

QVITEL 2016
montevideo

XLII Congreso de Químicos Teóricos de Expresión Latina
20/25 nov. 2016

**Computational Methods Applied to
Materials Science:**

Nanotechnology and Surface Phenomena

From Molecules to Solids

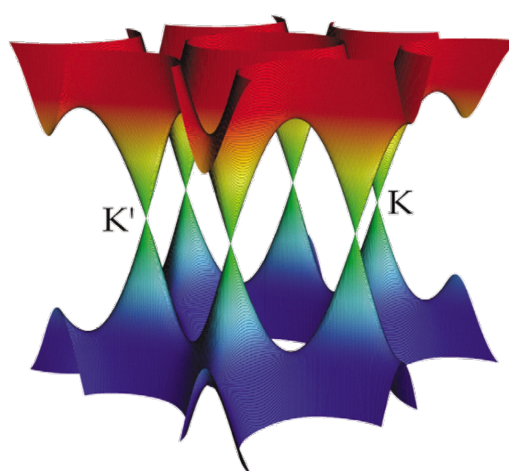
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UDELAR
FACULTAD DE QUÍMICA

UNIVERSIDAD DE LA REPÚBLICA
FÍSICA DAY

Outline

- LCAO
- Bloch Theorem
- Band
 - Width
 - Running
 - Folding
- 1D and 2D



Linear Combination of Atomic Orbitals

□ Diatomic molecule

$$\psi(r) = c_1\phi_1 + c_2\phi_2$$

$$E = \frac{c_1^2 \int \phi_1 \hat{H} \phi_1 dV + c_2^2 \int \phi_2 \hat{H} \phi_2 dV + 2c_1 c_2 \int \phi_1 \hat{H} \phi_2 dV}{c_1^2 \int \phi_1^2 dV + c_2^2 \int \phi_2^2 dV + 2c_1 c_2 \int \phi_1 \phi_2 dV}$$

$$\alpha_1 = \int \phi_1 \hat{H} \phi_1 dV$$

$$S_{12} = \int \phi_1 \phi_2 dV$$

$$\alpha_2 = \int \phi_2 \hat{H} \phi_2 dV$$

$$\beta_{12} = \int \phi_1 \hat{H} \phi_2 dV = \beta_{21} = \int \phi_2 \hat{H} \phi_1 dV$$

LCAO

$$E = \frac{c_1^2 \alpha_1 + c_2^2 \alpha_2 + 2c_1 c_2 \beta}{c_1^2 + c_2^2 + 2c_1 c_2 S} \quad \frac{\partial E}{\partial c_1} = 0 \quad \frac{\partial E}{\partial c_2} = 0$$

$$(\alpha_1 - E)c_1 + (\beta - ES)c_2 = 0$$

$$(\beta - ES)c_1 + (\alpha_2 - E)c_2 = 0$$

$$\begin{vmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{vmatrix}$$

$$\alpha - E = \pm(\beta - ES)$$

$$E_A = \frac{\alpha + \beta}{1 + S}$$

$$c_1 = c_2$$

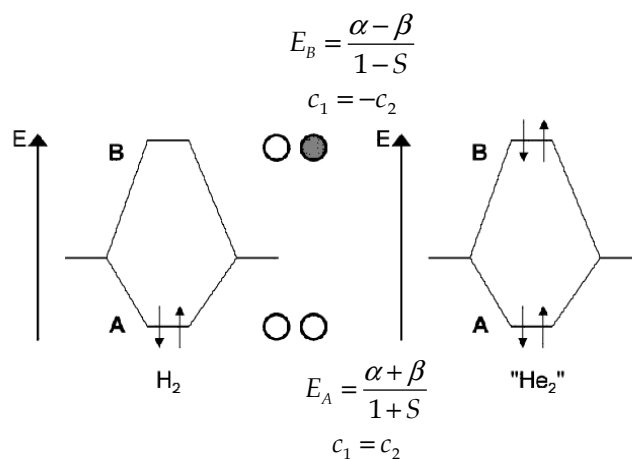
$$E_B = \frac{\alpha - \beta}{1 - S}$$

$$c_1 = -c_2$$

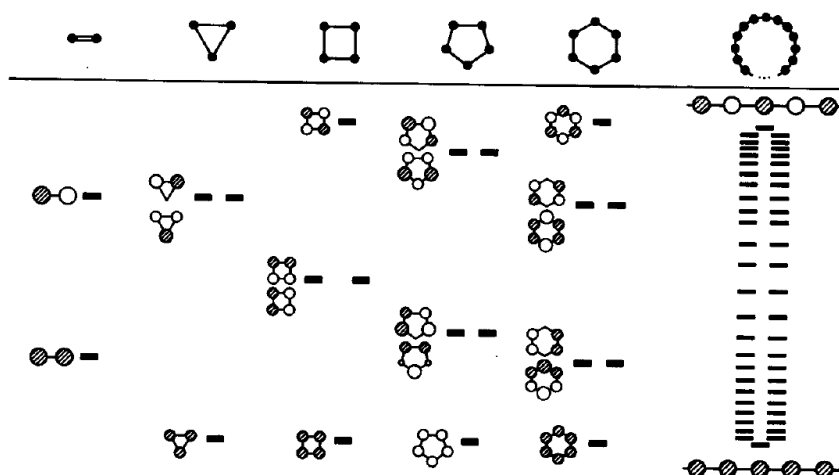
$$\alpha_1 = \alpha_2 = \alpha$$

LCAO: Diatomic molecule

▣ Identical atoms



Simple cyclic molecules

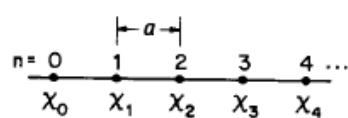


Blöch Theorem

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

$$\psi_k = \sum_n \chi_n e^{ikna}$$

Infinite chain of H: Blöch Theorem



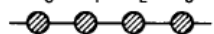
$$\psi_k = \sum_n e^{ikna} \chi_n$$

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

$$\psi_k = \sum_n \chi_n e^{ikna}$$

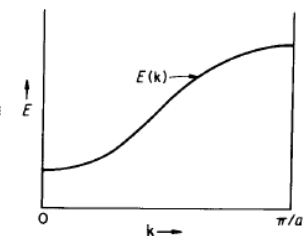
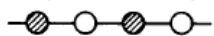
$$k=0 \quad \psi_0 = \sum_n e^{i0} \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



$$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



Other k-points

$$k = \pi/a$$

$$\Psi_{\pi/a} = \chi_0 + (\exp\{i\pi\})\chi_1 + (\exp\{i2\pi\})\chi_2 + (\exp\{i3\pi\})\chi_3 + \dots$$

$$\Psi_{\pi/2a} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \chi_4 + \dots$$

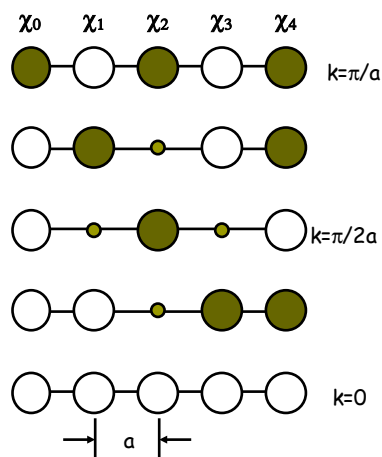
$$k = \pi/2a$$

$$\Psi_{\pi/2a} = \chi_0 + (\exp\{i\pi/2\})\chi_1 + (\exp\{i\pi\})\chi_2 + (\exp\{i3\pi/2\})\chi_3 + (\exp\{i2\pi\})\chi_4 + \dots$$

$$\Psi_{\pi/2a} = \chi_0 + 0 - \chi_2 + 0 + \chi_4 + \dots$$

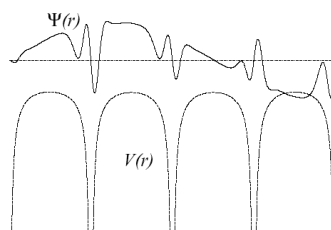
$$k = 0$$

$$\Psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4 + \dots$$

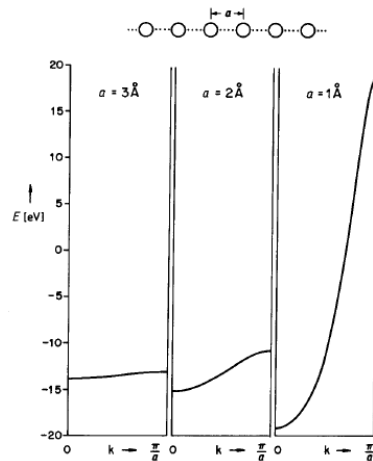


Blöch Theorem Properties

- ▣ We have as many k-points as unit cells in the crystal.
- ▣ The Wave-function is periodical in momentum space, and non-periodical in real space: $\psi_{n, \vec{k} + \vec{G}}(\vec{r}) = \psi_{n, \vec{k}}(\vec{r})$
- ▣ The charge density and the crystalline potential are periodical in real space: $\rho_n(\vec{r} + \vec{R}) = \rho_n(\vec{r})$
- ▣ We have as many bands as orbitals in the unit cell.
- ▣ Each band has as many k-points as unit cells the crystal have.



Band Width



$$E_{A/B} = \frac{\alpha \pm \beta}{1 \pm S}$$

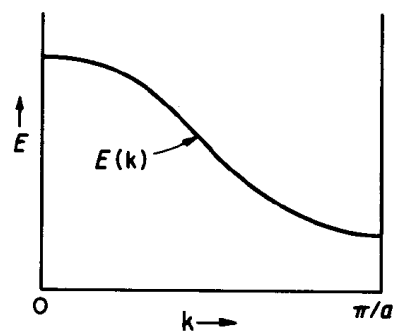
Band Running: P orbitals

□ Sigma bands

$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



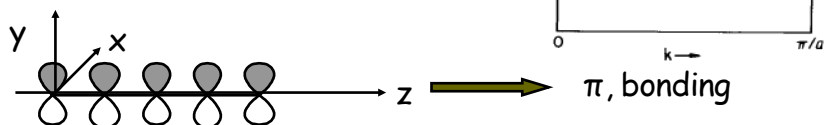
$$\psi_{\pi/a} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



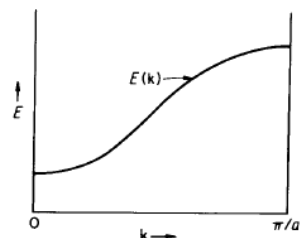
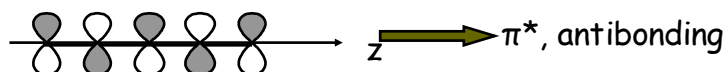
Band Running: P orbitals

□ n bands

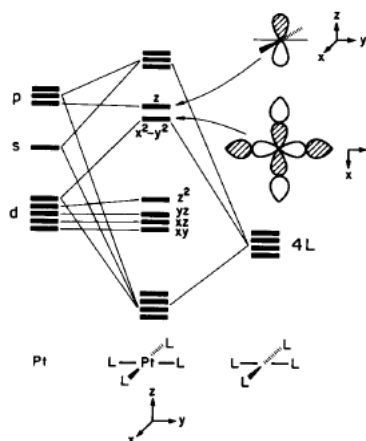
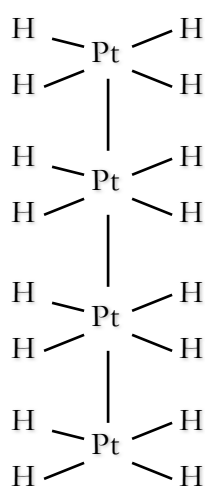
$$k=0, \quad \psi_0 = \sum \chi_n e^{i0} = \sum \chi_n$$



$$k=\pi/a, \quad \psi_{\pi/a} = \sum \chi_n e^{i\frac{\pi}{a}na} = \chi_0 - \chi_1 + \chi_2 \dots$$

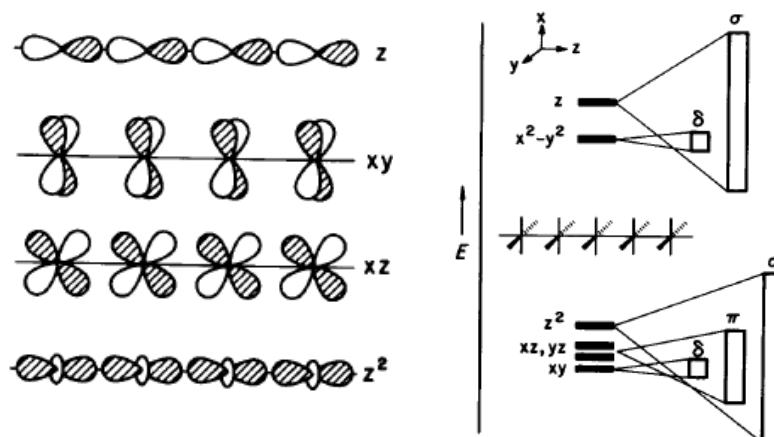


Linear chain: (PtL₄)_n



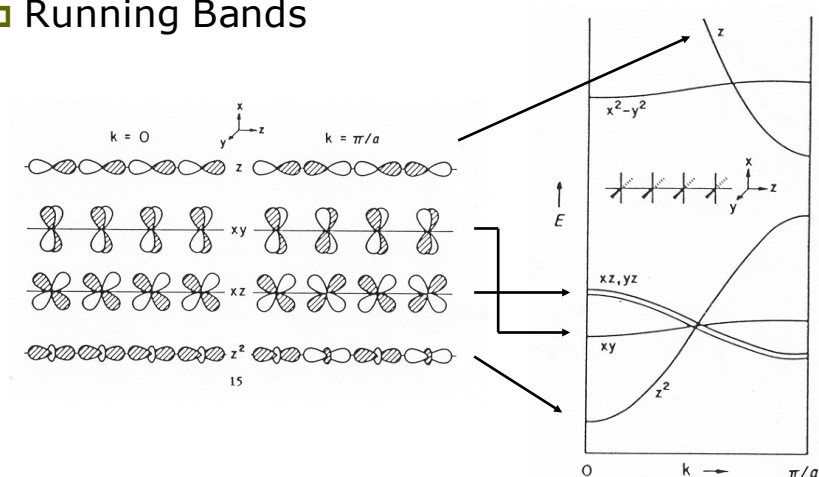
Linear chain: $(\text{PtL}_4)_n$

Comparative overlap



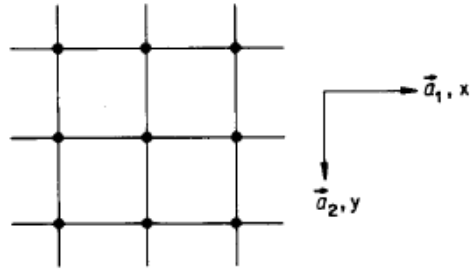
Linear chain: $(\text{PtL}_4)_n$

Running Bands

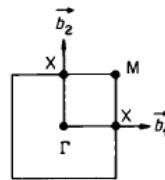


2D Crystals

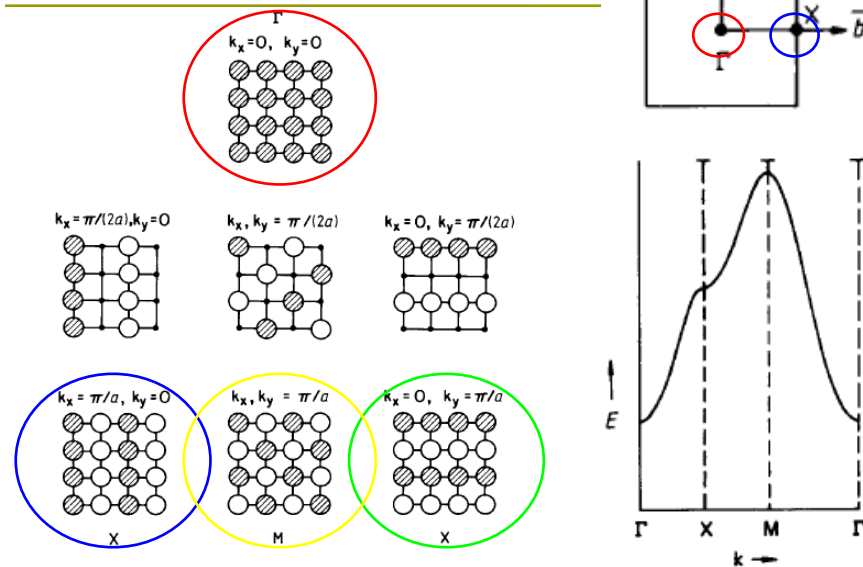
Direct Cell

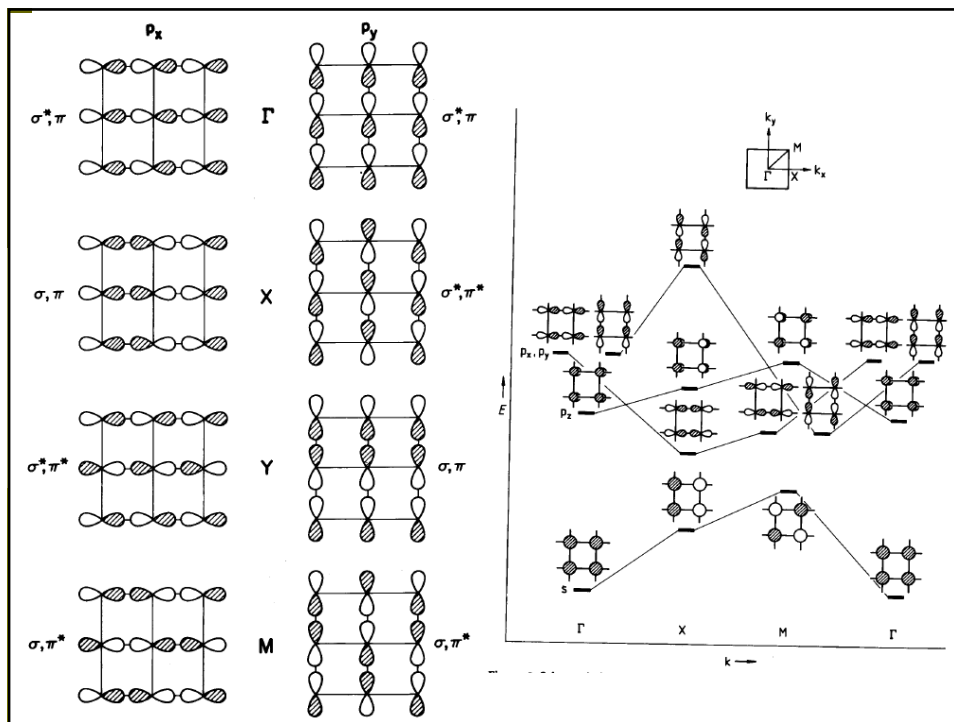


Reciprocal Lattice

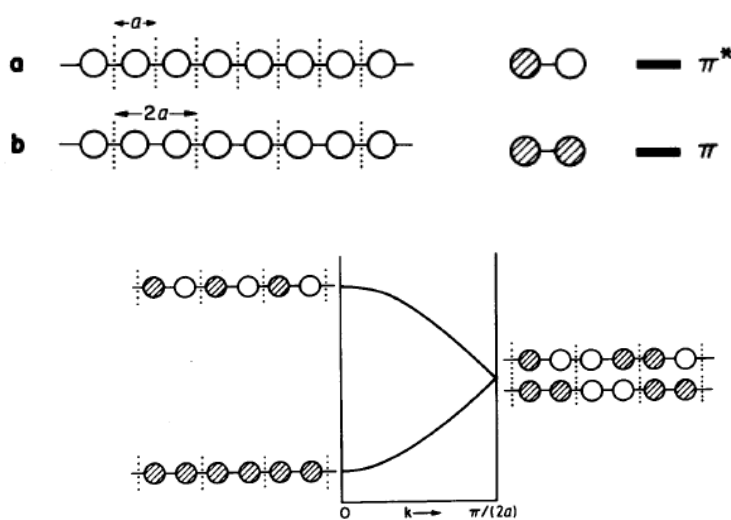


2-D Lattice of H atoms

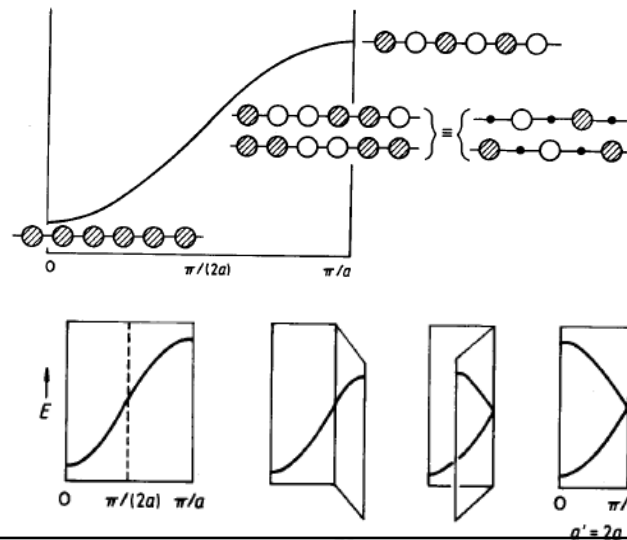




Band Folding (I): supercells

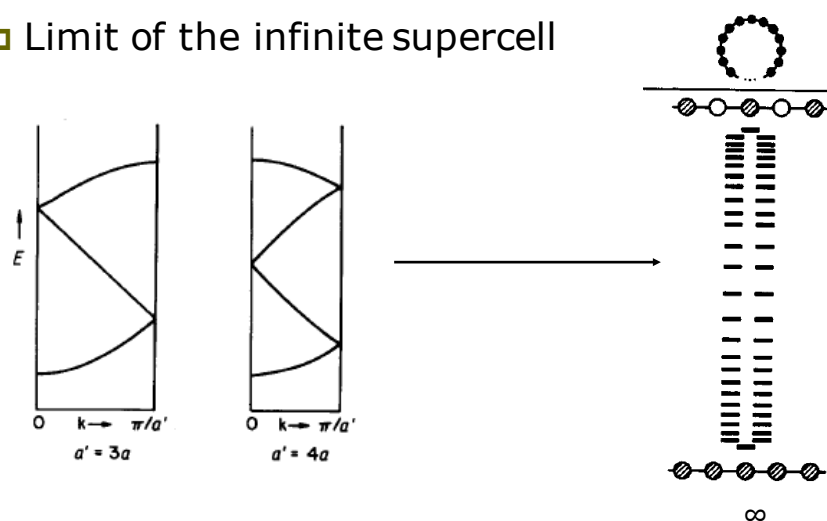


Band Folding (2)



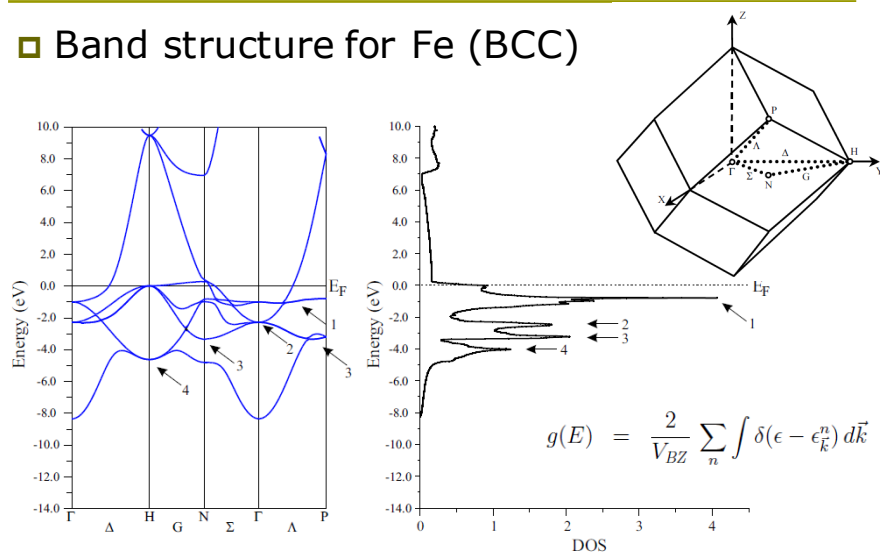
Band Folding (3)

□ Limit of the infinite supercell



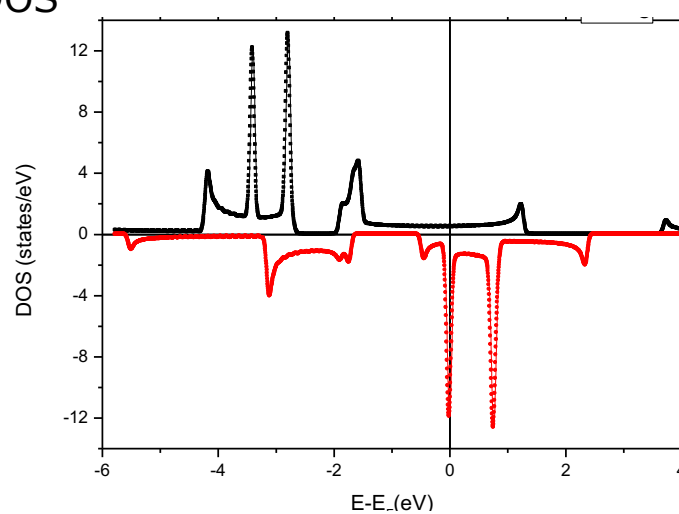
From Bands to DOS

Band structure for Fe (BCC)

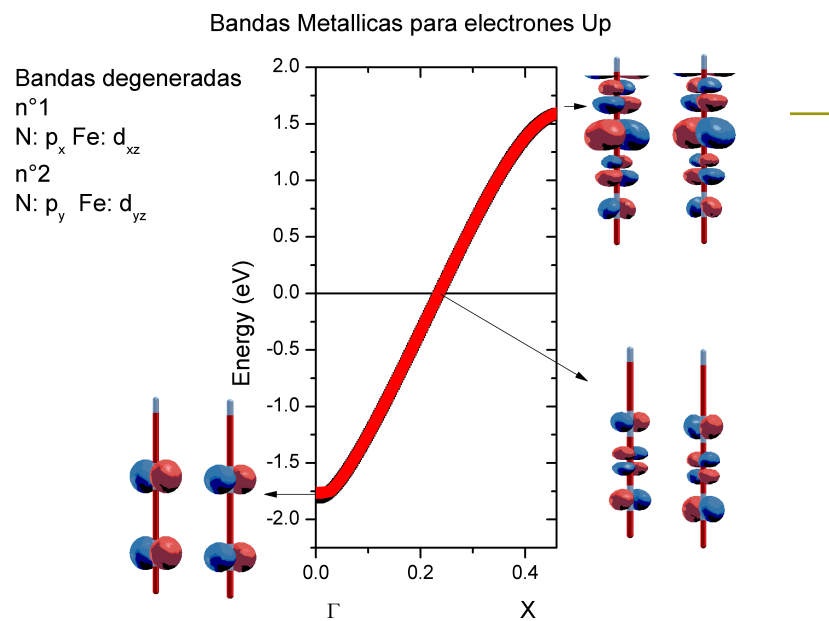
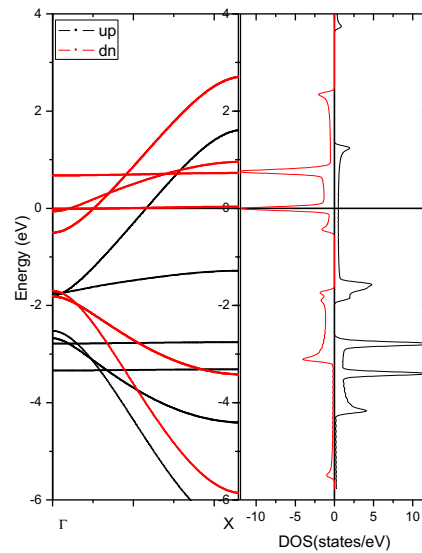


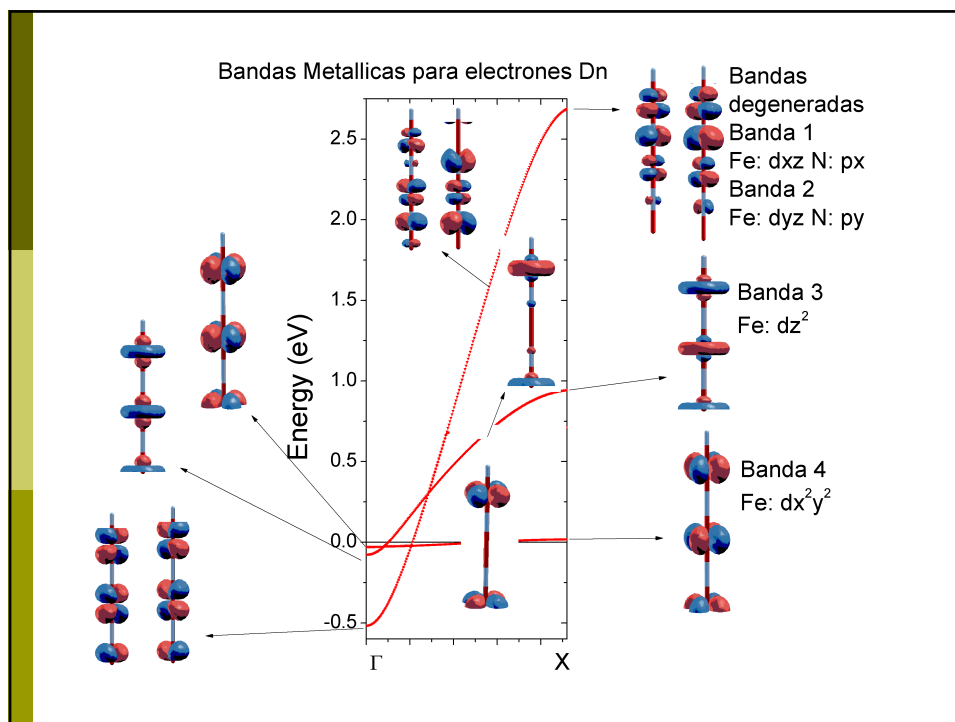
E.g.: infinite chain FeN

DOS



FeN: Band Structure & DOS





Bibliography

- ▣ *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures.* Roald Hoffmann. Wiley. ISBN: 0471187100
- ▣ Density Functional Theory and the Family of (L)APW-methods: a step-by-step introduction. S. Cottenier. ISBN 90-807215-1-4
- ▣ www.wien2k.at