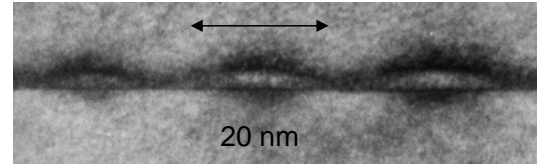
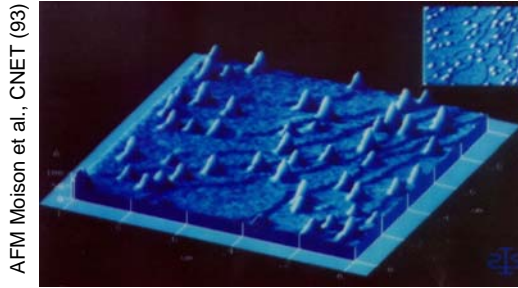


Examples : InAs/GaAs QDs

- **Stransky-Krastanov** growth of InAs on GaAs :

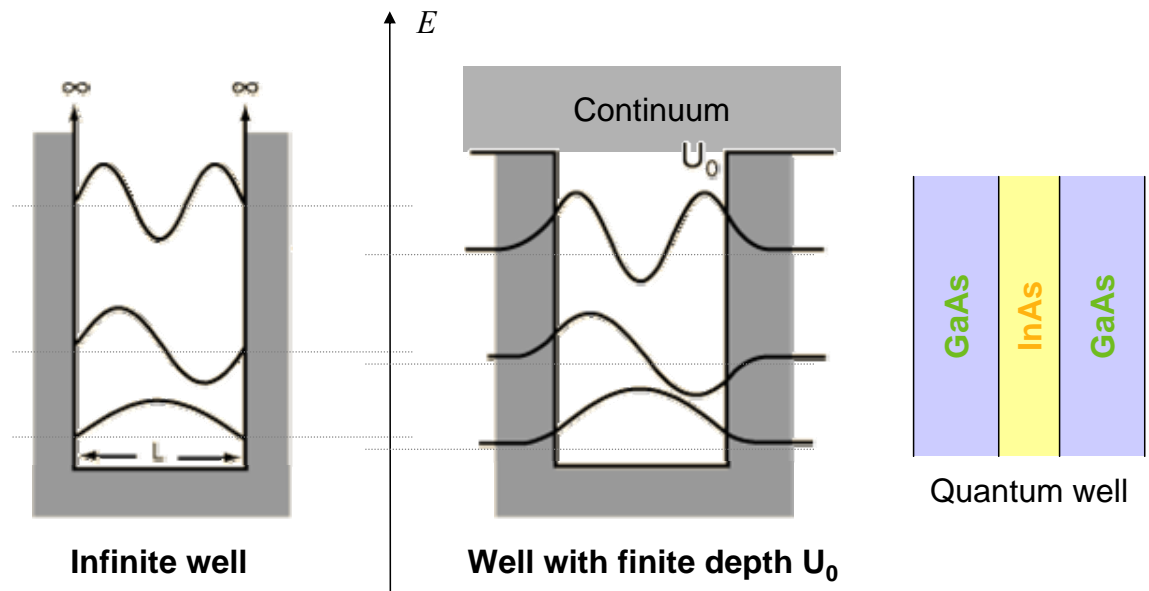


The InAs form pyramidal « droplets » on the GaAs surface. This transition from planar to 3D growth is driven by the lattice mismatch between InAs and GaAs : the bond length is indeed 6.69% larger in InAs than in GaAs.



Applications : Quantum dot lasers, ...

The $\mathbf{k}\cdot\mathbf{p}$ and effective mass approximations



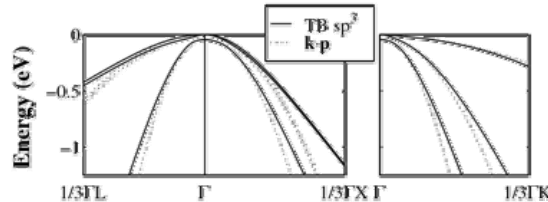
Effective mass approximation

$$\left\{ \begin{array}{l} \text{in bulk : } \varepsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m^*} \\ \text{in nanostructures : } -\frac{\hbar^2}{2m^*} \Delta_{\mathbf{r}} \psi(\mathbf{r}) + v_{slow}(\mathbf{r}) \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}) \end{array} \right.$$

The limits of the $\mathbf{k}\cdot\mathbf{p}$ approximation



- The $\mathbf{k}\cdot\mathbf{p}$ approximation is accurate in weakly confined nanostructures such as InAs/GaAs quantum dots and large nanocrystals.
- However the $\mathbf{k}\cdot\mathbf{p}$ approximation suffers from known deficiencies :
 - **It does not properly reproduce bulk bands** at large \mathbf{k} / high energy :



Si valence band structure

As a consequence the $\mathbf{k}\cdot\mathbf{p}$ approximation fails to describe the electronic properties of nanostructures at high energy (e.g. highly confined structures such as small nanocrystals).

- The $\mathbf{k}\cdot\mathbf{p}$ approximation can not handle **atomic-like boundary conditions**.

We need an atomistic method reproducing the bulk band structures over a wide energy range to overcome these deficiencies

An effective single-particle hamiltonian



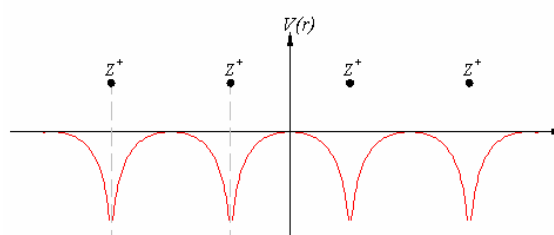
- We assume that the semiconductor crystal or nanostructure can be modeled by a one-particle hamiltonian :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\psi(\mathbf{r}) + v_{eff}(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

where the effective potential $v_{eff}(\mathbf{r})$ may be expanded as a sum of atomic contributions :

$$v_{eff}(\mathbf{r}) = \sum_i v_i(\mathbf{r} - \mathbf{R}_i)$$

\mathbf{R}_i being the atomic positions.



Introduction

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\psi(\mathbf{r}) + v_{eff}(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

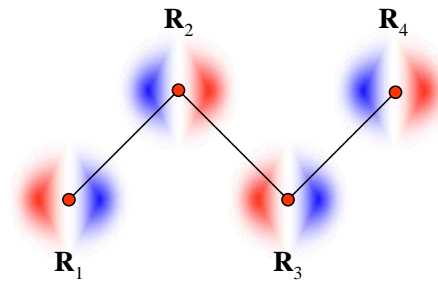


- Write the wavefunctions as **linear combination of atomic orbitals** (LCAO) :

$$\psi(\mathbf{r}) = \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$$

where $\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$ is an orbital of kind α centered on atom i with position \mathbf{R}_i . For example,

- $\alpha = 1 \leftrightarrow 1s$
- $\alpha = 2 \leftrightarrow 2s$
- $\alpha = 3 \leftrightarrow 2p_x$
- $\alpha = 4 \leftrightarrow 2p_y$
- $\alpha = 5 \leftrightarrow 2p_z$
- ...

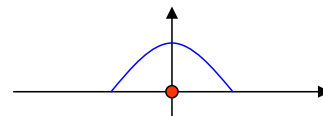
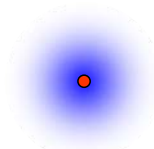


- Which orbitals to choose ?

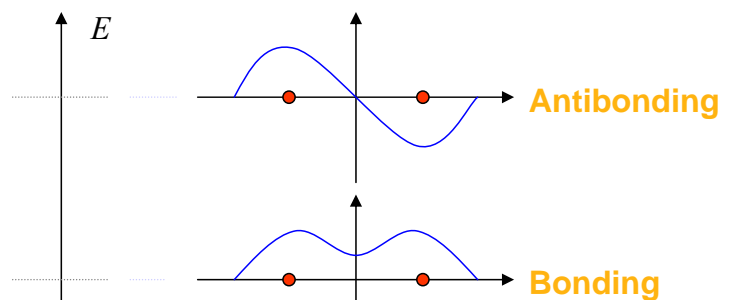
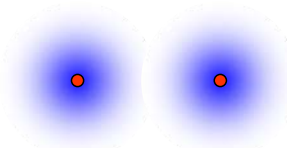
From the atom to the solid (I)



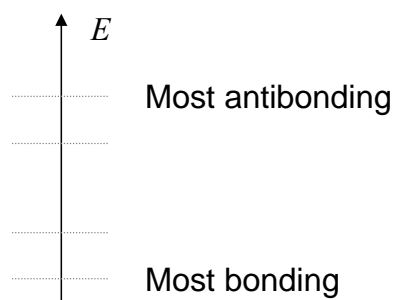
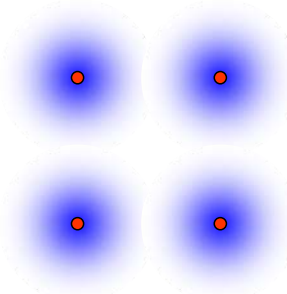
1 H

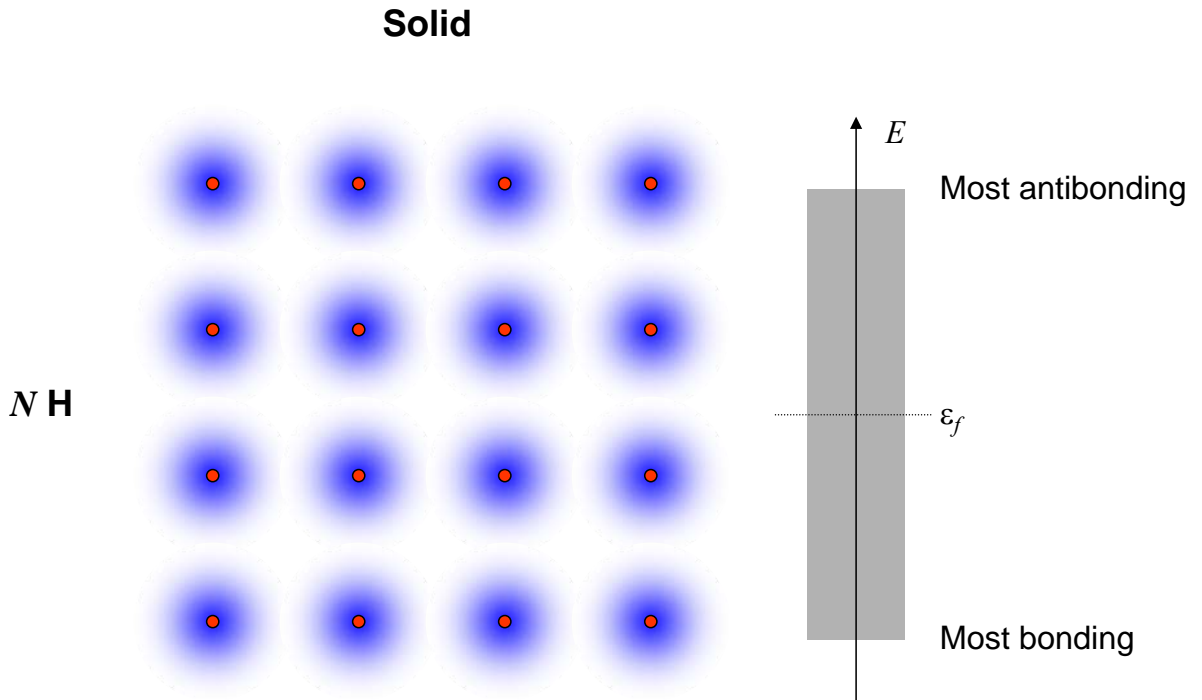


2 H

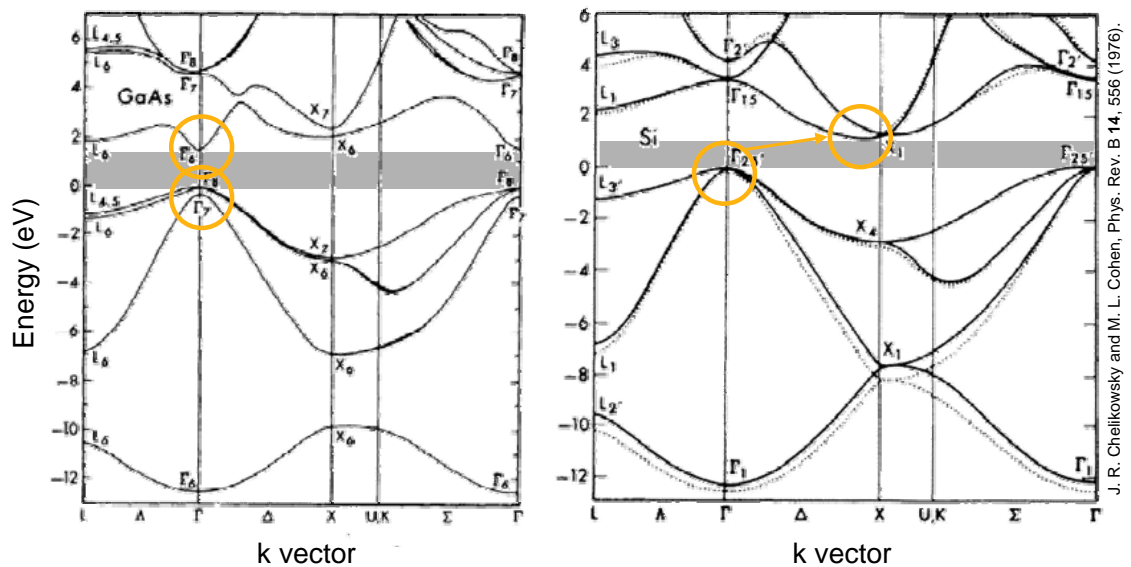


4 H



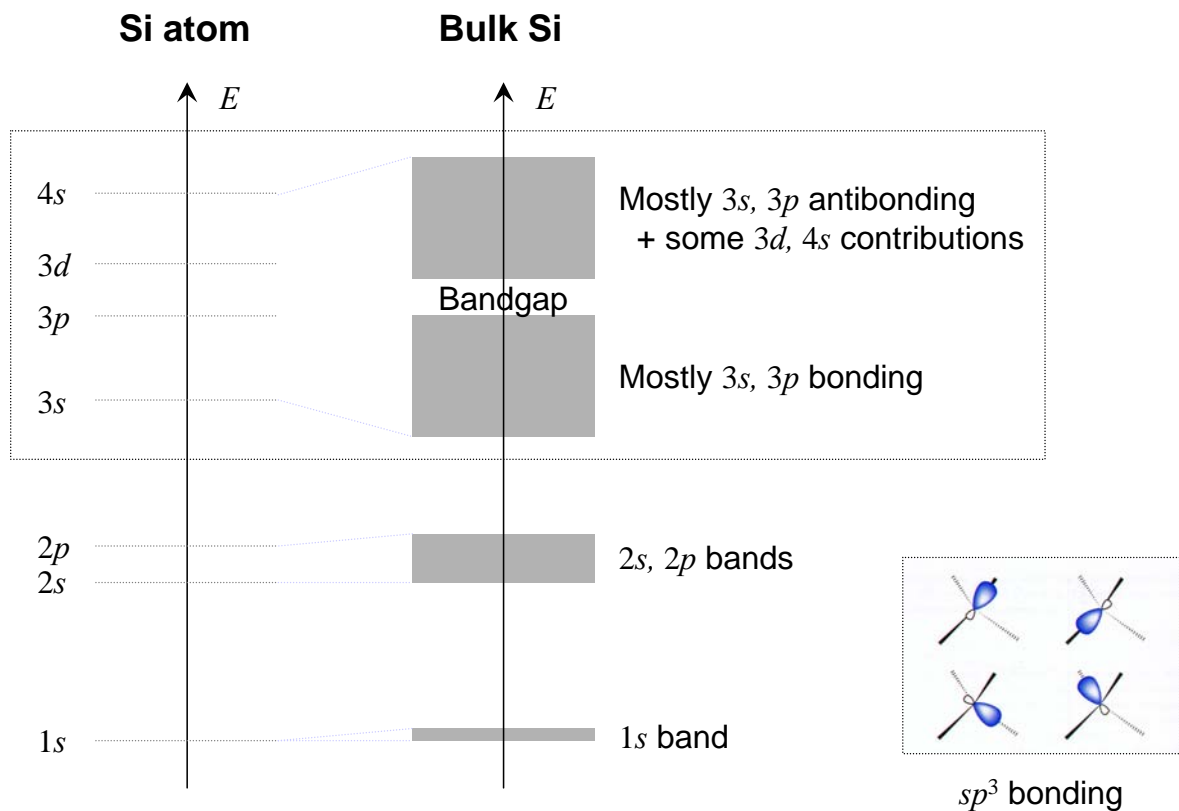


Semiconductor band structures

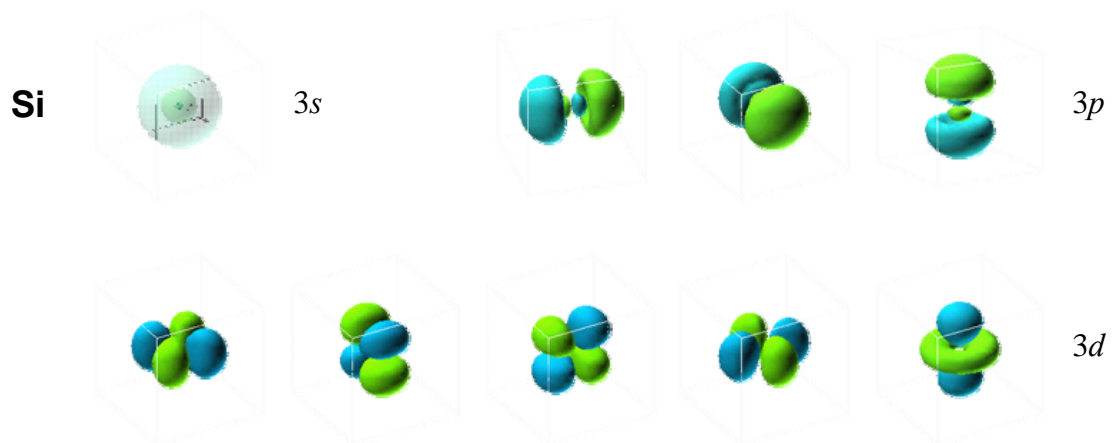


- **GaAs** : **Direct bandgap** material (the valence band maximum and conduction band minimum lie at the same k point).
- **Si** : **Indirect bandgap** material (the valence band maximum and conduction band minima lie at different k points).

Which orbitals to choose ? (I)



Which orbitals to choose ? (II)



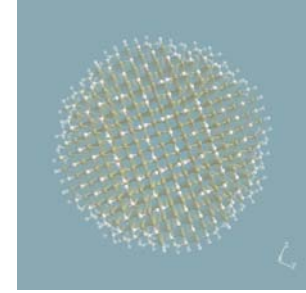
● Possible choices for Si :

- **sp^3 tight-binding model** : quite accurate for the valence bands, somewhat less for the conduction bands, especially at high energy.
- **sp^3d^5 tight-binding model** : accurate valence bands, pretty good conduction bands.
- **$sp^3d^5s^*$ tight-binding model** : accurate valence and conduction bands.

Application to nanocrystals and quantum dots (I)



$$-\frac{\hbar^2}{2m_0} \Delta_{\mathbf{r}} \psi(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}), \quad v_{\text{eff}}(\mathbf{r}) = \sum_{i=1}^N v_i(\mathbf{r} - \mathbf{R}_i)$$



- Write the wavefunctions as **linear combination of atomic orbitals** (LCAO) :

$$\psi(\mathbf{r}) = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$$

where $\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$ is an orbital of type α centered on atom i with position \mathbf{R}_i .
Hence :

$$h|\psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle$$

Application to nanocrystals and quantum dots (II)

$$h|\psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle$$



- We then project onto $|\varphi_{\beta}(\mathbf{r} - \mathbf{R}_j)\rangle$:

$$\begin{aligned} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle &= \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \\ &= \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \quad \forall (\beta, j) \end{aligned}$$

$$\langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} H_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} S_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \quad \forall (\beta, j)$$

where :

$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | h | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Hamiltonian matrix element]} \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Overlap matrix element]} \end{cases}$$

$H_{\alpha\alpha}(\mathbf{R}_i, \mathbf{R}_i)$ is an « on-site » energy while $H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j)$ is a « hopping » matrix element.

$$h|\psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle$$



- We then project onto $|\varphi_{\beta}(\mathbf{r} - \mathbf{R}_j)\rangle$:

$$\begin{aligned} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle &= \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \\ &= \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \forall (\beta, j) \\ \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle &= \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} H_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} S_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \forall (\beta, j) \end{aligned}$$

We last define the following $n \times n$ matrices ($n = N \times n_{orb}$) :

$$\begin{cases} \hat{\mathbf{H}} \text{ with elements } \hat{H}_{(j\beta)(i\alpha)} = H_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \\ \hat{\mathbf{S}} \text{ with elements } \hat{S}_{(j\beta)(i\alpha)} = S_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \end{cases}$$

and the vector $\hat{\mathbf{c}}$ with coordinates $c_{i\alpha}$. We thus end up with :

$$\hat{\mathbf{H}}\hat{\mathbf{c}} = \varepsilon\hat{\mathbf{S}}\hat{\mathbf{c}}$$

The semi-empirical tight-binding method



- What we need :

$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | h | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle \text{ [Hamiltonian matrix element]} \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle \text{ [Overlap matrix element]} \end{cases}$$

- « **Semi-empirical** » tight-binding :

- Consider these matrix elements as adjustable parameters.
- Fit them on the experimental or *ab initio* bulk band structures.
- Use the same matrix elements in nanostructures (« **transferability** »).

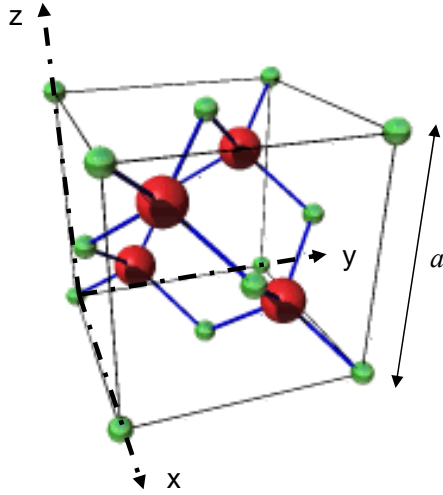
Transferability assumes that the effective potential created by each atom is the same in bulk and nanostructures.

Application to crystalline solids (I)

- In a crystalline solid, any atomic position \mathbf{R}_i can be split in two parts :



$$\mathbf{R}_i = \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p \quad \text{where} \quad \begin{cases} \tilde{\mathbf{R}}_{jkl} = j\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3 \text{ is a lattice vector } [(j,k,l) \in Z^3] \\ \mathbf{d}_p \text{ is the position of one of the } n_c \text{ atoms of the} \\ \text{reference unit cell at } \tilde{\mathbf{R}}_{000} \end{cases}$$



Example : The **Diamond/Zinc-Blende crystal** structure is a **face-centered cubic** (FCC) lattice with a two atom unit cell ($n_c = 2$) :

- one at $\mathbf{d}_1 = (0,0,0)$ [e.g. Ga].
- the other at $\mathbf{d}_2 = (1,1,1) a/4$ [e.g. As].

$$\text{Hence, } \psi(\mathbf{r}) = \sum_i \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \equiv \sum_{(j,k,l) \in Z^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha} \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)$$

Application to crystalline solids (II)



$$\psi(\mathbf{r}) = \sum_i \sum_{\alpha=1}^{n_{orb}} c_{i\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \equiv \sum_{(j,k,l) \in Z^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha} \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)$$

- Bloch's theorem :**

$$\psi(\mathbf{r}) \equiv \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad \text{where} \quad u_{n\mathbf{k}}(\mathbf{r} + u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3) = u_{n\mathbf{k}}(\mathbf{r}) \quad \forall (u,v,w) \in Z^3$$

As a consequence,

$$\psi_{n\mathbf{k}}(\mathbf{r} + \tilde{\mathbf{R}}_{uvw}) = e^{i\mathbf{k} \cdot (\mathbf{r} + \tilde{\mathbf{R}}_{uvw})} u_{n\mathbf{k}}(\mathbf{r} + \tilde{\mathbf{R}}_{uvw}) = e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} [e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})] = e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} \psi_{n\mathbf{k}}(\mathbf{r}) \quad \forall (u,v,w) \in Z^3$$

However,

$$\begin{aligned} \psi_{n\mathbf{k}}(\mathbf{r} + \tilde{\mathbf{R}}_{uvw}) &= \sum_{(j,k,l) \in Z^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha} (n\mathbf{k}) \varphi_{\alpha}(\mathbf{r} + \tilde{\mathbf{R}}_{uvw} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \\ &= \sum_{(j,k,l) \in Z^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha} (n\mathbf{k}) \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{(j-u)(k-v)(l-w)} - \mathbf{d}_p) \\ &= \sum_{(j,k,l) \in Z^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{(j+u)(k+v)(l+w)p\alpha} (n\mathbf{k}) \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \end{aligned}$$

Application to crystalline solids (III)

- Hence,

$$\begin{aligned}\psi_{\mathbf{nk}}(\mathbf{r} + \tilde{\mathbf{R}}_{uvw}) &= \sum_{(j,k,l) \in \mathbb{Z}^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{(j+u)(k+v)(l+w)p\alpha}(\mathbf{nk}) \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \\ &= e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} \psi(\mathbf{r}) \\ &= e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} \sum_{(j,k,l) \in \mathbb{Z}^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha}(\mathbf{nk}) \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)\end{aligned}$$

Since the LCAO expansion must be unique,

$$\begin{aligned}c_{(j+u)(k+v)(l+w)p\alpha}(\mathbf{nk}) &= e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} c_{jklp\alpha}(\mathbf{nk}) \\ c_{uvw p\alpha}(\mathbf{nk}) &= e^{i\mathbf{k} \cdot \tilde{\mathbf{R}}_{uvw}} c_{000p\alpha}(\mathbf{nk}) = e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{uvw} + \mathbf{d}_p)} \left[e^{-i\mathbf{k} \cdot \mathbf{d}_p} c_{000p\alpha}(\mathbf{nk}) \right] = e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{uvw} + \mathbf{d}_p)} b_{p\alpha}(\mathbf{nk})\end{aligned}$$

Finally,

$$\begin{aligned}\psi_{\mathbf{nk}}(\mathbf{r}) &= \sum_{(j,k,l) \in \mathbb{Z}^3} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} c_{jklp\alpha}(\mathbf{nk}) \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \\ &= \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{nk}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p)} \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)\end{aligned}$$

Application to crystalline solids (IV)

- Let :

$$h = -\frac{\hbar^2}{2m_0} \Delta_{\mathbf{r}} + v_{eff}(\mathbf{r}), \quad h|\psi_{\mathbf{nk}}\rangle = \varepsilon_{\mathbf{nk}}|\psi_{\mathbf{nk}}\rangle$$

We get :

$$\begin{aligned}h|\psi_{\mathbf{nk}}\rangle &= \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{nk}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p)} h|\varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)\rangle \\ &= \varepsilon_{\mathbf{nk}}|\psi_{\mathbf{nk}}\rangle = \varepsilon_{\mathbf{nk}} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{nk}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p)} |\varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p)\rangle\end{aligned}$$

- We then project on $e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{000} + \mathbf{d}_q)} |\varphi_{\beta}(\mathbf{r} - \tilde{\mathbf{R}}_{000} - \mathbf{d}_q)\rangle$:

$$\begin{aligned}\sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{nk}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} \langle \varphi_{\beta}(\mathbf{r} - \tilde{\mathbf{R}}_{000} - \mathbf{d}_q) | h | \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \rangle \\ = \varepsilon_{\mathbf{nk}} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{nk}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} \langle \varphi_{\beta}(\mathbf{r} - \tilde{\mathbf{R}}_{000} - \mathbf{d}_q) | \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \rangle \quad \forall (q, \beta)\end{aligned}$$

Application to crystalline solids (V)



$$\begin{aligned} & \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} \langle \varphi_{\beta}(\mathbf{r} - \tilde{\mathbf{R}}_{000} - \mathbf{d}_q) | h | \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \rangle \\ & = \varepsilon_{\mathbf{n}\mathbf{k}} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} \langle \varphi_{\beta}(\mathbf{r} - \tilde{\mathbf{R}}_{000} - \mathbf{d}_q) | \varphi_{\alpha}(\mathbf{r} - \tilde{\mathbf{R}}_{jkl} - \mathbf{d}_p) \rangle \quad \forall (q, \beta) \end{aligned}$$

- Let us define :

$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | h | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Hamiltonian matrix element]} \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Overlap matrix element]} \end{cases}$$

We get :

$$\begin{aligned} & \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} H_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \\ & = \varepsilon_{\mathbf{n}\mathbf{k}} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} S_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \quad \forall (q, \beta) \end{aligned}$$

Application to crystalline solids (VI)



$$\begin{aligned} & \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} H_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \\ & = \varepsilon_{\mathbf{n}\mathbf{k}} \sum_{p=1}^{n_c} \sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(\mathbf{n}\mathbf{k}) \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} S_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \quad \forall (q, \beta) \end{aligned}$$

- We last define the following $n_b \times n_b$ matrices ($n_b = n_c n_{orb}$) :

$$\begin{cases} \hat{\mathbf{H}}(\mathbf{k}) \text{ with elements } \hat{H}_{(q\beta)(p\alpha)}(\mathbf{k}) = \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} H_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \\ \hat{\mathbf{S}}(\mathbf{k}) \text{ with elements } \hat{S}_{(q\beta)(p\alpha)}(\mathbf{k}) = \sum_{(j,k,l) \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} S_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \end{cases}$$

and the vector $\hat{\mathbf{b}}_{\mathbf{n}\mathbf{k}}$ with coordinates $b_{p\alpha}(\mathbf{n}\mathbf{k})$. We thus end up with :

$$\hat{\mathbf{H}}(\mathbf{k}) \hat{\mathbf{b}}_{\mathbf{n}\mathbf{k}} = \varepsilon_{\mathbf{n}\mathbf{k}} \hat{\mathbf{S}}(\mathbf{k}) \hat{\mathbf{b}}_{\mathbf{n}\mathbf{k}}$$

We solve this generalized eigenvalue problem and get $n_b = n_c n_{orb}$ bands.

Further simplifications...

- What we need :

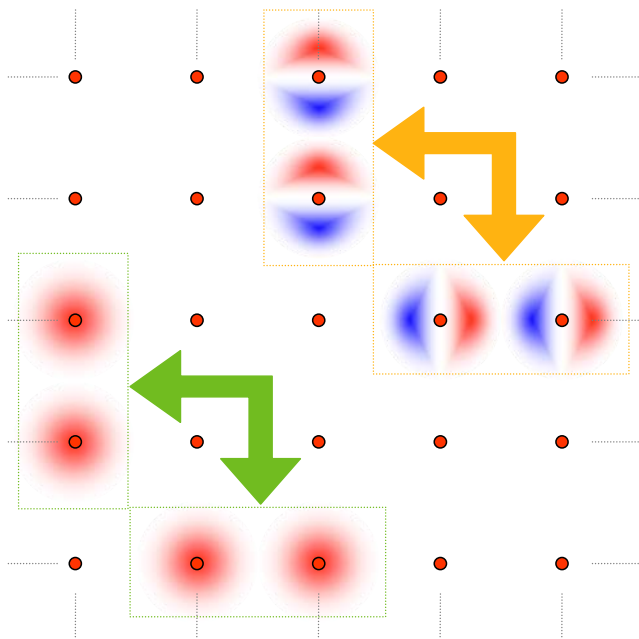


$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | h | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Hamiltonian matrix element]} \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Overlap matrix element]} \end{cases}$$

$H_{\alpha\alpha}(\mathbf{R}_i, \mathbf{R}_i)$ is an « on-site » energy while $H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j)$ is a « hopping » matrix element.

- We can use symmetries and make further approximations to reduce the number of matrix elements to compute :
 - Finite range tight-binding models.
 - Orthogonal/non-orthogonal tight-binding models.
 - Two/three centers tight-binding models.

The use of symmetries (I)

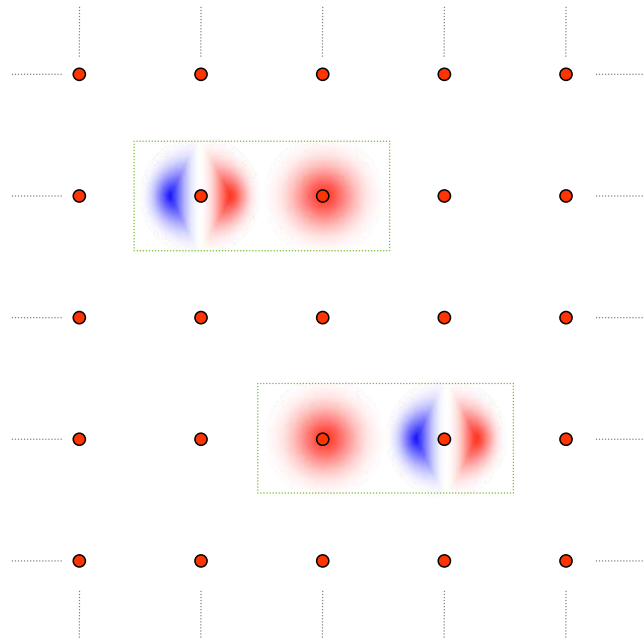


$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | h | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \end{cases}$$

- These hamiltonian and overlap matrix elements are **equal** by symmetry...

The use of symmetries (II)

cea

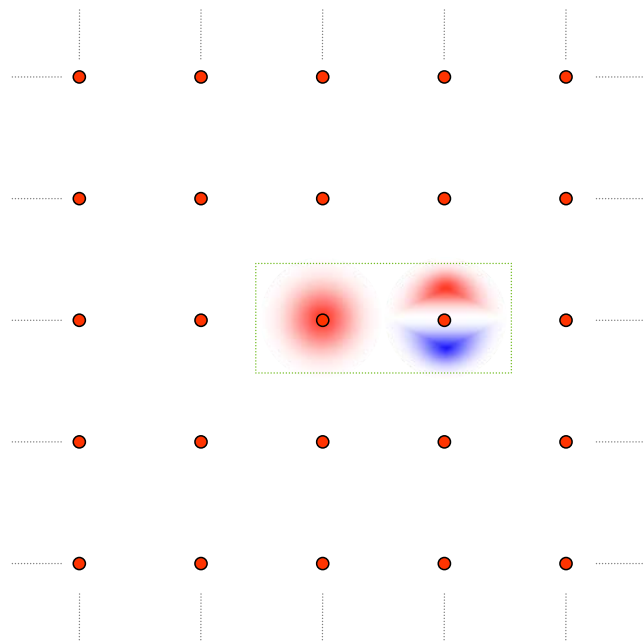


$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | h | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \end{cases}$$

- These hamiltonian and overlap matrix elements are **opposite** by symmetry...

The use of symmetries (III)

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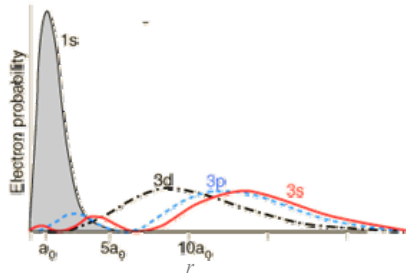


$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | h | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \end{cases}$$

- These hamiltonian and overlap matrix elements are **zero** by symmetry...

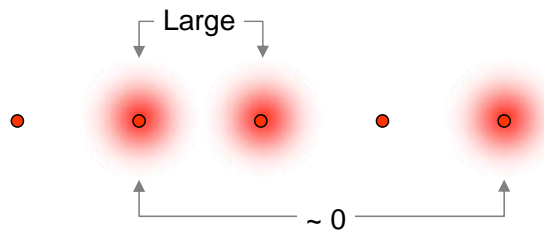
Finite range tight-binding models

- Atomic orbitals decay exponentially far enough from the nucleus :



$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | h | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \end{cases}$$

As a consequence, the hamiltonian and overlap matrix elements decrease very fast with $|\mathbf{R}_i - \mathbf{R}_j|$.



Assume zero hamiltonian and overlap matrix elements beyond first, second or third nearest neighbors.

Orthogonal tight-binding models (I)

- The atomic orbitals may be split into a radial and an angular part :



$$\varphi_\alpha(\mathbf{r}) = \underbrace{R_\alpha(r)}_{\text{Radial part}} \times \underbrace{Y_{l_\alpha m_\alpha}(\theta, \varphi)}_{\substack{\text{Spherical harmonic} \\ s, p, d, \dots}}$$

Different orbitals on the same atom are orthogonal (because the angular parts are) :

$$S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_i) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_i) \rangle = \delta_{\alpha\beta}$$

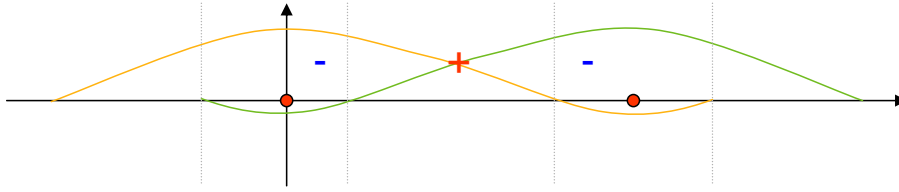
- The R_α 's of the free atoms are neither the only possible nor the best choice for the radial parts. Slightly different sets of R_α 's can indeed yield reasonable band structures. In particular, we may try to tune the $R_\alpha(r)$'s so as to minimize the overlaps between neighboring orbitals while retaining their overall free atom-like shapes, thus achieving :

$$S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \approx \delta_{ij} \delta_{\alpha\beta}$$

[Orthogonal tight-binding model]

Orthogonal tight-binding models (II)

- **Beware** : negligible overlap matrix elements does not mean that neighboring orbitals do not interpenetrate !!



$$S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \approx 0$$

On the contrary, making the orbitals quasi-orthogonal add wiggles that usually increase the range of the model.

Orthogonal tight-binding models (III)

- We have to solve :



$$\hat{\mathbf{H}}(\mathbf{k})\hat{\mathbf{b}}_{nk} = \varepsilon_{nk}\hat{\mathbf{S}}(\mathbf{k})\hat{\mathbf{b}}_{nk} \quad \begin{cases} \hat{H}_{(q\beta)(p\alpha)}(\mathbf{k}) = \sum_{(j,k,l) \in Z^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} H_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \\ \hat{S}_{(q\beta)(p\alpha)}(\mathbf{k}) = \sum_{(j,k,l) \in Z^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} S_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \end{cases}$$

Assuming $S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_\alpha(\mathbf{r} - \mathbf{R}_i) | \varphi_\beta(\mathbf{r} - \mathbf{R}_j) \rangle \approx \delta_{ij}\delta_{\alpha\beta}$,

$$\begin{aligned} \hat{S}_{(q\beta)(p\alpha)}(\mathbf{k}) &= \sum_{(j,k,l) \in Z^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} S_{\beta\alpha}(\tilde{\mathbf{R}}_{000} + \mathbf{d}_q, \tilde{\mathbf{R}}_{jkl} + \mathbf{d}_p) \\ &= \sum_{(j,k,l) \in Z^3} e^{i\mathbf{k} \cdot (\tilde{\mathbf{R}}_{jkl} - \tilde{\mathbf{R}}_{000} + \mathbf{d}_p - \mathbf{d}_q)} \delta_{j0}\delta_{k0}\delta_{l0}\delta_{qp}\delta_{\beta\alpha} \\ &= \delta_{\beta\alpha}\delta_{qp} \equiv \delta_{(q\beta)(p\alpha)} \end{aligned}$$

We are thus back to a simpler standard eigenvalue problem :

$$\hat{\mathbf{H}}(\mathbf{k})\hat{\mathbf{b}}_{nk} = \varepsilon_{nk}\hat{\mathbf{b}}_{nk}$$

Two and three center tight-binding models

- Let :

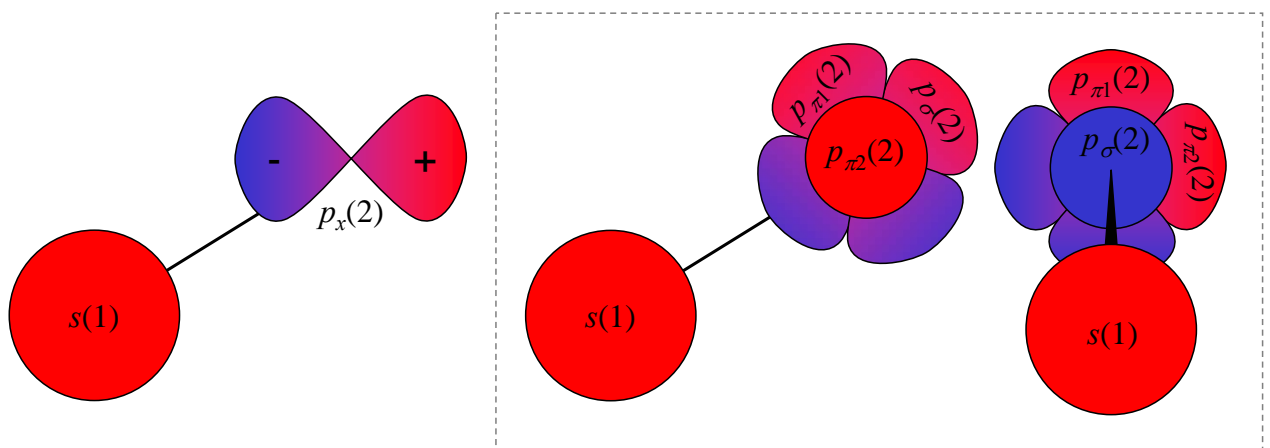
$$h = -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_{\text{eff}}(\mathbf{r}) \text{ and } v_{\text{eff}}(\mathbf{r}) = \sum_k v_k(\mathbf{r} - \mathbf{R}_k)$$

Then,

$$\begin{aligned} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) &= \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | h | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle \\ &= \left\langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + \sum_k v_k(\mathbf{r} - \mathbf{R}_k) \right| \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \right\rangle \\ &= \left\langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} \right| \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \right\rangle + \sum_k \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | v_k(\mathbf{r} - \mathbf{R}_k) | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle \end{aligned}$$

- Keep part or all $k \neq i$ and $k \neq j$ terms : « **Three center** tight-binding model ».
- Only keep (most important) $k = i$ or $k = j$ terms : « **Two center** tight-binding model ».

Two center tight-binding models



$$p_x(\mathbf{r} - \mathbf{R}_2) = l p_{\sigma}(\mathbf{r} - \mathbf{R}_2) + m p_{\pi_1}(\mathbf{r} - \mathbf{R}_2) + n p_{\pi_2}(\mathbf{r} - \mathbf{R}_2) \text{ where } l = \frac{\mathbf{x} \cdot (\mathbf{R}_2 - \mathbf{R}_1)}{|\mathbf{R}_2 - \mathbf{R}_1|}$$

$$\begin{aligned} H_{sx}(\mathbf{R}_1, \mathbf{R}_2) &= \left\langle s(\mathbf{r} - \mathbf{R}_1) \left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_1(\mathbf{r} - \mathbf{R}_1) + v_2(\mathbf{r} - \mathbf{R}_2) \right| p_x(\mathbf{r} - \mathbf{R}_2) \right\rangle \\ &= l \left\langle s(\mathbf{r} - \mathbf{R}_1) \left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_1(\mathbf{r} - \mathbf{R}_1) + v_2(\mathbf{r} - \mathbf{R}_2) \right| p_{\sigma}(\mathbf{r} - \mathbf{R}_2) \right\rangle + m \dots \end{aligned}$$

$$H_{sx}(\mathbf{R}_1, \mathbf{R}_2) = l V_{sp\sigma}(\mathbf{R}_2 - \mathbf{R}_1)$$

Spin-orbit coupling within tight-binding



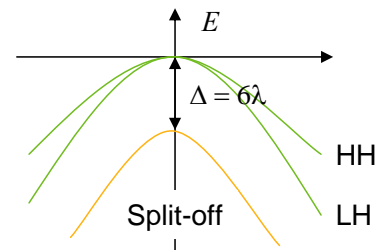
$$-\frac{\hbar^2}{2m_0} \Delta_{\mathbf{r}} \psi(\mathbf{r}) + v_{eff}(\mathbf{r}) \psi(\mathbf{r}) + \underbrace{\left[\frac{1}{2m_0^2 c^2} (\mathbf{S} \times \nabla_{\mathbf{r}} v_{ion}) \cdot \mathbf{p} \right]}_{\text{Spin-orbit coupling term}} \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

- Spin-orbit mainly couples the orbitals of each atom among themselves. We can indeed make the following on-site approximation :

$$H_i^{so} \approx \lambda_i \mathbf{L}_i \cdot \mathbf{S}$$

where \mathbf{S} is the electron spin and \mathbf{L} is the orbital momentum operator on atom i . As a consequence, a spin-augmented basis must be used with one $|\uparrow\rangle$ and one $|\downarrow\rangle$ orbital of each kind. In most cases, spin-orbit coupling is taken into account between p orbitals only, which is enough to split the valence bands :

$$H_i^{so} = -\lambda_i \begin{bmatrix} 0 & -i & 0 & 0 & 0 & 1 \\ i & 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & -1 & i & 0 \\ 0 & 0 & -1 & 0 & i & 0 \\ 0 & 0 & -i & -i & 0 & 0 \\ 1 & i & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} p_x \uparrow \\ p_y \uparrow \\ p_z \uparrow \\ p_x \downarrow \\ p_y \downarrow \\ p_z \downarrow \end{bmatrix}$$



The semi-empirical tight-binding method



- What we need :

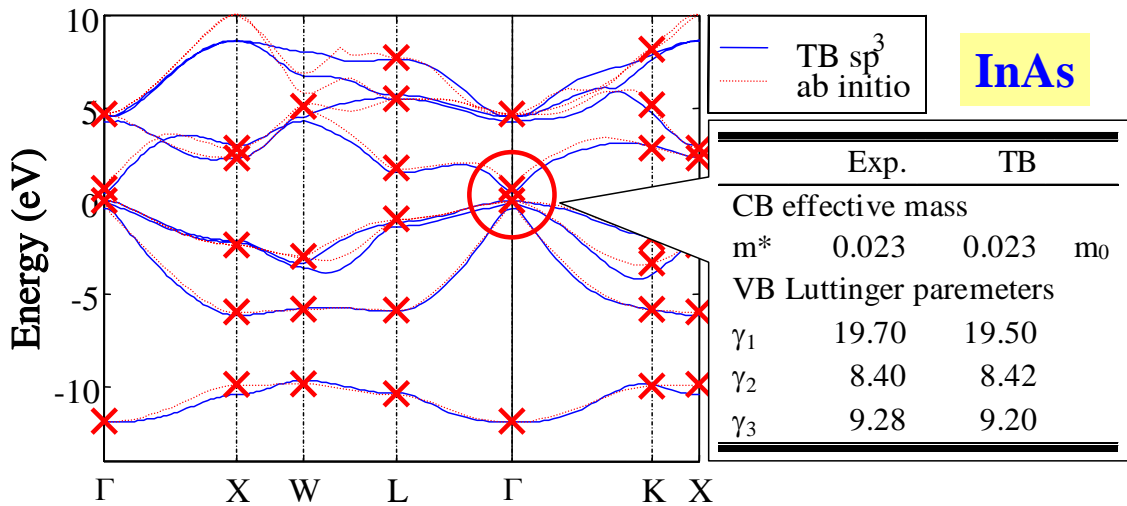
$$\begin{cases} H_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | h | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Hamiltonian matrix element]} \\ S_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) = \langle \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle & \text{[Overlap matrix element]} \end{cases}$$

- « **Semi-empirical** » tight-binding :

- Consider these matrix elements as adjustable parameters.
- Fit them on the experimental or *ab initio* bulk band structures.
- Use the same matrix elements in nanostructures (« **transferability** »).

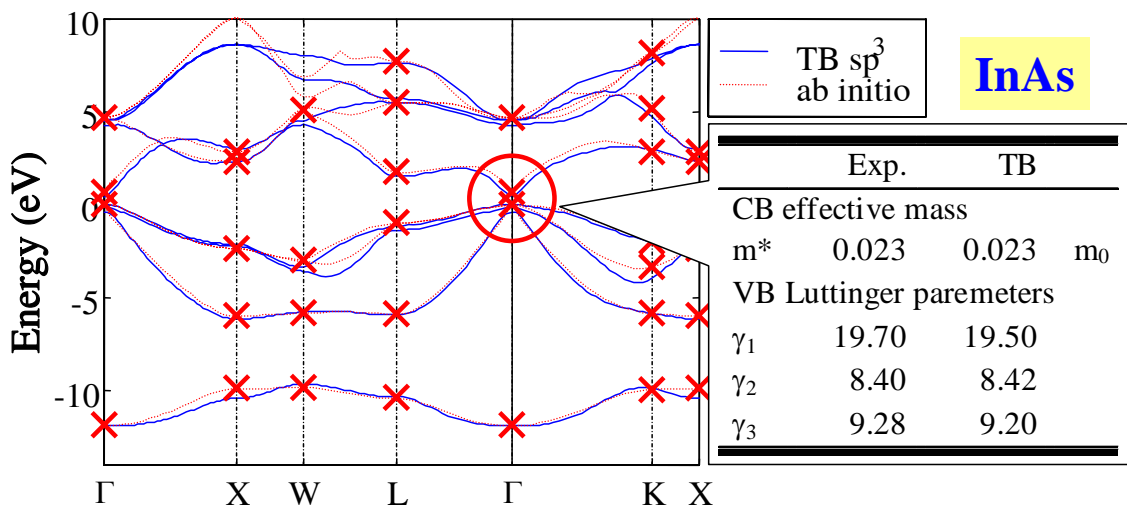
Transferability assumes that the effective potential created by each atom is the same in bulk and nanostructures.

Fitting tight-binding parameters (I)



- Fit the tight-binding parameters onto selected experimental or « ab initio » band energies and effective masses.

Fitting tight-binding parameters (II)



- Minimize the squared error with respect to the tight-binding parameters :

$$\text{Err}^2 = \sum_{\text{selected } nk} \alpha_{nk} (\varepsilon_{nk}^{\text{tight-binding}} - \varepsilon_{nk}^{\text{target}})^2 + \frac{\hbar^4 k_0^4}{4} \sum_{\text{selected masses}} \beta_i \left(\frac{1}{m_i^{\text{tight-binding}}} - \frac{1}{m_i^{\text{target}}} \right)^2$$

α_{nk} and β_i are weighting coefficients and k_0 is an arbitrary wavevector (for consistency & overall weighting of the masses with respect to the band energies).

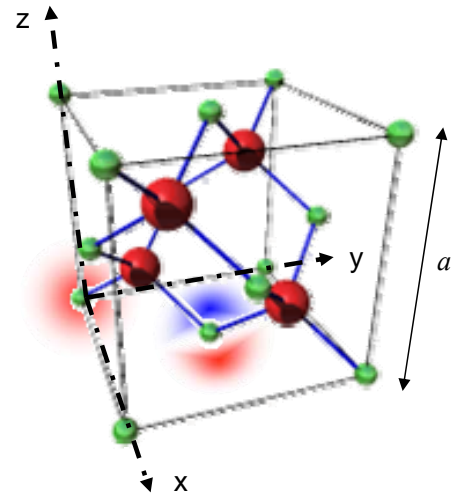
Fitting tight-binding parameters (III)

- Third nearest neighbors, three centers orthogonal sp^3 tight-binding model for Si :



$E_{ss}(000)$	-6.17334 eV	$E_{ss}(111)$	-1.78516 eV
$E_{xx}(000)$	2.39585 eV	$E_{sx}(111)$	0.78088 eV
Δ	0.04500 eV	$E_{xx}(111)$	0.35657 eV
		$E_{xy}(111)$	1.47649 eV
$E_{ss}(220)$	0.23010 eV	$E_{ss}(311)$	-0.06857 eV
$E_{sx}(220)$	-0.21608 eV	$E_{sx}(311)$	0.25209 eV
$E_{sx}(022)$	-0.02496 eV	$E_{sx}(113)$	-0.17098 eV
$E_{xx}(220)$	0.02286 eV	$E_{xx}(311)$	0.13968 eV
$E_{xx}(022)$	-0.24379 eV	$E_{xx}(113)$	-0.04580 eV
$E_{xy}(220)$	-0.05462 eV	$E_{xy}(311)$	-0.03625 eV
$E_{xy}(022)$	-0.12754 eV	$E_{xy}(113)$	0.06921 eV

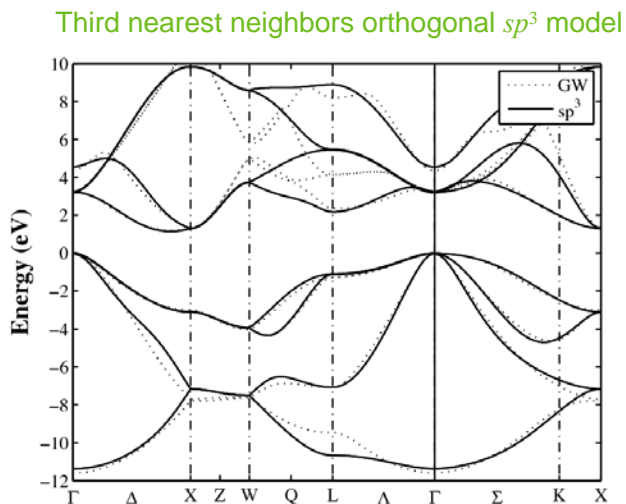
Y. M. Niquet et al., Phys. Rev. B **62**, 5109 (2000)



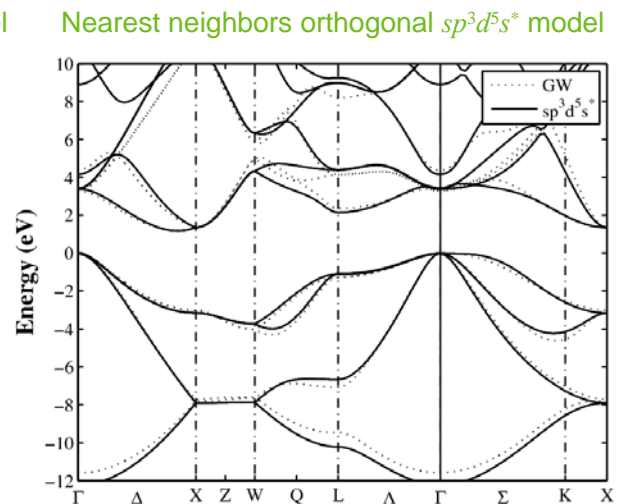
Example : $E_{sx}(220)$ = Hamiltonian matrix element between a s orbital at $(0,0,0)$ and a p_x orbital at $(2,2,0)a/4$. Δ is the spin-orbit coupling parameter.

- **Atomic orbitals remain unknown !!**

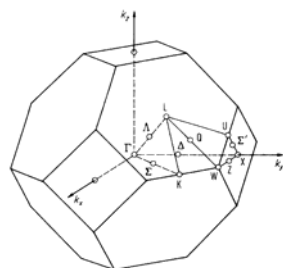
Comparison between a sp^3 and a $sp^3d^5s^*$ model for Si



Y. M. Niquet et al., Phys. Rev. B **62**, 5109 (2000)



J. M. Jancu et al., Phys. Rev. B **57**, 6493 (1998)

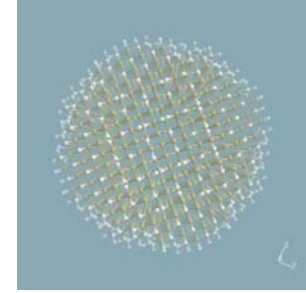


- GW = « ab initio » method (no adjustable parameters).
- The $sp^3d^5s^*$ model provides a better description (especially on the conduction band side), but at a higher computational cost.

Application to nanocrystals and quantum dots (I)



$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\psi(\mathbf{r}) + v_{\text{eff}}(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}), \quad v_{\text{eff}}(\mathbf{r}) = \sum_{k=1}^N v_k(\mathbf{r} - \mathbf{R}_k)$$



- Write the wavefunctions as **linear combination of atomic orbitals** (LCAO) :

$$\psi(\mathbf{r}) = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$$

where $\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$ is an orbital of type α centered on atom i with position \mathbf{R}_i .
We get :

$$h|\psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle$$

Application to nanocrystals and quantum dots (II)

$$h|\psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} h|\varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i)\rangle$$



- We then project onto $|\varphi_{\beta}(\mathbf{r} - \mathbf{R}_j)\rangle$:

$$\begin{aligned} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle &= \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \\ &= \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} \langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \rangle \quad \forall (\beta, j) \end{aligned}$$

$$\langle \varphi_{\beta}(\mathbf{r} - \mathbf{R}_j) | h | \psi \rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} H_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) = \varepsilon \sum_{i=1}^N \sum_{\alpha=1}^{n_{\text{orb}}} c_{i\alpha} S_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \quad \forall (\beta, j)$$

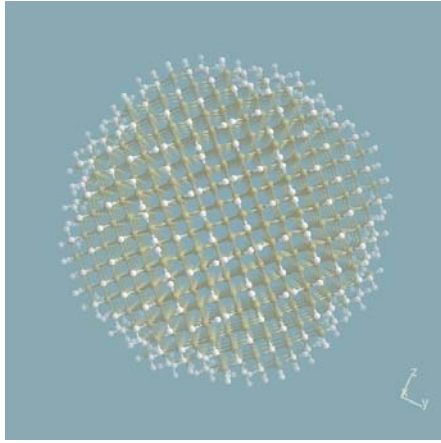
We last define the following $n \times n$ matrices ($n = N \times n_{\text{orb}}$) :

$$\begin{cases} \hat{\mathbf{H}} \text{ with elements } \hat{H}_{(j\beta)(i\alpha)} = H_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \\ \hat{\mathbf{S}} \text{ with elements } \hat{S}_{(j\beta)(i\alpha)} = S_{\beta\alpha}(\mathbf{R}_j, \mathbf{R}_i) \end{cases}$$

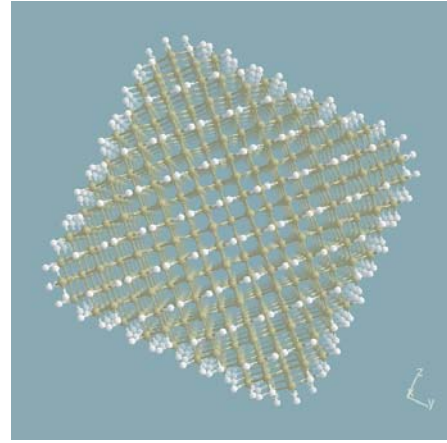
and the vector $\hat{\mathbf{c}}$ with coordinates $c_{i\alpha}$. We thus end up with :

$$\hat{\mathbf{H}}\hat{\mathbf{c}} = \varepsilon\hat{\mathbf{S}}\hat{\mathbf{c}} \quad [\hat{\mathbf{S}} = \hat{\mathbf{I}} \text{ for orthogonal tight-binding models}]$$

Application : Confinement in Si nanocrystals (I)



Spherical Si nanocrystals with diameter d



Cubic Si nanocrystals with side a and « effective » diameter d such that :

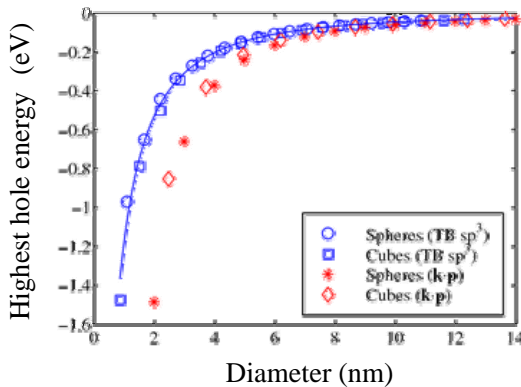
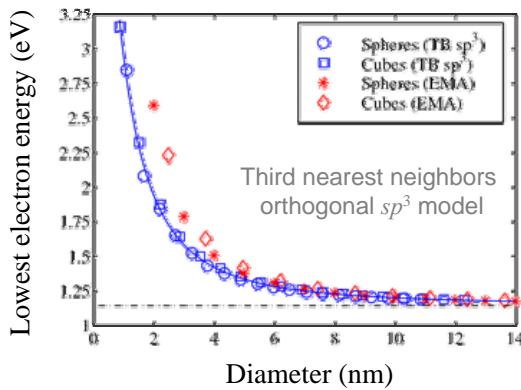
$$\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = a^3$$

The dangling bonds at the surface of the nanocrystals are saturated with H atoms.

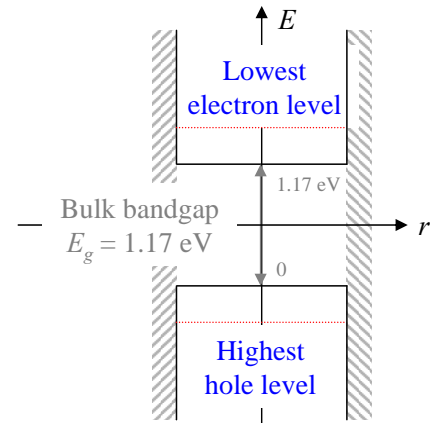
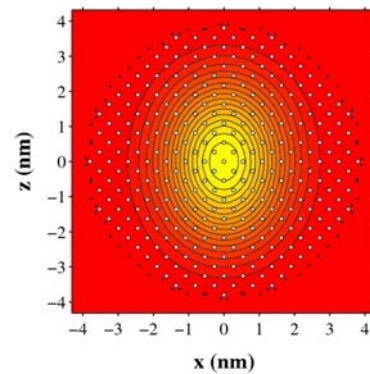
Application : Confinement in Si nanocrystals (II)

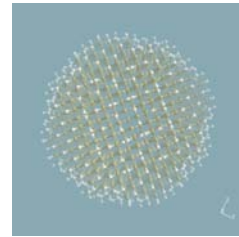
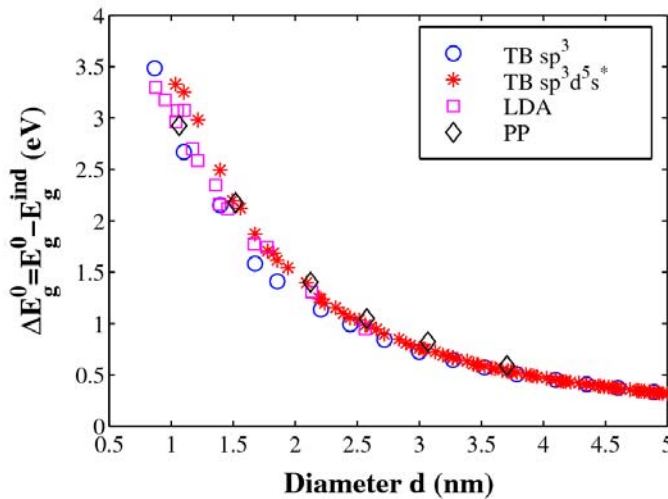


Y. M. Niquet et al., Phys. Rev. B **62**, 5109 (2000)



Lowest electron level $|\psi(\mathbf{r})|^2$





$$\Delta E_g^0 = E_g(d) - E_g(\text{bulk Si})$$

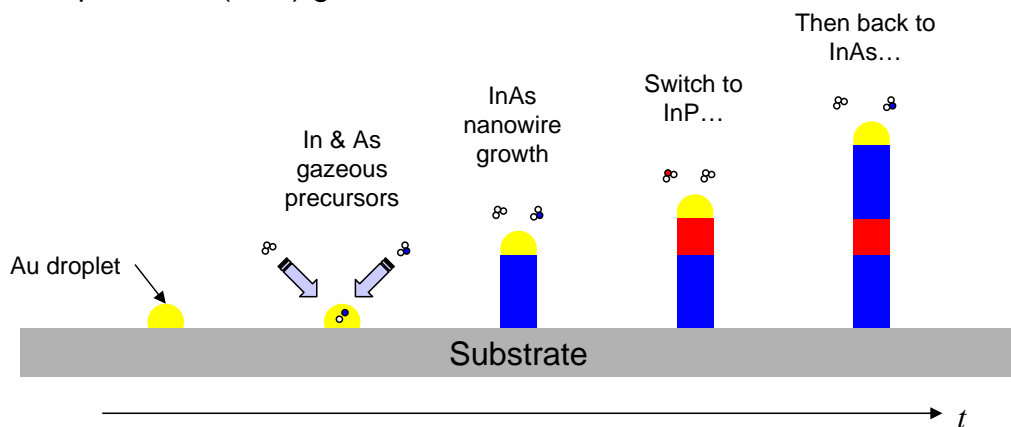
where $E_g(\text{bulk Si}) = 1.17 \text{ eV}$

- Comparison between a third nearest neighbors orthogonal sp^3 **tight-binding model**, a nearest neighbors orthogonal $sp^3 d^5 s^*$ **tight-binding model**, the **semi-empirical pseudopotential** (PP) method [the wavefunction is expanded in plane waves instead of atomic orbitals] and an **ab initio** method [the local density approximation (LDA), involving no « adjustable » parameters like semi-empirical methods].

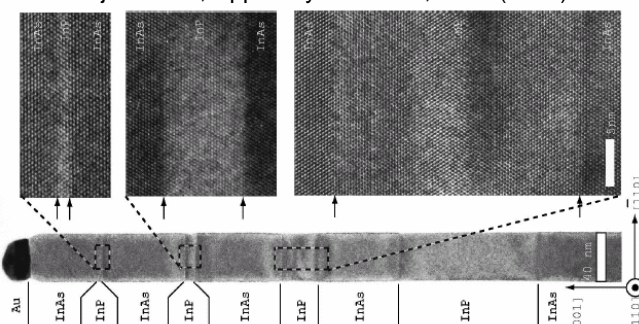
Nanowires (I)



- Vapor-Liquid-Solid (VLS) growth :



M. T. Björk *et al.*, Appl. Phys. Lett. **80**, 1058 (2002)



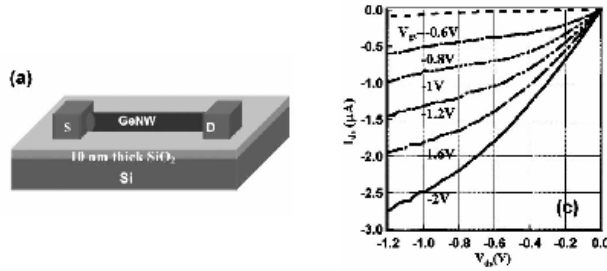
« **Nanowire heterostructure** »

Nanowires (II)



- **Applications (examples) :**

- Nanowire field effect transistor :

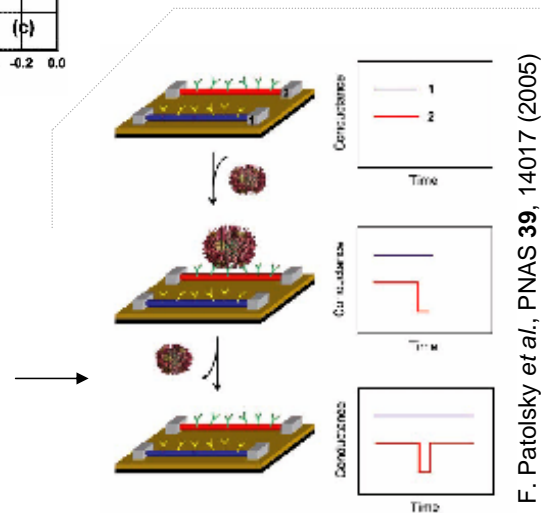


D. Wang *et al.*, Appl. Phys. Lett. **83**, 2432 (2003)

The current between the drain and source is controlled by the gate voltage.

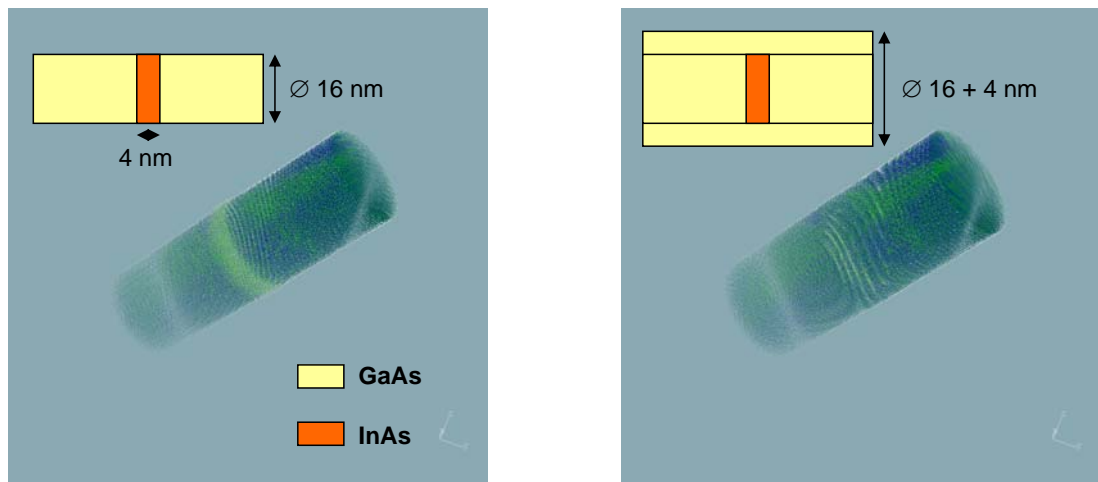
- Detection of single molecules/viruses :

The surface of the nanowire is capped with molecules that bind to specific targets (DNA, viruses). The conductance of the nanowire changes each time the target binds to the wire.



F. Patolsky *et al.*, PNAS **39**, 14017 (2005)

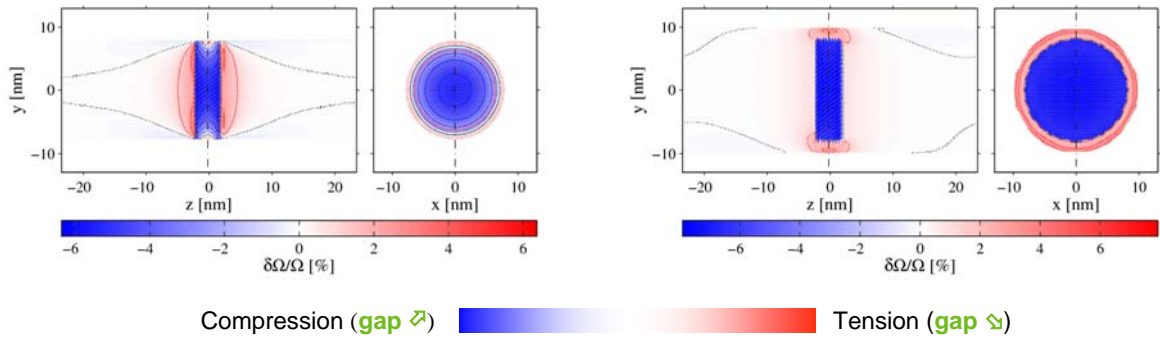
Application : Nanowire heterostructures (I)



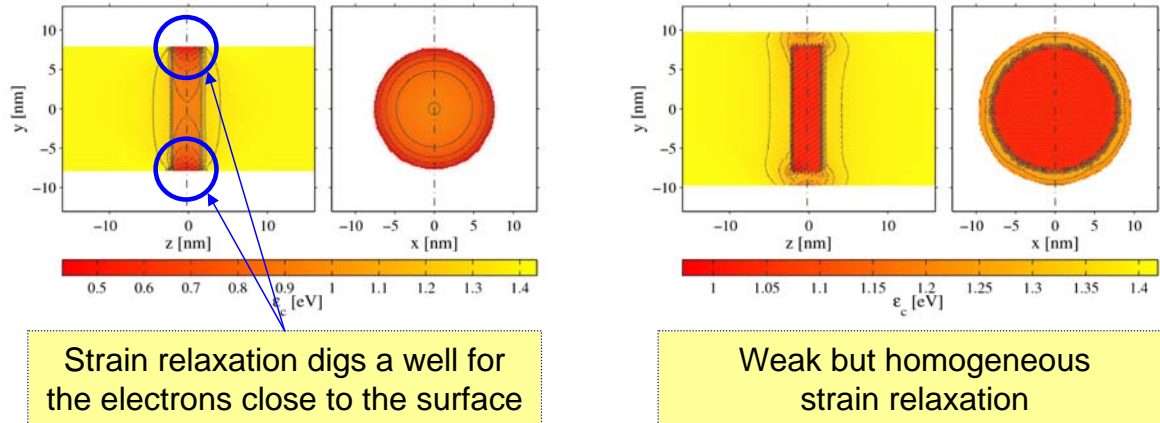
- The GaAs shell move surface traps away from the InAs/GaAs active core...

- **Strained system** : The interatomic distance is 6.69% larger in InAs than in GaAs. The thin InAs layer is thus comprimed by the GaAs core, but can (partly) relax strains at the surface of the nanowire.

Application : Nanowire heterostructures (II)



- The bandgap opens under compression and closes under tension :

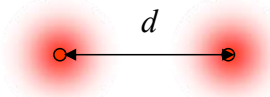


Strains in tight-binding



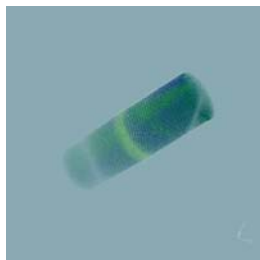
- To account for strains, we need bond length dependent tight binding parameters. Example for two center tight binding models (generalized Harrison's law) :

$$V_{ss\sigma}(d) = V_{ss\sigma}(d_0) \left(\frac{d_0}{d} \right)^{\alpha_{ss\sigma}}$$

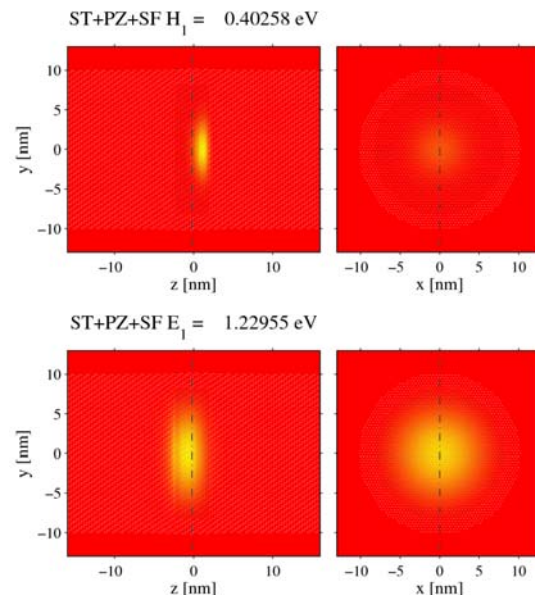
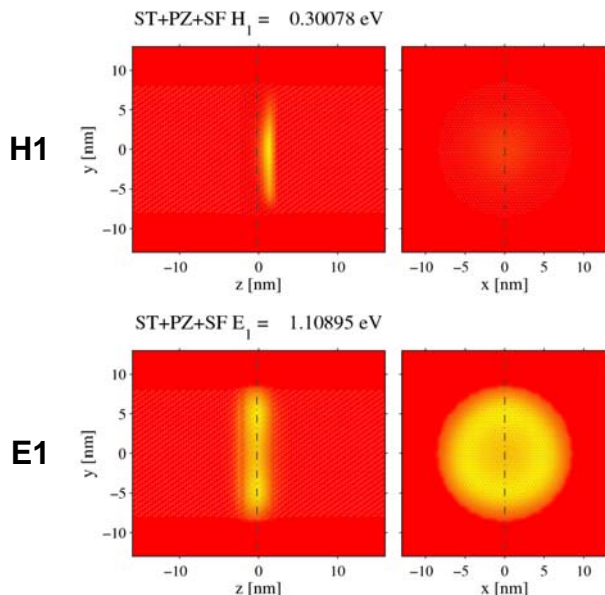
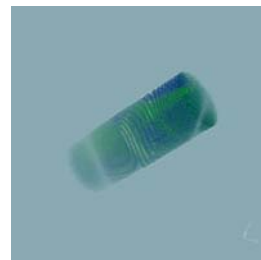


where d_0 is the equilibrium bond length and $\alpha_{ss\sigma}$ is an exponent (around 2).

Application : Nanowire heterostructures (III)



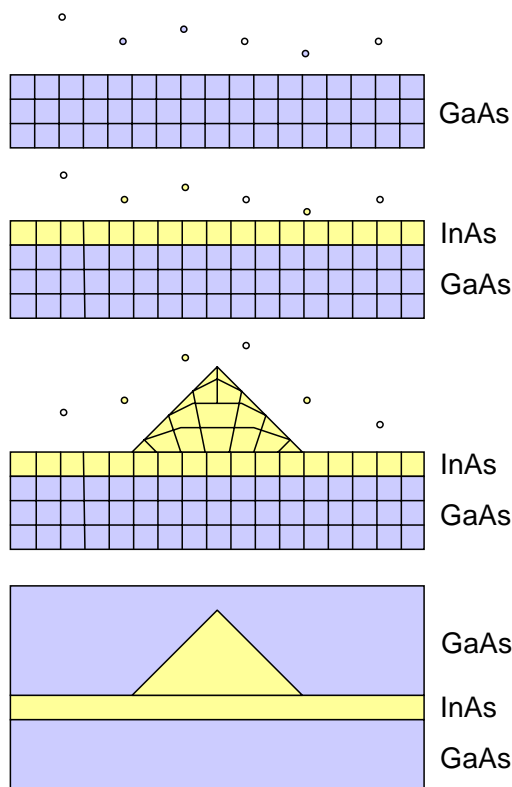
Nearest neighbors
 $sp^3d^5s^*$ tight-binding model



InAs/GaAs dots (I)



● Stransky-Krastanov growth :



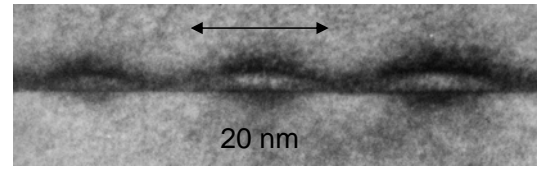
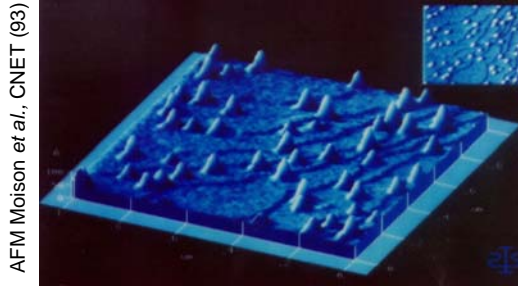
Semiconductor structures can be grown layer by layer using « molecular beam epitaxy ».

The bond length is 6.7% larger in InAs than in GaAs. The InAs layer is thus compressed by the thick GaAs substrate...

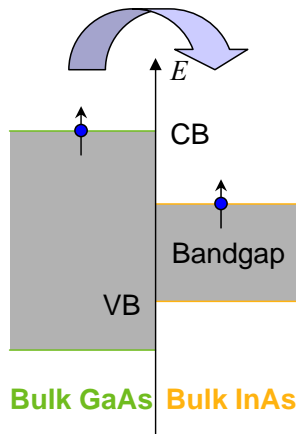
InAs pyramids finally grow onto the thin InAs « wetting layer ». The free surfaces of the pyramids indeed help relaxing strains.

The pyramids can last be embedded in a thick, overgrown GaAs layer.

InAs/GaAs dots (II)



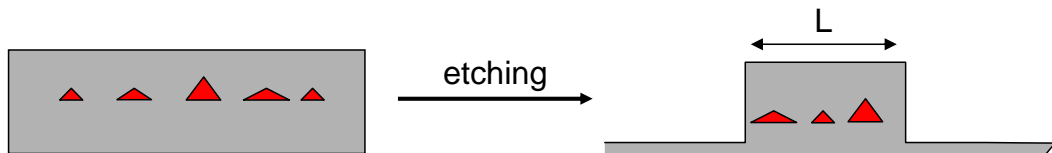
TEM A. Ponchet CNRS (95)



- InAs has a lower bandgap energy (~ 0.5 eV) than GaAs (~ 1.5 eV). The electrons and holes are thus confined in the InAs « quantum dots ».

InAs/GaAs dots (III)

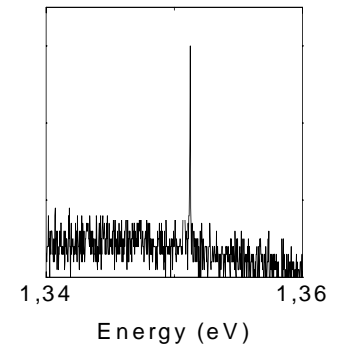
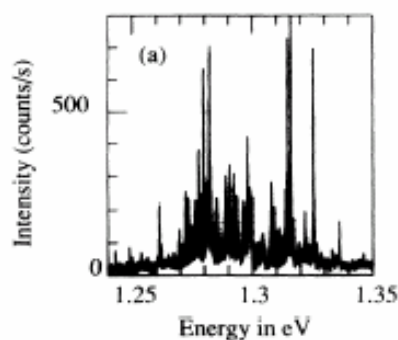
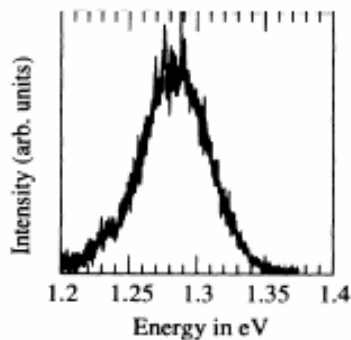
J.Y. Marzin *et al.*, Phys. Rev. Lett. **73**, 716 (1994)



$L = 5 \mu\text{m}$: **10000** QDs

$L = 0.5 \mu\text{m}$: **100** QDs

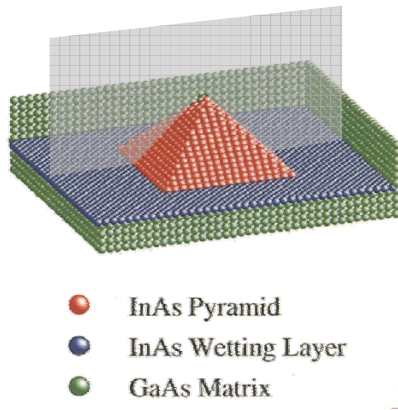
$L \sim 50 \text{ nm}$: **1** QD



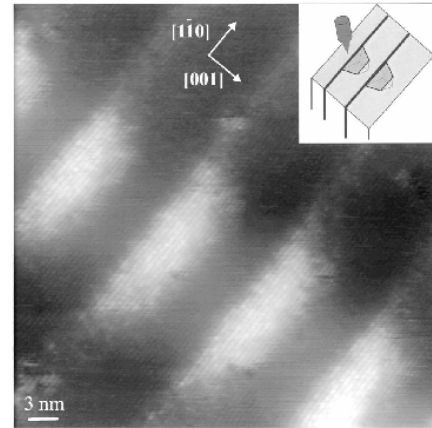
- Very sharp emission from a single InAs quantum dot (QD).
Applications : Quantum dots lasers...

Application : Wavefunction imaging (I)

InAs/GaAs quantum dots

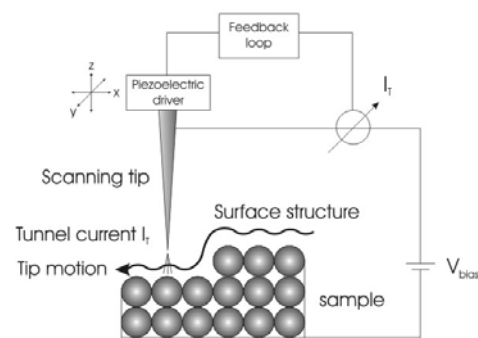
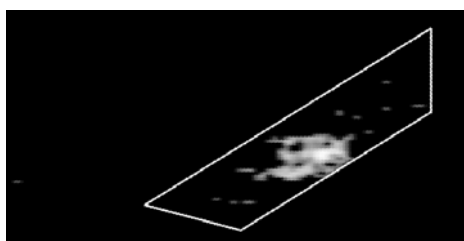
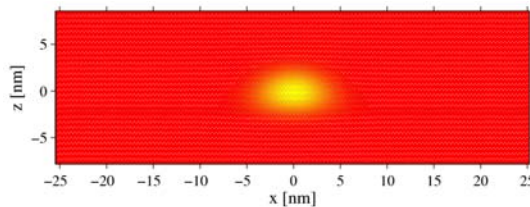
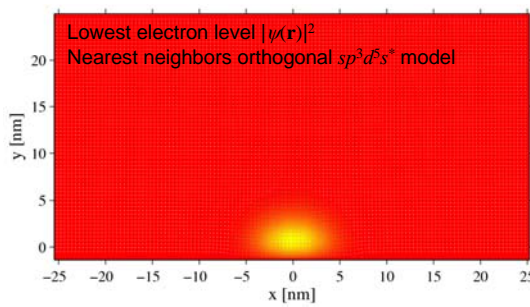


- InAs Pyramid
- InAs Wetting Layer
- GaAs Matrix



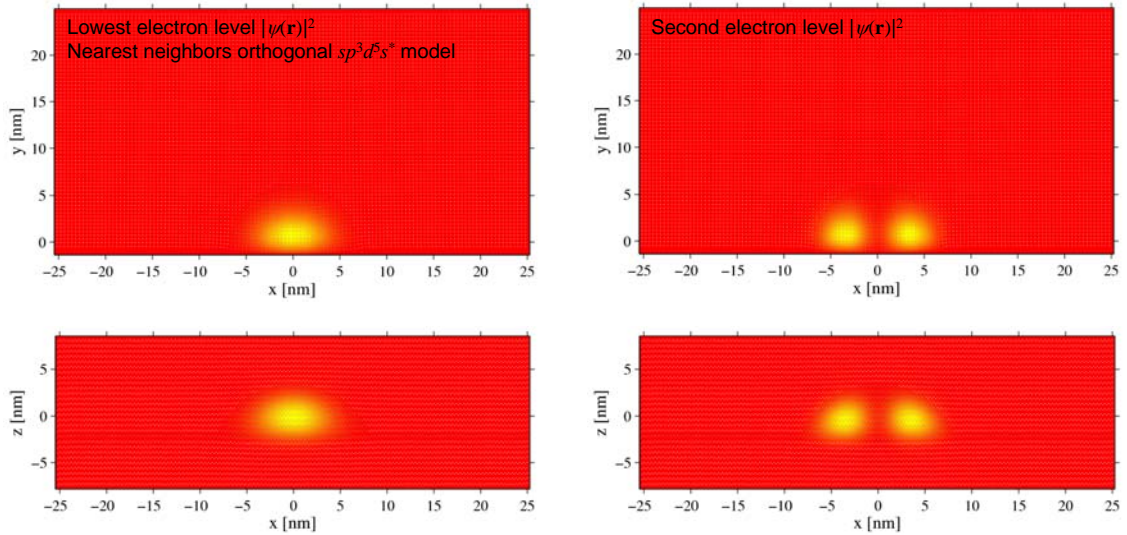
- The sample is cleaved (cut in two pieces along a crystallographic plane). The cleavage plane goes through some InAs quantum dots, that show on the surface of the sample. The cleavage plane is then imaged with a scanning tunneling microscope (STM). The InAs dots appear as bright spots, that tend to align along columns.

Application : Wavefunction imaging (II)

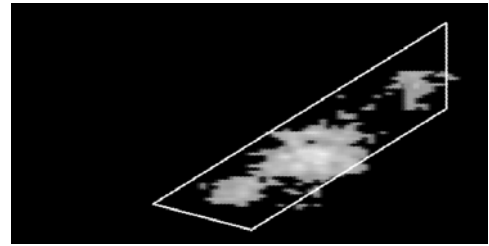


- The current flowing through the tip is plotted as a function of tip position (at constant tip-sample distance). This roughly provides an image of the wavefunctions of the levels the electrons are tunneling onto.
- **V = 0.69 V : The electrons can only tunnel onto the lowest level.**

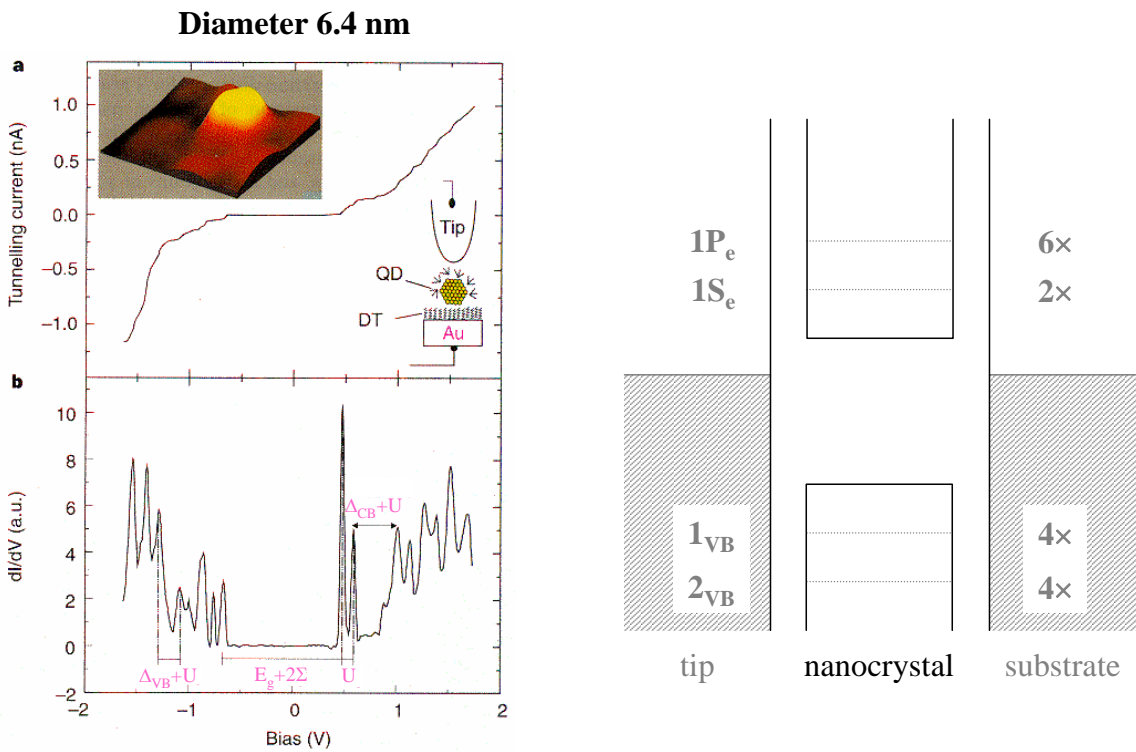
Application : Wavefunction imaging (III)



● **V = 0.82 V** : The electrons can tunnel onto the first two levels.

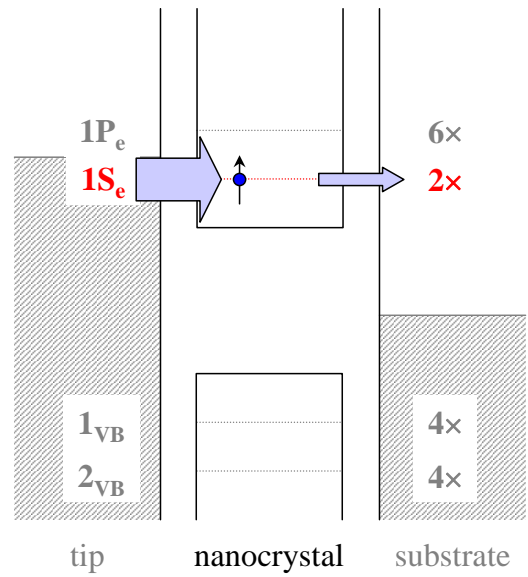
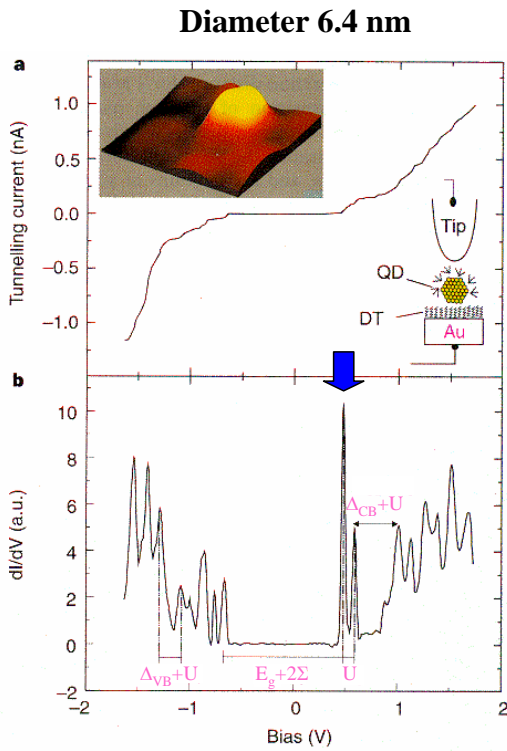


Application : Tunneling spectroscopy (I)



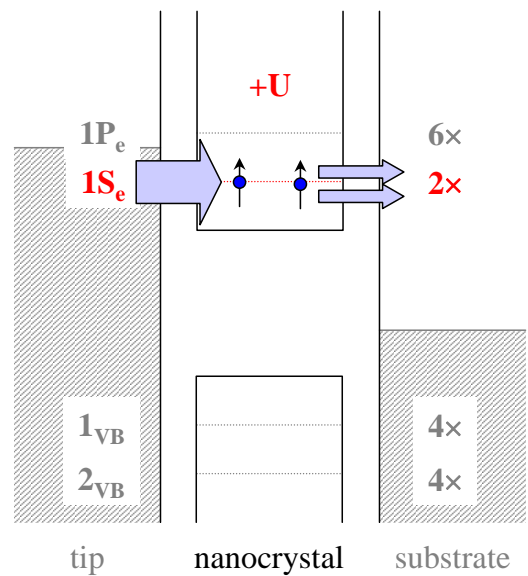
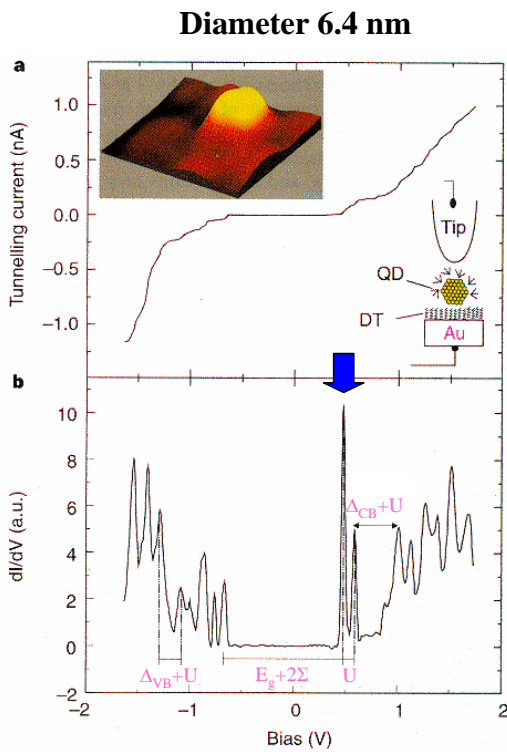
U. Banin *et al.*, Nature **400**, 542 (1999).

Applications : Tunneling spectroscopy (II)



U. Banin *et al.*, Nature **400**, 542 (1999).

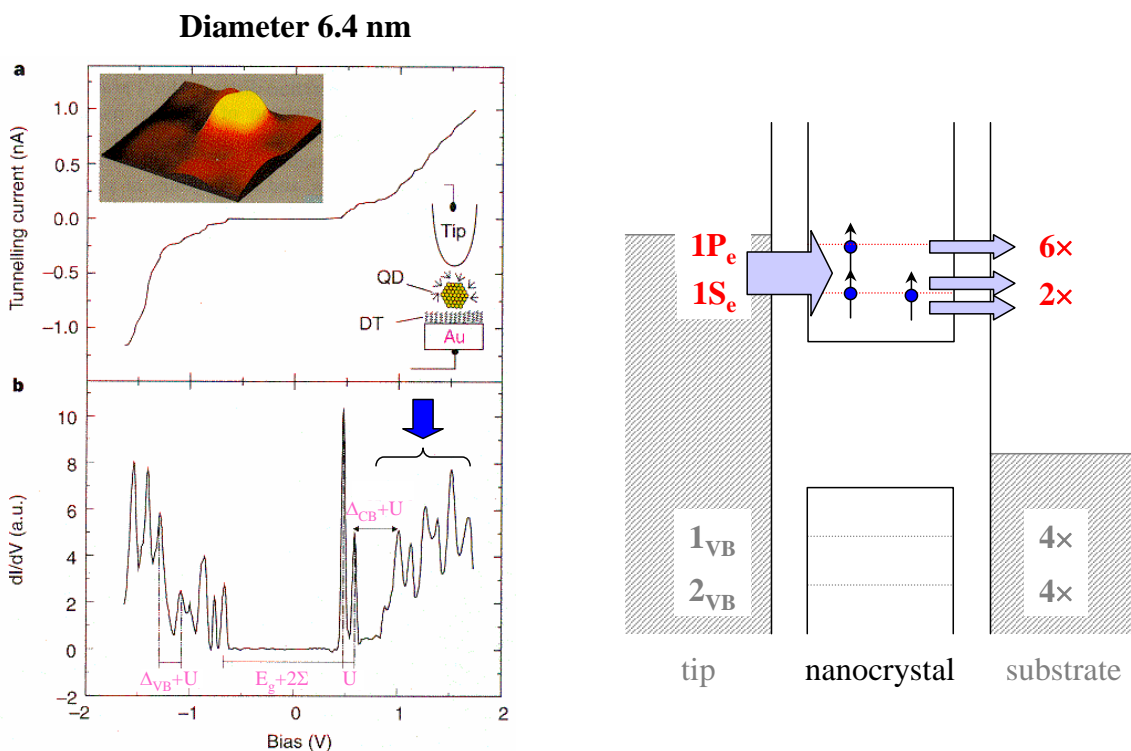
Applications : Tunneling spectroscopy (III)



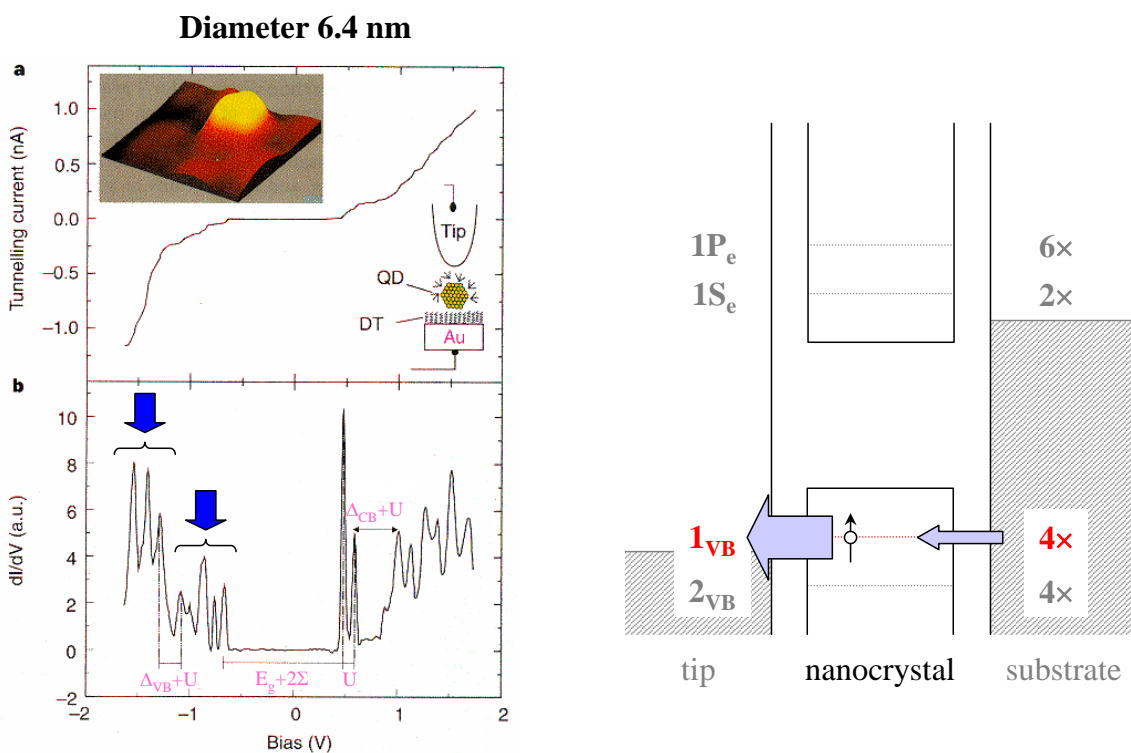
U : Addition energy

U. Banin *et al.*, Nature **400**, 542 (1999).

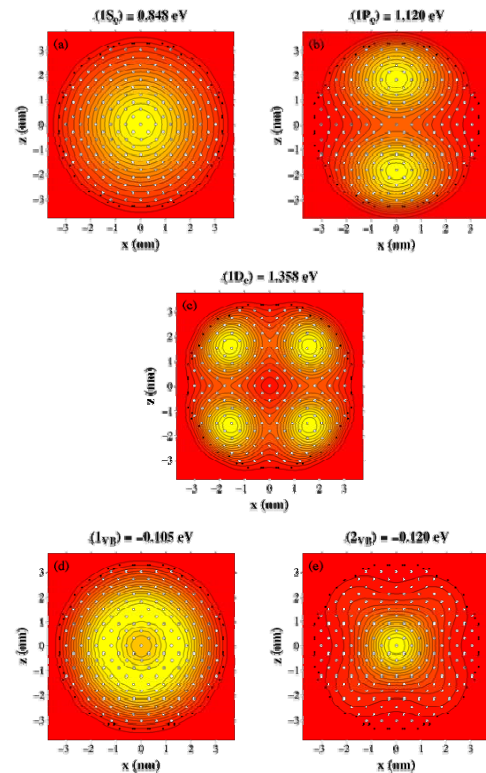
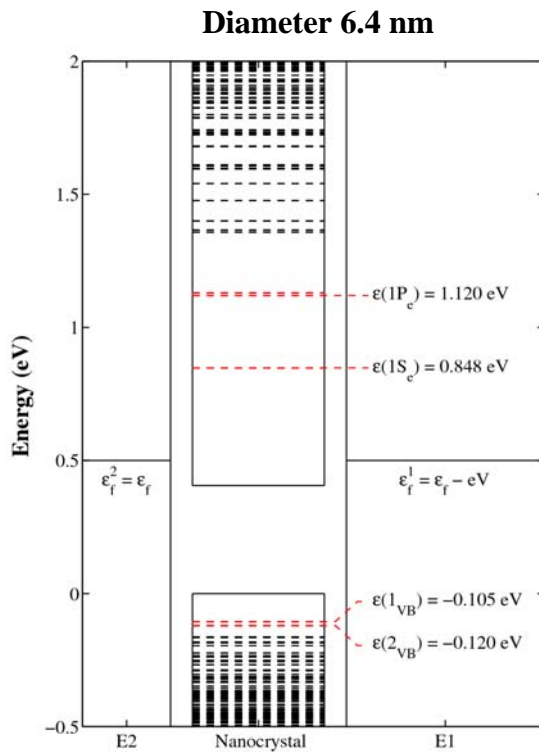
Applications : Tunneling spectroscopy (IV)



Applications : Tunneling spectroscopy (V)

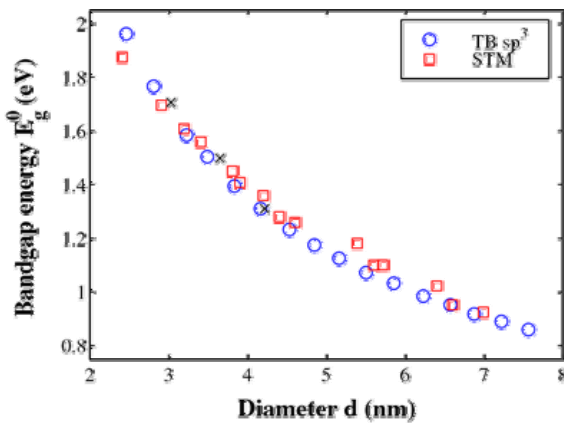


Applications : Tunneling spectroscopy (VI)

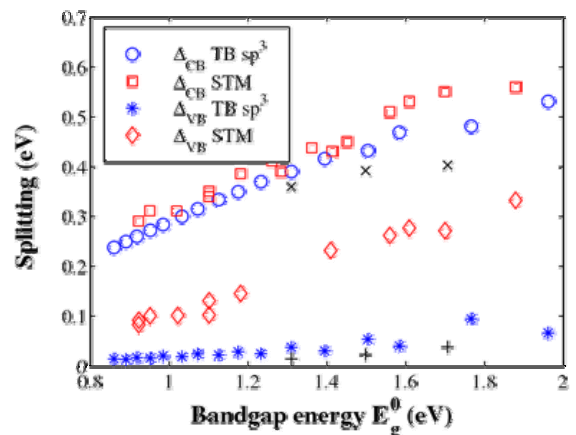
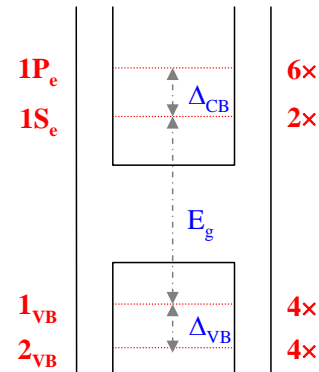


Second nearest-neighbors orthogonal sp^3 model

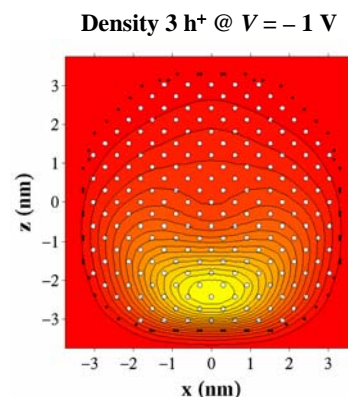
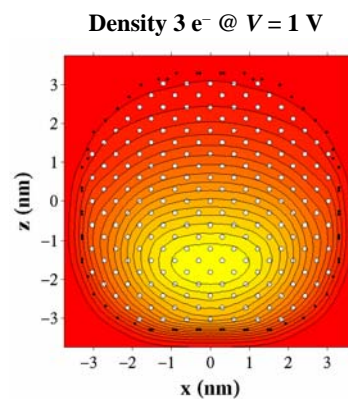
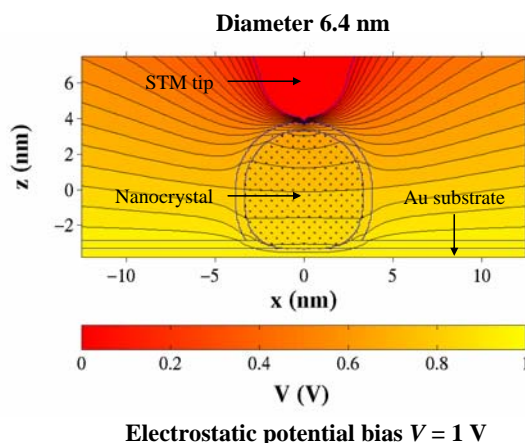
Applications : Tunneling spectroscopy (VII)



- The calculated **bandgap energies** and **electron levels splittings** are in very good agreement with the experiment.
- **Controversy** about the interpretation of Δ_{VB} .

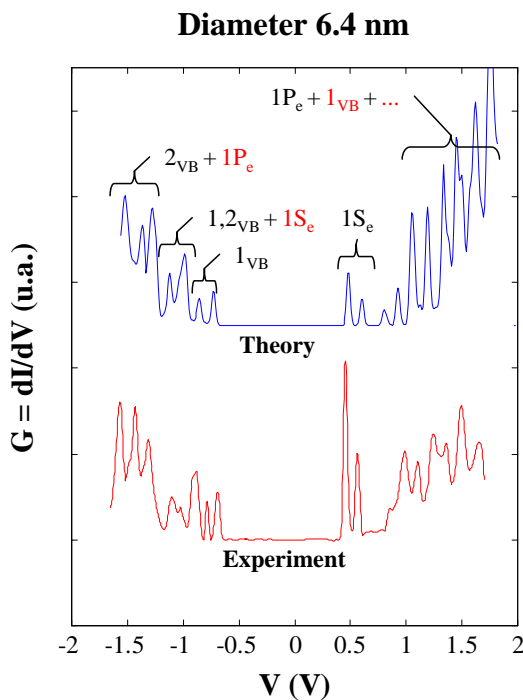


Applications : Tunneling spectroscopy (VIII)

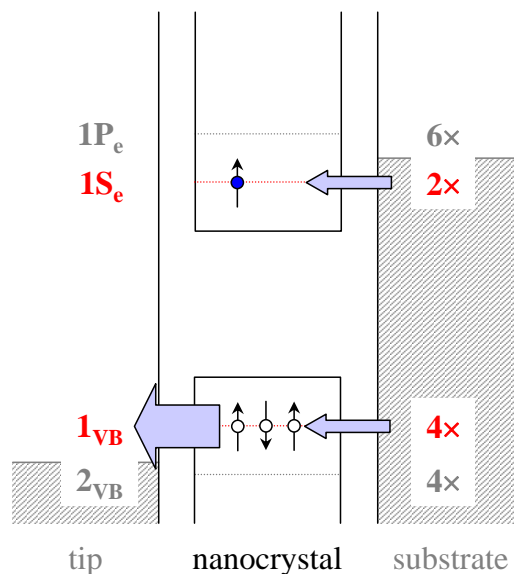


- We have computed the full $I(V)$ curve using the so-called orthodox theory. Electron-electron interactions were taken into account self-consistently.

Applications : Tunneling spectroscopy (IX)



Y. M. Niquet et al., Phys. Rev. B **64**, 113305 (2001)



- **Injection of both electrons and holes** at high enough positive or negative bias.
- Measurement of Δ_{VB} practically impossible.

Comparison : $k \cdot p$ versus tight-binding



	$k \cdot p$	Tight-binding
Description of bulk band structure	Accurate right around the conduction band minimum and valence band maximum	Accurate throughout the whole first Brillouin zone
Description of nanostructures	Accurate in weakly confined systems	Usually accurate even in highly confined systems (small nanocrystals). Can handle atomic-like boundary conditions (e.g. surface reconstructions, ...)
Computational cost	Continuum model : does not depend on the size of the system	Increasing at least linearly with the number of atoms

- **$k \cdot p$ and tight-binding are semi-empirical methods** : they are based on a parametrization of the bulk band structure (through effective masses or tight-binding parameters) and implicitly assume that the effective potential created by each atom is the same in bulk and nanostructures (**transferability**). This, of course, is an approximation that always break down in small enough systems.