO in light semiconductors is small

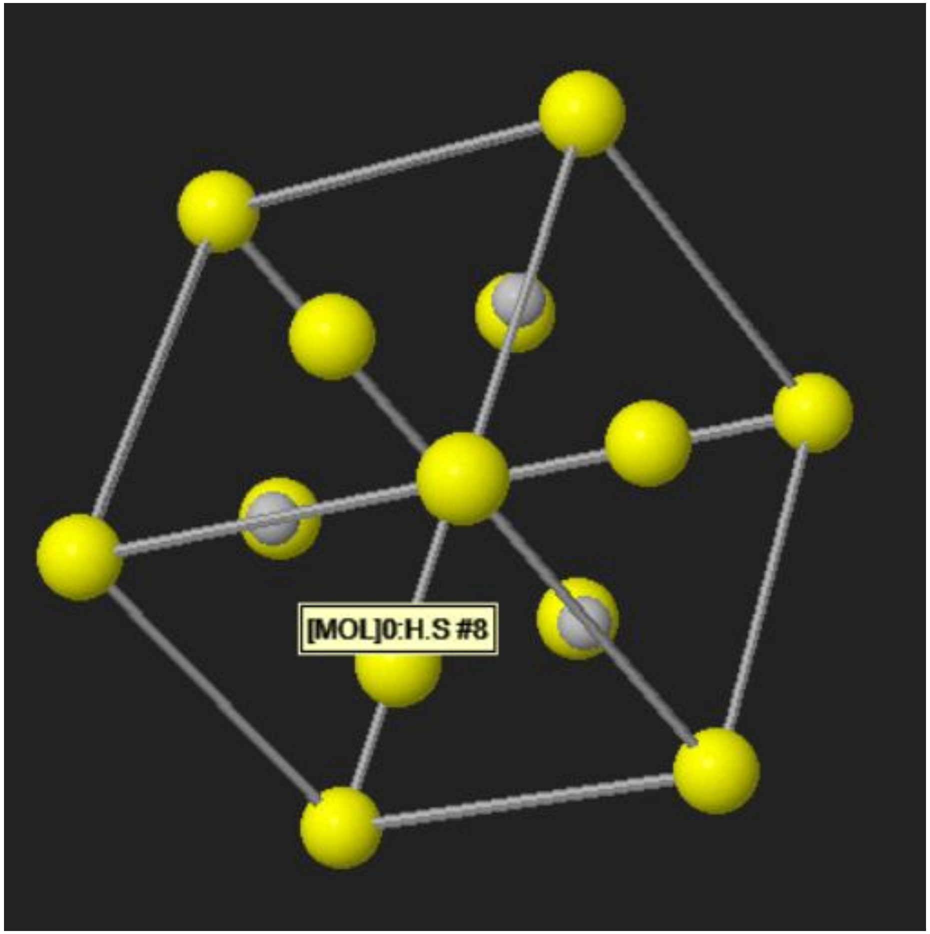
More precisely: Valence band is dominated by p states coming from N: SO larger in GaAs than in GaN, but comparable in AlN and GaN



Wurtzite GaN

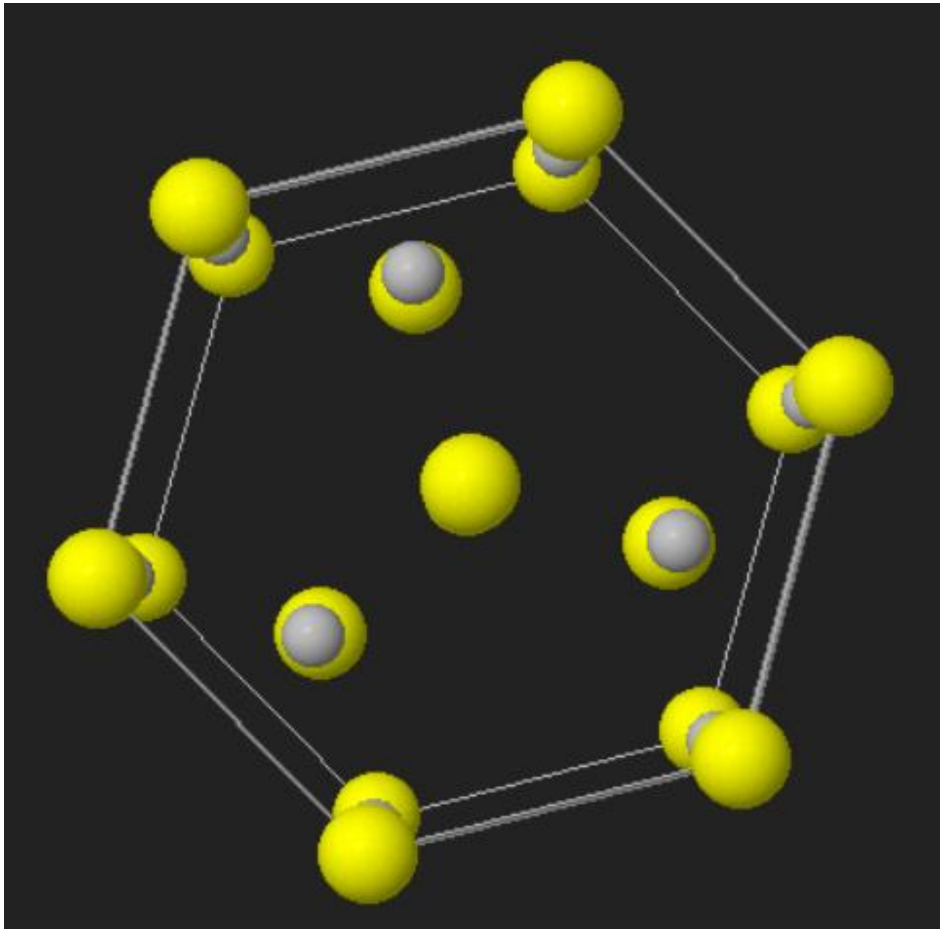
we focus on the k=0 (Γ) point

Zinc blend



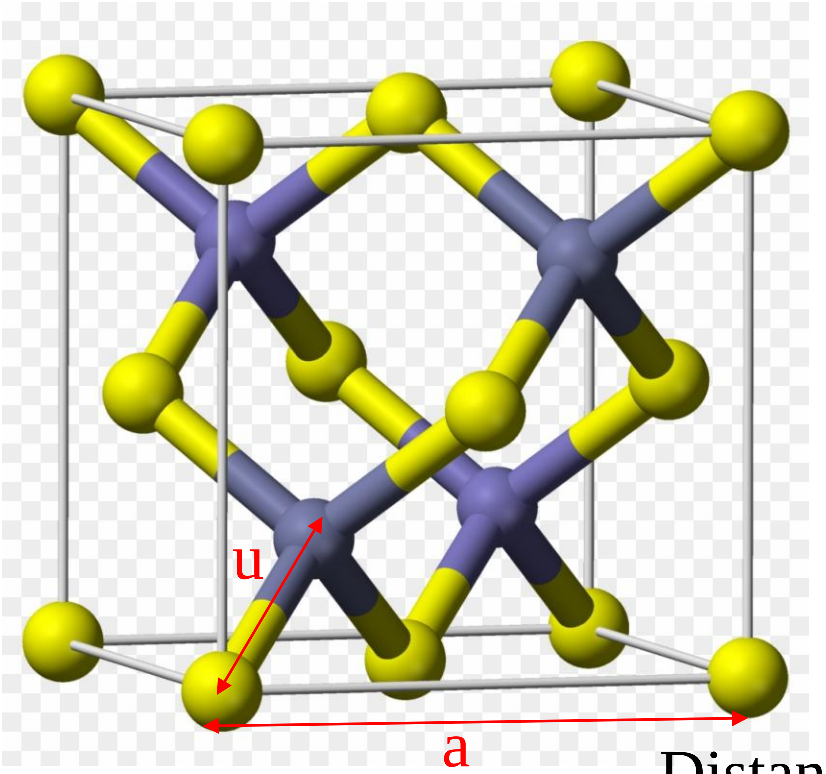
A,B,C, A,B,C…

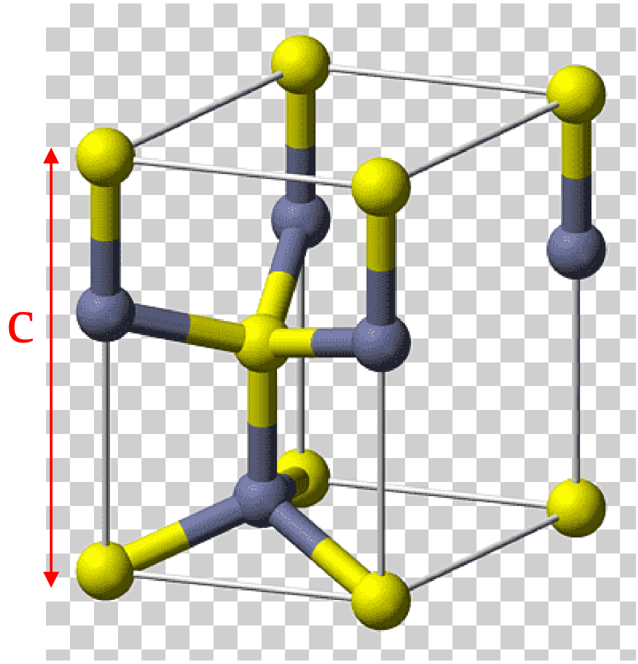
Wurtzite



A,B, A,B,…

From cubic to wurzite

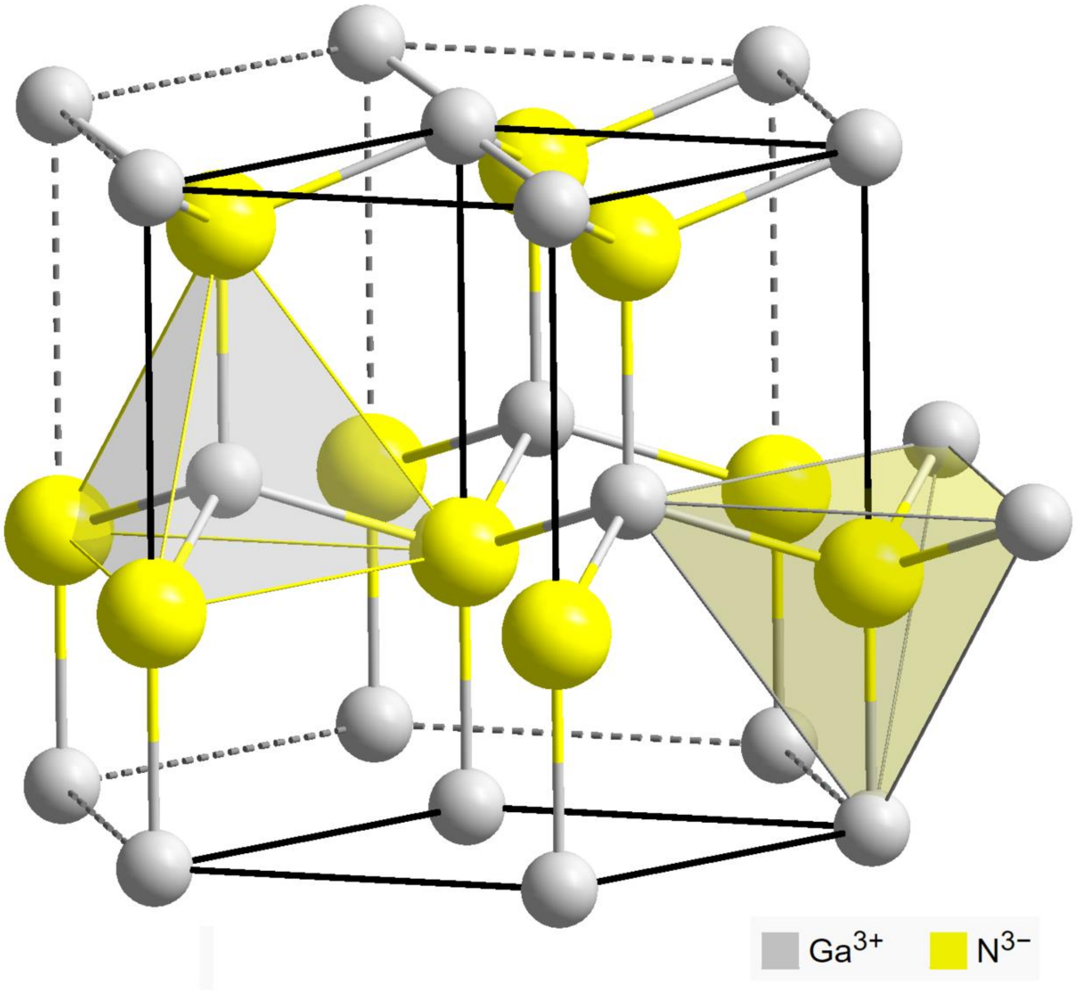


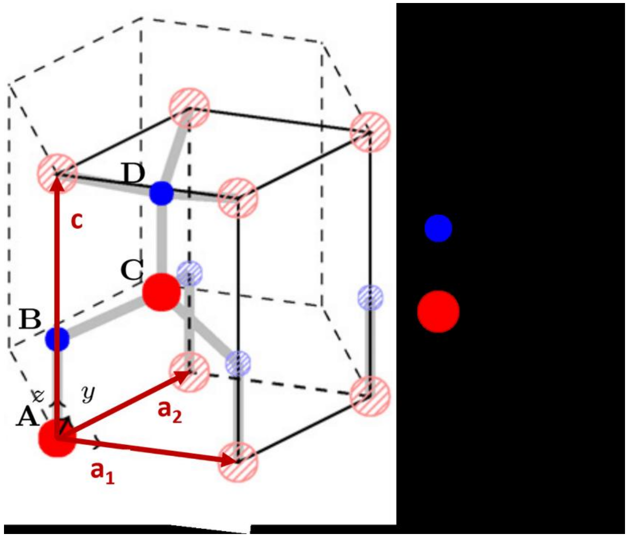


Distance Ga to Ga

#	n	cubic	n	wurzite
1st	**12**	$a = u\sqrt{8/3} = 1.63u$	**12**	$a = u\sqrt{8/3} = 1.63u$
2nd	**3**	$a\sqrt{2} = 4u\sqrt{1/3} = 2.30u$	**3**	$a\sqrt{2} = 4u\sqrt{1/3} = 2.30u$
3rd	**6**	$a\sqrt{3} = u\sqrt{8} = 2.82u$	**2**	$c = 8/3u = 2.66u$

Wurtzite, Space groupe : n° 186; $P6_3mc$; C_{6v}



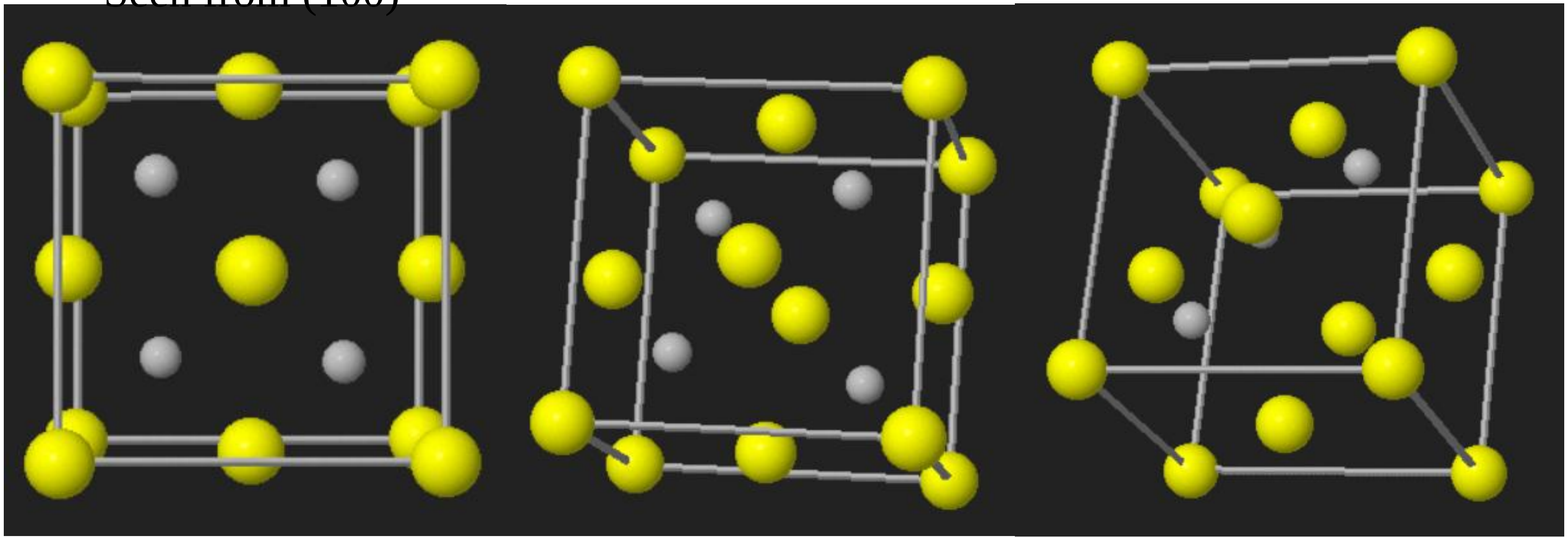


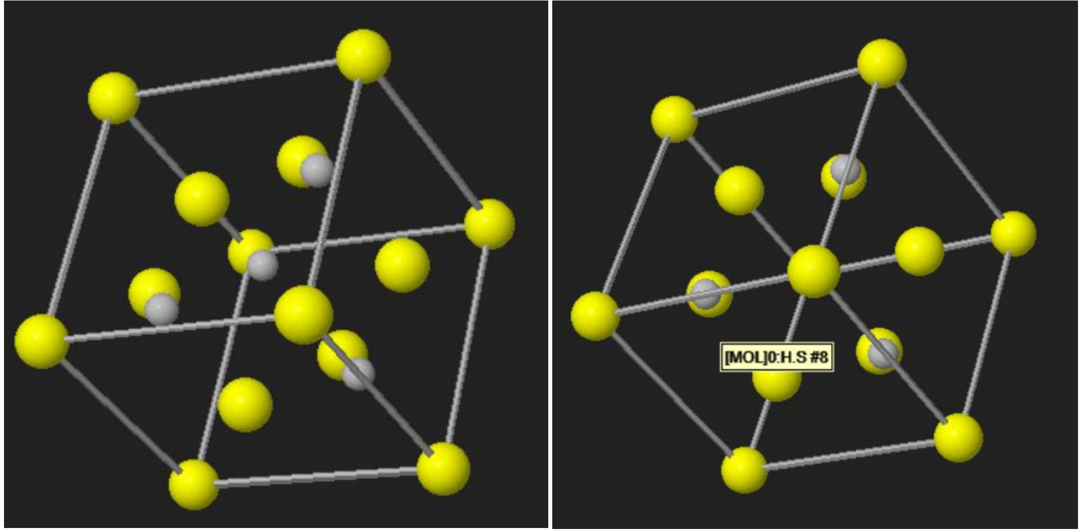
Unitary cell:

- 2 Ga et 2 N in wurtzite = 4 atoms
- 1 Ga et 1 N in zinc blend = 2 atoms

From zinc blend to wurtzite

Seen from (100)





Seen from (111) of cubic

60° rotation around the (111) axis

From zinc blend to wurtzite

We have calculated the H in the cubic referencial with the x,y,z axes. At k=0, for the valence band, we have:

$$H_{x,y,z}=\begin{pmatrix} E_{px} & 0 & 0 \\ 0 & E_{py} & 0 \\ 0 & 0 & E_{pz} \end{pmatrix}$$

Neglecting spin, at k=0, we have $E_{px}=E_{py}=E_{pz}$ (3×degeneracy)

We want to express the H in the wurtzite referencial (X,Y,Z) where the c axis is the (111) direction of the cube.

Rotation (100) to (111)

When the base is rotated by R, the Hamiltonian becomes

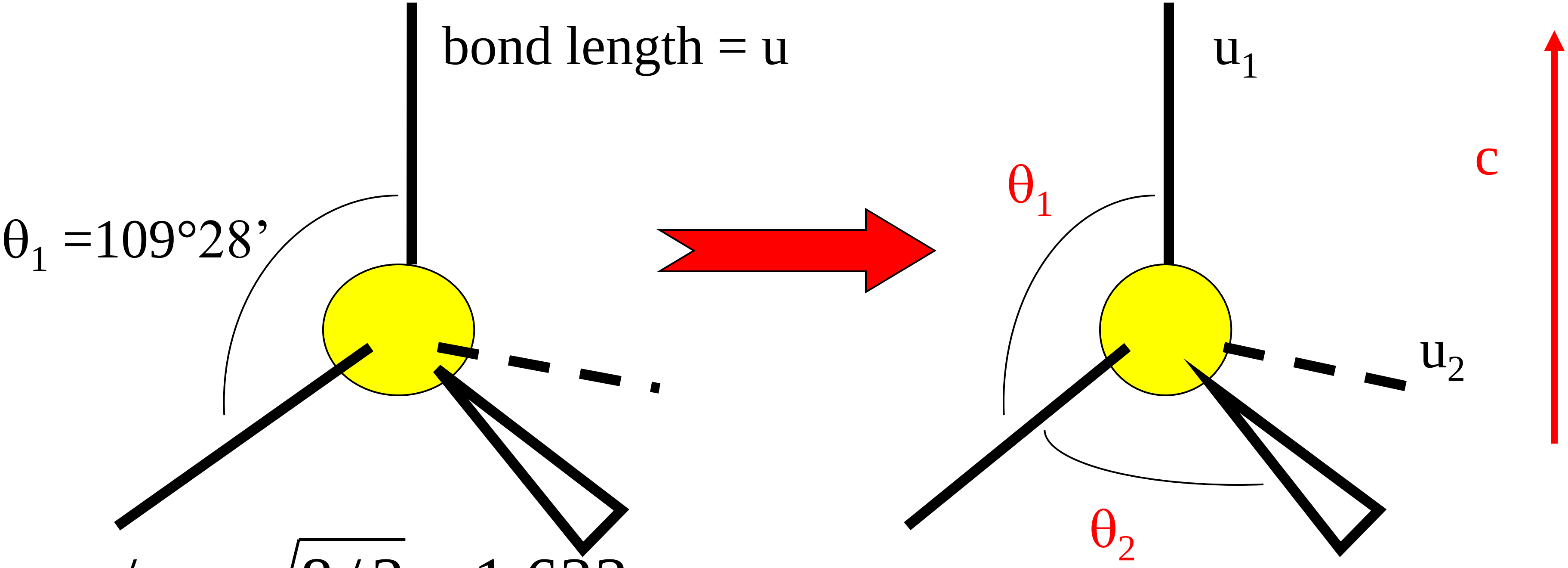
$$H' = R\,H\,R^{-1}$$

$$H_{x,y,z} = \begin{pmatrix} E_{px} & 0 & 0 \\ 0 & E_{py} & 0 \\ 0 & 0 & E_{pz} \end{pmatrix} = \mathrm{E}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E\hat{1}$$

$$H_{X,Y,Z} = RH_{x,y,z}R^{-1} = RE\hat{1}R^{-1} = E\hat{1}RR^{-1} = E\hat{1} = H_{x,y,z}$$

Real structure of wurtzite GaN

The GaN_4 tetrahedron is distorted in the w-GaN crystal due to the electronic environnement !



$$c/a = \sqrt{8/3} = 1.633$$

$$c/u = 8/3 = 2.666$$

$$c/a \neq \sqrt{8/3} = 1.633$$

$$c/u \neq 8/3 = 2.666$$

Real structure of wurtzite GaN

	a(nm)	c(nm)	c/a	c/u
GaN	0.3189	0.5185	1.626	2.652
AlN	0.3113	0.4982	1.600	2.618
InN	0.3538	0.5703	1.612	2.652

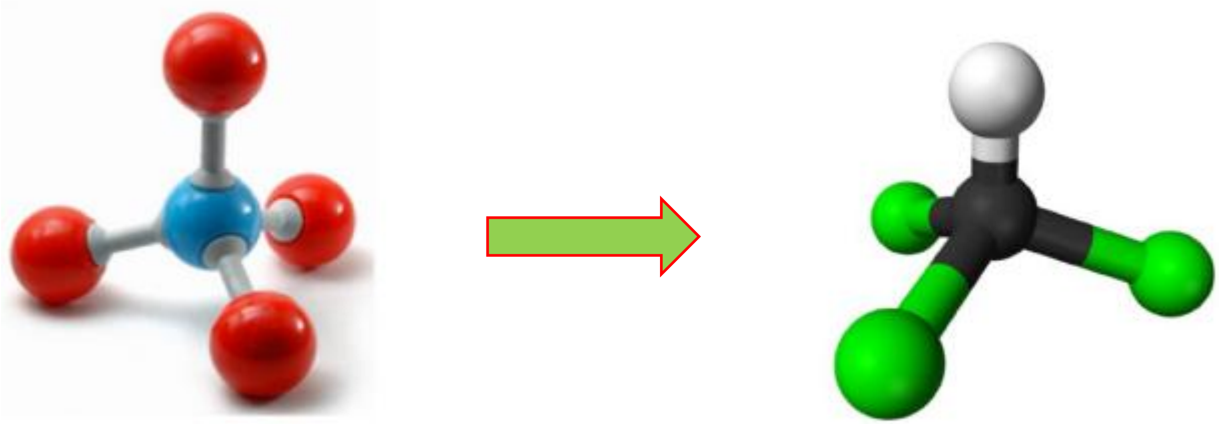
Ideal wurtzite

c/a	c/u
1.633	2.666

The cell is distorted

c shorter = tetrahedron compressed along c

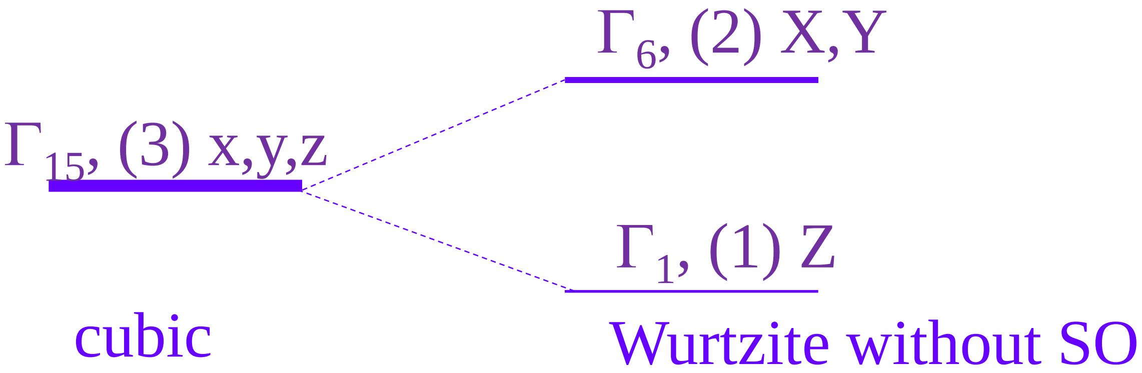
From cubic to wurtzite



$$H = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{pmatrix} \qquad H = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E + \Delta \end{pmatrix}$$

	GaN	AlN	InN
Δcr (meV)	10	-200	25 ?

NB: Δ_{cr} strongly varies with strain (see B.Gil's plot)



Γ_6, (2) X,Y

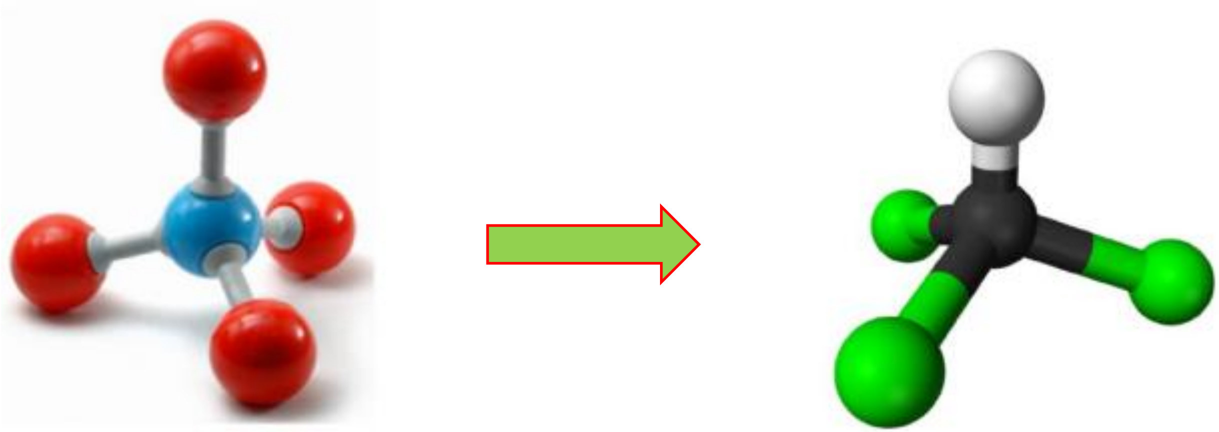
Γ_{15}, (3) x,y,z

Γ_1, (1) Z

cubic

Wurtzite without SO

A remark



$$H = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{pmatrix} \qquad H = \begin{pmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E+\Delta \end{pmatrix}$$

Δ= the energy difference for the z function would appear even **without** terahedron deformation, as the electronic clouds are deformed in the reduced symmetry system (same as for spontaneous polarization) but it would be smaller

Spin orbit coupling in wurzite

$$H_{SO} = \Delta_2 L_z S_z + \Delta_3 (L_x S_x + L_y S_y)$$

- H_{SO} is not diagonal in the X,Y,Z basis and terms are difficult to express

- H_{SO} is not diagonal in the J basis in the wurzite case (contrary to cubic) as $\Delta_2 \neq \Delta_3$. H_{cr} is not diagonal in the J basis as crystal fields does not depend on spin

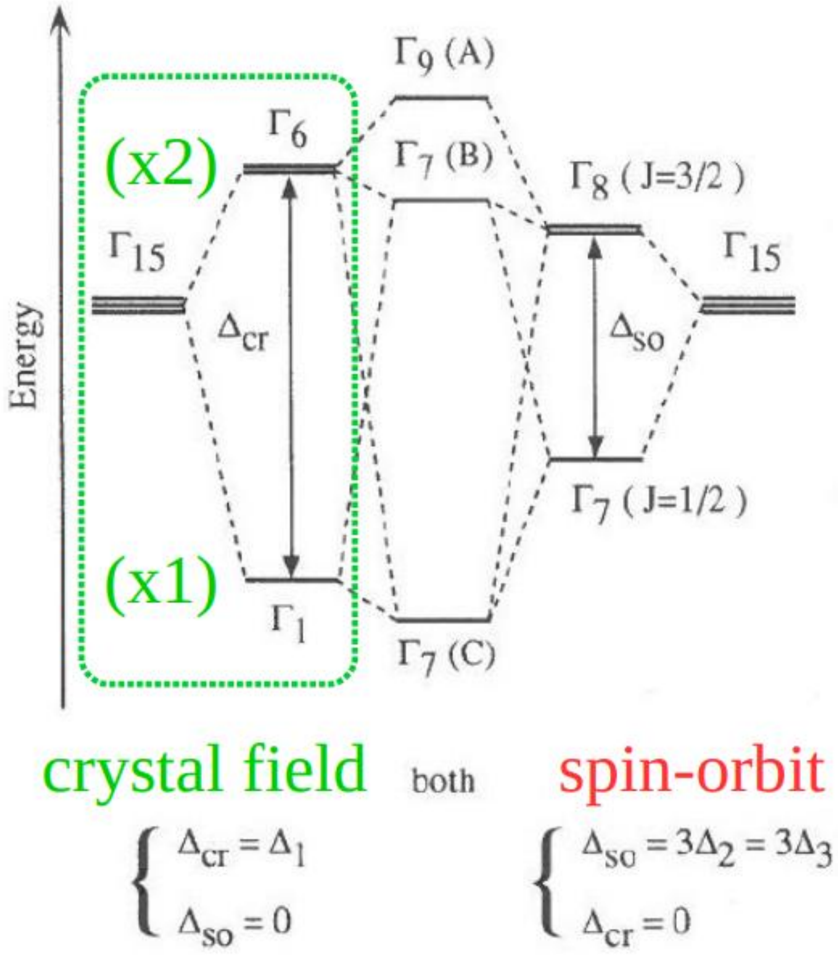
- H_{SO} is not diagonal in the L,S basis but can be expressed easily

⇒ Rewrite the crystal field term in the L, S basis

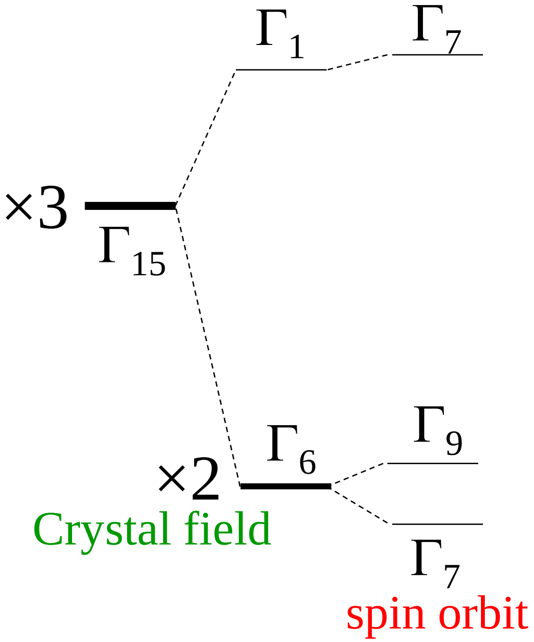
⇒ Diagonalise H_{SO} + H_{cr} to find the new eigen states for the valence band

GaN valence band

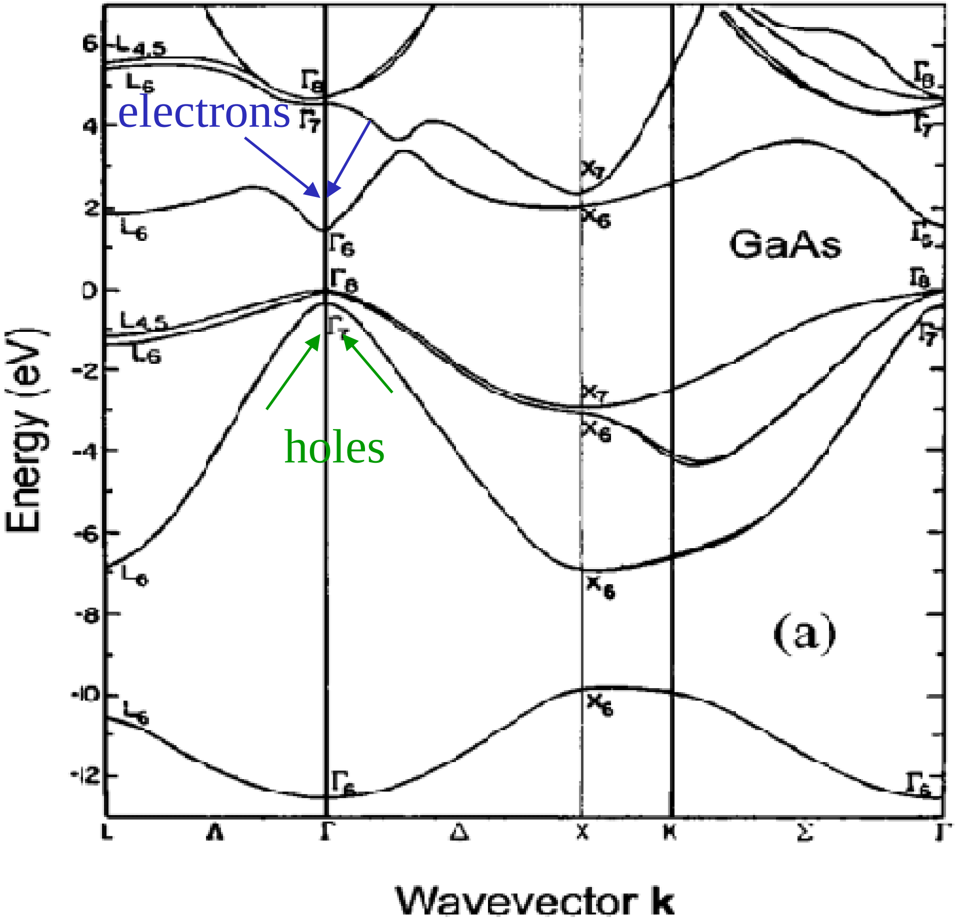
GaN



AlN



Why was it important
and relevant to focus
on the Γ point ?



The Γ point is where all recombinations and emission will happen.

It is also the onset of optical absorption and where gain appears in lasers

It is also where the effective masses are defined for electronics, at least at low field

Any experiment/device implying other states than Γ ?

Auger, high electric field (avalanche, velocity saturation…)

CONCLUSION

- Bands appear in solids because of the overlap of a large number of atomic orbitals. Periodicity is not necessary for bands. However, periodicity give rise to specific features (bands and gaps)
- A quite small number (<10) of periods is needed to generate the band structure
- LCAO gives a good description of covalent semiconductors and also III-V semiconductors
- The crystal symmetry has an impact on the band degeneracy at high symmetry point (Γ, X….): The higher the symmetry, the larger the degeneracy (up to 3)