Part II

Electronic structure methods

Outline

- **II.1** :
  The *ab initio* density functional theory
- **II.2** :
  The semi-empirical tight-binding method
- **II.3** :
  The $\mathbf{k}\cdot\mathbf{p}$ approximation

II.1 : The *ab initio* density functional theory

The many-particle hamiltonian…

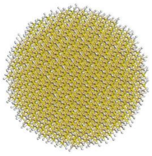
- We do not live in a non-interacting world !..
  The hamiltonian of the N-electron system actually reads :

$$\hat{H}_N = \hat{T} + \hat{V} + \hat{V}_{ee}$$

where $\hat{T} = -\frac{\hbar^2}{2m_0}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i}$ is the kinetic energy of the electrons

$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$ is their potential energy $\left[v(\mathbf{r}) = -\sum_{j=1}^{N_{at}} \frac{Z_j e^2}{|\mathbf{r}-\mathbf{R}_j|} \right]$

$\hat{V}_{ee} = \sum_{i=1}^{N}\sum_{j<i}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}$ is the Coulomb interaction.



- The ground-state wavefunction $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ is not a single-Slater determinant !
  The ground-state density reads :

$$n(\mathbf{r}) = N\int d^3\mathbf{r}_2 \ldots \int d^3\mathbf{r}_N \left|\Psi_0(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\right|^2$$

The Hohenberg-Kohn theorem

- Obviously,

$$\begin{tikzcd} v(\mathbf{r}) \arrow[r] & \Psi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \arrow[r] & n(\mathbf{r}) \arrow[ll, bend left] \end{tikzcd}$$

Hohenberg-Kohn Theorem
[Phys. Rev. B **136**, B864 (1964)]

- There is a one to one correspondance between the one-body potential $v(\mathbf{r})$ and the ground-state density $n(\mathbf{r})$.

  As a consequence, the ground-state energy :

$$E = \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle \equiv E_{GS}[v] \equiv E_{GS}[n]$$

  can either be considered as a ***functional* of the one-body potential $v(\mathbf{r})$ or of the ground-state density $n(\mathbf{r})$.**

The variational principle

- $E_{GS}[n]$ can be split as follows :

$$\begin{aligned} E_{GS}[n] &= \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{T} + \hat{V} + \hat{V}_{ee} | \Psi_0 \rangle \\ &= \underbrace{\langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle}_{F[n]} + \int d^3\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

- Let us now introduce :

$$E[n,v] = \underbrace{\langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle}_{F[n]} + \int d^3\mathbf{r} v(\mathbf{r}) n(\mathbf{r})$$

  as a functional of n ***for a given one-body potential*** v.

  $E[n,v]$ has minimum $E[n_v,v] = E_{GS}[n_v]$ when $n(\mathbf{r})$ is the ground-state density $n_v(\mathbf{r})$ corresponding to $v(\mathbf{r})$ [otherwise there would exist a Ψ_0 with energy lower than the ground-state energy !!].

The Hohenberg-Kohn theorem : Proof

- Proof *ad absurdum*. Let us assume that :
  - the potential $v(\mathbf{r})$ with ground-state wavefunction $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$,

  and :
  - the potential $v'(\mathbf{r})$ with ground-state wavefunction $\Psi_0'(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$

  give rise to the *same* density $n(\mathbf{r})$.

- Let :

  $$E = \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle \text{ and } E' = \langle \Psi_0' | \hat{H}_N' | \Psi_0' \rangle$$

  be the corresponding ground-state energies.

- First, $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ and $\Psi_0'(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ must be different (unless v-v' is a constant) because they satisfy different Schrödinger equations.

The Hohenberg-Kohn theorem : Proof

- Proof *ad absurdum*. Let us assume that :
  - the potential $v(\mathbf{r})$ with ground-state wavefunction $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$,

  and :
  - the potential $v'(\mathbf{r})$ with ground-state wavefunction $\Psi_0'(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$

  give rise to the *same* density $n(\mathbf{r})$.

- Let :

  $$E = \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle \text{ and } E' = \langle \Psi_0' | \hat{H}_N' | \Psi_0' \rangle$$

  be the corresponding ground-state energies.

- Then (variational principle on the wavefunction),

  $$E' = \langle \Psi_0' | \hat{H}_N' | \Psi_0' \rangle < \langle \Psi_0 | \hat{H}_N' | \Psi_0 \rangle = \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}' - \hat{V} | \Psi_0 \rangle$$

  $$E' < E + \int d^3\mathbf{r} [v'(\mathbf{r}) - v(\mathbf{r})] n(\mathbf{r})$$

  Likewise,

  $$E = \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle < \langle \Psi_0' | \hat{H}_N | \Psi_0' \rangle = \langle \Psi_0' | \hat{H}_N' | \Psi_0' \rangle + \langle \Psi_0' | \hat{V} - \hat{V}' | \Psi_0' \rangle$$

  $$E < E' + \int d^3\mathbf{r} [v(\mathbf{r}) - v'(\mathbf{r})] n(\mathbf{r})$$

  $E' + E < E + E'$!

  Absurd

The HK theorem applied to non-interacting electrons

- The Hohenberg-Kohn theorem also holds for non-interacting electrons in a one-body potential $v_s(\mathbf{r})$:

$$\begin{aligned} E_s &= \left\langle \Psi_0^s \middle| \hat{H}_N \middle| \Psi_0^s \right\rangle \\ &= \left\langle \Psi_0^s \middle| \hat{T} + \hat{V}_s \middle| \Psi_0^s \right\rangle \\ &= \underbrace{\left\langle \Psi_0^s \middle| \hat{T} \middle| \Psi_0^s \right\rangle}_{T_s[n]} + \int d^3\mathbf{r}\, v_s(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

- <u>Variational principle</u> : $E_s[n,v_s]$ is minimum when $n(\mathbf{r})$ is the GS density for $v_s(\mathbf{r})$.

$$\frac{\delta E_s[n,v_s]}{\delta n(\mathbf{r})} = 0 = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) \quad \forall \mathbf{r}$$

- Although this equation looks very complicated, we know its solution !

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_i(\mathbf{r}) + v_s(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

[ε_i twofold spin degenerate]

The Kohn-Sham equations (I)

- Back to the interacting electrons problem…

$$\begin{aligned} E &= \langle \Psi_0 | \hat{H}_N | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{T} + \hat{V} + \hat{V}_{ee} | \Psi_0 \rangle \\ &= \underbrace{\langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle}_{F[n]} + \int d^3\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

E can further be split as follows :

$$E = T_s[n] + \int d^3\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) + \underbrace{\frac{1}{2}\int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\substack{\text{Electrostatic energy} \\ \text{(Hartree energy)}}} + E_{xc}[n]$$

where $\begin{cases} T_s[n] \text{ is the kinetic energy of a non-interacting electron gas with density } n(\mathbf{r}) \\ E_{xc}[n] = F[n] - T_s[n] - \frac{1}{2}\int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{cases}$

- $E_{xc}[n]$ is the so-called « exchange-correlation » energy, that accounts for :
  - The Coulomb interactions beyond the mean-field (Hartree) approximation.
  - The increase of kinetic energy due to these interactions (T-T_s).

The Kohn-Sham equations (II)

$$E = T_s[n] + \int d^3\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) + \underbrace{\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\substack{\text{Electrostatic energy}\\ \text{(Hartree energy)}}} + E_{xc}[n]$$

- <u>Variational principle</u> : $E[n,v]$ is minimum when $n(\mathbf{r})$ is the GS density for $v(\mathbf{r})$.

$$\frac{\delta E[n,v]}{\delta n(\mathbf{r})} = 0 = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + \underbrace{\int d^3\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\substack{\text{Hartree potential}\\ v_h(\mathbf{r})}} + \underbrace{\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}}_{\substack{\text{"Exchange}-\text{correlation}\\ \text{potential" } v_{xc}(\mathbf{r})}} \qquad \forall \mathbf{r}$$

$$\frac{\delta E[n,v]}{\delta n(\mathbf{r})} = 0 = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\text{KS}}(\mathbf{r}), \text{ where } v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_h(\mathbf{r}) + v_{xc}(\mathbf{r})$$

This last equation is the same as the one found for non-interacting electrons in a one-body potential $v_{\text{KS}}(\mathbf{r})$!!

The Kohn-Sham equations (III)

$$E = T_s[n] + \int d^3\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) + \underbrace{\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\substack{\text{Electrostatic energy}\\ \text{(Hartree energy)}}} + E_{xc}[n]$$

- The ground-state density $n(\mathbf{r})$ satisfies :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_i(\mathbf{r}) + v(\mathbf{r})\varphi_i(\mathbf{r}) + v_h(\mathbf{r})\varphi_i(\mathbf{r}) + v_{xc}(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \qquad [\varepsilon_i \text{ twofold spin degenerate}]$$

$$n(\mathbf{r}) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2$$

where :

$$\begin{cases} v_h(\mathbf{r}) = \int d^3\mathbf{r}'\,\dfrac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} & \text{is the Hartree potential} \\ v_{xc}(\mathbf{r}) = \dfrac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} & \text{is the exchange - correlation potential} \end{cases}$$

- <u>Note</u> : The Hartree and exchange-correlation potentials depend on the density !!
  These equations must be solved « self-consistently ».

The local density approximation (I)

$$E = T_s[n] + \int d^3\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) + \underbrace{\frac{1}{2}\int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Electrostatic energy (Hartree energy)}} + E_{xc}[n]$$

- We know everything, except $E_{xc}[n]$!!
  This is an unknown and incredibly complex functional !!

  We must therefore choose approximations at this stage.

- The simplest, yet most widely useed approximation is the so-called « **local density approximation** (LDA) ».

  It assumes that the electrons behave locally as a homogeneous electron gas :

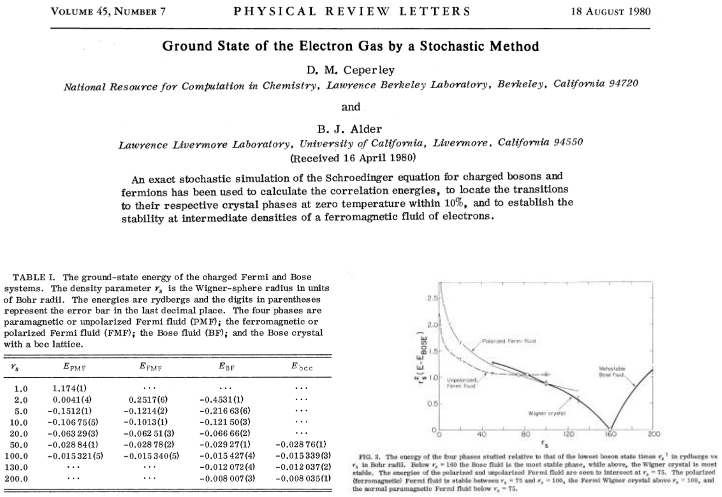
  $$E_{xc}[n] = \int d^3\mathbf{r}\, n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}))$$

  where $\varepsilon_{xc}(n)$ is the exchange-correlation energy per particle of a homogeneous electron gas with density n. The LDA exchange-correlation potential is :

  $$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \varepsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \frac{d\varepsilon_{xc}(n(\mathbf{r}))}{dn}$$

The local density approximation (II)

- $\varepsilon_{xc}(n)$ has been tabulated using « Quantum Monte Carlo » methods.



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Ground State of the Electron Gas by a Stochastic Method

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(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

TABLE I. The ground-state energy of the charged Fermi and Bose systems. The density parameter r_s is the Wigner-sphere radius in units of Bohr radii. The energies are rydbergs and the digits in parentheses represent the error bar in the last decimal place. The four phases are paramagnetic or unpolarized Fermi fluid (PMF); the ferromagnetic or polarized Fermi fluid (FMF); the Bose fluid (BF); and the Bose crystal with a bcc lattice.

r_s	$E_{\rm PMF}$	$E_{\rm FMF}$	$E_{\rm BF}$	$E_{\rm bcc}$
1.0	1.174(1)	...	...	...
2.0	0.0041(4)	0.2517(6)	−0.4531(1)	...
5.0	−0.1512(1)	−0.1214(2)	−0.216 63(6)	...
10.0	−0.106 75(5)	−0.1013(1)	−0.121 50(3)	...
20.0	−0.063 29(3)	−0.062 51(3)	−0.066 66(2)	...
50.0	−0.028 84(1)	−0.028 78(2)	−0.029 27(1)	−0.028 76(1)
100.0	−0.015 321(5)	−0.015 340(5)	−0.015 427(4)	−0.015 339(3)
130.0	...	...	−0.012 072(4)	−0.012 037(2)
200.0	...	...	−0.008 007(3)	−0.008 035(1)

FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$.

Beyond the local density approximation

- The local density approximation only works (in principle) for almost homogeneous electron systems. Yet it is accurate enough (in practice) for many solids and molecules !!

- Beyond the LDA :

  - The « Generalized Gradient Approximation (GGA) » :

    $$E_{xc}[n] = \int d^3\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}), ...)$$

    Still a (semi-)local functional…

  - Non-local functionals (« Exact exchange » and beyond) :
    More accurate, but also much more expensive… Still being explored…

What can be computed with DFT ?

- **Ground-state energy** of solids and molecules.
  Ground-state density.

- Derivatives of the ground-state energies :

  - Forces $F_{i\alpha} = -\nabla_{\mathbf{R}_{i\alpha}} E$ $\Rightarrow$ **Structural relaxation and optimization**.

  - Dynamical matrices $D_{X_i X_j} = \dfrac{\partial^2 E}{\partial X_i \partial X_j}$ $\Rightarrow$ **Vibrations modes (phonons)**.

  - **Linear (or higher order) response coefficients** :
    Polarizabilities ($\mathbf{P} = \alpha\mathbf{E}$), piezoelectric constants, etc…

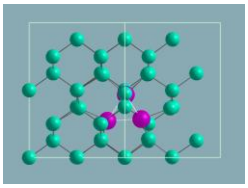
Example : GeMn structure (I)

- GeMn is a « **diluted magnetic semi-conductor** ».
  It is ferromagnetic at $T < 400$ K ⇒ Applications for « spintronic ».

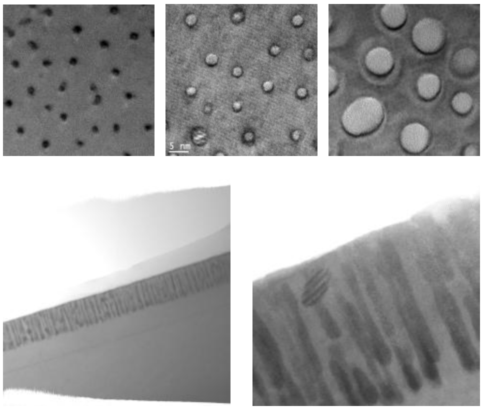
- Mn forms **nanocolumns** when inserted in a Ge matrix.

- **What is the structure of these nanocolumns ?**

Ab initio simulation of a periodic 64 atoms box :



Wavefunctions expanded in plane waves

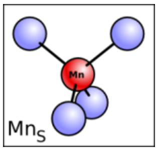


Thibaut DEVILLERS, Matthieu JAMET, CEA Grenoble

Example : GeMn structure (II)

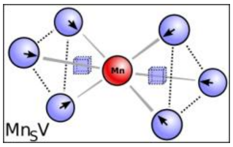
- Formation energies (FE) :

Substitutional



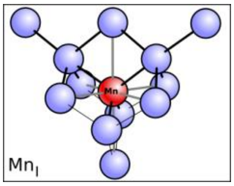
FE = 0 eV

Split-vacancy

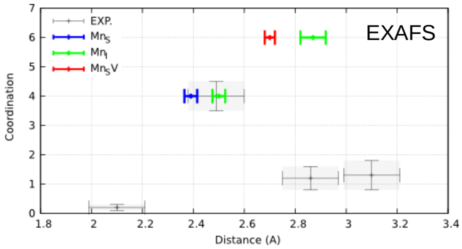


FE = -0.2 eV

Tetrahedral interstitial



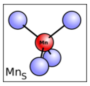
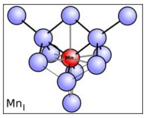
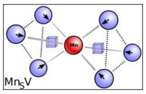
FE = +1.5 eV



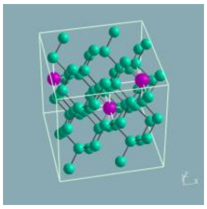
- None of these defects reproduce the distances & coodinations !
- 1 Mn in a 64-site box = 1.6 % much lower than exp. conc.

Increase the number of Mn in the box !

Example : GeMn structure (III)

		# of Mn	1	2	3
		[Mn]	1.6 %	3.1 %	4.7 %
Formation Energy (FE)			0 eV	0.3 eV	0.5 eV
			1.5 eV	1.5 eV	1.5 eV
			-0.2 eV	0.5 eV	-

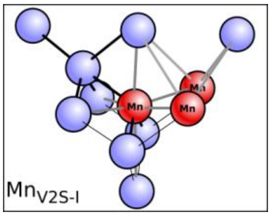
Formation Energy (eV/Mn) as a function of [Mn] for isolated defects



- FE does not decrease with [Mn] !!
- What about clusters ?

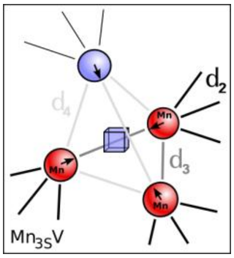
Example : GeMn structure (IV)

Interstitial cluster

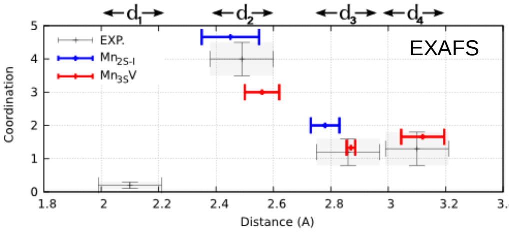


FE = 0.4 eV

Vacancy cluster



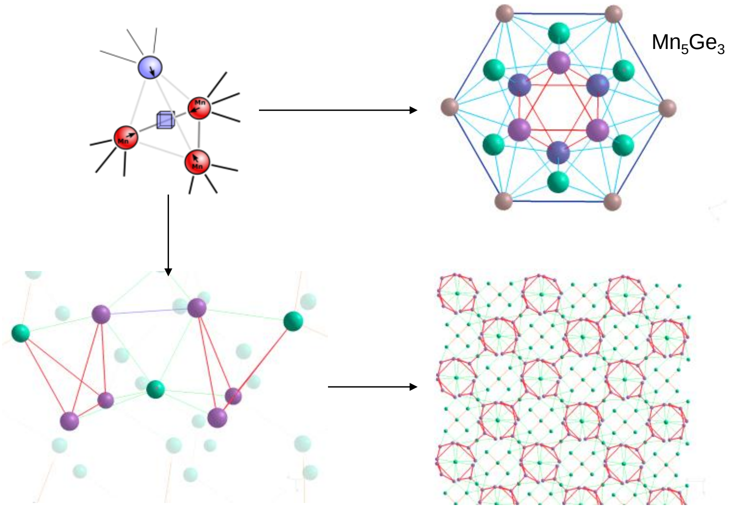
FE = 0.3 eV



- Distances and coordinations well reproduced by the vacancy cluster.
- These tetrahedra are the building blocks of Mn_5Ge_3 & Mn_8Ge_{11} (known to be stable).

Structure of Mn-rich GeMn nanocolumns : A combined EXAFS and ab initio calculations study.
E. Arras *et al*., submitted to PRL.

Example : GeMn structure (V)

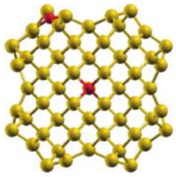


Bridged tetrahedron

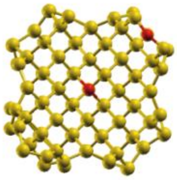
Possible chessboard-like structure of GeMn columns ?

Example : Doping silicon nanowires (I)

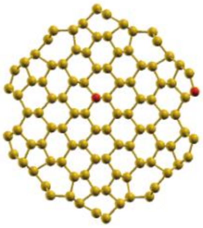
- Doping of small ⟨110⟩-oriented, unpassivated Si nanowires :



Wire a



Wire b



Wire c

X. Blase, …

Surface segregation energies

	Si(001)-2x1	Wire a	Wire b	Wire c
B	-0.7 eV	-0.03 eV	-0.14 eV	-0.99 eV
P	-1.08 eV	-0.98 eV	-1.05 eV	-1.10 eV

- **The dopants prefer being at the surface where they are electrically inactive** !..

Surface segregation and backscattering in doped silicon nanowires,
M.V. Fernandez-Serra, Ch. Adessi and X. Blase, Phys. Rev. Lett. **96**, 166805 (2006).

Example : Doping silicon nanowires (II)

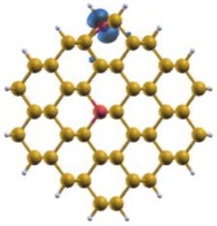
- In perfectly passivated nanowires : No clear tendency for surface diffusion.

But :
- $>10^{12}$ cm^{-2} dangling bond (P_b) defects at Si/SiO$_2$ interface
- 10^{18}-10^{19} cm^{-3} dopants in bulk (n_{Mott} (P:Si)=3×10^{18} cm^{-3})

As many surface traps as impurities for wires up to several nanometers in diameter !!

Segregation energy at P_b defect

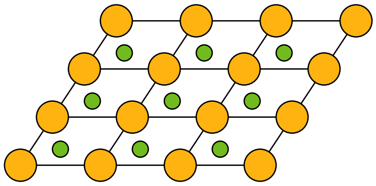
B	-0.99 eV
P	-1.62 eV



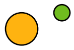
Surface segregation and backscattering in doped silicon nanowires,
M.V. Fernandez-Serra, Ch. Adessi and X. Blase, Phys. Rev. Lett. **96**, 166805 (2006).

DFT in crystals

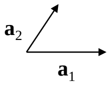
- A crystal is a periodic structure characterized by its **unit cell** and **lattice vectors** $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Example in 2D :



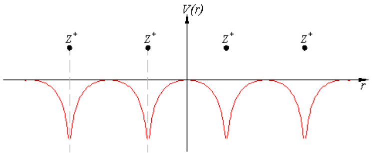
Unit cell :



Lattice vectors :



- The potential $v(\mathbf{r})$ is **periodic** in a crystal :



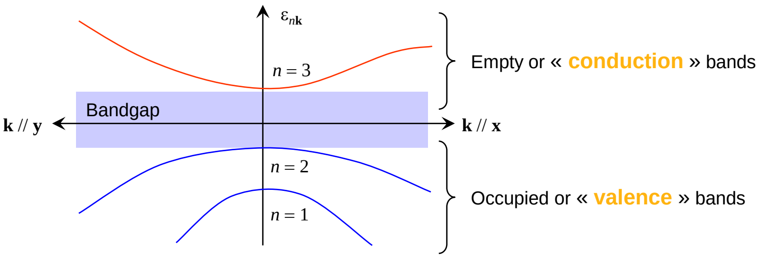
$$v(\mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3) = v(\mathbf{r}) \quad \forall (n_1,n_2,n_3)\in Z^3$$

Bloch's theorem

- **Bloch's theorem** : The one-particle wavefunctions $\varphi(\mathbf{r})$ in a periodic potential $v(\mathbf{r})$ can be split as follows :

$$\varphi(\mathbf{r}) \equiv \varphi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \text{ where } u_{n\mathbf{k}}(\mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3) = u_{n\mathbf{k}}(\mathbf{r}) \ \forall (n_1,n_2,n_3) \in Z^3$$

$\mathbf{k}$ is a (wave)vector and n is an integer. The one-particle energies $\varepsilon_{n\mathbf{k}}$ can thus be sorted into « bands » (same n, different $\mathbf{k}$) :



$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r}) + v(\mathbf{r})\varphi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{r})$$

The reciprocal lattice (I)

- Let us introduce the following vectors :

$$\begin{cases} \mathbf{b}_1 = \dfrac{2\pi}{\Omega}\mathbf{a}_2 \wedge \mathbf{a}_3 \\ \mathbf{b}_2 = \dfrac{2\pi}{\Omega}\mathbf{a}_3 \wedge \mathbf{a}_1 \\ \mathbf{b}_3 = \dfrac{2\pi}{\Omega}\mathbf{a}_1 \wedge \mathbf{a}_2 \end{cases} \text{ where } \Omega = \mathbf{a}_1\cdot(\mathbf{a}_2\wedge\mathbf{a}_3) = \mathbf{a}_2\cdot(\mathbf{a}_3\wedge\mathbf{a}_1) = \mathbf{a}_3\cdot(\mathbf{a}_1\wedge\mathbf{a}_2)$$

- Then,

$$\begin{cases} \mathbf{a}_1\cdot\mathbf{b}_1 = \dfrac{2\pi}{\Omega}\mathbf{a}_1\cdot(\mathbf{a}_2\wedge\mathbf{a}_3) = \dfrac{2\pi}{\mathbf{a}_1\cdot(\mathbf{a}_2\wedge\mathbf{a}_3)}\mathbf{a}_1\cdot(\mathbf{a}_2\wedge\mathbf{a}_3) = 2\pi \\ \mathbf{a}_1\cdot\mathbf{b}_2 = \dfrac{2\pi}{\Omega}\mathbf{a}_1\cdot(\mathbf{a}_3\wedge\mathbf{a}_1) = 0 \text{ because } \mathbf{u}\wedge\mathbf{v} \text{ always } \perp \text{ to } \mathbf{u} \text{ and } \mathbf{v} \\ \mathbf{a}_1\cdot\mathbf{b}_3 = \dfrac{2\pi}{\Omega}\mathbf{a}_1\cdot(\mathbf{a}_1\wedge\mathbf{a}_2) = 0 \end{cases}$$

and, in general,

$$\mathbf{a}_i\cdot\mathbf{b}_j = 2\pi\delta_{ij}$$

The reciprocal lattice (II)

- The reciprocal lattice is the lattice of $\mathbf{G}$ vectors defined by :

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \quad \forall(m_1, m_2, m_3) \in Z^3$$

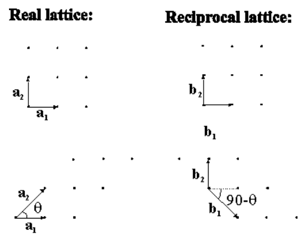
Then for any $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, $(n_1, n_2, n_3) \in Z^3$,

$$\mathbf{G}\cdot\mathbf{R} = 2\pi(m_1n_1 + m_2n_2 + m_3n_3) \text{ since } \mathbf{a}_i\cdot\mathbf{b}_j = 2\pi\delta_{ij}$$

$$\Downarrow$$

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1$$

Examples in 2D :



$\mathbf{a}_i\cdot\mathbf{b}_j = 2\pi\delta_{ij}$

The first Brillouin zone (I)

- The **band structure** is **periodic** in reciprocal space.
  Let us indeed consider a one-particle wavefunction $\varphi_{n\mathbf{k}}(\mathbf{r})$ with energy $\varepsilon_{n\mathbf{k}}$ and a lattice vector $\mathbf{G} \neq \mathbf{0}$:

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r}) + v(\mathbf{r})\varphi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{r})$$

We may as well write :

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\left[e^{-i\mathbf{G}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})\right] = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\tilde{u}(\mathbf{r})$$

Then for any $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, $(n_1, n_2, n_3) \in Z^3$,

$$\tilde{u}(\mathbf{r}+\mathbf{R}) = e^{-i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})}u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{-i\mathbf{G}\cdot\mathbf{R}}\left[e^{-i\mathbf{G}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})\right] = \tilde{u}(\mathbf{r}) \text{ since } e^{i\mathbf{G}\cdot\mathbf{R}} = 1$$

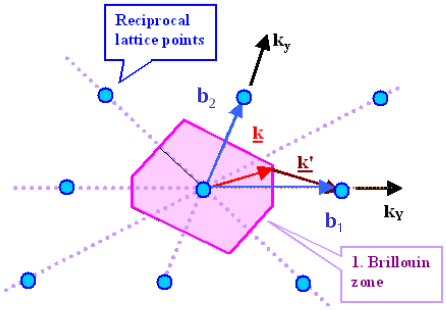
As a consequence, $\varphi_{n\mathbf{k}}(\mathbf{r})$ and $\varepsilon_{n\mathbf{k}}$ are also one-particle wavefunction and energy for $\mathbf{k}' = \mathbf{k} + \mathbf{G}$.

The band structure has the periodicity of the reciprocal lattice !

The first Brillouin zone (II)

- We thus only need to compute the band structure in an elementary unit cell around $\mathbf{k} = \mathbf{0}$. We define the **first Brillouin zone** (FBZ) as the set of $\mathbf{k}$'s that is closer to $\mathbf{G} = \mathbf{0}$ than to any other reciprocal lattice point.

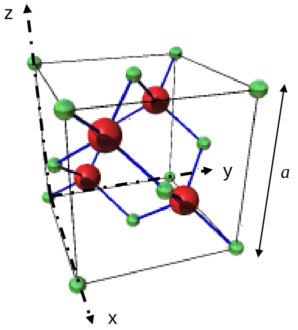
Example in 2D :



The reciprocal space can indeed be covered with FBZ-like tiles translated along $\mathbf{b}_1$ and $\mathbf{b}_2$.

Crystal structure

- Most usual semiconductors crystallize in the cubic **Diamond/Zinc-Blende** structure.



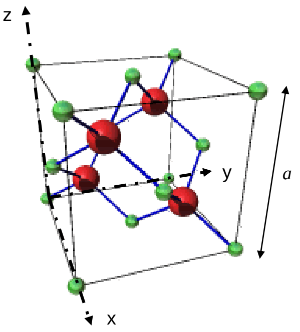
It is a **face-centered cubic** (FCC) lattice with a two atom unit cell :
  – one at (0,0,0).
  – the other at a(1,1,1)/4.

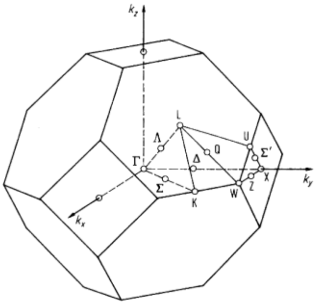
In the **Zinc-Blende** structure, each FCC sublattice is occupied by a different atom (e.g. Ga/As, In/P).

In the **Diamond** structure, the two sublattices are occupied by the same atom (e.g. Si, Ge, C).

- Alloys can also be synthetized, e.g. $\mathrm{In_{0.8}Ga_{0.2}As}$.
  One FCC sublattice is occupied by the In/Ga atoms (80% In+20% Ga ~ randomly distributed), the other by the As atoms.

Reciprocal lattice

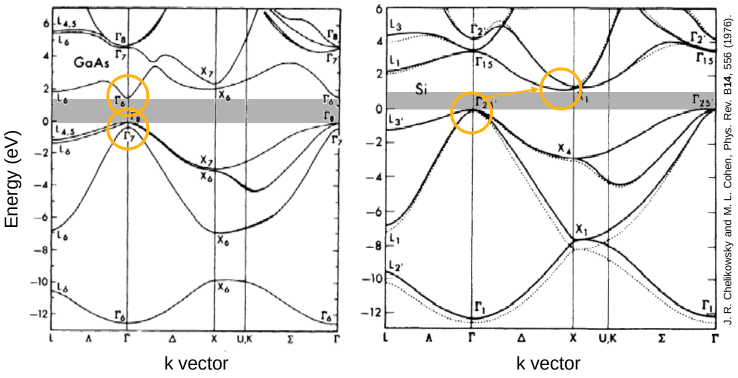




$$\begin{cases} \mathbf{a}_1 = \frac{a}{2}(0,1,1) \\ \mathbf{a}_2 = \frac{a}{2}(1,0,1) \\ \mathbf{a}_3 = \frac{a}{2}(1,1,0) \end{cases} \Rightarrow \begin{cases} \mathbf{b}_1 = \frac{2\pi}{a}(\bar{1},1,1) \\ \mathbf{b}_2 = \frac{2\pi}{a}(1,\bar{1},1) \\ \mathbf{b}_3 = \frac{2\pi}{a}(1,1,\bar{1}) \end{cases}$$

The reciprocal of a **face-centered cubic** lattice with side a is a **body-centered cubic** lattice with side $2\pi/a$.
The **first Brillouin zone** is the above truncated octahedron.

Direct vs indirect bandgap materials

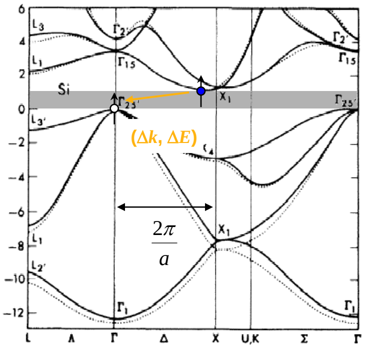


J. R. Chelikowsky and M. L. Cohen, Phys. Rev. **B14**, 556 (1976).

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

Bulk Si can not emit light !

Why bulk Si can not emit light…



A photon with wavelength λ has :

– Energy $E = h\nu = hc/\lambda$

– Momentum $k = 2\pi/\lambda$

- Optical transitions must preserve :
  - **Energy** : $h\nu = hc/\lambda = E_g$.
    λ is in the μm range for typical bandgap energies E_g ~ eV.
  - **Momentum** : $\Delta k = 2\pi/\lambda$.
    But $\lambda << a \Rightarrow \Delta k << 2\pi/a$.

Optical transitions are quasi-vertical in reciprocal space !!

The DFT band structure (I)

- Kohn-Sham equations :

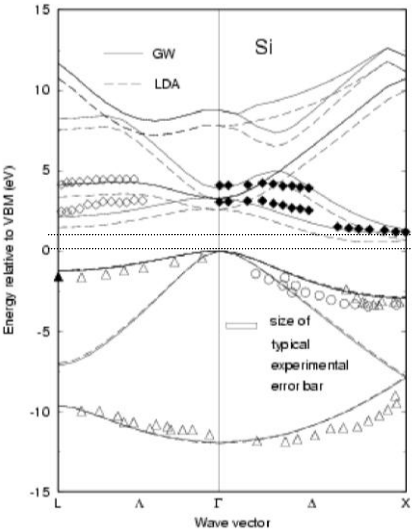
$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_i(\mathbf{r})+v(\mathbf{r})\varphi_i(\mathbf{r})+v_h(\mathbf{r})\varphi_i(\mathbf{r})+v_{xc}(\mathbf{r})\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

[ε_i twofold spin degenerate]

$$n(\mathbf{r})=\sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2$$

In principle, the Kohn-Sham energies have no physical meaning…
Let us have a look anyway at the LDA band structure of silicon…

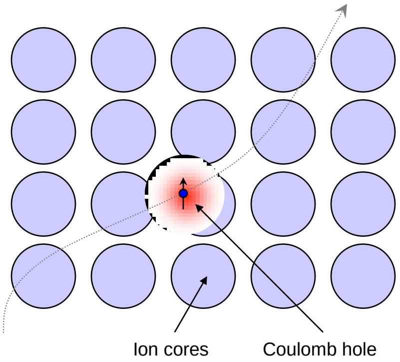
The DFT band structure (II)



- The LDA band structure of silicon is rather **good**, but **misses** one of the most important feature : **the bandgap energy**. The latter is ~0.5 eV too small.
- The DFT is a ground-state theory !
- What are single particle wavefunctions and energies in an interacting system ?

Interacting systems : « Quasi-electrons » (I)

- Let us add an electron to an otherwise neutral solid...



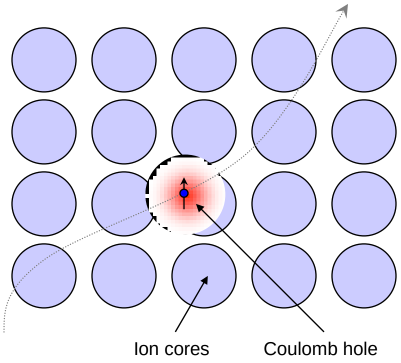
This electron repells nearby valence electrons, thus leaving partially « naked » ion cores around him.

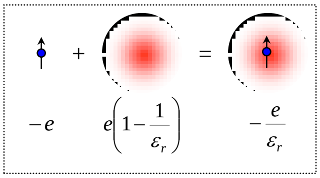
The electron is thus « clothed » by a cloud of positive charges (also known as a **Coulomb hole**) that screens its interactions with the other particles. This Coulomb hole follows the electron travelling in the solid.

- The electron plus its Coulomb hole is called a « **quasi-electron** ».

Interacting systems : « Quasi-electrons » (II)

- Let us add an electron to an otherwise neutral solid...

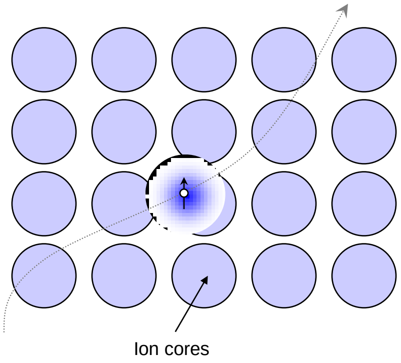




- Far enough from the quasi-electron at $\mathbf{r}$, $V(\mathbf{r},\mathbf{r}') = -\frac{e}{\varepsilon_r|\mathbf{r}-\mathbf{r}'|}$.

Interacting systems : « Quasi-holes » (I)

- Let us remove an electron from an otherwise neutral solid...



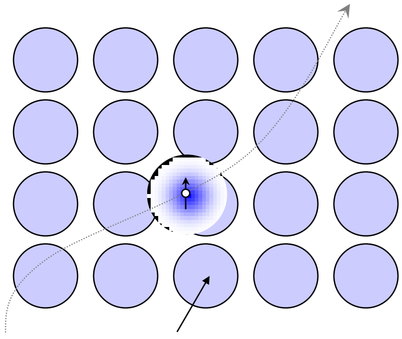
This leaves a positive charge (hole) in the solid that gets surrounded by a cloud of valence electrons.

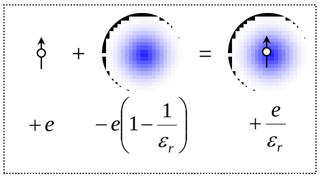
This cloud of electrons is dragged by the hole as it moves in the solid.

- The hole plus its cloud of electrons is called a « **quasi-hole** ».

Interacting systems : « Quasi-holes » (II)

- Let us remove an electron from an otherwise neutral solid...





- Far enough from the quasi-hole at $\mathbf{r}$, $V(\mathbf{r},\mathbf{r}') = +\dfrac{e}{\varepsilon_r|\mathbf{r}-\mathbf{r}'|}$.

The quasiparticle equation (I)

- Can we still describe the dynamics of quasi-electrons and quasi-holes with one-particle wavefunctions ?

  - i.e., looking on the **quasi-electron** side :

    Can we find one-particle energies E_n and one-particle wavefunctions $\varphi_n(\mathbf{r})$ such that :

    - $|\varphi_n(\mathbf{r})|^2$ is the probability to find the electron at $\mathbf{r}$.
    - $E_0(N)+E_n$ is the energy of the $(N+1)$-electron system ?

  - or, looking on the **quasi-hole** side :

    Can we find one-particle energies E_n and one-particle wavefunctions $\varphi_n(\mathbf{r})$ such that :

    - $|\varphi_n(\mathbf{r})|^2$ is the probability to find the hole at $\mathbf{r}$.
    - $E_0(N)-E_n$ is the energy of the $(N-1)$-electron system ?

- The answer is **yes**, but with conditions.

The quasiparticle equation (II)

- The quasiparticle wavefunctions and energies can be shown to satisfy the so-called quasiparticle equation :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v(\mathbf{r})\varphi_n(\mathbf{r})+v_h(\mathbf{r})\varphi_n(\mathbf{r})+\int d^3r'\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_n)\varphi_n(\mathbf{r}')=E_n\varphi_n(\mathbf{r})$$

where :

  - $v(\mathbf{r})$ is the « external » (ionic) potential.
  - $v_h(\mathbf{r})=e^2\int d^3r'\frac{\rho_N(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the average potential created by the ground-state electron density (also known as the Hartree potential).
  - $\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_n)$ is the « **self-energy** ». It describes how valence electrons dynamically act back onto the additional electron/hole at $\mathbf{r}$.

- The self-energy is an incredibly complex operator. Approximations can be found within many-body perturbation theory (e.g., the « *GW* » method).

The quasiparticle equation (III)

- The quasiparticle equation :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v(\mathbf{r})\varphi_n(\mathbf{r})+v_h(\mathbf{r})\varphi_n(\mathbf{r})+\int d^3r'\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_n)\varphi_n(\mathbf{r}')=E_n\varphi_n(\mathbf{r})$$

is a Schrödinger-like equation whose effective potential $\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_n)$ is :

  - **Non-local** (depends on both $\mathbf{r}$ and $\mathbf{r}'$).
    The range of the self-energy is of the order of the Coulomb hole size (~ 2 Å) in solids. But see later discussion in nanostructures !
  - **Complex and energy dependent**.
    As a consequence, the quasiparticle « hamiltonian » is **not** hermitian and the quasiparticle energies are complex numbers.

$$\boxed{E_n=\varepsilon_n\pm i\Gamma_n}$$

What does that mean ??

The quasiparticle lifetime

- Quasiparticles have a **finite lifetime** $\tau_n \sim 1/\Gamma_n$:

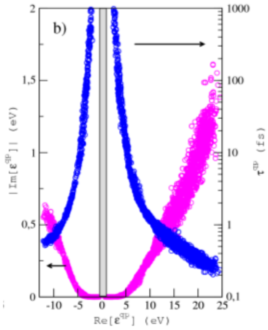
$$\varphi_n(\mathbf{r};t) = \varphi_n(\mathbf{r}) e^{-\frac{i}{\hbar}E_n t} = \left[\varphi_n(\mathbf{r}) e^{-\frac{i}{\hbar}\varepsilon_n t} \right] e^{-\Gamma_n t}$$

The quasiparticles decay into other many-body excitations... They propagate as single particles only on « short » time scales $\tau << \tau_n$.

- How long is τ_n ??

Back to the quasiparticle lifetime...

- Quasiparticle lifetime in bulk Si, as calculated with the so-called *GW* method :



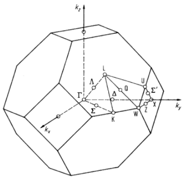
B. Arnaud et al.

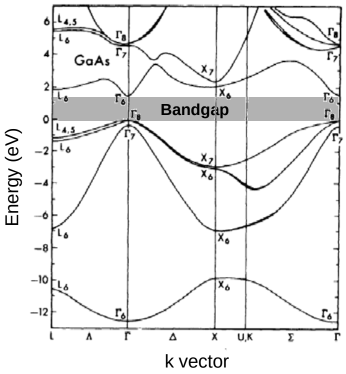
- The quasiparticle lifetime diverges at the conduction and valence band edges !

There are well defined, long-lived quasiparticles around the gap.

The quasiparticle band structure of a solid

- Bloch theorem still applies. In a solid, the quasiparticle wavefunctions and energies can be labelled with a wavevector $\mathbf{k}$ and a band index n :





Quasi-electron bands
« **Conduction bands** »

Quasi-hole bands
« **Valence bands** »

An effective single-particle hamiltonian

- Most of the interesting physics takes place around the gap...
  Let us now forget about :
  - finite quasiparticle lifetimes...
  - self-energy non-locality...

and assume that we can find a local potential $v_{self}(\mathbf{r})$ that yields the same quasiparticle wavefunctions and energies as the self-energy operator $\Sigma_{xc}(\mathbf{r}, \mathbf{r}';E_n)$ at least around the gap :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v(\mathbf{r})\varphi_n(\mathbf{r})+v_h(\mathbf{r})\varphi_n(\mathbf{r})+\int d^3r'\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_n)\varphi_n(\mathbf{r}')=E_n\varphi_n(\mathbf{r})$$

$$\Downarrow$$

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v(\mathbf{r})\varphi_n(\mathbf{r})+v_h(\mathbf{r})\varphi_n(\mathbf{r})+v_{self}(\mathbf{r})\varphi_n(\mathbf{r})=\varepsilon_n\varphi_n(\mathbf{r})$$

$$\Downarrow$$

$$\boxed{-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v_{eff}(\mathbf{r})\varphi_n(\mathbf{r})=\varepsilon_n\varphi_n(\mathbf{r})}$$

where $v_{eff}(\mathbf{r}) = v(\mathbf{r}) + v_h(\mathbf{r}) + v_{self}(\mathbf{r})$.

II.2 : The semi-empirical tight-binding method

Introduction

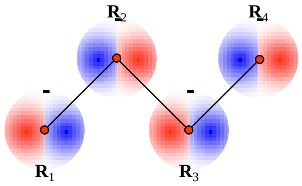
$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\psi(\mathbf{r})+v_{eff}(\mathbf{r})\psi(\mathbf{r})=\varepsilon\psi(\mathbf{r})$$

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

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

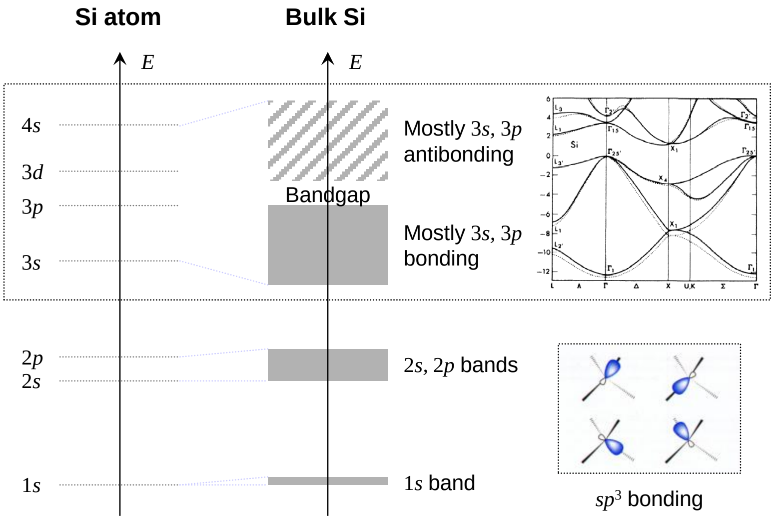
where $\varphi_\alpha(\mathbf{r}-\mathbf{R}_i)$ is an orbital of kind α centered on atom i with position $\mathbf{R}_i$. For example,

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



- Which orbitals to choose ?

Which orbitals to choose ? (I)



Si atom

Bulk Si

E

E

4*s*

3*d*

3*p*

3*s*

Bandgap

Mostly 3*s*, 3*p* antibonding

Mostly 3*s*, 3*p* bonding

2*p*

2*s*

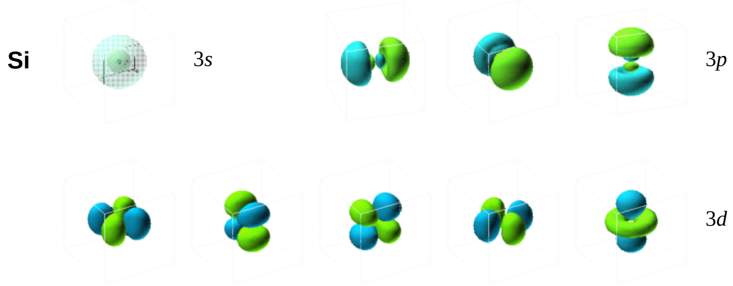
2*s*, 2*p* bands

1*s*

1*s* band

sp^3 bonding

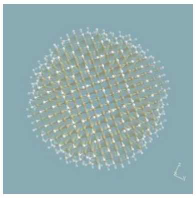
Which orbitals to choose ? (II)



- 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)

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



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

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

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

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

Application to nanocrystals and quantum dots (II)

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

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

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

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

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.

Application to nanocrystals and quantum dots (III)

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

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

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

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

We last define the following n x 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 :

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

Further simplifications…

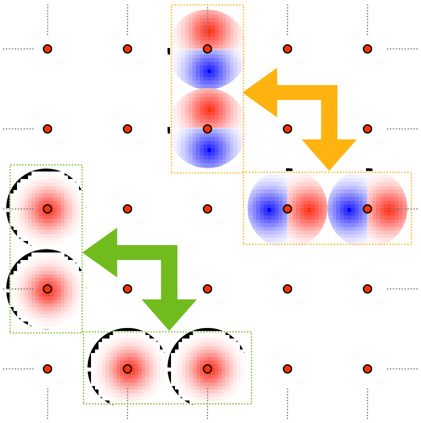
- What we need :

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

$H_{\alpha\alpha}(\mathbf{R}_i, \mathbf{R}_i)$ 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.

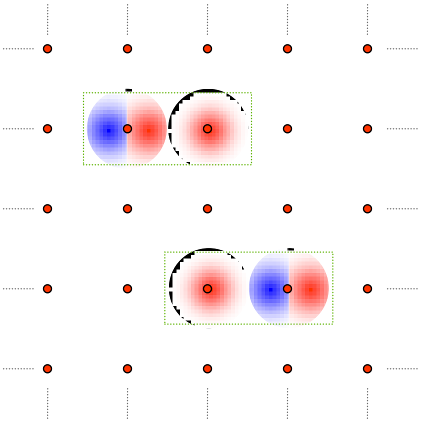
The use of symmetries (I)



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

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

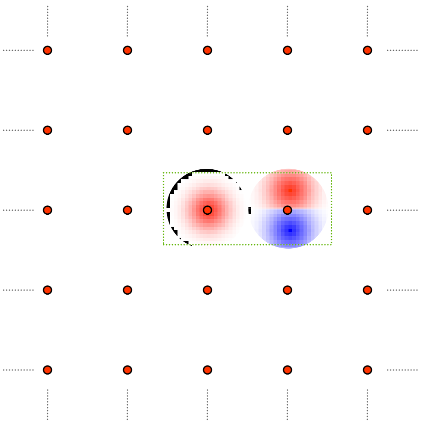
The use of symmetries (II)



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

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

The use of symmetries (III)

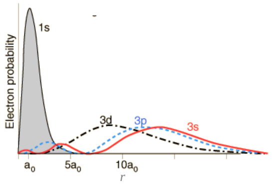


$$\left\{\begin{array}{l} H_{\alpha\beta}(\mathbf{R}_i,\mathbf{R}_j)=\langle\varphi_\alpha(\mathbf{r}-\mathbf{R}_i)|h|\varphi_\beta(\mathbf{r}-\mathbf{R}_j)\rangle \\ S_{\alpha\beta}(\mathbf{R}_i,\mathbf{R}_j)=\langle\varphi_\alpha(\mathbf{r}-\mathbf{R}_i)|\varphi_\beta(\mathbf{r}-\mathbf{R}_j)\rangle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

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

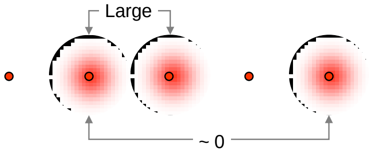
Finite range tight-binding models

- Atomic orbitals decay exponentially far enough from the nucleus :



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

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 :

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

Different orbitals on the same atom are orthogonal (because their ang. 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. 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 :

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

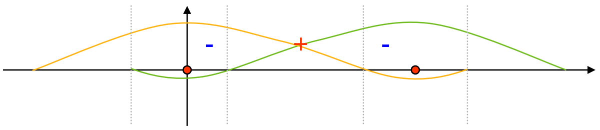
- We are back to a simpler standard eigenvalue problem :

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

[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.

Two and three center tight-binding models

- Let :

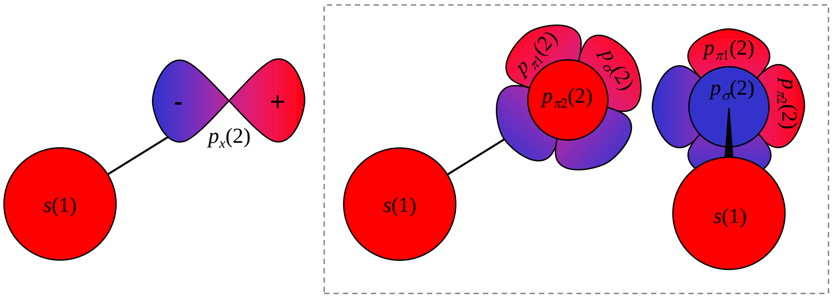
$$h = -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_{eff}(\mathbf{r}) \text{ and } v_{eff}(\mathbf{r}) = \sum_{k=1}^{N} v_k(\mathbf{r}-\mathbf{R}_k)$$

Then,

$$\begin{aligned} H_{\alpha\beta}(\mathbf{R}_i,\mathbf{R}_j) &= \langle \varphi_\alpha(\mathbf{r}-\mathbf{R}_i)|h|\varphi_\beta(\mathbf{r}-\mathbf{R}_j)\rangle \\ &= \left\langle \varphi_\alpha(\mathbf{r}-\mathbf{R}_i)\left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + \sum_{k=1}^{N} v_k(\mathbf{r}-\mathbf{R}_k) \right| \varphi_\beta(\mathbf{r}-\mathbf{R}_j)\right\rangle \\ &= \left\langle \varphi_\alpha(\mathbf{r}-\mathbf{R}_i)\left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_i(\mathbf{r}-\mathbf{R}_i) + v_j(\mathbf{r}-\mathbf{R}_j) \right| \varphi_\beta(\mathbf{r}-\mathbf{R}_j)\right\rangle \\ &+ \left\langle \varphi_\alpha(\mathbf{r}-\mathbf{R}_i)\left| \sum_{k\neq i,j}^{N} v_k(\mathbf{r}-\mathbf{R}_k) \right| \varphi_\beta(\mathbf{r}-\mathbf{R}_j)\right\rangle \end{aligned}$$

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

Two center tight-binding models (I)



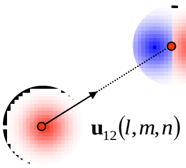
$$p_x(r-\mathbf{R}_2) = lp_\sigma(r-\mathbf{R}_2) + lp_{\pi_1}(r-\mathbf{R}_2) + np_{\pi 2}(r-\mathbf{R}_2) \text{ where } l = \frac{\mathbf{x}\cdot(\mathbf{R}_1-\mathbf{R}_2)}{|\mathbf{R}_1-\mathbf{R}_2|}\ldots$$

$$\begin{aligned} H_{\alpha\beta}(\mathbf{R}_1,\mathbf{R}_2) &= \left\langle s(\mathbf{r}-\mathbf{R}_1)\left| -\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}} + v_1(\mathbf{r}-\mathbf{R}_1) + v_2(\mathbf{r}-\mathbf{R}_2) \right| p_x(\mathbf{r}-\mathbf{R}_2)\right\rangle \\ &= l\langle s(\mathbf{r}-\mathbf{R}_1)|h_{12}|p_\sigma(\mathbf{r}-\mathbf{R}_2)\rangle + m\underbrace{\langle s(\mathbf{r}-\mathbf{R}_1)|h_{12}|p_{\pi_1}(\mathbf{r}-\mathbf{R}_2)\rangle}_{0 \text{ by symmetry}} + n\ldots \end{aligned}$$

$$H_{\alpha\beta}(\mathbf{R}_1,\mathbf{R}_2) = l\langle s(\mathbf{r}-\mathbf{R}_1)|h_{12}|p_\sigma(\mathbf{r}-\mathbf{R}_2)\rangle = lV_{sp\sigma}(|\mathbf{R}_1-\mathbf{R}_2|)$$

Two center tight-binding models (II)

$$\begin{cases} l = \mathbf{x}\cdot\mathbf{u}_{12} \\ m = \mathbf{y}\cdot\mathbf{u}_{12} \\ n = \mathbf{z}\cdot\mathbf{u}_{12} \end{cases} \qquad \mathbf{u}_{12} = \frac{\mathbf{R}_1 - \mathbf{R}_2}{\left|\mathbf{R}_1 - \mathbf{R}_2\right|}$$



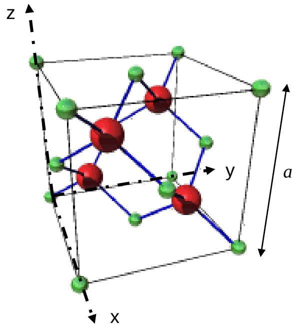
$$\begin{aligned} \left\langle s(\mathbf{r}-\mathbf{R}_1)\middle|h_{12}\middle|p_x(\mathbf{r}-\mathbf{R}_2)\right\rangle &= lV_{sp\sigma}\left(\left|\mathbf{R}_1-\mathbf{R}_2\right|\right) \\ \left\langle s(\mathbf{r}-\mathbf{R}_1)\middle|h_{12}\middle|p_y(\mathbf{r}-\mathbf{R}_2)\right\rangle &= mV_{sp\sigma}\left(\left|\mathbf{R}_1-\mathbf{R}_2\right|\right) \\ \left\langle s(\mathbf{r}-\mathbf{R}_1)\middle|h_{12}\middle|p_z(\mathbf{r}-\mathbf{R}_2)\right\rangle &= n\ \underbrace{V_{sp\sigma}\left(\left|\mathbf{R}_1-\mathbf{R}_2\right|\right)}_{\text{Only depends on }\left|\mathbf{R}_1-\mathbf{R}_2\right|\text{!}} \end{aligned}$$

- Advantages of the two-center approximation :
  - The tight-binding matrix elements only depend on **a few “Slater-Koster parameters”** (e.g. $V_{sp\sigma}$).
  - **Explicit angular dependence** (through the cosine directors l, m and n).
  - Complete **separation between the angular and interatomic distance dependences**.

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].

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

Application to crystalline solids (II)

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

- **Bloch's theorem** :

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

As a consequence,

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

However,

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

Application to crystalline solids (III)

- Hence,

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

Since the LCAO expansion must be unique,

$$c_{(j+u)(k+v)(l+w)p\alpha}(n\mathbf{k}) = e^{i\mathbf{k}\cdot\tilde{\mathbf{R}}_{uvw}} c_{jklp\alpha}(n\mathbf{k})$$

$$c_{uvwp\alpha}(n\mathbf{k}) = e^{i\mathbf{k}\cdot\tilde{\mathbf{R}}_{uvw}} c_{000p\alpha}(n\mathbf{k}) = e^{i\mathbf{k}\cdot\left(\tilde{\mathbf{R}}_{uvw} + \mathbf{d}_p\right)} \left[e^{-i\mathbf{k}\cdot\mathbf{d}_p} c_{000p\alpha}(n\mathbf{k})\right] = e^{i\mathbf{k}\cdot\left(\tilde{\mathbf{R}}_{uvw} + \mathbf{d}_p\right)} b_{p\alpha}(n\mathbf{k})$$

Finally,

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

Application to crystalline solids (IV)

- Let :

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

We get :

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

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

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

Application to crystalline solids (V)

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

- 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 :

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

Application to crystalline solids (VI)

$$\sum_{p=1}^{n_c}\sum_{\alpha=1}^{n_{orb}} b_{p\alpha}(n\mathbf{k}) \sum_{(j,k,l)\in Z^3} e^{i\mathbf{k}\cdot\left(\tilde{\mathbf{R}}_{jkl}-\tilde{\mathbf{R}}_{000}+\mathbf{d}_p-\mathbf{d}_q\right)} H_{\beta\alpha}\left(\tilde{\mathbf{R}}_{000}+\mathbf{d}_q,\tilde{\mathbf{R}}_{jkl}+\mathbf{d}_p\right)$$

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

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

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

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

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

We solve this generalized eigenvalue problem and get $n_b = n_c n_{orb}$ bands (see examples in next slides).

The semi-empirical tight-binding method

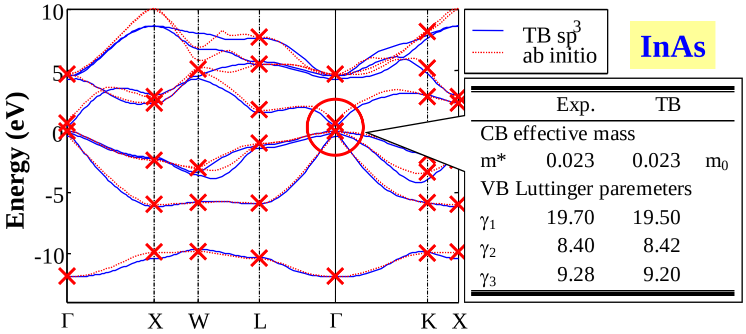
- What we need :

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

- « **Semi-empirical** » tight-binding :
    - Consider these matrix elements as adjustable parameters…
    - …fitted on the experimental or *ab initio* (corrected DFT/GW) bulk band structures.
    - Use the same matrix elements in nanostructures (« **transferabilty** »).

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

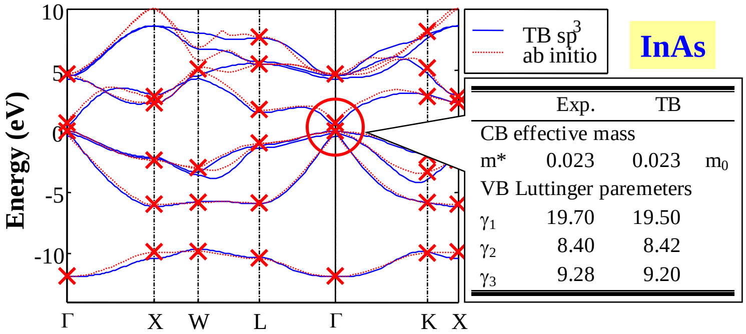
Fitting tight-binding parameters (I)



	Exp.	TB	
CB effective mass			
m*	0.023	0.023	m_0
VB Luttinger paremeters			
γ_1	19.70	19.50	
γ_2	8.40	8.42	
γ_3	9.28	9.20	

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

Fitting tight-binding parameters (II)



	Exp.	TB	
CB effective mass			
m*	0.023	0.023	m_0
VB Luttinger paremeters			
γ_1	19.70	19.50	
γ_2	8.40	8.42	
γ_3	9.28	9.20	

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

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

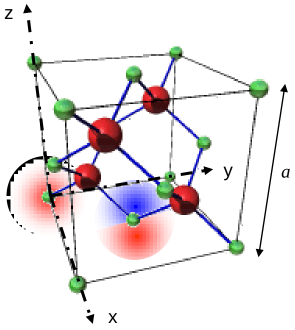
$\alpha_{n\mathbf{k}}$ and β_i are weighting coefficients and k_0 is an arbitrary wavevector (for consistency & overall weighting of the masses with respect to the band energies).

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)

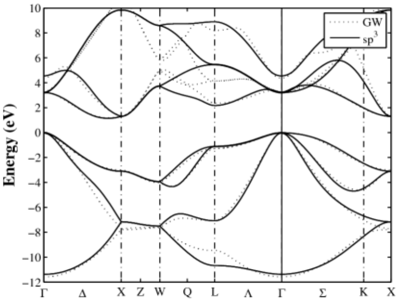


Example : $E_{sx}(220)$ = Hamiltonian matrix element between a s orbital at $(0,0,0)$ and a p_x orbital at $(2,2,0)a/4$. Δ is the spin-orbit coupling parameter.

- **Atomic orbitals remain unknown !!**

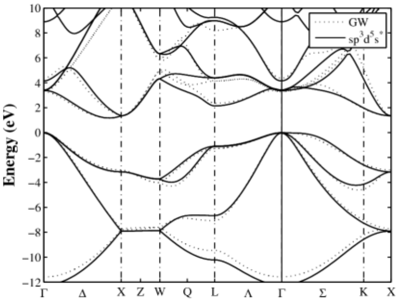
Comparison between a sp^3 and a $sp^3d^5s^*$ model for Si

Third nearest neighbors orthogonal sp^3 model

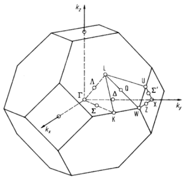


Y. M. Niquet et al., Phys. Rev. B **62**, 5109 (2000)

Nearest neighbors orthogonal $sp^3d^5s^*$ model



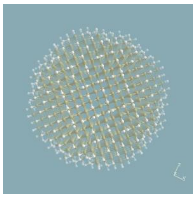
J. M. Jancu et al., Phys. Rev. B **57**, 6493 (1998)



- GW = « ab initio » method (no adjustable paremeters).
- 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)

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



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

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

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 :

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

Application to nanocrystals and quantum dots (II)

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

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

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

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

We last define the following n x 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 :

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

Numerical issues

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

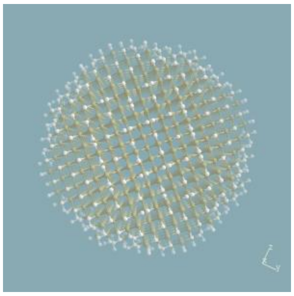
- **H** and **S** are large *n* x *n* matrices ($n = N \times n_{orb}$). It is not possible to solve this eigenvalue problem using standard libraries (e.g., Lapack).

  H and **S** are however **sparse** matrices : most of the elements are zero because atoms only interact with their nearest neighbors. The matrix-vector products (**Hc** and **Sc**) can thus be implemented very efficiently : only the position and value of the non-zero elements of **H** and **S** need to be stored in memory.

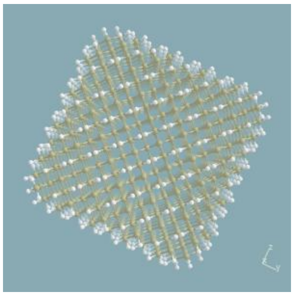
  A few wavefunctions and energies can then be computed around the gap using an iterative diagonalization technique : a trial vector is updated step by step until it has become an eigenstate of **H**. Each optimization step only requires one or more **Hc** / **Sc** products (no explicit transformations on **H** and **S**) :
  - Lanczos,
  - Conjugate gradients,
  - Jacobi-Davidson…

  10-50 eigenstates of **H** can be computed in few hours for ~ 10 000 000 orbitals or more.

Application : Confinement in Si nanocrystals (I)



Spherical Si nanocrystals with diameter *d*



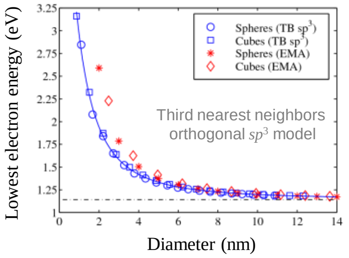
Cubic Si nanocrystals with side *a* and « effective » diameter *d* such that :

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

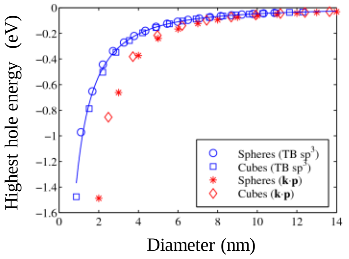
The dangling bonds at the surface of the nanocrystals are saturated with H atoms.

Application : Confinement in Si nanocrystals (II)

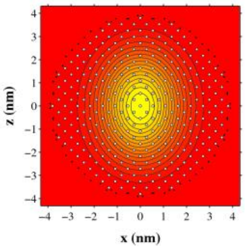
Y. M. Niquet et al., Phys. Rev. B **62**, 5109 (2000)

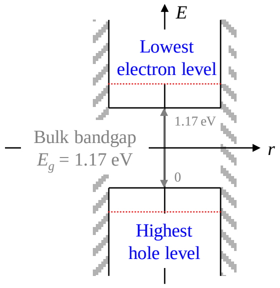


Third nearest neighbors orthogonal sp^3 model



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





E

Lowest electron level

1.17 eV

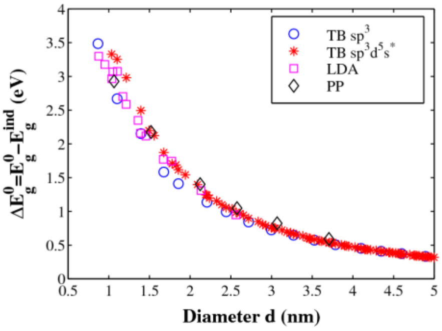
Bulk bandgap E_g = 1.17 eV

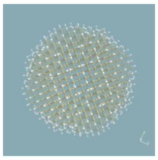
r

0

Highest hole level

Application : Confinement in Si nanocrystals (III)





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

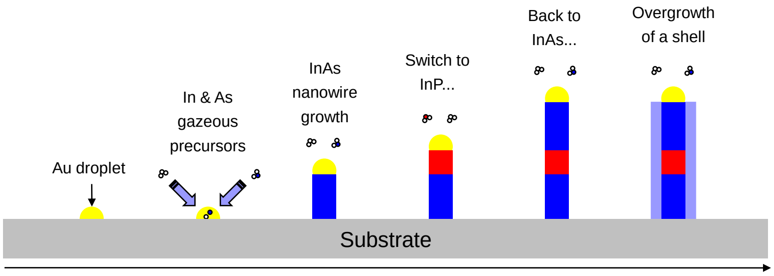
where $E_g(\text{bulk Si}) = 1.17$ eV

- Comparison between a third nearest neighbors orthogonal ***sp^3* tight-binding (TB) model**, a nearest neighbors orthogonal ***$sp^3d^5s^*$* TB model**, the **semi-empirical pseudopotential** (PP) method [the wavefunction is expanded in plane waves instead of atomic orbitals] and the *ab initio* **local density approximation** (LDA).

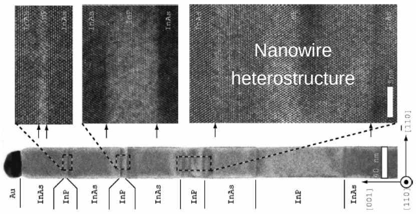
- **Note** : The LDA is wrong on E_g, but is believed to be ~ OK on ΔE_g !

Application : Nanowire heterostructures (I)

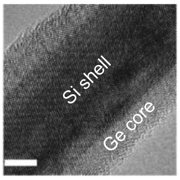
- Vapor-Liquid-Solid (VLS) growth :



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



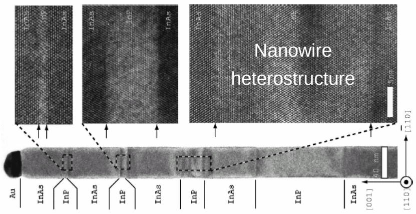
W. Lu *et al.*, PNAS. **102**, 10046 (2005)



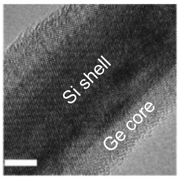
Application : Nanowire heterostructures (II)

- Large interest in nanowire « heterostructures » for optics & transport :

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



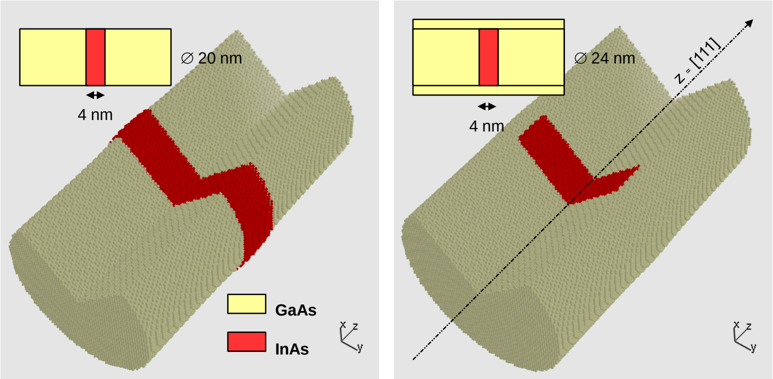
W. Lu *et al.*, PNAS. **102**, 10046 (2005)



- **Strain relaxation is believed to be efficient** in these structures, likely allowing the growth of thick lattice mismatched layers.

- A few issues :
  - **What is the effect of strain relaxation on the electronic properties of nanowire heterostructures ?**
  - **What is the effect of an overgrown shell ?**

Application : Nanowire heterostructures (III)



- The bond length is 6.7% shorter in GaAs than in InAs. The InAs layer is thus **compressed** by the GaAs core, but can partly **relax** strains at the surface of the nanowire.

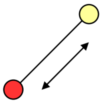
- The GaAs shell move surface traps away from the InAs layer, but prevents strain relaxation.

Application : Nanowire heterostructures (IV)

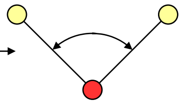
- Assuming coherent growth, strain relaxation can be computed using Keating's Valence Force Field model :

$$E = \frac{1}{2}\sum_i \sum_j^{NN} \frac{3\alpha_{ij}}{8\left(d_{ij}^0\right)^2}\left[\left(\mathbf{R}_j - \mathbf{R}_i\right)^2 - \left(d_{ij}^0\right)^2\right]^2$$

$$+\sum_i \sum_{j,k>j}^{NN} \frac{3\beta_{ijk}}{8\left(d_{ij}^0\right)\left(d_{ik}^0\right)}\left[\left(\mathbf{R}_j - \mathbf{R}_i\right)\left(\mathbf{R}_k - \mathbf{R}_i\right) + \frac{1}{3}\left(d_{ij}^0\right)\left(d_{ik}^0\right)\right]^2$$



Bond stretching constant α

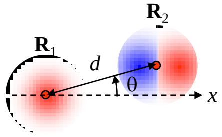


Bond bending constant β

	InAs	GaAs
d_0	2,623 Å	2,448 Å
α	32,65 N/m	39,85 N/m
β	7,35 N/m	10,86 N/m

Application : Nanowire heterostructures (V)

- We need to account for the dependence on the tight-binding parameters on the atomic positions.



For two center tight-binding models :

$$H_{sx}(\mathbf{R}_1,\mathbf{R}_2)=\langle\varphi_s(\mathbf{r}-\mathbf{R}_1)|h|\varphi_x(\mathbf{r}-\mathbf{R}_2)\rangle$$

$$=l\times\underbrace{V_{sp\sigma}(|\mathbf{R}_2-\mathbf{R}_1|)}_{\text{Bond length dependence}}\quad\text{where}\quad\underbrace{l=\cos\theta=\frac{\mathbf{x}\cdot(\mathbf{R}_2-\mathbf{R}_1)}{|\mathbf{R}_2-\mathbf{R}_1|}}_{\text{Bond angle dependence}}$$

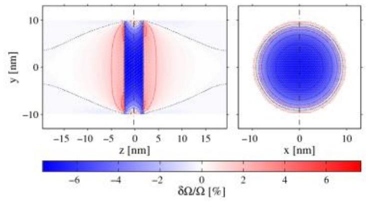
where :

$$V_{sp\sigma}(d)=V_{sp\sigma}(d_0)\left(\frac{d_0}{d}\right)^{\alpha_{sp\sigma}}\qquad\text{[Harisson's law]}$$

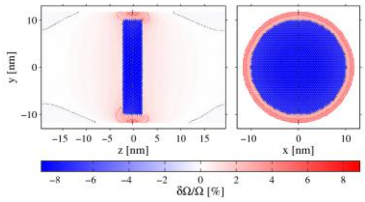
d_0 is the equilibrium bond length and $\alpha_{sp\sigma}$ is an exponent (around 2).

Application : Nanowire heterostructures (VI)

Core



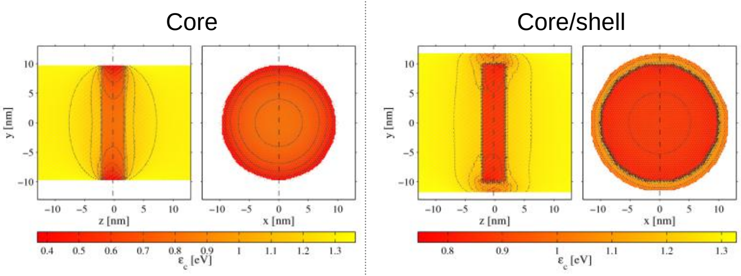
Core/shell



- Strain relaxation is very **efficient** in core-only heterostructures. The InAs layer protrudes outwards and distorts the surface of the nanowire. The strain distribution is however very **inhomogeneous** : the surface is overrelaxed while the center of the InAs layer is still significantly compressed.

- The GaAs shell **limits strain relief** in the InAs layer. The strain distribution is however much more **homogeneous**.

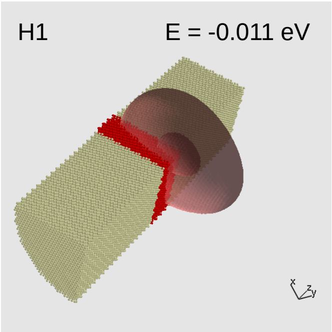
Application : Nanowire heterostructures (VII)

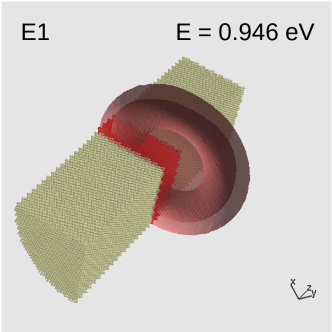


$$\boxed{\delta E_c = a_c \frac{\delta\Omega}{\Omega} = a_c\left(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}\right)}$$

- Strain relaxation in core-only heterostructures digs a **well in the conduction band** at the surface of the nanowire !

Application : Nanowire heterostructures (VIII)

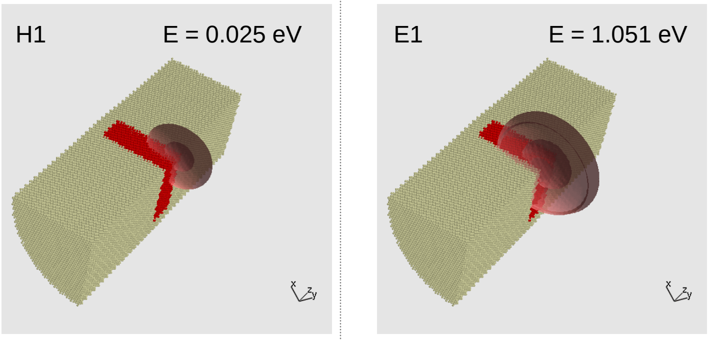




- The **electron** (E1) **is trapped** near the surface of the nanowire by the inhomogeneous strain relaxation.

- **No significant overlap** between H1 and E1 !!

Application : Nanowire heterostructures (IX)

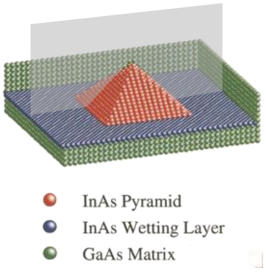


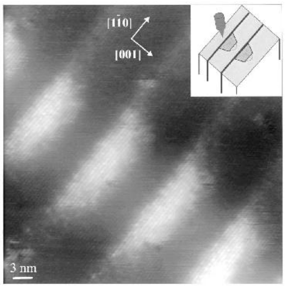
Y. M. Niquet, Nano Lett. **7**, 1105 (2007).

- Both particles are now well confined in the InAs layer.
- **Large overlap** between H1 and E1.

Application : Wavefunction imaging (I)

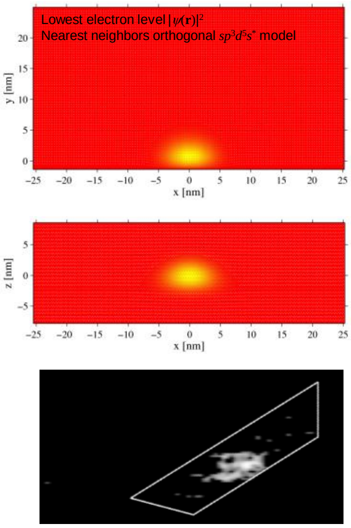
InAs/GaAs quantum dots

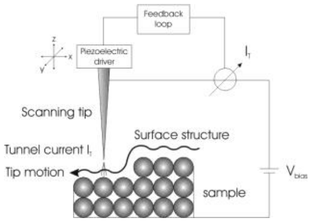




- The sample is cleaved (cut in two pieces along a crystallographic plane). The cleavage plane goes through some InAs quantum dots, that show on the surface of the sample.
  The cleavage plane is then imaged with a scanning tunneling microscope (STM).
  The InAs dots appear as bright spots, that tend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

Application : Wavefunction imaging (II)

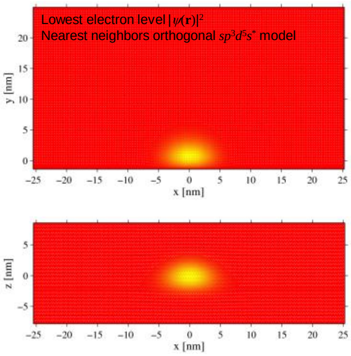


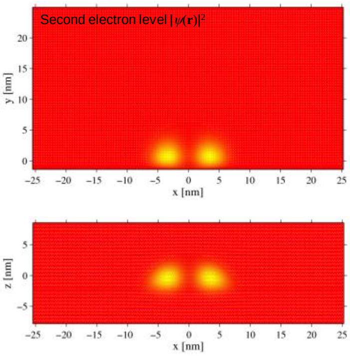


- The current flowing through the tip is plotted as a function of the tip position (at constant tip-sample distance). This roughly provides an image of the wavefunctions of the levels the electrons are tunneling onto.

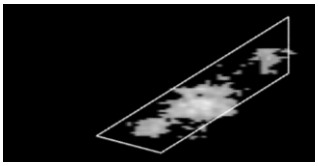
- **V = 0.69 V : The electrons can only tunnel onto the lowest level.**

Application : Wavefunction imaging (III)



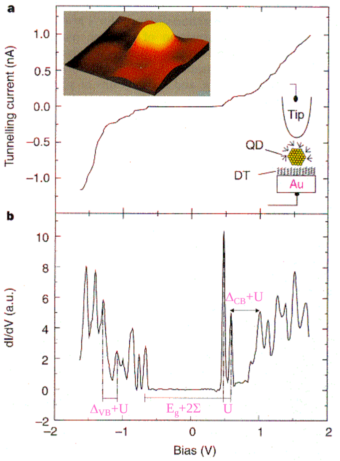


- **V = 0.82 V : The electrons can tunnel onto the first two levels.**

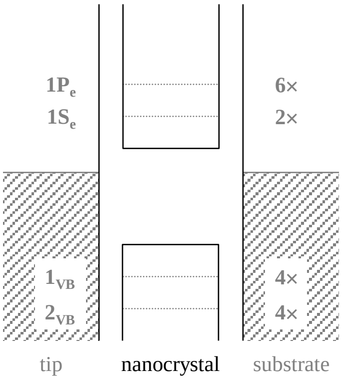


Application : Tunneling spectroscopy (I)

Diameter 6.4 nm

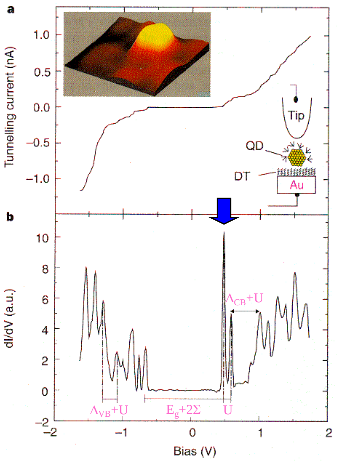


U. Banin *et al.*, Nature **400**, 542 (1999).

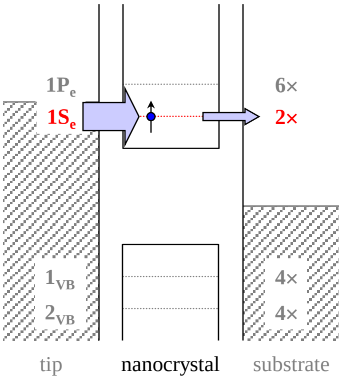


Applications : Tunneling spectroscopy (II)

Diameter 6.4 nm

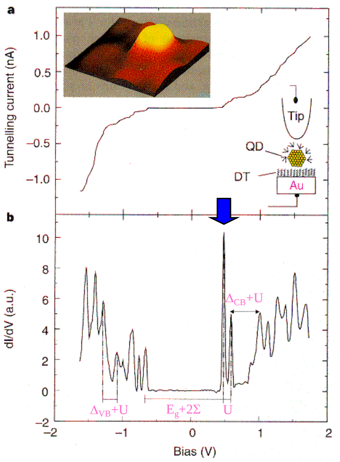


U. Banin *et al.*, Nature **400**, 542 (1999).

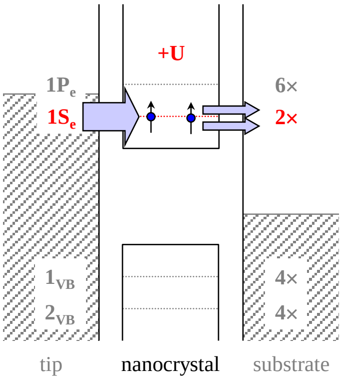


Applications : Tunneling spectroscopy (III)

Diameter 6.4 nm



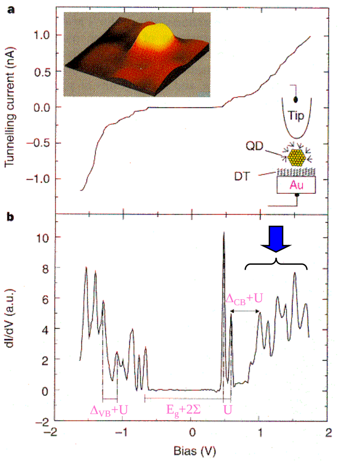
U. Banin *et al.*, Nature **400**, 542 (1999).



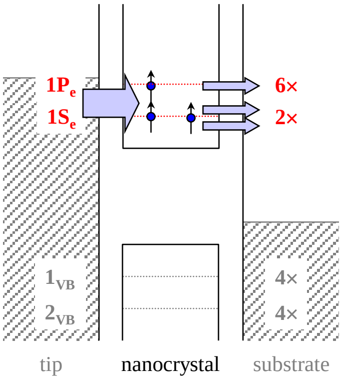
U : Addition energy

Applications : Tunneling spectroscopy (IV)

Diameter 6.4 nm

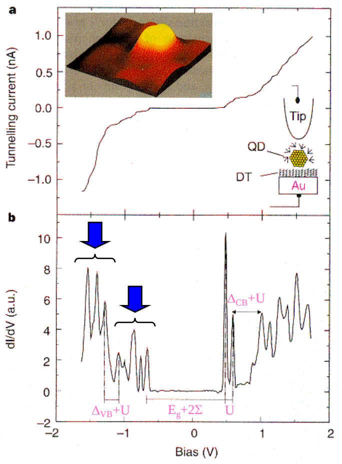


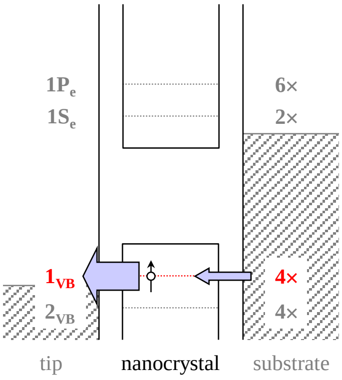
U. Banin *et al.*, Nature **400**, 542 (1999).



Applications : Tunneling spectroscopy (V)

Diameter 6.4 nm

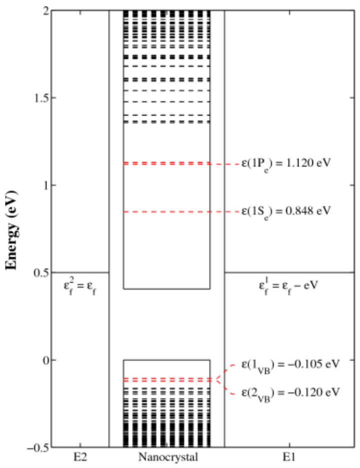


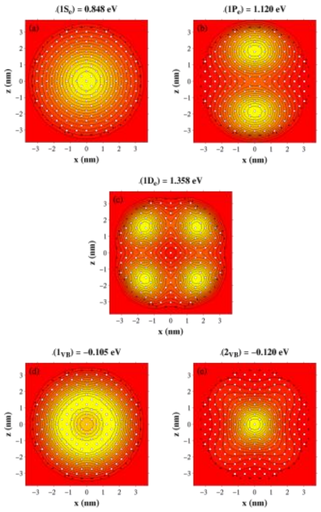


U. Banin *et al.*, Nature **400**, 542 (1999).

Applications : Tunneling spectroscopy (VI)

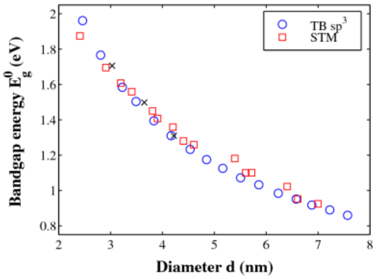
Diameter 6.4 nm

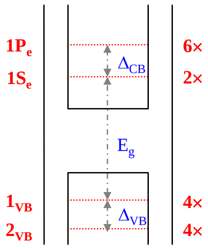




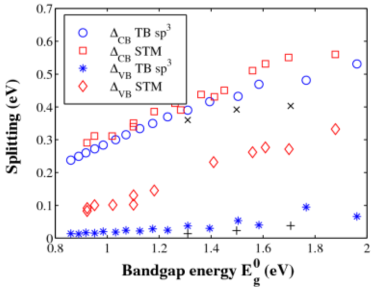
Second nearest-neighbors orthogonal sp^3 model

Applications : Tunneling spectroscopy (VII)

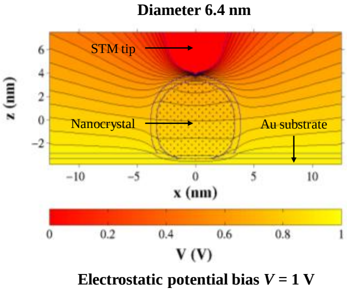




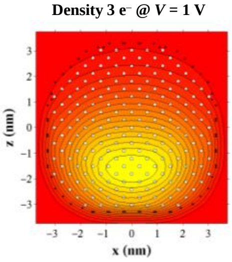
- The calculated **bandgap energies** and **electron levels splittings** are in very good agreement with the experiment.
- **Controversy** about the interpretation of Δ_{VB}.

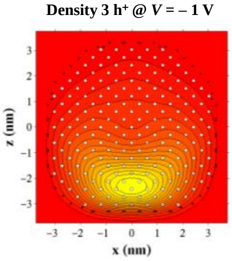


Applications : Tunneling spectroscopy (VIII)


Diameter 6.4 nm

Electrostatic potential bias $V = 1$ V

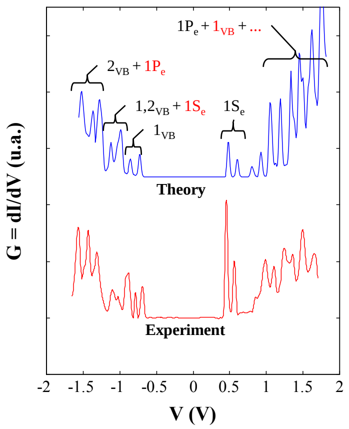

Density 3 e$^-$ @ $V = 1$ V


Density 3 h$^+$ @ $V = -1$ V

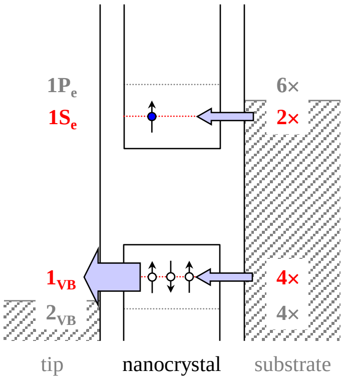
- We have computed the full $I(V)$ curve using the so-called orthodox theory. Electron-electron interactions were taken into account self-consistently.

Applications : Tunneling spectroscopy (IX)

Diameter 6.4 nm



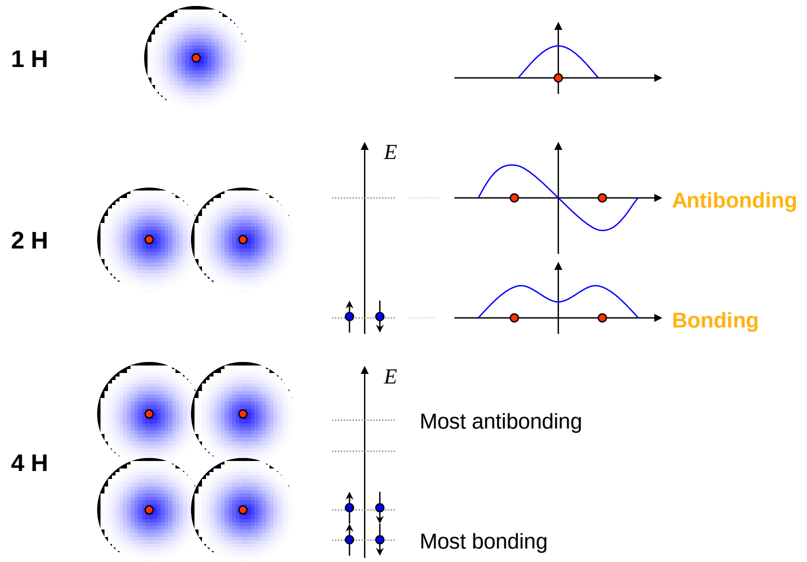
Y. M. Niquet et al., Phys. Rev. B **64**, 113305 (2001)



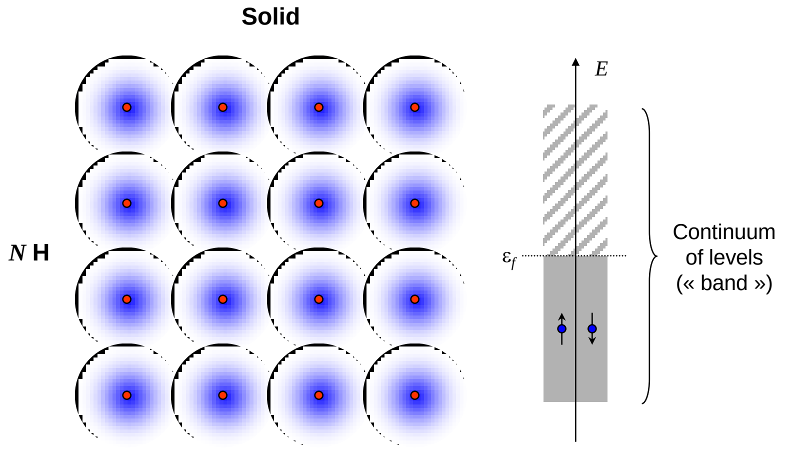
- **Injection of both electrons and holes** at high enough positive or negative bias.
- Measurement of Δ_{VB} practically impossible.

II.3 : The **k·p** approximation

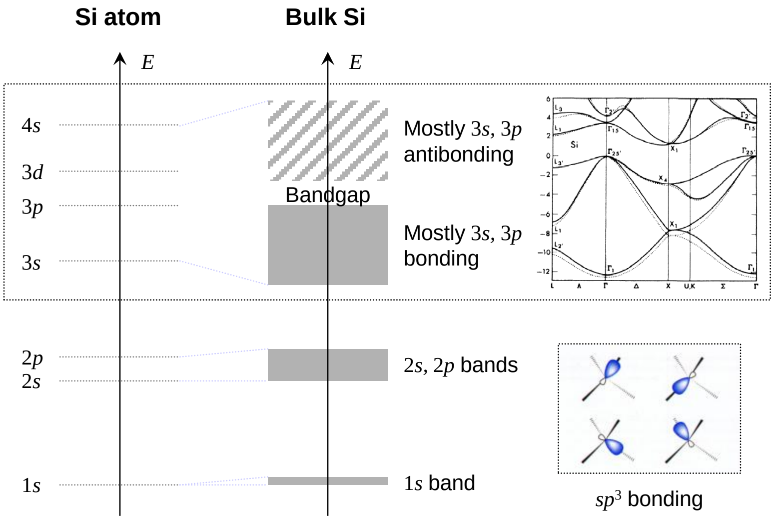
From the atom to the solid (I)



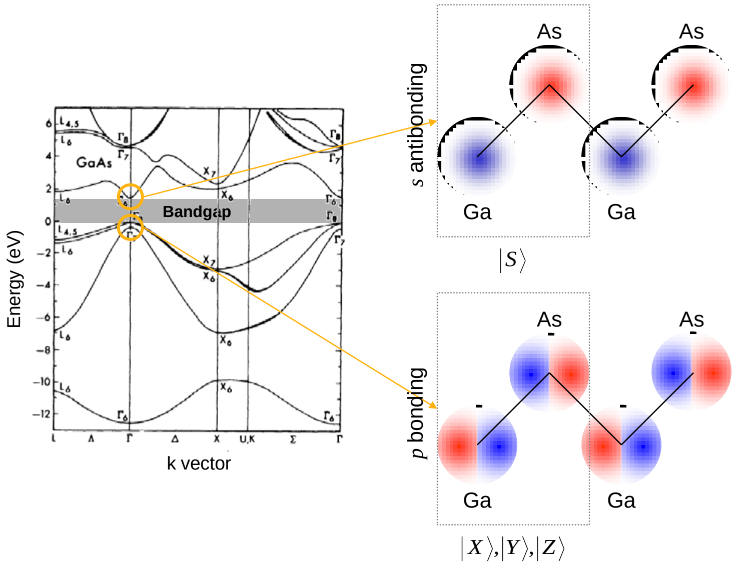
From the atom to the solid (II)



The case of bulk semiconductors (I)



The case of bulk semiconductors (II)



The equation for the periodic part of Bloch waves (I)

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})+v_{eff}(\mathbf{r})\varphi_{n\mathbf{k}}(\mathbf{r})=\varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{r}),\ \ \varphi_{n\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

- **Equation for** $u_{n\mathbf{k}}(\mathbf{r})$:

$$\bullet\ \Delta_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})=\mathrm{div}\ \mathbf{grad}\ \varphi_{n\mathbf{k}}(\mathbf{r})=\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})$$

$$\begin{aligned}\bullet\ \nabla_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})&=\nabla_{\mathbf{r}}\left[e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})\right]=i\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})\\&=e^{i\mathbf{k}\cdot\mathbf{r}}\left[\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+i\mathbf{k}u_{n\mathbf{k}}(\mathbf{r})\right]\end{aligned}$$

$$\begin{aligned}\bullet\ \nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}}\varphi_{n\mathbf{k}}(\mathbf{r})&=\nabla_{\mathbf{r}}\cdot\left(e^{i\mathbf{k}\cdot\mathbf{r}}\left[\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+i\mathbf{k}u_{n\mathbf{k}}(\mathbf{r})\right]\right)\\&=ie^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{k}\cdot\left[\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+i\mathbf{k}u_{n\mathbf{k}}(\mathbf{r})\right]\\&\quad+e^{i\mathbf{k}\cdot\mathbf{r}}\left[\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+i\mathbf{k}\cdot\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})\right]\\&=e^{i\mathbf{k}\cdot\mathbf{r}}\left[\Delta_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})+2i\mathbf{k}\cdot\nabla_{\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})-\mathbf{k}^2u_{n\mathbf{k}}(\mathbf{r})\right]\end{aligned}$$

$$\bullet\ -\frac{\hbar^2}{2m_0}e^{i\mathbf{k}\cdot\mathbf{r}}\left[\Delta_{\mathbf{r}}+2i\mathbf{k}\cdot\nabla_{\mathbf{r}}-\mathbf{k}^2\right]u_{n\mathbf{k}}(\mathbf{r})+v_{eff}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})=\varepsilon_{n\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

$$\frac{1}{2m_0}\left[\mathbf{p}^2+(\hbar\mathbf{k})^2+2\hbar\mathbf{k}\cdot\mathbf{p}\right]u_{n\mathbf{k}}(\mathbf{r})+v_{eff}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})=\varepsilon_{n\mathbf{k}}u_{n\mathbf{k}}(\mathbf{r})$$

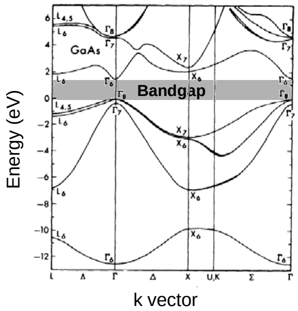
The equation for the periodic part of Bloch waves (II)

$$\frac{1}{2m_0}\left[\mathbf{p}^2+(\hbar\mathbf{k})^2+2\hbar\mathbf{k}\cdot\mathbf{p}\right]u_{n\mathbf{k}}(\mathbf{r})+v_{eff}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})=\varepsilon_{n\mathbf{k}}u_{n\mathbf{k}}(\mathbf{r})\ \ \text{[k - dependent hamiltonian]}$$

- One equation for each $\mathbf{k}$.
  The solutions must be chosen **periodic** with the real space lattice :

$$u_{n\mathbf{k}}(\mathbf{r}+n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3)=u_{n\mathbf{k}}(\mathbf{r})\ \ \forall(n_1,n_2,n_3)\in Z^3$$

Periodic boundary conditions on unit cell volume $\Omega_0 \Rightarrow$ discrete spectrum (bands).



We define the following dot product for the periodic $u_{n\mathbf{k}}$'s :

$$\langle u_{m\mathbf{k}'}|u_{n\mathbf{k}}\rangle_{\Omega_0}=\frac{1}{\Omega_0}\int_{\Omega_0}d^3r\,u^*_{m\mathbf{k}'}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})$$

We normalize the $u_{n\mathbf{k}}$'s such that :

$$\langle u_{m\mathbf{k}}|u_{n\mathbf{k}}\rangle_{\Omega_0}=\delta_{nm}$$

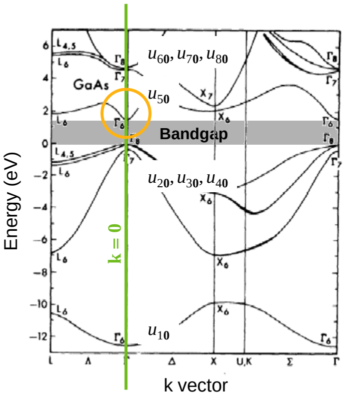
Beware :

$$\langle u_{m\mathbf{k}'}|u_{n\mathbf{k}}\rangle_{\Omega_0}\neq 0\ \text{ if }\mathbf{k}\neq\mathbf{k}'$$

k·**p** theory in bulk solids (I)

- Let us assume that we were (hardly !) able to solve this equation for a $\mathbf{k}$ point of utmost interest (e.g. $\mathbf{k} = \mathbf{0}$) :

$$\frac{\mathbf{p}^2}{2m_0} u_{n\mathbf{0}}(\mathbf{r}) + v_{eff}(\mathbf{r}) u_{n\mathbf{0}}(\mathbf{r}) = \varepsilon_{n\mathbf{0}} u_{n\mathbf{0}}(\mathbf{r})$$



We now want to get the lowest conduction band energy $\varepsilon_{5\mathbf{k}}$ around $\mathbf{k} = \mathbf{0}$ without having to do this laborious calculation again for each $\mathbf{k}$…

---

k·**p** theory in bulk solids (II)

- What we know :

$$\frac{\mathbf{p}^2}{2m_0} u_{n\mathbf{0}}(\mathbf{r}) + v_{eff}(\mathbf{r}) u_{n\mathbf{0}}(\mathbf{r}) = \varepsilon_{n\mathbf{0}} u_{n\mathbf{0}}(\mathbf{r})$$

- What we want :

$$\frac{1}{2m_0}\left[\mathbf{p}^2 + (\hbar\mathbf{k})^2 + 2\hbar\mathbf{k}\cdot\mathbf{p}\right] u_{5\mathbf{k}}(\mathbf{r}) + v_{eff}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) = \varepsilon_{5\mathbf{k}} u_{5\mathbf{k}}(\mathbf{r}) \quad \text{for small } \mathbf{k}$$

$$\frac{\mathbf{p}^2}{2m_0} u_{5\mathbf{k}}(\mathbf{r}) + v_{eff}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) + \frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p}u_{5\mathbf{k}}(\mathbf{r}) = \left[\varepsilon_{5\mathbf{k}} - \frac{\hbar^2\mathbf{k}^2}{2m_0}\right] u_{5\mathbf{k}}(\mathbf{r})$$

- What to do :
  - The $\mathbf{k}\cdot\mathbf{p}$ term is the only one that changes $u_{50}(\mathbf{r})$ into $u_{5\mathbf{k}}(\mathbf{r})$!
  - We are only interested in small $\mathbf{k}$'s.
  - The conduction band $\varepsilon_{5\mathbf{k}}$ is well separated from the others.

Treat the k·p term in perturbation !!

First-order perturbation theory

- We get at once :

$$\varepsilon_{5\mathbf{k}} - \frac{\hbar^2\mathbf{k}^2}{2m_0} = \varepsilon_{50} + \frac{\hbar}{m_0}\mathbf{k}\cdot\langle u_{50}|\mathbf{p}|u_{50}\rangle_{\Omega_0}$$

However, $u_{50}(\mathbf{r})$ periodic $\Rightarrow \langle u_{50}|\mathbf{p}|u_{50}\rangle_{\Omega_0} = -i\hbar\langle u_{50}|\nabla_{\mathbf{r}}|u_{50}\rangle_{\Omega_0} = \mathbf{0}$

As a consequence,

$$\varepsilon_{5\mathbf{k}} = \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m_0} \quad \text{(Free electron band)}$$

Far from the actual result !!

Second-order perturbation theory (I)

- Let us proceed with second-order perturbation theory :

$$\varepsilon_{5\mathbf{k}} = \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{n\neq 5}\frac{\left|\mathbf{k}\cdot\boldsymbol{\pi}_{n5}\right|^2}{\varepsilon_{50}-\varepsilon_{n\mathbf{0}}} \quad \text{where} \quad \boldsymbol{\pi}_{n5} = \langle u_{n\mathbf{0}}|\mathbf{p}|u_{50}\rangle_{\Omega_0}$$

$$= \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{n\neq 5}\frac{\left|\sum_{\alpha=x,y,z}k_\alpha\pi_{n5}^\alpha\right|^2}{\varepsilon_{50}-\varepsilon_{n\mathbf{0}}} \quad \text{where } k_\alpha = \boldsymbol{\alpha}\cdot\mathbf{k} \text{ and } \pi_{n5}^\alpha = \boldsymbol{\alpha}\cdot\boldsymbol{\pi}_{n5}$$

$$= \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{n\neq 5}\sum_{\alpha=x,y,z}\sum_{\beta=x,y,z}k_\alpha\frac{\pi_{n5}^\alpha\pi_{n5}^{\beta*}}{\varepsilon_{50}-\varepsilon_{n\mathbf{0}}}k_\beta$$

It can be shown that for symmetry reasons (only for the lowest conduction band at $\mathbf{k} = \mathbf{0}$ in direct gap semiconductors !) :

- The $\alpha \neq \beta$ terms cancel each other.
- The remaining $\alpha = \beta$ terms are all equal.

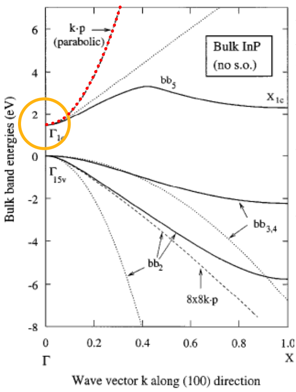
$$\varepsilon_{5\mathbf{k}} = \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m_0} + \frac{\hbar^2}{m_0^2}\sum_{n\neq 5}\frac{\pi_{n5}^z\pi_{n5}^{z*}}{\varepsilon_{50}-\varepsilon_{n\mathbf{0}}}\left(k_x^2+k_y^2+k_z^2\right)$$

$$\varepsilon_{5\mathbf{k}} = \varepsilon_{50} + \frac{\hbar^2\mathbf{k}^2}{2m^*} \quad \text{where} \quad \frac{1}{m^*} = \frac{1}{m_0} + \frac{2}{m_0^2}\sum_{n\neq 5}\frac{\left|\langle u_{n\mathbf{0}}|p_z|u_{50}\rangle_{\Omega_0}\right|^2}{\varepsilon_{50}-\varepsilon_{n\mathbf{0}}}$$

The effective mass

$$\varepsilon_{5\mathbf{k}} = \varepsilon_{5\mathbf{0}} + \frac{\hbar^2 \mathbf{k}^2}{2m^*} \quad \text{where} \quad \frac{1}{m^*} = \frac{1}{m_0} + \frac{2}{m_0^2} \sum_{n\neq 5} \frac{\left| \langle u_{n\mathbf{0}} | p_z | u_{5\mathbf{0}} \rangle_{\Omega_0} \right|^2}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_{5\mathbf{k}}}{\partial k^2}$$

- Free-electron-like band with an **effective mass** m^* :



H. Fu, L.-W. Wang and A. Zunger, Phys. Rev. B **57**, 9971 (1998).

Only works well around $\mathbf{k} = \mathbf{0}$.
This is just second order perturbation theory !

Lower m^* ⇒ more dispersive band !

Practically m^* is known from, e.g., cyclotron resonance experiments.

	m^* (m_0)
InAs	0.023
GaAs	0.067
CdSe	0.130

The first-order $u_{5\mathbf{k}}$

- First-order perturbation theory (for the wavefunction) :

$$u_{5\mathbf{k}}(\mathbf{r}) = u_{5\mathbf{0}}(\mathbf{r}) + \frac{\hbar}{m_0} \sum_{n\neq 5} \frac{\mathbf{k}\cdot\boldsymbol{\pi}_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} u_{n\mathbf{0}}(\mathbf{r}) \quad \text{where} \quad \boldsymbol{\pi}_{n5} = \langle u_{n\mathbf{0}} | \mathbf{p} | u_{5\mathbf{0}} \rangle_{\Omega_0}$$

As a consequence,

$$\langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = \underbrace{\langle u_{5\mathbf{0}} | u_{5\mathbf{0}} \rangle_{\Omega_0}}_{1} + \frac{\hbar}{m_0} \sum_{n\neq 5} \frac{\mathbf{k}\cdot\boldsymbol{\pi}_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} \underbrace{\langle u_{5\mathbf{0}} | u_{n\mathbf{0}} \rangle_{\Omega_0}}_{0}$$

$$+ \frac{\hbar}{m_0} \sum_{n\neq 5} \frac{\mathbf{k}'\cdot\boldsymbol{\pi}^*_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} \underbrace{\langle u_{n\mathbf{0}} | u_{5\mathbf{0}} \rangle_{\Omega_0}}_{0} + \frac{\hbar^2}{m_0^2} \sum_{n\neq 5} \sum_{m\neq 5} \frac{\mathbf{k}'\cdot\boldsymbol{\pi}^*_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{m\mathbf{0}}} \frac{\mathbf{k}\cdot\boldsymbol{\pi}_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} \underbrace{\langle u_{m\mathbf{0}} | u_{n\mathbf{0}} \rangle_{\Omega_0}}_{\delta_{nm}}$$

$$\langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = 1 + \frac{\hbar^2}{m_0^2} \sum_{n\neq 5} \frac{\mathbf{k}'\cdot\boldsymbol{\pi}^*_{m5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}} \frac{\mathbf{k}\cdot\boldsymbol{\pi}_{n5}}{\varepsilon_{5\mathbf{0}} - \varepsilon_{n\mathbf{0}}}$$

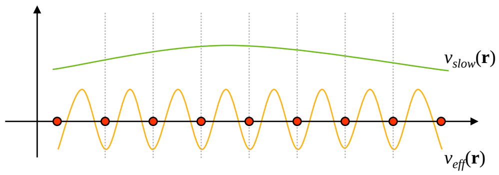
$$\langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = 1 + O(kk')$$

Electrons in slowly varying potentials

- Let us now add a « slowly » varying potential $v_{slow}(\mathbf{r})$ to the effective potential $v_{eff}(\mathbf{r})$ (for example the potential created by external electrodes). The one-particle wavefunctions $\varphi_n(\mathbf{r})$ and energies ε_n now satisfy :

$$-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}\varphi_n(\mathbf{r})+v_{eff}(\mathbf{r})\varphi_n(\mathbf{r})+v_{slow}(\mathbf{r})\varphi_n(\mathbf{r})=\varepsilon_n\varphi_n(\mathbf{r})$$

NB : « slowly » varying means that $v_{slow}(\mathbf{r})$ does not change much on the scale of the unit cell :



The effective mass equation (I)

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

- We look for the lowest-lying electron states.
  We expand $\varphi(\mathbf{r})$ in Bloch waves :

$$\varphi(\mathbf{r})=\sum_{n\mathbf{k}}\alpha_{n\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

and assume $|\alpha_{n\mathbf{k}}| << |\alpha_{5\mathbf{k}}|$, $n \neq 5$. Since $v_{slow}(\mathbf{r})$ is slowly varying, we also expect $|\alpha_{5\mathbf{k}}|$ to decrease rapidly with $|\mathbf{k}|$.
We then easily get, dropping all $n \neq 5$ terms :

$$\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}\left[-\frac{\hbar^2}{2m_0}\Delta_{\mathbf{r}}+v_{eff}(\mathbf{r})+v_{slow}(\mathbf{r})\right]e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})=\varepsilon\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})$$
$$\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}\left[\varepsilon_{5\mathbf{k}}+v_{slow}(\mathbf{r})\right]e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})=\varepsilon\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})$$
$$\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}\left[\varepsilon_{5\mathbf{k}}-\varepsilon+v_{slow}(\mathbf{r})\right]e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})=0$$

The effective mass equation (II)

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}} \left[\varepsilon_{5\mathbf{k}} - \varepsilon + v_{slow}(\mathbf{r})\right] e^{i\mathbf{k}\cdot\mathbf{r}} u_{5\mathbf{k}}(\mathbf{r}) = 0$$

- We next multiply by $e^{-i\mathbf{k}'\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r})$ and integrate over space :

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}} \left[(\varepsilon_{5\mathbf{k}} - \varepsilon)\int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) + \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})\right] = 0 \quad \forall \mathbf{k}'$$

We have :

$$\int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) = \delta(\mathbf{k}'-\mathbf{k}) \text{ [Bloch waves orthogonality]}$$

The effective mass equation (III)

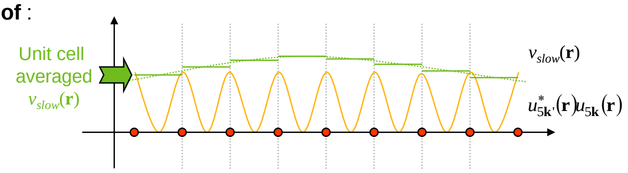
- For small enough |**k**| and |**k'**|,

$$\int d^3r \underbrace{e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r})}_{\text{Slowly varying}} \underbrace{u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})}_{\text{Rapidly varying}} \approx \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) \frac{1}{\Omega_0} \int_{\Omega_0} d^3r u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})$$

$$\approx \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) \langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0}$$

- **Proof** :

.



$$\int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3} \int_{\Omega_0} d^3r \underbrace{e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}+\mathbf{R})} v_{slow}(\mathbf{r}+\mathbf{R})}_{\substack{\text{Almost constant within } \Omega_0 \\ \text{Replace with its average value} \\ \text{in the unit cell}}} u^*_{5\mathbf{k}'}(\mathbf{r}+\mathbf{R}) u_{5\mathbf{k}}(\mathbf{r}+\mathbf{R})$$

$$\approx \sum_{\mathbf{R}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3} \frac{1}{\Omega_0} \int_{\Omega_0} d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}+\mathbf{R})} v_{slow}(\mathbf{r}+\mathbf{R}) \int_{\Omega_0} d^3r u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})$$

$$\approx \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) \frac{1}{\Omega_0} \int_{\Omega_0} d^3r u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})$$

The effective mass equation (IV)

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}} \left[\varepsilon_{5\mathbf{k}} - \varepsilon + v_{slow}(\mathbf{r})\right] e^{i\mathbf{k}\cdot\mathbf{r}} u_{5\mathbf{k}}(\mathbf{r}) = 0$$

- We next multiply by $e^{-i\mathbf{k}'\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r})$ and integrate over space :

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}} \left[(\varepsilon_{5\mathbf{k}} - \varepsilon)\int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) + \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r})\right] = 0 \quad \forall \mathbf{k}'$$

We have :

$$\begin{cases} \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) = \delta(\mathbf{k}'-\mathbf{k}) & \text{[Bloch waves orthogonality]} \\ \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v_{slow}(\mathbf{r}) u^*_{5\mathbf{k}'}(\mathbf{r}) u_{5\mathbf{k}}(\mathbf{r}) \approx \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) \langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} & [v_{slow}(\mathbf{r}) \text{ slowly varying]} \end{cases}$$

Hence we get :

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}'} (\varepsilon_{5\mathbf{k}'} - \varepsilon) \delta(\mathbf{k}'-\mathbf{k}) + \alpha_{5\mathbf{k}} \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) \langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = 0 \quad \forall \mathbf{k}'$$

The effective mass equation (V)

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}'} (\varepsilon_{5\mathbf{k}'} - \varepsilon) \delta(\mathbf{k}'-\mathbf{k}) + \alpha_{5\mathbf{k}} \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) \langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = 0 \quad \forall \mathbf{k}'$$

- We then use $\mathbf{k}\cdot\mathbf{p}$ theory for $\varepsilon_{5\mathbf{k}'}$ and $\langle u_{5\mathbf{k}'}|u_{5\mathbf{k}}\rangle_\Omega$:

$$\begin{cases} \varepsilon_{5\mathbf{k}'} = \varepsilon_{50} + \dfrac{\hbar^2 \mathbf{k}'^2}{2m^*} + \ldots \\ \langle u_{5\mathbf{k}'} | u_{5\mathbf{k}} \rangle_{\Omega_0} = 1 + O(kk') \end{cases}$$

Dropping all terms that couple $\mathbf{k}$ and $v_{slow}(\mathbf{r})$ [i.e. O(kk')], we end up with :

$$\sum_{\mathbf{k}} \alpha_{5\mathbf{k}'} \left(\varepsilon_{50} + \frac{\hbar^2 \mathbf{k}'^2}{2m^*} - \varepsilon \right) \delta(\mathbf{k}'-\mathbf{k}) + \alpha_{5\mathbf{k}} \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) = 0 \quad \forall \mathbf{k}'$$

- We last go back to real space - We multiply by $e^{i\mathbf{k}'\cdot\mathbf{r}}$ and sum over $\mathbf{k}'$:

$$\sum_{\mathbf{k}'} \sum_{\mathbf{k}} \alpha_{5\mathbf{k}'} \left(\varepsilon_{50} + \frac{\hbar^2 \mathbf{k}'^2}{2m^*} - \varepsilon \right) \delta(\mathbf{k}'-\mathbf{k}) e^{i\mathbf{k}'\cdot\mathbf{r}} + \sum_{\mathbf{k}'} \sum_{\mathbf{k}} \alpha_{5\mathbf{k}} \hat{v}_{slow}(\mathbf{k}'-\mathbf{k}) e^{i\mathbf{k}'\cdot\mathbf{r}} = 0$$

The effective mass equation (VI)

- We easily get :

$$\sum_{\mathbf{k}'}\sum_{\mathbf{k}}\alpha_{5\mathbf{k}'}\left(\varepsilon_{50}+\frac{\hbar^2\mathbf{k}'^2}{2m^*}-\varepsilon\right)\delta(\mathbf{k}'-\mathbf{k})e^{i\mathbf{k}'\cdot\mathbf{r}}+\sum_{\mathbf{k}'}\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}\hat{v}_{slow}(\mathbf{k}'-\mathbf{k})e^{i\mathbf{k}'\cdot\mathbf{r}}=0$$

$$\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\left(\varepsilon_{50}+\frac{\hbar^2\mathbf{k}^2}{2m^*}-\varepsilon\right)+\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{k}'}\hat{v}_{slow}(\mathbf{k}'-\mathbf{k})e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}=0$$

$$\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\left(\varepsilon_{50}+\frac{\hbar^2\mathbf{k}^2}{2m^*}-\varepsilon\right)+\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\underbrace{\sum_{\mathbf{k}''}\hat{v}_{slow}(\mathbf{k}'')e^{i\mathbf{k}''\cdot\mathbf{r}}}_{v_{slow}(\mathbf{r})}=0\quad[\mathbf{k}''=\mathbf{k}'-\mathbf{k}]$$

- Let us finally introduce :

$$\psi(\mathbf{r})=\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Rightarrow\nabla_{\mathbf{r}}\psi(\mathbf{r})=\sum_{\mathbf{k}}i\mathbf{k}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Rightarrow\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}}\psi(\mathbf{r})=\Delta_{\mathbf{r}}\psi(\mathbf{r})=-\sum_{\mathbf{k}}\mathbf{k}^2\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

$\psi(\mathbf{r})$ thus satisfies the following equation :

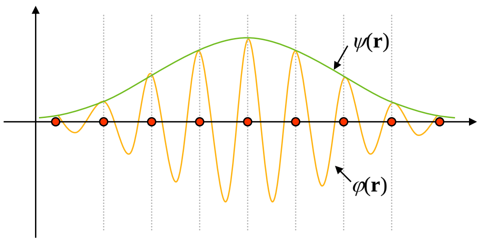
$$\left(\varepsilon_{50}-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}-\varepsilon\right)\psi(\mathbf{r})+v_{slow}(\mathbf{r})\psi(\mathbf{r})=0$$

The effective mass equation (VII)

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r})+v_{slow}(\mathbf{r})\psi(\mathbf{r})=(\varepsilon-\varepsilon_{50})\psi(\mathbf{r})$$

- $\psi(\mathbf{r})$ is called the « **envelope** » function. The **true** conduction band wavefunction indeed reads :

$$\varphi(\mathbf{r})=\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{5\mathbf{k}}(\mathbf{r})\approx\sum_{\mathbf{k}}\alpha_{5\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{50}(\mathbf{r})\approx\psi(\mathbf{r})u_{50}(\mathbf{r})$$



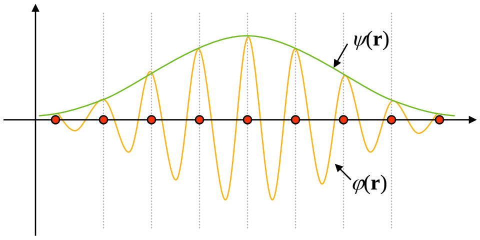
The effective mass equation (VIII)

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r})+v_{slow}(\mathbf{r})\psi(\mathbf{r})=(\varepsilon-\varepsilon_{50})\psi(\mathbf{r})$$

- NB : If $v_{slow}(\mathbf{r}) = 0$, we recover Bloch waves as the solutions of the effective mass equation :

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r})=(\varepsilon-\varepsilon_{50})\psi(\mathbf{r})\Rightarrow\begin{cases}\varepsilon=\varepsilon_{50}+\dfrac{\hbar^2\mathbf{k}^2}{2m^*}\\ \psi(\mathbf{r})\propto e^{i\mathbf{k}\cdot\mathbf{r}}\ \left[\varphi(\mathbf{r})=\psi(\mathbf{r})u_{50}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{50}(\mathbf{r})\right]\end{cases}$$

Interpretation of the envelope function



- $|\varphi(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2\ |u_{50}(\mathbf{r})|^2$ is the probability to find the electron at $\mathbf{r}$.
  The probability $p(\mathbf{r})$ to find the electron in an unit cell around $\mathbf{r}$ is therefore :

$$p(\mathbf{r})=\int_{\Omega_0}d^3v\left|\varphi(\mathbf{r}+\mathbf{v})\right|^2=\int_{\Omega_0}d^3v\underbrace{\left|\psi(\mathbf{r}+\mathbf{v})\right|^2}_{\text{Slowly varying}}\left|u_{50}(\mathbf{r}+\mathbf{v})\right|^2$$

$$\approx\int_{\Omega_0}d^3v\left|\psi(\mathbf{r}+\mathbf{v})\right|^2\underbrace{\frac{1}{\Omega_0}\int_{\Omega_0}d^3v\left|u_{50}(\mathbf{r}+\mathbf{v})\right|^2}_{1}\approx\int_{\Omega_0}d^3v\left|\psi(\mathbf{r}+\mathbf{v})\right|^2\approx\Omega_0\left|\psi(\mathbf{r})\right|^2$$

$|\psi(\mathbf{r})|^2=p(\mathbf{r})/\Omega_0$ is thus the unit cell-averaged probability to find the electron at $\mathbf{r}$.

Ehrenfest's theorem

- Time-dependent version of the effective mass equation :

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r};t)+v_{slow}(\mathbf{r})\psi(\mathbf{r};t)=i\hbar\frac{\partial\psi(\mathbf{r};t)}{\partial t}$$

Ehrenfest's theorem for the average position $\mathbf{r}$ and « impulsion » $\mathbf{p}=-i\hbar\nabla_{\mathbf{r}}$:

$$\begin{cases}\dfrac{d}{dt}\langle\mathbf{r}\rangle(t)=\dfrac{1}{m^*}\langle\mathbf{p}\rangle(t)\\ \dfrac{d}{dt}\langle\mathbf{p}\rangle(t)=-\langle\nabla_{\mathbf{r}}v_{slow}\rangle(t)\end{cases}\quad\text{where }\langle\mathbf{A}\rangle(t)=\langle\psi(\mathbf{r};t)|\mathbf{A}|\psi(\mathbf{r};t)\rangle$$

(**Semi-)classical limit** : if $\psi(\mathbf{r};t)$ is localized enough with respect to $v_{slow}(\mathbf{r})$, the electron appears as a classical particle with position $\mathbf{r}_e=\langle\mathbf{r}\rangle(t)$ and impulsion $\mathbf{p}_e=\langle\mathbf{p}\rangle(t)$:

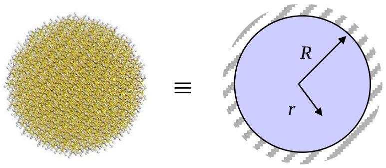
$$\begin{cases}\dfrac{d}{dt}\mathbf{r}_e(t)\approx\dfrac{1}{m^*}\mathbf{p}_e(t)\\ \dfrac{d}{dt}\mathbf{p}_e(t)\approx-\nabla_{\mathbf{r}}v_{slow}[\mathbf{r}_e(t)]=\mathbf{F}_{class}\end{cases}$$

Newton's equations with an effective mass m^*

Application : The spherical nanocrystal (I)

Infinite spherical well model :

$$\begin{cases}v_{conf}(r)=0\ \text{ if }\ r<R\\ v_{conf}(r)=+\infty\ \text{ if }\ r>R\end{cases}$$



- We are looking for the lowest conduction band state. The latter satisfies :

$$\begin{cases}-\dfrac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r})=(\varepsilon-\varepsilon_{50})\psi(\mathbf{r})\ \text{ if } r<R\\ \psi(\mathbf{r})=0\ \text{ if } r>R\end{cases}$$

We now take $\varepsilon_{50}=0$ as the reference of energies for simplicity.

- Since the potential has spherical symmetry, we may split $\psi(\mathbf{r})$ as follows :

$$\psi(\mathbf{r})\equiv\underbrace{R_{nl}(r)}_{\text{Radial part}}\times\underbrace{Y_{lm}(\theta,\varphi)}_{\text{Spherical harmonic}}$$

The lowest electron state will likely be s-like ($Y_{lm}=Y_{00}$ = constant) :

$$\psi(\mathbf{r})\equiv R_{n0}(r)$$

Application : The spherical nanocrystal (II)

- The effective mass equation then simplifies into :

$$\begin{cases} -\dfrac{\hbar^2}{2m^*}\dfrac{1}{r}\dfrac{\partial^2[rR_{n0}(r)]}{\partial r^2} = \varepsilon_{n0}R_{n0}(r) \text{ if } r < R \ [\text{Laplacian in spherical coordinates}] \\ R_{n0}(r) = 0 \text{ if } r > R \end{cases}$$

We look for $R_{n0}(r)$ in the form $R_{n0}(r) = f_{n0}(r)/r$:

$$\begin{cases} \dfrac{\partial^2[f_{n0}(r)]}{\partial r^2} = -\dfrac{2m^*}{\hbar^2}\varepsilon_{n0} f_{n0}(r) \text{ if } r < R \\ \lim\limits_{r\to 0} f_{n0}(r) = 0 \text{ and } f_{n0}(r) = 0 \text{ if } r > R \end{cases}$$

The solutions of this equation read :

$$f_{n0}(r) = A\cos(kr) + B\sin(kr) \text{ if } r < R, \text{where } \hbar k = \sqrt{2m^*\varepsilon_{n0}}$$

We last enforce the boundary conditions :

$$\begin{cases} \lim\limits_{r\to 0} f_{n0}(r) = 0 \Rightarrow A = 0 \\ f_{n0}(R) = 0 \Rightarrow B\sin(kR) = 0 \ \Rightarrow k = \dfrac{\sqrt{2m^*\varepsilon_{n0}}}{\hbar} = \dfrac{(n+1)\pi}{R}, n > 0 \end{cases}$$

Application : The spherical nanocrystal (III)

- We thus finally get :

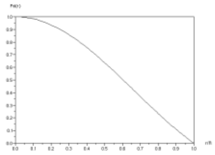
$$\begin{cases} \psi_{n0}(r) = B\dfrac{1}{r}\sin\left[\dfrac{(n+1)\pi}{R}r\right] \text{ if } r < R \\ \psi_{n0}(r) = 0 \text{ if } r > R \end{cases} \text{ with energy } \varepsilon_{n0} = \frac{\hbar^2\pi^2(n+1)^2}{2m^*R^2}$$

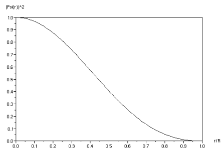
B is a normalization constant such that $\int d^3r|\psi_{n0}(\mathbf{r})|^2 = 1.$

- In particular,

$$\begin{cases} \psi_{00}(r) = \dfrac{1}{\sqrt{2\pi R}}\dfrac{1}{r}\sin\left[\dfrac{\pi}{R}r\right] \text{ if } r < R \\ \psi_{00}(r) = 0 \text{ if } r > R \end{cases} \text{ with energy } \varepsilon_{00} = \frac{\hbar^2\pi^2}{2m^*R^2}$$

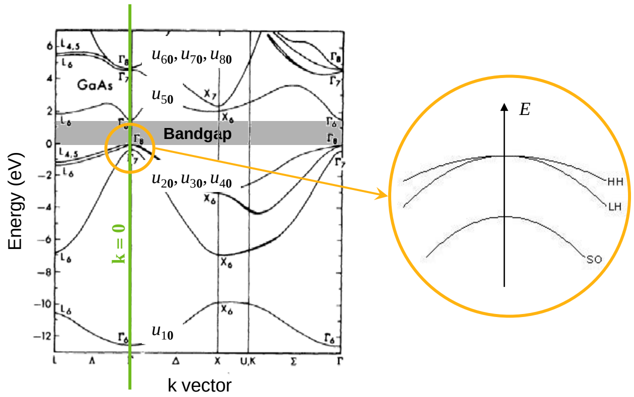
The $1/R^2$ dependence of the confinement energy is typical of the effective mass approximation with infinite barrier heights.





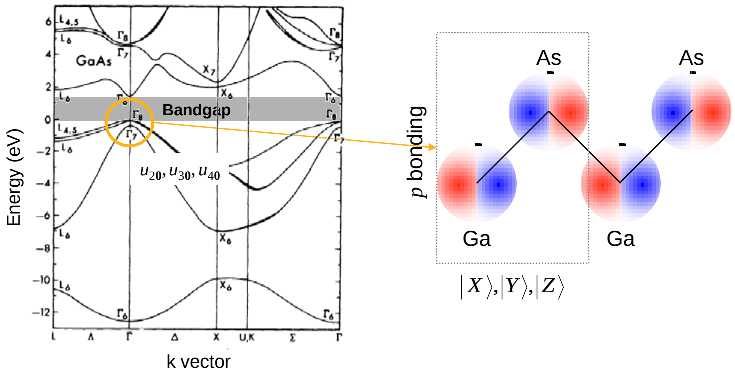
The valence band problem (I)

- We now wish to do $\mathbf{k}\cdot\mathbf{p}$ theory for, e.g., the highest valence band energy $\varepsilon_{4\mathbf{k}}$ around $\mathbf{k} = \mathbf{0}$…



Problem : There are three nearly degenerate highest valence bands around $\mathbf{k} = \mathbf{0}$. Standard second order perturbation theory will fail !

The valence band problem (II)



- According to this picture, there should be three degenerate highest valence bands at $\mathbf{k} = \mathbf{0}$, corresponding to bonding combinations of p_x, p_y, and p_z orbitals.

  This degeneracy is lifted by the so-called « **spin-orbit coupling** ».

Spin-orbit coupling

- Spin-orbit coupling is a **relativistic** effect…

Semi-classical image : Imagine you are riding an electron… The nuclei appear as moving charges in your frame ; they thus create a magnetic field that acts upon the spin of the electron.

The orbital motion of the electron thus couples to its spin ; hence the name « **spin-orbit coupling** ». The hamiltonian now reads :

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

where $v_{ion}(\mathbf{r})$ is the ionic potential and $\mathbf{S}$ is the electron spin.

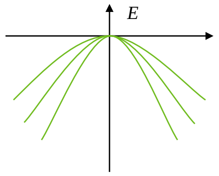
- As a consequence there are no more pure |↑> / |↓> states, but only mixed states :

$$\varphi(\mathbf{r})\equiv\varphi_{\uparrow}(\mathbf{r})\left|\uparrow\right\rangle+\varphi_{\downarrow}(\mathbf{r})\left|\downarrow\right\rangle$$ [Spatial modulation of spin]

Spin-orbit coupling actually has no effect on *s*-like atomic orbitals, thus little effect on the lowest conduction band.

The valence band structure at $\mathbf{k}=\mathbf{0}$

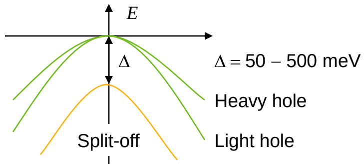
Without spin-orbit



$\left|X\uparrow\right\rangle,\left|X\downarrow\right\rangle,\left|Y\uparrow\right\rangle,\left|Y\downarrow\right\rangle,\left|Z\uparrow\right\rangle,\left|Z\downarrow\right\rangle$

all degenerate at $\mathbf{k}=\mathbf{0}$

With spin-orbit



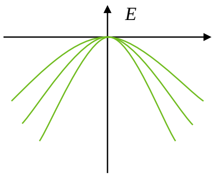
The highest valence bands $u_{n\mathbf{0}}$'s can be mapped onto the following eigenstates of $\mathbf{J}=\mathbf{L}+\mathbf{S}$ and J_z (where $\mathbf{L}$ is the orbital momentum) :

$$\left.\begin{aligned}\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle&=\frac{1}{\sqrt{2}}\left|(X-iY)\downarrow\right\rangle\\ \left|\tfrac{3}{2},+\tfrac{3}{2}\right\rangle&=\frac{1}{\sqrt{2}}\left|(X+iY)\uparrow\right\rangle\\ \left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle&=-\frac{1}{\sqrt{6}}\left|(X-iY)\uparrow\right\rangle-\sqrt{\frac{2}{3}}\left|Z\downarrow\right\rangle\\ \left|\tfrac{3}{2},+\tfrac{1}{2}\right\rangle&=\frac{1}{\sqrt{6}}\left|(X+iY)\downarrow\right\rangle-\sqrt{\frac{2}{3}}\left|Z\uparrow\right\rangle\end{aligned}\right\}\text{Heavy and light holes}$$

$$\left.\begin{aligned}\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle&=-\frac{1}{\sqrt{3}}\left|(X-iY)\uparrow\right\rangle+\frac{1}{\sqrt{3}}\left|Z\downarrow\right\rangle\\ \left|\tfrac{1}{2},+\tfrac{1}{2}\right\rangle&=\frac{1}{\sqrt{3}}\left|(X+iY)\downarrow\right\rangle+\frac{1}{\sqrt{3}}\left|Z\uparrow\right\rangle\end{aligned}\right\}\text{Split-off band}$$

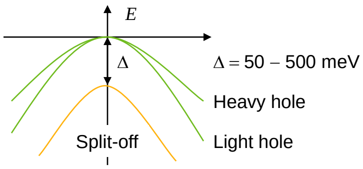
Kramers degeneracy

Without spin-orbit



The bands are **twofold** spin-degenerate (one |↑> and one |↓> band)

With spin-orbit



The bands remain **twofold** degenerate.

This is the so-called **Kramers** degeneracy, that has to do with time-reversal symmetry.

The degeneracy between |↑> and |↓> bands without spin-orbit coupling is just a special case of Kramers degeneracy

---

$\mathbf{k}\cdot\mathbf{p}$ theory for the valence band (I)

- We want to compute the effect of the $\mathbf{k}\cdot\mathbf{p}$ term on the highest valence bands away from $\mathbf{k}=\mathbf{0}$ (here leaving out the spin-orbit term for simplicity) :

$$\frac{\mathbf{p}^2}{2m_0}u_{n\mathbf{k}}(\mathbf{r})+v_{eff}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})+\frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p}u_{n\mathbf{k}}(\mathbf{r})=\left[\varepsilon_{n\mathbf{k}}-\frac{\hbar^2\mathbf{k}^2}{2m_0}\right]u_{n\mathbf{k}}(\mathbf{r})$$

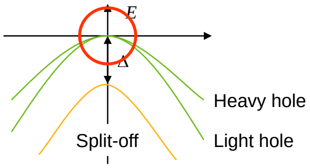
But we still have to face this near-degeneracy problem : straightforward second-order perturbation theory is bound to fail…

- **Solution** :
  - Treat exactly the $\mathbf{k}\cdot\mathbf{p}$ couplings in the $|J,m_j>$ manifold.
  - Treat the $\mathbf{k}\cdot\mathbf{p}$ couplings with remote bands in perturbation.

k·p theory for the valence band (II)

- **Example** : Suppose we are interested in the heavy and light hole bands right around $\mathbf{k} = \mathbf{0}$, within an energy range << Δ…

  We build the matrix of the $\mathbf{k}$–dependent hamiltonian in the basis :



$$\left\{\left|\frac{3}{2},+\frac{3}{2}\right\rangle,\left|\frac{3}{2},+\frac{1}{2}\right\rangle,\left|\frac{3}{2},-\frac{1}{2}\right\rangle,\left|\frac{3}{2},-\frac{3}{2}\right\rangle\right\}$$

We then correct the elements of this 4x4 matrix for the coupling with remote bands using second order perturbation theory.

We last diagonalize the 4x4 matrix and actually get twofold degenerate bands…

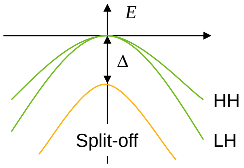
Luttinger's hamiltonian

- The 4x4 matrix in the $\left\{\left|\frac{3}{2},+\frac{3}{2}\right\rangle,\left|\frac{3}{2},+\frac{1}{2}\right\rangle,\left|\frac{3}{2},-\frac{1}{2}\right\rangle,\left|\frac{3}{2},-\frac{3}{2}\right\rangle\right\}$ basis reads :

$$H(\mathbf{k})=\frac{\hbar^2}{2m_0}\begin{bmatrix}-P-Q & -S & R & 0\\ -S^* & -P+Q & 0 & R\\ R^* & 0 & -P+Q & S\\ 0 & R^* & S^* & -P-Q\end{bmatrix} \quad \text{where} \quad \begin{cases}P=\gamma_1\mathbf{k}^2\\ Q=\gamma_2\left(k_x^2+k_y^2-2k_z^2\right)\\ R=\sqrt{3}\left[\gamma_2\left(k_x^2-k_y^2\right)-2i\gamma_3k_xk_y\right]\\ S=-2\sqrt{3}\gamma_3k_z\left(k_x-ik_y\right)\end{cases}$$

γ_1, γ_2 and γ_3 are the so-called « **Luttinger parameters** ». They can be expressed, like the conduction band effective mass, as a function of the $\boldsymbol{\pi}_{nm} = \langle u_{n\mathbf{0}}|\mathbf{p}|u_{m\mathbf{0}}\rangle$'s. Practically, we use experimental values derived from measurements of the valence band structure around $\mathbf{k} = \mathbf{0}$.

Light and heavy hole bands



- The eigenvalues of $H(\mathbf{k})$ are :

$$E(\mathbf{k}) = -\frac{\hbar^2}{2m_0}\gamma_1\mathbf{k}^2 \pm \frac{\hbar^2}{m_0}\sqrt{\gamma_2^2\mathbf{k}^4 + 3\left(\gamma_3^2-\gamma_2^2\right)\left(k_x^2k_y^2+k_y^2k_z^2+k_x^2k_z^2\right)}$$

- Let $\mathbf{k} = (0,0,k)$. We then get :

$$\begin{cases} E_{HH}(\mathbf{k}) = -\dfrac{\hbar^2}{2m_0}(\gamma_1-2\gamma_2)k^2 = -\dfrac{\hbar^2k^2}{2m^*_{HH}[001]} \text{ where } m^*_{HH}[001] = \dfrac{m_0}{\gamma_1-2\gamma_2} \\ E_{LH}(\mathbf{k}) = -\dfrac{\hbar^2}{2m_0}(\gamma_1+2\gamma_2)k^2 = -\dfrac{\hbar^2k^2}{2m^*_{LH}[001]} \text{ where } m^*_{LH}[001] = \dfrac{m_0}{\gamma_1+2\gamma_2} \end{cases}$$

Let $\mathbf{k} = (k,k,k)/\sqrt{3}$. We then get :

$$\begin{cases} E_{HH}(\mathbf{k}) = -\dfrac{\hbar^2}{2m_0}(\gamma_1-2\gamma_3)k^2 = -\dfrac{\hbar^2k^2}{2m^*_{HH}[111]} \text{ where } m^*_{HH}[111] = \dfrac{m_0}{\gamma_1-2\gamma_3} \\ E_{LH}(\mathbf{k}) = -\dfrac{\hbar^2}{2m_0}(\gamma_1+2\gamma_3)k^2 = -\dfrac{\hbar^2k^2}{2m^*_{LH}[111]} \text{ where } m^*_{LH}[111] = \dfrac{m_0}{\gamma_1+2\gamma_3} \end{cases}$$

Anisotropic heavy and light hole masses !

Valence band warping

Shape of the heavy hole band
energy surfaces in Si

Shape of the light hole band
energy surfaces in Si

- The energy surfaces around $\mathbf{k} = \mathbf{0}$ are are deformed or « warped » spheres. As a consequence the valence bands can not be characterized by a single effective mass.

- It is not possible to make an accurate single band approximation for the holes except in special circumstances (some quantum wells and strained systems). A full 4 bands (Luttinger hamiltonian), 6 bands (including the split-off bands in the basis) and sometimes even 8 bands (also treating the conduction band on the same footing) $\mathbf{k}\cdot\mathbf{p}$ model is needed.

Holes in slowly varying potentials (I)

- Let us again add a « slowly » varying potential $v_{slow}(\mathbf{r})$ to the effective potential $v_{eff}(\mathbf{r})$… Can we write for the holes an equation similar to the effective mass equation for the electrons ?

  The answer is yes, though the derivation is a bit more involved…

- In the case of the four bands Luttinger hamiltonian, the hole wavefunctions $\varphi(\mathbf{r})$ in $v_{slow}(\mathbf{r})$ can be written :

$$\varphi(\mathbf{r}) = \psi_{+3/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},+\frac{3}{2}\right\rangle + \psi_{+1/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},+\frac{1}{2}\right\rangle + \psi_{-1/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},-\frac{1}{2}\right\rangle + \psi_{-3/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},-\frac{3}{2}\right\rangle$$

Holes in slowly varying potentials (II)

- The four envelope functions $\psi_{+3/2}(\mathbf{r})$, $\psi_{+1/2}(\mathbf{r})$, $\psi_{-1/2}(\mathbf{r})$ and $\psi_{-3/2}(\mathbf{r})$ satisfy :

$$H\begin{bmatrix}\psi_{+3/2}(\mathbf{r})\\ \psi_{+1/2}(\mathbf{r})\\ \psi_{-1/2}(\mathbf{r})\\ \psi_{-3/2}(\mathbf{r})\end{bmatrix} + v_{slow}(\mathbf{r})\begin{bmatrix}\psi_{+3/2}(\mathbf{r})\\ \psi_{+1/2}(\mathbf{r})\\ \psi_{-1/2}(\mathbf{r})\\ \psi_{-3/2}(\mathbf{r})\end{bmatrix} = \varepsilon\begin{bmatrix}\psi_{+3/2}(\mathbf{r})\\ \psi_{+1/2}(\mathbf{r})\\ \psi_{-1/2}(\mathbf{r})\\ \psi_{-3/2}(\mathbf{r})\end{bmatrix}$$

where H is Luttinger's 4x4 Hamiltonian with the substitution :

$$\begin{cases} k_x \rightarrow -i\,\partial/\partial_x \\ k_y \rightarrow -i\,\partial/\partial_y \\ k_y \rightarrow -i\,\partial/\partial_z \end{cases}$$

Holes in slowly varying potentials (III)

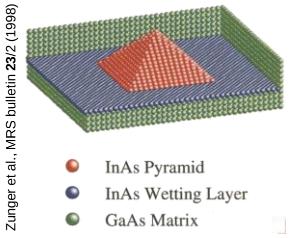
$$\varphi(\mathbf{r}) = \psi_{+3/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},+\frac{3}{2} \right\rangle + \psi_{+1/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},+\frac{1}{2} \right\rangle + \psi_{-1/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},-\frac{1}{2} \right\rangle + \psi_{-3/2}(\mathbf{r})\left\langle \mathbf{r} \middle| \frac{3}{2},-\frac{3}{2} \right\rangle$$

$$H\begin{bmatrix} \psi_{+3/2}(\mathbf{r}) \\ \psi_{+1/2}(\mathbf{r}) \\ \psi_{-1/2}(\mathbf{r}) \\ \psi_{-3/2}(\mathbf{r}) \end{bmatrix} + v_{slow}(\mathbf{r})\begin{bmatrix} \psi_{+3/2}(\mathbf{r}) \\ \psi_{+1/2}(\mathbf{r}) \\ \psi_{-1/2}(\mathbf{r}) \\ \psi_{-3/2}(\mathbf{r}) \end{bmatrix} = \varepsilon\begin{bmatrix} \psi_{+3/2}(\mathbf{r}) \\ \psi_{+1/2}(\mathbf{r}) \\ \psi_{-1/2}(\mathbf{r}) \\ \psi_{-3/2}(\mathbf{r}) \end{bmatrix}$$

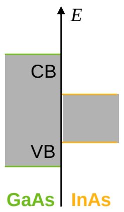
$$H = \frac{\hbar^2}{2m_0}\begin{bmatrix} -P-Q & -S & R & 0 \\ -S^* & -P+Q & 0 & R \\ R^* & 0 & -P+Q & S \\ 0 & R^* & S^* & -P-Q \end{bmatrix} \quad \text{where} \quad \begin{cases} P = -\gamma_1 \Delta_{\mathbf{r}} \\ Q = -\gamma_2\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} - 2\dfrac{\partial^2}{\partial z^2}\right) \\ R = -\sqrt{3}\left[\gamma_2\left(\dfrac{\partial^2}{\partial x^2} - \dfrac{\partial^2}{\partial y^2}\right) - 2i\gamma_3\dfrac{\partial^2}{\partial x \partial y}\right] \\ S = +2\sqrt{3}\gamma_3\dfrac{\partial}{\partial z}\left(\dfrac{\partial}{\partial x} - i\dfrac{\partial}{\partial y}\right) \end{cases}$$

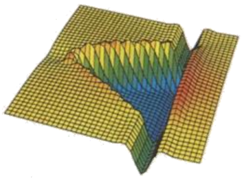
System of coupled differential equations

Confinement in semiconductor heterostructures (I)



Zunger et al., MRS bulletin **23**/2 (1998)





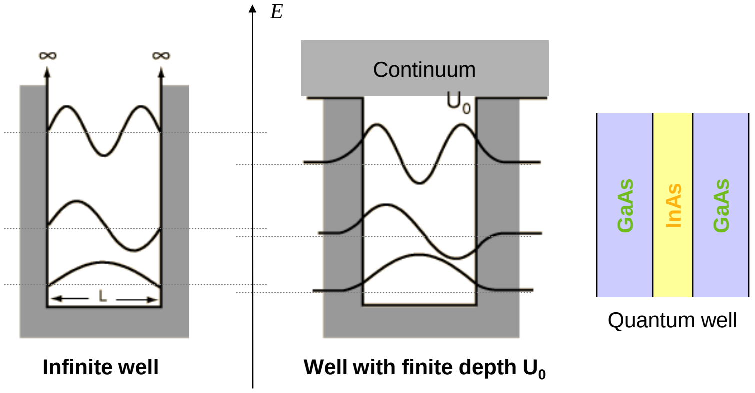
Conduction band profile

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r}) + v_{slow}(\mathbf{r})\psi(\mathbf{r}) = [\varepsilon - \varepsilon_{50}(\mathbf{r})]\psi(\mathbf{r})$$

$$-\frac{\hbar^2}{2m^*}\Delta_{\mathbf{r}}\psi(\mathbf{r}) + v_{slow}(\mathbf{r})\psi(\mathbf{r}) + \varepsilon_{50}(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

- The conduction band profile acts as a potential for the electrons (there are actually some subtleties due to the variation of the effective mass across the interfaces).

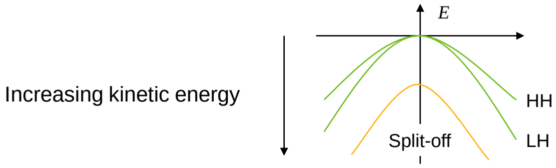
Confinement in semiconductor heterostructures (II)



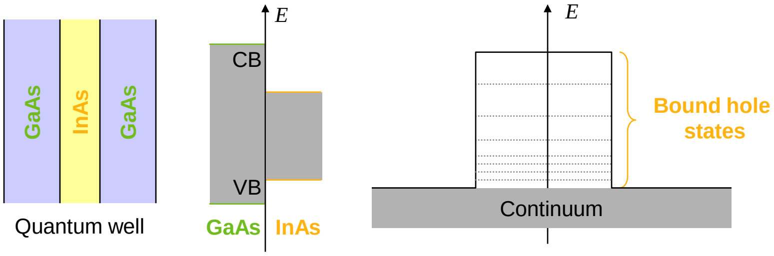
- A finite well only binds a limited number of states.

Confinement of the holes

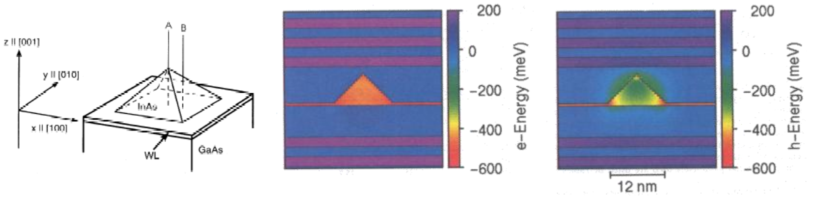
- Holes have negative dispersion in the solid :



We are looking for the highest hole wavefunctions (lowest ionization energies) :



Application : InAs/GaAs quantum dots (I)



M. Grundmann et al., Phys. Rev. B **52**, 11969 (1995)
O. Stier et al., Phys. Rev. B **59**, 5688 (1999)

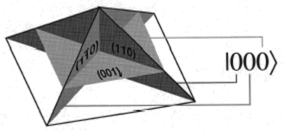
- Eight bands **k·p** calculation in the basis :

$$\left\{ |X\uparrow\rangle, |X\downarrow\rangle, |Y\uparrow\rangle, |Y\downarrow\rangle, |Z\uparrow\rangle, |Z\downarrow\rangle, |S\uparrow\rangle, |S\downarrow\rangle \right\}$$

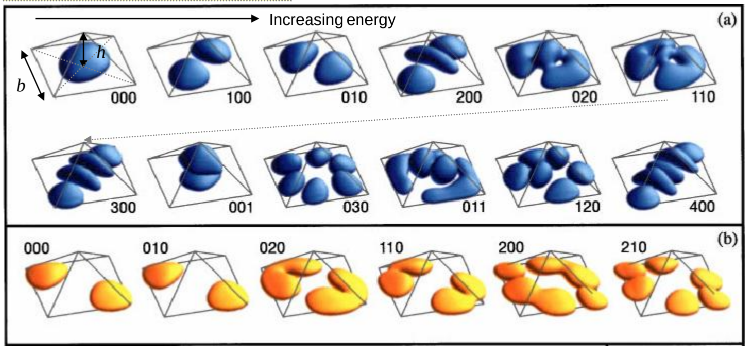
The **k·p** coupling between the highest valence bands and the lowest conduction band is thus fully taken into account (i.e. beyond second order perturbation theory). The effects of strains have also been included in the calculation.

Application : InAs/GaAs quantum dots (II)

Electron and hole states, labelled according to the number of nodal surfaces parallel to each of the three planes on the right.



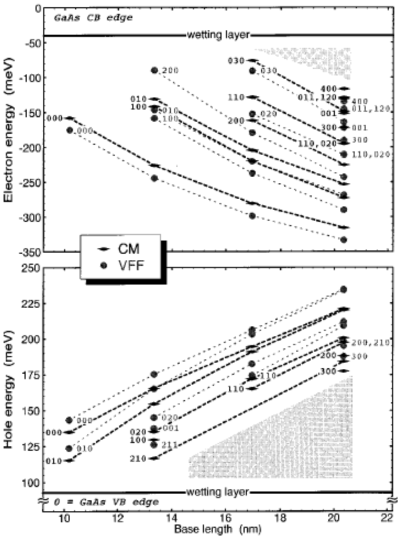
b = 13.6 nm ; $h = b/2$ = 6.8 nm



O. Stier et al., Phys. Rev. B **59**, 5688 (1999)

Application : InAs/GaAs quantum dots (III)

O. Stier et al., Phys. Rev. B **59**, 5688 (1999)



- **Energy of the electron and hole states as a function of base length *b*.**

  The zero of energy is the bulk conduction band edge in GaAs on the electron side, and the bulk valence band edge in GaAs on the hole side.
  CM and VFF are two different model for the strain distribution in the system.
  « Wetting layer » is the energy of the electrons and holes in the thin InAs layer running below the pyramids.

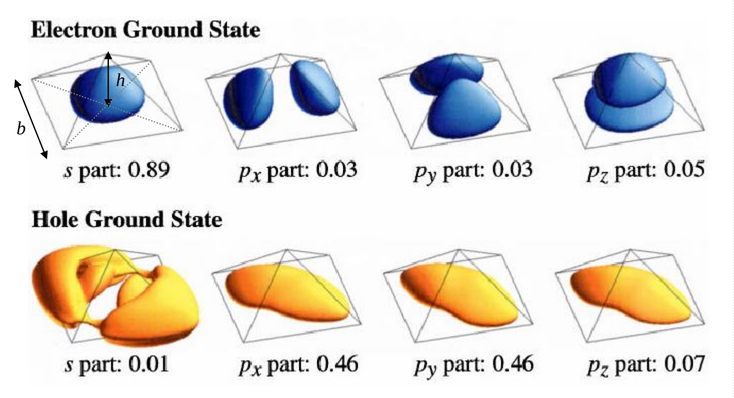
- **As expected, the bandgap energy increases with decreasing base length due to quantum confinement.**

Application : InAs/GaAs quantum dots (IV)

- Eight bands $\mathbf{k}\cdot\mathbf{p}$ calculation in the basis :

$$\left\{ |X\uparrow\rangle, |X\downarrow\rangle, |Y\uparrow\rangle, |Y\downarrow\rangle, |Z\uparrow\rangle, |Z\downarrow\rangle, |S\uparrow\rangle, |S\downarrow\rangle \right\}$$

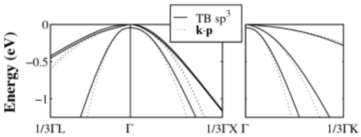
b = 13.6 nm ; $h = b/2$ = 6.8 nm



O. Stier et al., Phys. Rev. B **59**, 5688 (1999)

The limits of the **k·p** approximation

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



Si valence band structure

As a consequence the **k·p** approximation fails to describe the electronic properties of nanostructures at high electron/hole energy (e.g. highly confined structures such as small nanocrystals).

  - The **k·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

---

Comparison : **k·p** versus tight-binding

	k·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	Increase at least linearly with the number of atoms

- **k·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 implicitely 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.

Part III

Self-energy and excitonic corrections in nanostructures

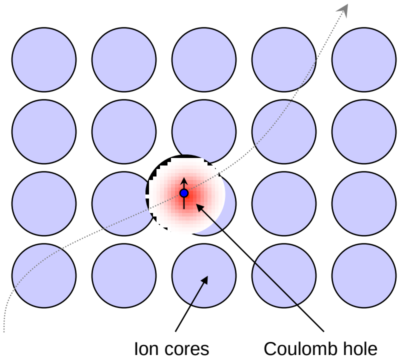
Outline

- **III.1** :
  The « self-energy » correction
- **III.2** :
  The exciton

III.1 : The « self-energy » correction

The self-energy problem (I)

- Let us add an electron to an otherwise neutral solid...

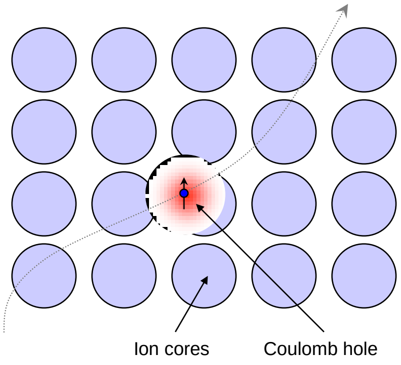


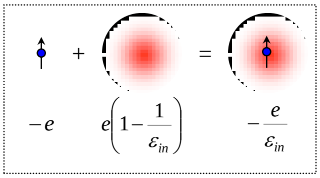
This electron repells nearby valence electrons, thus leaving partially « naked » ion cores around him.

The electron is thus « clothed » by a cloud of positive charges (also known as a **Coulomb hole**) that screens its interactions with the other particles. This Coulomb hole follows the electron travelling in the solid.

The self-energy problem (II)

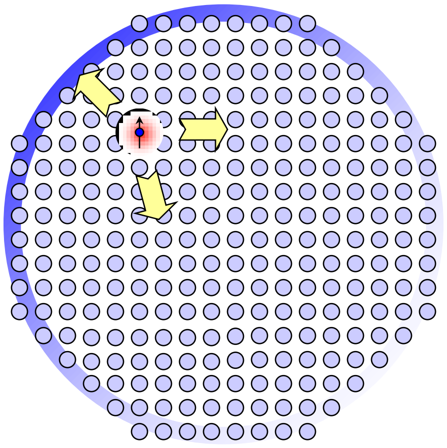
- Let us add an electron to an otherwise neutral solid...





- The charge $q = -e(1-1/\varepsilon_{in})$ cast out from the Coulomb hole is expelled to « infinity » and does not interact any more with the additional electron…

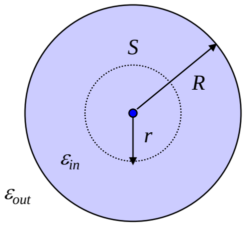
The self-energy problem (III)



- In finite-size nanostructures however, the charge cast out from the Coulomb hole is expelled onto the surfaces of the system, and thus still interacts with the additional electron…

- The interaction of the electron with the so-called **image or polarization charges** it has **itself** induced on the surfaces of the system is responsible for large « **self-energy** » corrections to the electronic structure.

Classical electrostatics (I)



- Gauss theorem for a single electron at the center of a nanocrystal with radius R and dielectric constant ε_{in} embedded in a medium with dielectric constant ε_{out} :

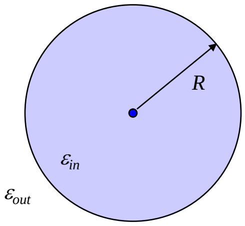
$$\int_S \varepsilon \mathbf{E}\cdot d\mathbf{S} = 4\pi r^2 \varepsilon(r)E(r) = 4\pi Q_i = -4\pi e$$

$$\begin{cases} 4\pi\varepsilon_{in} r^2 E(r) = -4\pi e \text{ if } r<R \\ 4\pi\varepsilon_{out} r^2 E(r) = -4\pi e \text{ if } r>R \end{cases} \Rightarrow \begin{cases} E(r) = -\dfrac{e}{\varepsilon_{in} r^2} \text{ if } r<R \\ E(r) = -\dfrac{e}{\varepsilon_{out} r^2} \text{ if } r>R \end{cases} \Rightarrow \begin{cases} V(r) = -\dfrac{e}{\varepsilon_{in} r} + C \text{ if } r<R \\ V(r) = -\dfrac{e}{\varepsilon_{out} r} \text{ if } r>R \end{cases}$$

where C is a constant such that $\lim_{r\to R^-} V(r) = \lim_{r\to R^+} V(r)$, ie :

$$C = -\frac{e}{\varepsilon_{out} R} + \frac{e}{\varepsilon_{in} R}$$

Classical electrostatics (II)



$$\begin{aligned} V(r) &= -\frac{e}{\varepsilon_{in} r} + \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{R} \text{ if } r<R \\ V(r) &= -\frac{e}{\varepsilon_{out} r} \text{ if } r>R \end{aligned}$$

- The potential created by the electron can be split in two parts $V(r) = V_b(r) + V_s(r)$, where :

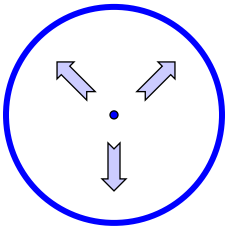
$$V_b(r) = -\frac{e}{\varepsilon_{in} r}$$

$$V_s(r) = \begin{cases} \left(\dfrac{1}{\varepsilon_{in}} - \dfrac{1}{\varepsilon_{out}}\right)\dfrac{e}{R} \text{ if } r<R \\ \left(\dfrac{1}{\varepsilon_{in}} - \dfrac{1}{\varepsilon_{out}}\right)\dfrac{e}{r} \text{ if } r>R \end{cases}$$

$V_b(r)$ is the potential created in vacuum by the electron plus its « local » Coulomb hole.

$V_s(r)$ is the potential created in vacuum by the (uniform) image charge distribution at the surface of the nanocrystal.

Classical electrostatics (III)

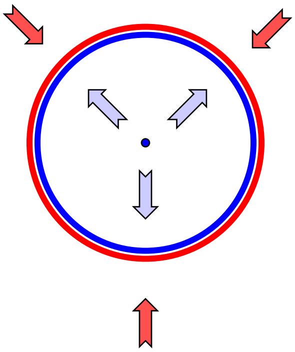


$$V_s(r)=\begin{cases}\left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{R} & \text{if } r<R\\ \left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{r} & \text{if } r>R\end{cases}$$

is actually the potential created in vacuum by a surface charge density $\sigma_s=\left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{4\pi R^2}$.

- If $\varepsilon_{out}=1$, $4\pi R^2\sigma_s=-e(1-1/\varepsilon_{in})$ is, as expected, the charge expelled from the Coulomb hole around the electron. In particular, the total charge of the system (electron + Coulomb hole + surface polarization charges) is $-e$, so that the potential outside the nanocrystal is just $V(r)=-e/r$.

Classical electrostatics (IV)

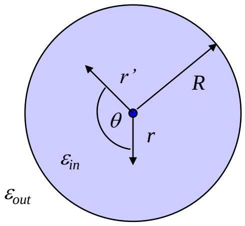


$$V_s(r)=\begin{cases}\left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{R} & \text{if } r<R\\ \left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{r} & \text{if } r>R\end{cases}$$

is actually the potential created in vacuum by a surface charge density $\sigma_s=\left(\frac{1}{\varepsilon_{in}}-\frac{1}{\varepsilon_{out}}\right)\frac{e}{4\pi R^2}$.

- If $\varepsilon_{out}\neq 1$, $4\pi R^2\sigma_s=-e(1/\varepsilon_{out}-1/\varepsilon_{in})$ can be seen as the charge $q=-e(1-1/\varepsilon_{in})$ expelled from the Coulomb hole plus a charge $q' = e(1-1/\varepsilon_{out})$ brought by the outer medium to screen the electron. In particular, $\sigma_s=0$ if $\varepsilon_{in}=\varepsilon_{out}$.

Classical electrostatics (V)



- **Generalization** : The potential created at point $\mathbf{r}'$ by an electron at point $\mathbf{r}$ in a nanocrystal with radius R and dielectric constant ε_{in} embedded in a medium with dielectric constant ε_{out} is :

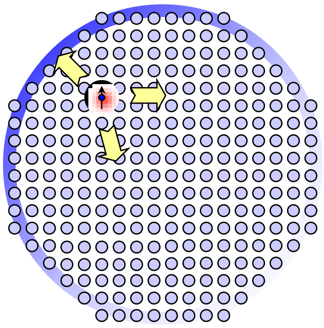
$$V(\mathbf{r},\mathbf{r}') = V_b(\mathbf{r},\mathbf{r}') + V_s(\mathbf{r},\mathbf{r}')$$

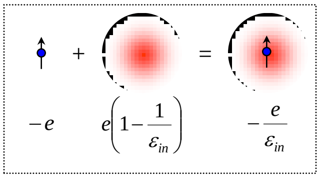
where :

$$\begin{cases} V_b(\mathbf{r},\mathbf{r}') = -\dfrac{e}{\varepsilon_{in}|\mathbf{r}-\mathbf{r}'|} \\ V_s(\mathbf{r},\mathbf{r}') = -e\displaystyle\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})|\mathbf{r}|^n|\mathbf{r}'|^n P_n(\cos\theta)}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}} \quad \text{if } r<R \text{ and } r'<R \end{cases}$$

$P_n(x)$ is the Legendre ploynomial of order n (cf. spherical harmonics).

The self-energy correction : semi-classical theory (I)





- Let us consider an additional electron at point $\mathbf{r}$. This electron creates at point $\mathbf{r}'$ a potential :

$$V(\mathbf{r},\mathbf{r}') = V_b(\mathbf{r},\mathbf{r}') + V_s(\mathbf{r},\mathbf{r}')$$

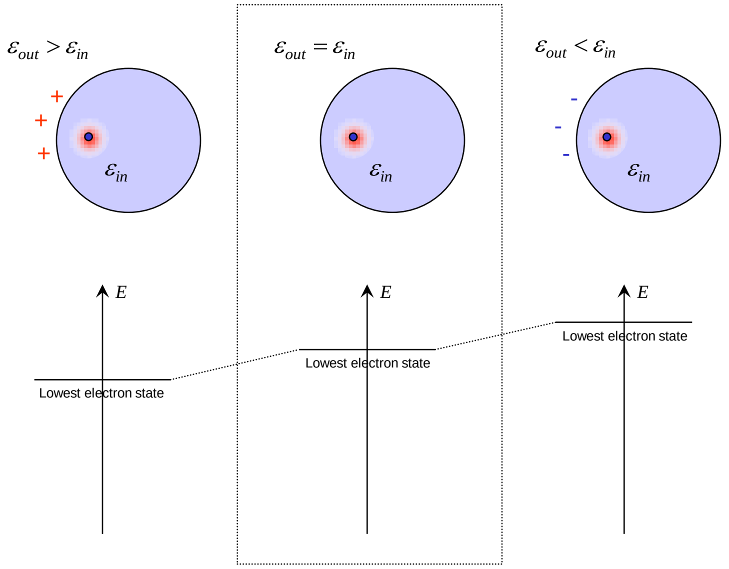
where $V_b(\mathbf{r},\mathbf{r}') = -e/\varepsilon_{in}|\mathbf{r}-\mathbf{r}'|$ is the potential created by the electron plus its Coulomb hole and $V_s(\mathbf{r},\mathbf{r}')$ is the potential created by the surface polarization charges. The latter thus act back onto the electrons with a potential :

$$\Sigma_e(\mathbf{r}) = -eV_s(\mathbf{r},\mathbf{r})$$

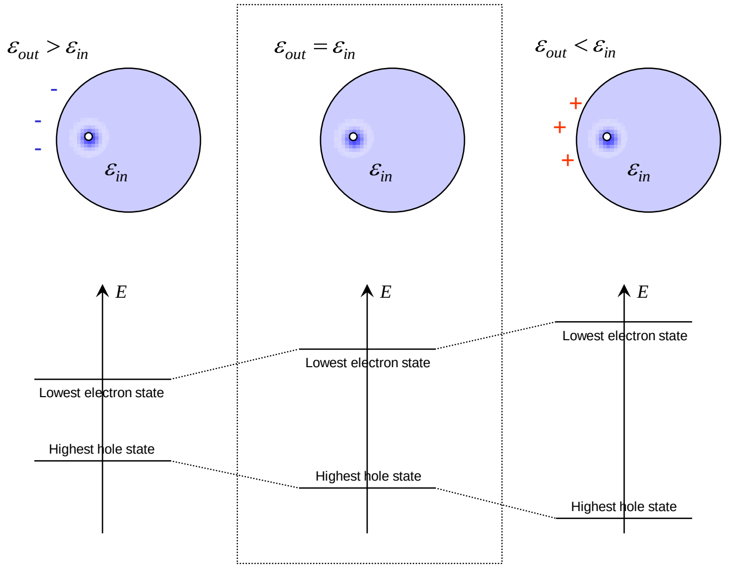
A more refined theory where the electron is introduced « adiabatically » into the system actually yields :

$$\Sigma_e(\mathbf{r}) = -eV_s(\mathbf{r},\mathbf{r})/2$$

The self-energy correction : semi-classical theory (II)

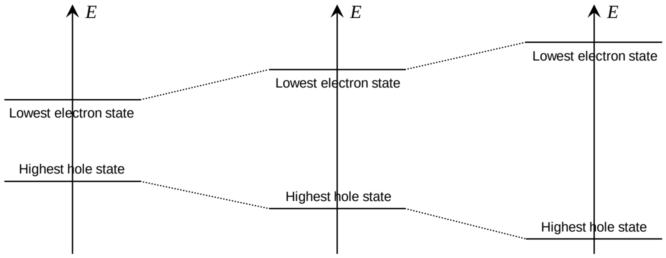


The self-energy correction : semi-classical theory (III)

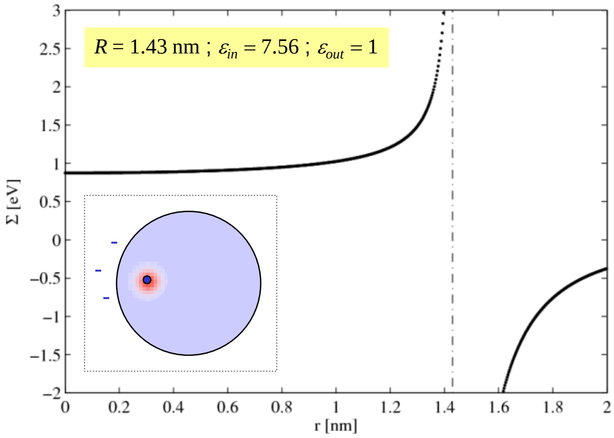


The self-energy correction : semi-classical theory (IV)

The hole feels a potential $\Sigma_h(\mathrm{r}) = -\Sigma_e(\mathrm{r})$!!



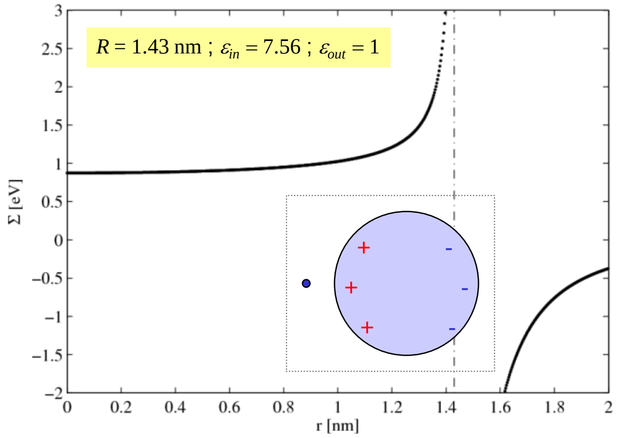
The self-energy potential $\Sigma_e(\mathrm{r})$ (I)



- The semi-classical self-energy potential $\Sigma_e(\mathrm{r})$ is positive inside the nanocrystal…

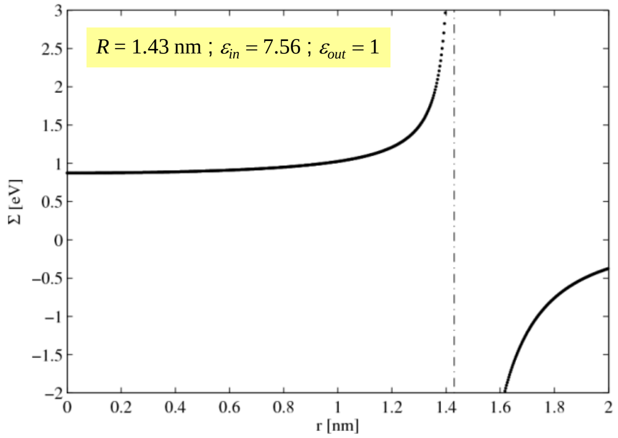
$$\Sigma_e(\mathbf{r}) = -\frac{e}{2}V_s(\mathbf{r},\mathbf{r}) = \frac{e^2}{2}\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})|\mathbf{r}|^{2n}}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}} \quad \text{if } r<R$$

The self-energy potential $\Sigma_e(r)$ (II)



- …negative outside (the electron polarizes the nanocrystal and attract positive charges on its side),…

The self-energy potential $\Sigma_e(r)$ (III)



- …and diverges as the electron approaches the image charges at the surface of the nanocrystal (this divergence actually disappears in a more refined many-body approach such as the *GW* approximation).

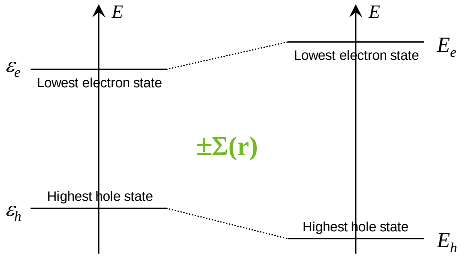
First-order perturbation theory (I)

- Let :

$$\begin{cases} \varphi_e(\mathbf{r}) \text{ and } \varepsilon_e \text{ be the lowest electron wavefunction and energy} \\ \varphi_h(\mathbf{r}) \text{ and } \varepsilon_h \text{ be the highest hole wavefunct ion and energy} \end{cases}$$

… without self-energy potential. The first-order self-energy corrections read :

$$\begin{cases} E_e = \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle \\ E_h = \varepsilon_h - \langle \varphi_h | \Sigma | \varphi_h \rangle \end{cases} \text{ where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$



E

ε_e Lowest electron state

ε_h Highest hole state

$\pm\Sigma(\mathbf{r})$

E

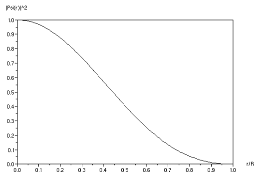
Lowest electron state E_e

Highest hole state E_h

First-order perturbation theory (II)

- We can hopefully get a reasonnable approximation for $\langle \varphi_e | \Sigma | \varphi_e \rangle$ and $\langle \varphi_h | \Sigma | \varphi_h \rangle$ using an effecive mass ansatz for the wavefunctions $\varphi_e(\mathbf{r})$ and $\varphi_h(\mathbf{r})$:

$$\begin{cases} \varphi(r) = \dfrac{1}{\sqrt{2\pi R}} \dfrac{1}{r} \sin\left[\dfrac{\pi}{R} r\right] \text{ if } r < R \\ \varphi(r) = 0 \text{ if } r > R \end{cases}$$



Then,

$$\langle \varphi | \Sigma | \varphi \rangle = \int d^3 r \Sigma(\mathbf{r}) |\varphi(\mathbf{r})|^2 = 4\pi \int_0^R dr \Sigma(r) |\varphi(r)|^2$$

where :

$$\Sigma(r) = \frac{e^2}{2} \sum_{n=0}^{\infty} \frac{(n+1)(\varepsilon_{in} - \varepsilon_{out}) r^{2n}}{\varepsilon_{in} [\varepsilon_{out} + n(\varepsilon_{in} + \varepsilon_{out})] R^{2n+1}}$$

First-order perturbation theory (III)

- This finally yields, in the limit $\varepsilon_{in} + \varepsilon_{out} >> 1$,

$$\begin{cases} E_e = \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle \\ E_h = \varepsilon_h - \langle \varphi_h | \Sigma | \varphi_h \rangle \end{cases} \text{ where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$

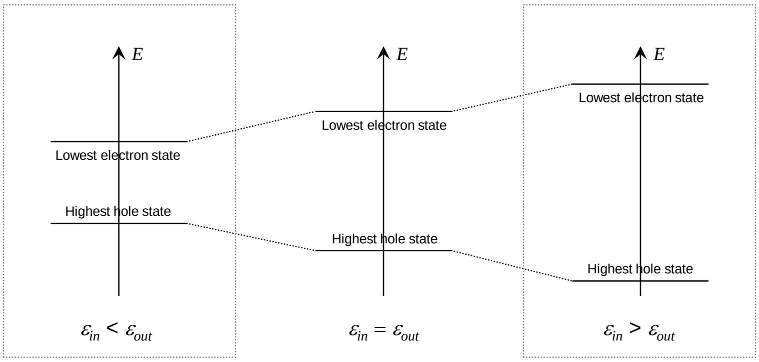
and :

$$\langle \varphi_e | \Sigma | \varphi_e \rangle \approx \langle \varphi_h | \Sigma | \varphi_h \rangle \approx \frac{1}{2}\left(\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right)\frac{e^2}{R} + 0.47\frac{e^2}{\varepsilon_{in} R}\left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}\right)$$

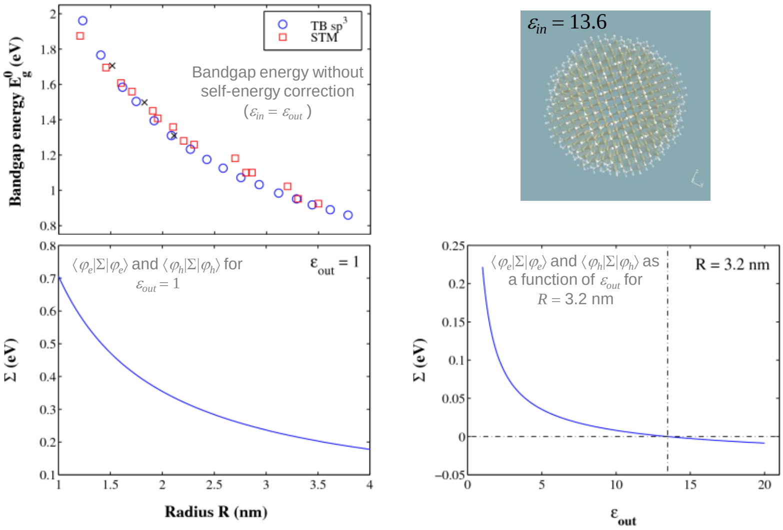
First-order perturbation theory (IV)

$$\langle \varphi_e | \Sigma | \varphi_e \rangle \approx \langle \varphi_h | \Sigma | \varphi_h \rangle \approx \frac{1}{2}\left(\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right)\frac{e^2}{R} + 0.47\frac{e^2}{\varepsilon_{in} R}\left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}\right)$$

- The self-energy corrections open (resp. close) the quasiparticle gap when $\varepsilon_{in} > \varepsilon_{out}$ (resp. $\varepsilon_{out} > \varepsilon_{in}$). **They decrease in $1/R$, slower than quantum confinement**. They are thus far from negligible in most experimental setups !!



Application : InAs nanocrystals



III.2 : The exciton

The exciton

- Let us imagine the following experience :
  - We remove one electron from the system, thus leaving a hole with energy ε_N.
  - We add an electron with energy ε_{N+1} far away from the hole.

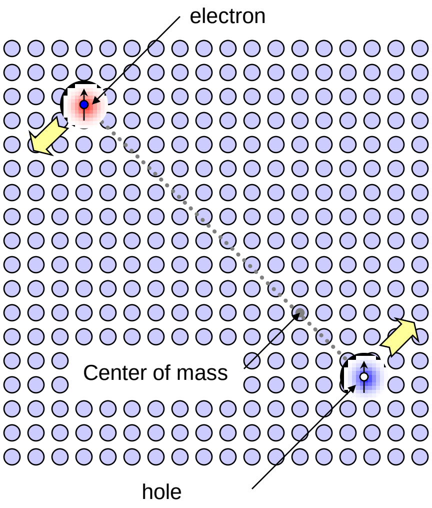
We then wait for electron-hole recombination [i.e. the system returns to its ground state] and collect the emitted photon (if any).

Is the energy of the photon $h\nu = \varepsilon_{N+1} - \varepsilon_N$?

NO !

Before recombination the quasi-electron and hole will bind in a lower energy state called an **exciton**.

The exciton in bulk materials (I)



The electron at $\mathbf{r}_e$ and the hole at $\mathbf{r}_h$ attract each other with an effective Coulomb interaction :

$$W(\mathbf{r}_e,\mathbf{r}_h) = -\frac{e^2}{\varepsilon_r |\mathbf{r}_e - \mathbf{r}_h|}$$

provided $|\mathbf{r}_e - \mathbf{r}_h|$ is not too small.

The attraction reduces the energy of the electron-hole pair by the « **exciton binding energy** » ε_x :

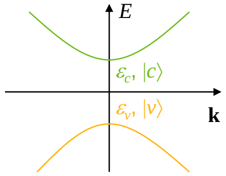
$$h\nu = \varepsilon_{N+1} - \varepsilon_N - \varepsilon_x$$

The **exciton** is (in a first approximation) an hydrogenoid-like bound state between the electron and the hole.

The exciton in bulk materials (II)

- We assume that the independent electron and hole can be described by a single band effective mass model :

$$\begin{cases} -\dfrac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi_e(\mathbf{r}_e) = (\varepsilon_e-\varepsilon_c)\psi_e(\mathbf{r}_e) \\ +\dfrac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi_h(\mathbf{r}_h) = (\varepsilon_h-\varepsilon_v)\psi_h(\mathbf{r}_h) \end{cases}$$



The solution of these equations are Bloch waves :

$$\begin{cases} \varepsilon_e = \varepsilon_c + \dfrac{\hbar^2\mathbf{k}_e^2}{2m_e^*} \text{ and } \psi_e(\mathbf{r}_e) \propto e^{i\mathbf{k}_e\cdot\mathbf{r}_e}\ \left[\varphi_e(\mathbf{r}_e) = \psi_e(\mathbf{r}_e)\langle\mathbf{r}_e|c\rangle \propto e^{i\mathbf{k}_e\cdot\mathbf{r}_e}\langle\mathbf{r}_e|c\rangle\right] \\ \varepsilon_h = \varepsilon_v - \dfrac{\hbar^2\mathbf{k}_h^2}{2m_h^*} \text{ and } \psi_h(\mathbf{r}_h) \propto e^{i\mathbf{k}_h\cdot\mathbf{r}_h}\ \left[\varphi_h(\mathbf{r}_h) = \psi_h(\mathbf{r}_h)\langle\mathbf{r}_h|v\rangle \propto e^{i\mathbf{k}_h\cdot\mathbf{r}_h}\langle\mathbf{r}_h|v\rangle\right] \end{cases}$$

We now introduce the electron-hole pair energy $\varepsilon = \varepsilon_e - \varepsilon_h$ and « uncorrelated » envelope function $\psi(\mathbf{r}_e, \mathbf{r}_h) = \psi_e(\mathbf{r}_e)\psi_h(\mathbf{r}_h)$, which satisfy :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{r}_e,\mathbf{r}_h) = (\varepsilon-\varepsilon_g)\psi(\mathbf{r}_e,\mathbf{r}_h)$$

The exciton in bulk materials (III)

- We last switch on the screened Coulomb interaction between the electron and the hole :

$$W(\mathbf{r}_e,\mathbf{r}_h) = -\frac{e^2}{\varepsilon_r|\mathbf{r}_e-\mathbf{r}_h|}$$

The electron-hole pair energy ε and envelope function $\psi(\mathbf{r}_e, \mathbf{r}_h)$ now satisfy :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{e^2}{\varepsilon_r|\mathbf{r}_e-\mathbf{r}_h|}\psi(\mathbf{r}_e,\mathbf{r}_h) = (\varepsilon-\varepsilon_g)\psi(\mathbf{r}_e,\mathbf{r}_h)$$

$\psi(\mathbf{r}_e, \mathbf{r}_h)$ can not be written any more as a product $\psi(\mathbf{r}_e, \mathbf{r}_h) = \psi_e(\mathbf{r}_e)\psi_h(\mathbf{r}_h)$ of one electron and one hole wavefunction. Still, the center of mass motion can be decoupled from the relative motion of the electron-hole pair. Let us indeed introduce :

$$\begin{cases} \mathbf{r} = \mathbf{r}_e - \mathbf{r}_h \\ \mathbf{R} = \dfrac{m_e^*}{m_e^*+m_h^*}\mathbf{r}_e + \dfrac{m_h^*}{m_e^*+m_h^*}\mathbf{r}_h \end{cases} \Rightarrow \begin{cases} \mathbf{r}_e = \mathbf{R} + \dfrac{m_h^*}{m_e^*+m_h^*}\mathbf{r} \\ \mathbf{r}_h = \mathbf{R} - \dfrac{m_e^*}{m_e^*+m_h^*}\mathbf{r} \end{cases}$$

The exciton in bulk materials (IV)

$$\begin{cases}\mathbf{r}=\mathbf{r}_e-\mathbf{r}_h\\ \mathbf{R}=\dfrac{m_e^*}{m_e^*+m_h^*}\mathbf{r}_e+\dfrac{m_h^*}{m_e^*+m_h^*}\mathbf{r}_h\end{cases}\Rightarrow\begin{cases}\mathbf{r}_e=\mathbf{R}+\dfrac{m_h^*}{m_e^*+m_h^*}\mathbf{r}\\ \mathbf{r}_h=\mathbf{R}-\dfrac{m_e^*}{m_e^*+m_h^*}\mathbf{r}\end{cases}\quad \text{and } \psi(\mathbf{r}_e,\mathbf{r}_h)\equiv\psi(\mathbf{R},\mathbf{r})$$

- We get :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=(\varepsilon-\varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2m_e^*}\frac{m_e^{*2}}{(m_e^*+m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2m_h^*}\frac{m_h^{*2}}{(m_e^*+m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=(\varepsilon-\varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2}\frac{m_e^*+m_h^*}{(m_e^*+m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=(\varepsilon-\varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2(m_e^*+m_h^*)}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=(\varepsilon-\varepsilon_g)\psi(\mathbf{R},\mathbf{r})\ \text{where}\ \frac{1}{\mu^*}=\frac{1}{m_e^*}+\frac{1}{m_h^*}$$

The exciton in bulk materials (V)

$$-\frac{\hbar^2}{2(m_e^*+m_h^*)}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=(\varepsilon-\varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

- $\mathbf{R}$ and $\mathbf{r}$ are uncoupled : we can indeed split $\psi(\mathbf{R},\mathbf{r})=\psi_m(\mathbf{R})\psi_x(\mathbf{r})$, $\varepsilon=\varepsilon_g+\varepsilon_m-\varepsilon_x$ and solve :

$$\begin{cases}-\dfrac{\hbar^2}{2(m_e^*+m_h^*)}\Delta_{\mathbf{R}}\psi_m(\mathbf{R})=\varepsilon_m\psi_m(\mathbf{R})\\ -\dfrac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi_x(\mathbf{r})-\dfrac{e^2}{\varepsilon_r|\mathbf{r}|}\psi_x(\mathbf{r})=-\varepsilon_x\psi_x(\mathbf{r})\end{cases}$$

The solution of the center of mass equation is just :

$$\varepsilon_m=\frac{\hbar^2\mathbf{K}^2}{2(m_e^*+m_h^*)}\quad\text{and}\quad\psi_m(\mathbf{R})\propto e^{i\mathbf{K}\cdot\mathbf{R}}$$

where $\mathbf{K}$ is an arbitrary wavevector. The ground-state energy for the center of mass motion is thus :

$$\varepsilon_m^0=0$$

The exciton in bulk materials (VI)

$$\begin{cases} -\dfrac{\hbar^2}{2\left(m_e^*+m_h^*\right)}\Delta_{\mathbf{R}}\psi_m(\mathbf{R}) = \varepsilon_m\psi_m(\mathbf{R}) \\ -\dfrac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi_x(\mathbf{r}) - \dfrac{e^2}{\varepsilon_r|\mathbf{r}|}\psi_x(\mathbf{r}) = -\varepsilon_x\psi_x(\mathbf{r}) \end{cases}$$

- The equation for the relative motion of the electron and hole is similar to the hamiltonian of the Hydrogen atom, with m_0 replaced by μ^* and e^2 replaced by e^2/ε_r. The ground-state wavefunction and energy for the relative electron-hole motion are therefore :

$$\begin{cases} \varepsilon_x^0 = \dfrac{\mu e^4}{2\hbar^2\varepsilon_r^2} \quad \text{[the exciton binding energy]} \\ \varphi_x^0(\mathbf{r}) = \dfrac{1}{\sqrt{\pi a_x^3}}e^{-|\mathbf{r}|/a_x} \quad \text{where } a_x = \dfrac{\hbar^2\varepsilon_r}{\mu e^2} \quad \text{[the exciton radius]} \end{cases}$$

The exciton in bulk materials (VII)

- Summary : The lowest electron-hole pair energy and wavefunction are :

$$\begin{cases} \varepsilon = \varepsilon_g + \varepsilon_m^0 - \varepsilon_x^0 = \varepsilon_g - \varepsilon_x^0 \quad \text{where } \varepsilon_x^0 = \dfrac{\mu e^4}{2\hbar^2\varepsilon_r^2} \text{ is the exciton binding energy,} \\ \psi(\mathbf{R},\mathbf{r}) \propto e^{-|\mathbf{r}|/a_x} \quad \text{where } a_x = \dfrac{\hbar^2\varepsilon_r}{\mu e^2} \text{ is the exciton radius.} \end{cases}$$

Alternatively,

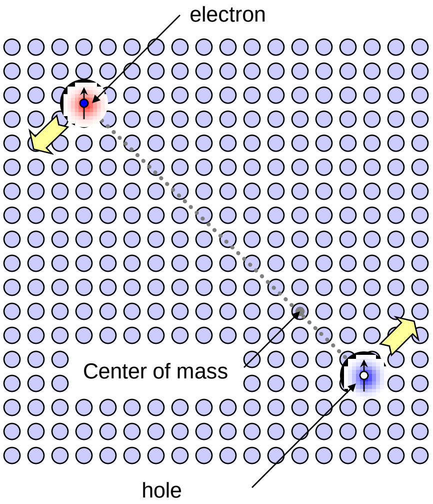
$$\psi(\mathbf{r}_e,\mathbf{r}_h) \propto e^{-|\mathbf{r}_e-\mathbf{r}_h|/a_x}$$

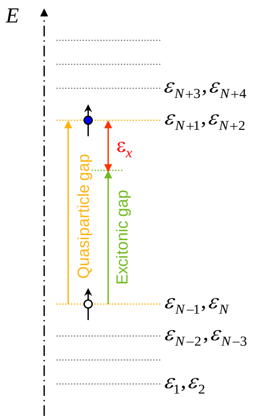
This wavefunction describes a bound electron-hole pair freely moving in the solid.

- **Application** : The exciton in GaAs.

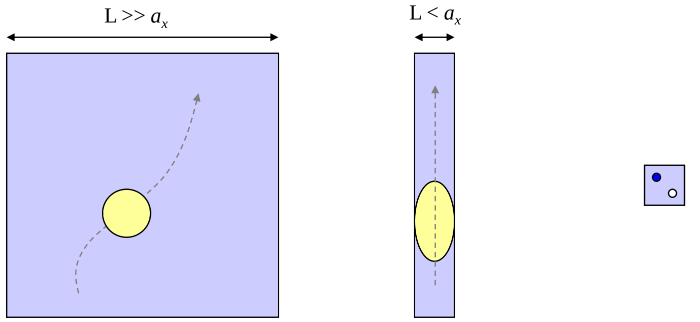
$$\begin{cases} m_e^* = 0.067m_0 \\ m_e^* = 0.45m_0 \\ \varepsilon_r = 11 \end{cases} \Rightarrow \mu^* = 0.06m_0, \varepsilon_x^0 = 6.7\text{ meV and } a_x = 9.7\text{ nm}$$

The exciton in bulk materials (VIII)





Confining the exciton



Center of mass confinement

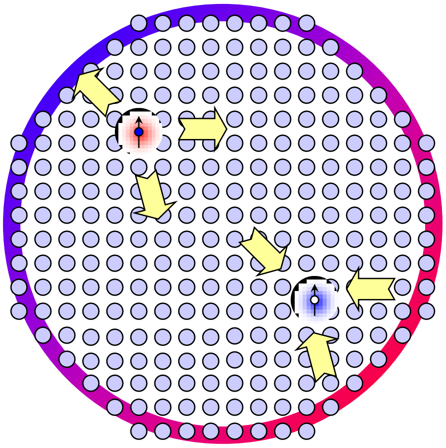
Laterally squeezed exciton

Single-particle confinement

- When all the dimensions of the system become significantly lower than the bulk exciton radius a_x, the Coulomb interaction can not efficiently couple any more the motion of the electron and hole because their kinetic energy is too high. Thus,

$$\varphi(\mathbf{r}_e,\mathbf{r}_h) \approx \varphi_e(\mathbf{r}_e)\varphi_h(\mathbf{r}_h)$$ [Uncorrelated electron-hole pair]

The exciton in nanocrystals (I)



- In a nanocrystal, the electron interacts with the hole and its cloud of screening charge, including the polarization charges at the surface of the nanocrystal. The effective electron-hole interaction is thus :

$$W(\mathbf{r},\mathbf{r}') = W_b(\mathbf{r},\mathbf{r}') + W_s(\mathbf{r},\mathbf{r}')$$

where $W_b(\mathbf{r},\mathbf{r}') = -e^2/\varepsilon_{in}\,|\mathbf{r}-\mathbf{r}'|$ and $W_s(\mathbf{r},\mathbf{r}')$ is the interaction with the surface polarization charges.

The exciton in nanocrystals (II)

- Since the diameter of the nanocrystals is usually much lower than the bulk exciton radius a_x, we can deal with the electron-hole attraction using first-order perturbation theory, which amounts to assume :

$\varphi(\mathbf{r}_e, \mathbf{r}_h) \approx \varphi_e(\mathbf{r}_e)\varphi_h(\mathbf{r}_h)$ [Uncorrelated electron-hole pair]

The exciton binding energy then reads :

$$\begin{aligned}\varepsilon_x &= \langle\varphi|W|\varphi\rangle\\ &= \int d^3r\int d^3r'\,\varphi_e(\mathbf{r})\varphi_h(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\varphi_e(\mathbf{r})\varphi_h(\mathbf{r}')\\ &= \int d^3r\int d^3r'\,|\varphi_e(\mathbf{r})|^2 W(\mathbf{r},\mathbf{r}')|\varphi_h(\mathbf{r}')|^2\end{aligned}$$

Using again an effective mass ansatz for the wavefunctions $\varphi_e(\mathbf{r})$ and $\varphi_h(\mathbf{r})$:

$$\varphi(r) = \frac{1}{\sqrt{2\pi R}}\frac{1}{r}\sin\left[\frac{\pi}{R}r\right] \text{ if } r < R \text{ and } \varphi(r) = 0 \text{ if } r > R$$

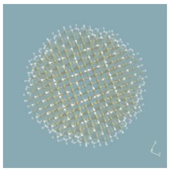
as well as:

$$W(\mathbf{r},\mathbf{r}') = -\frac{e^2}{\varepsilon_{in}|\mathbf{r}-\mathbf{r}'|} - e^2\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})|\mathbf{r}|^n|\mathbf{r}'|^n P_n(\cos\theta)}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}} \text{ if } r < R \text{ and } r' < R$$

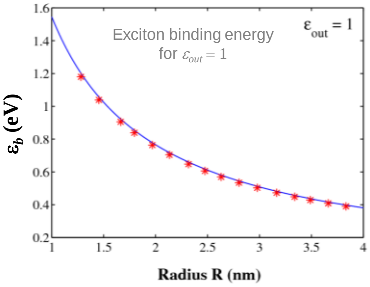
The exciton in nanocrystals (III)

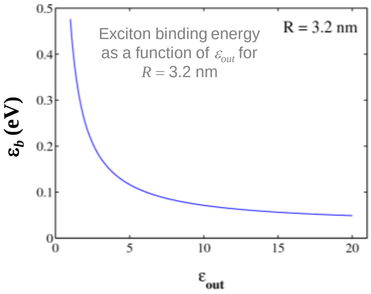
- We finally end up with :

$$\varepsilon_x = \left(\frac{1}{\varepsilon_{out}} + \frac{0.79}{\varepsilon_{in}}\right)\frac{e^2}{R}$$



- Application : InAs nanocrystals (ε_{in} = 13.6).





From the tight-binding to the optical gap (I)

- Let :

$$\begin{cases}\varphi_e(\mathbf{r}) \text{ and } \varepsilon_e \text{ be the lowest electron wavefunction and energy}\\ \varphi_h(\mathbf{r}) \text{ and } \varepsilon_h \text{ be the highest hole wavefunction and energy}\end{cases}$$

… without self-energy potential. The first-order self-energy corrections read :

$$\begin{cases}E_c = \varepsilon_e + \langle\varphi_e|\Sigma|\varphi_e\rangle\\ E_h = \varepsilon_h - \langle\varphi_h|\Sigma|\varphi_h\rangle\end{cases} \text{ where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$

while the first-order excitonic correction read :

$$\varepsilon_x = \int d^3r \int d^3r' |\varphi_e(\mathbf{r})|^2 W(\mathbf{r},\mathbf{r}') |\varphi_h(\mathbf{r}')|^2$$

Using effective mass wavefunctions one gets :

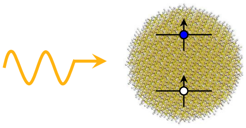
$$\begin{cases}\langle\varphi_e|\Sigma|\varphi_e\rangle \approx \langle\varphi_h|\Sigma|\varphi_h\rangle \approx \frac{1}{2}\left(\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right)\frac{e^2}{R} + 0.47\frac{e^2}{\varepsilon_{in}R}\left(\frac{\varepsilon_{in}-\varepsilon_{out}}{\varepsilon_{in}+\varepsilon_{out}}\right)\\ \varepsilon_x = \left(\frac{1}{\varepsilon_{out}} + \frac{0.79}{\varepsilon_{in}}\right)\frac{e^2}{R}\end{cases}$$

From the tight-binding to the optical gap (II)

- The optical (excitonic) gap is thus :

$$\begin{aligned} h\nu &= E_e - E_h - \varepsilon_b \\ &= \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle - \left(\varepsilon_h + \langle \varphi_h | \Sigma | \varphi_h \rangle \right) - \varepsilon_x \\ &= \varepsilon_e - \varepsilon_h + 2 \langle \varphi | \Sigma | \varphi \rangle - \varepsilon_x \end{aligned}$$

$$h\nu = \varepsilon_e - \varepsilon_h + \frac{1.79e^2}{\varepsilon_{in} R} - \frac{0.94e^2}{\varepsilon_{in} R} \left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} \right)$$



$$h\nu = \Delta E$$

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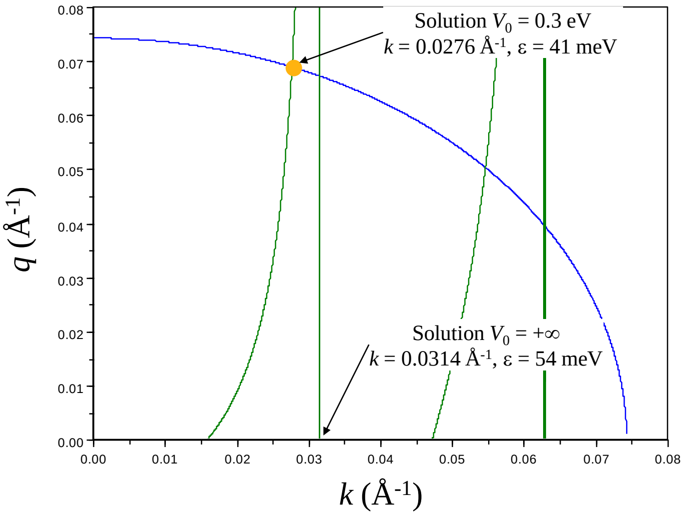
The End

Solution R = 10 nm, V_0 = 0.3 eV, m^* = 0.07m_0



Solution V_0 = 0.3 eV
k = 0.0276 Å^{-1}, ε = 41 meV

Solution V_0 = +∞
k = 0.0314 Å^{-1}, ε = 54 meV

Graphene bands