

CEA Grenoble, DSM/DRFMC/SP2M

History and vocabulary**Tight-binding : Solid State Physics point of view**

Mott and Jones, Slater and the pioneering works of Friedel in the 60's.

Huckel,(LCAO) : The chemists worldSemi-empirical method**TIGHT-BINDING METHODS**

**SIMPLE CONCEPTS
AND
EXAMPLES**

SIZE

1.000.000

10.000

1000

100

EMPIRICAL POTENTIALS

- large systems
- low transferability
- no electronic structure

TIGHT-BINDING (SEMI-EMPIRICAL)

- transferability depends on the system and on the parametrization
- "reasonable size"
- electronic structure

AB-INITIO

- good transferability
- small systems
- electronic structure

TRANSFERABILITY

Most tight-binding methods are parametrized. The parameters of the model are fitted either on experimental or on ab-initio results (the most popular procedure nowadays).

The jungle

There is a huge number of tight-binding methods depending on :

- parametrization.
- level of approximation : orthogonal or non-orthogonal, environment dependence..
- degree of "ab-initio".

OVERVIEW

Electronic Structure

- 1) Basic principles
- 2) Some important quantities
- 3) A simple example : simple cubic s-band model
- 4) Self consistent Tight-Binding
- 5) Doing tight-binding

Total Energy

- 1) Decomposition of the energy
- 2) Forces
- 3) Empirical potentials
- 4) DFT justification

Some examples of application

BIBLIOGRAPHY

Concepts in Surface Physics (Chapter 5)

M.C. Desjonquères and D. Spanjaard. Springer Verlag

Order and Phase Stability in alloys (Chapter 6)

F. Ducastelle. North Holland

Electronic Structure of Materials

A. P. Sutton. Oxford University Press.

Electronic Structure and the Properties of Solids.

W. Harrison. Dover.

Solid State Physics : Problems and Solutions.

L. Mihaly and C. Martin. Wiley-Interscience.

Tight-Binding Modelling of materials.

Goringe et al. Rep. Prog. Phys. 1997.

Linear Scaling electronic structure methods.

S. Goedecker. Review of Modern Physics, 1999.

BASIC PRINCIPLES

a) the basis set

The basic approximation of the tight-binding (TB) scheme is to assume that all electronic wave function of interest can be described within a restricted Hilbert space spanned by atomic-like orbitals.

$$\Psi(\mathbf{r}) = \sum_{n,\lambda} c_{n\lambda} \phi_{\lambda}(\mathbf{r} - \mathbf{n}) \quad , \quad |\Psi\rangle = \sum_{n\lambda} c_{n\lambda} |n\lambda\rangle$$

n : site index, ($n = 1, N_{at}$) λ : orbital index ($\lambda = 1, l$)

$$\lambda = \underbrace{s}_1, \underbrace{p_x, p_y, p_z}_3, \underbrace{d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{3z^2-r^2}}_5 \text{ : Transition Metals}$$

4 : semi-conductors 9 : Transition Metals

Overlaps integrals

$$S_{n,m}^{\lambda,\mu} = \langle n\lambda | m\mu \rangle = \int d\mathbf{r} \phi_{\lambda}(\mathbf{r} - \mathbf{n}) \phi_{\mu}(\mathbf{r} - \mathbf{m})$$

orthogonal tight-binding :

For “convenience” it is often assumed that the TB basis is orthogonal

$$S_{n,m}^{\lambda,\mu} = \langle n\lambda | m\mu \rangle = \delta_{nm} \delta_{\lambda\mu}$$

closure relation :

$$\sum_{n\lambda} |n\lambda\rangle \langle n\lambda| = Id$$

b) the Hamiltonian

$$H = T + V_{eff} = T + \sum_n V_n^{at}$$

T : kinetic energy. V_{eff} : one electron potential.

$$\langle n\lambda | H | m\mu \rangle = \langle n\lambda | T + V_m | m\mu \rangle + \langle n\lambda | \sum_{p \neq m} V_p^{at} | m\mu \rangle$$

$|n\lambda\rangle$ obeys the Schrodinger equation for a single atom :

$$H_{nm}^{\lambda,\mu} = \epsilon_n^{at,\lambda} \delta_{mn} \delta_{\lambda,\mu} + \langle n\lambda | \sum_{p \neq m} V_p^{at} | m\mu \rangle$$

Three center integrals are neglected

$$\langle n\lambda | \sum_{p \neq m} V_p^{at} | m\mu \rangle \simeq \langle n\lambda | V_n^{at} | m\mu \rangle = \beta_{nm}^{\lambda\mu}$$

Intra-atomic matrix elements

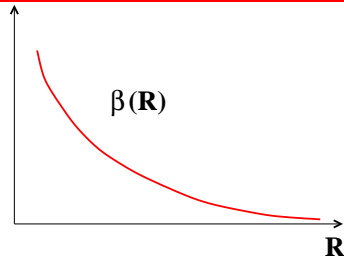
$$H_{nm}^{\lambda\mu} = \epsilon_{n\lambda}^{at} \delta_{\lambda\mu} + \langle n\lambda | \sum_{p \neq m} V_p^{at} | n\mu \rangle$$

$\left\{ \begin{array}{l} \epsilon_{n\lambda}^{at} \text{ atomic level of orbital } |n\lambda\rangle \\ \alpha_n^{\lambda\mu} = \langle n\lambda | \sum_{p \neq m} V_p^{at} | n\mu \rangle \text{ crystal field integral.} \end{array} \right.$

$$H_{nn}^{\lambda\mu} = \epsilon_{n\lambda}^0 \delta_{\lambda\mu}$$

Inter-atomic matrix elements :

$$H_{nm}^{\lambda\mu} = \beta_{nm}^{\lambda\mu}(\mathbf{m} - \mathbf{n}), \quad n \neq m$$



Hopping integrals are the crucial ingredient of TB schemes since they measure the ability of electrons to “jump” from one atom to the other.

c) Schrödinger equation

$$H |\psi_\alpha\rangle = \epsilon_\alpha |\psi_\alpha\rangle$$

Expanding $|\psi_\alpha\rangle$ in the TB basis we get

$$\tilde{H} \tilde{C}^\alpha = \epsilon_\alpha \tilde{C}^\alpha$$

$$\tilde{H} = \begin{pmatrix} (\tilde{H}_{11}) & \cdots & (\tilde{H}_{1m}) & \cdots & (\tilde{H}_{1N_{at}}) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ (\tilde{H}_{n1}) & \cdots & \cdots & \cdots & \cdots \\ \vdots & & & \ddots & \\ (\tilde{H}_{N_{at}1}) & & & & (\tilde{H}_{N_{at}N_{at}}) \end{pmatrix} \text{ and } \tilde{C}^\alpha = \begin{pmatrix} (\tilde{C}_1^\alpha) \\ \vdots \\ (\tilde{C}_n^\alpha) \\ \vdots \\ (\tilde{C}_{N_{at}}^\alpha) \end{pmatrix}$$

$$\left\{ \begin{array}{l} (\tilde{H}_{nm}) = \{H_{nm}^{\lambda\mu}\}_{(\lambda=1,l,\mu=1,l)} \text{ submatrix of size } l \times l \\ (\tilde{C}_n^\alpha) = \{c_{n\lambda}^\alpha\}_{(\lambda=1,l)} \text{ subvector of size } l \end{array} \right.$$

Eigenvalue matrix equation of size $(lN_{at} \times lN_{at})$

Periodic system : Bloch theorem.

$$H |\psi_\alpha(\mathbf{k})\rangle = \epsilon_\alpha(\mathbf{k}) |\psi_\alpha(\mathbf{k})\rangle$$

$|\psi_\alpha(\mathbf{k})\rangle$ is expanded in Bloch waves $|k\lambda\rangle$:

$$|k\lambda\rangle = \frac{1}{\sqrt{N_{at}}} \sum_n e^{i\mathbf{k}\cdot\mathbf{n}} |n\lambda\rangle, \quad |\psi_\alpha(\mathbf{k})\rangle = \sum_\lambda c_\lambda^\alpha(\mathbf{k}) |k\lambda\rangle$$

The eigenvalue matrix equation then reads :

$$\tilde{H}(\mathbf{k}) \tilde{C}^\alpha(\mathbf{k}) = \epsilon_\alpha(\mathbf{k}) \tilde{C}^\alpha(\mathbf{k})$$

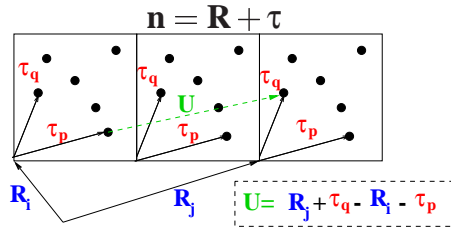
$$\left\{ \begin{array}{l} \tilde{C}^\alpha(\mathbf{k}) = \{c_\lambda^\alpha(\mathbf{k})\}_{(\lambda=1,l)} \text{ vector of size } l \\ \tilde{H}(\mathbf{k}) = \sum_n e^{i\mathbf{k}\cdot\mathbf{n}} \tilde{H}(\mathbf{n}) \text{ matrix of size } l \times l \end{array} \right.$$

If there are N_c atoms per unit cell we get the same type of equation matrix $\tilde{H}(\mathbf{k})$ is of size $(lN_c \times lN_c)$ (see *).

This eigenvalue matrix equation is easily solved at any \mathbf{k} point of Brillouin zone. The solution yields to the dispersion curve $\epsilon_\alpha(\mathbf{k})$.

Several atoms per unit cell

Let us consider the general case of N_c atoms per unit cell. Each atom of the crystal is indexed by two parameters :



We define Bloch waves associated with each atom τ of the unit cell :

$$|k\tau\lambda\rangle = \frac{e^{i\mathbf{k}\cdot\boldsymbol{\tau}}}{\sqrt{N_{at}}} \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} |(i\tau)\lambda\rangle$$

$e^{i\mathbf{k}\cdot\boldsymbol{\tau}}$ arbitrary phase factor introduced for convenience .

The eigen state $|\psi_\alpha(\mathbf{k})\rangle$ is expanded in Bloch waves :

$$|\psi_\alpha(\mathbf{k})\rangle = \sum_\lambda c_{\tau\lambda}^\alpha(\mathbf{k}) |k\tau\lambda\rangle$$

The eigenvalue matrix equation then reads :

$$\tilde{H}(\mathbf{k}) \tilde{C}^\alpha(\mathbf{k}) = \varepsilon_\alpha(\mathbf{k}) \tilde{C}^\alpha(\mathbf{k})$$

$$\tilde{H}(\mathbf{k}) = \begin{pmatrix} (\tilde{H}_{11}) & \cdots & (\tilde{H}_{1q}) & \cdots & (\tilde{H}_{1N_c}) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ (\tilde{H}_{p1}) & \cdots & \cdots & \cdots & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ (\tilde{H}_{N_c 1}) & \cdots & \cdots & \cdots & (\tilde{H}_{N_c N_c}) \end{pmatrix} \text{ and } \tilde{C}^\alpha = \begin{pmatrix} (\tilde{C}_1^\alpha) \\ \vdots \\ (\tilde{C}_p^\alpha) \\ \vdots \\ (\tilde{C}_{N_c}^\alpha) \end{pmatrix}$$

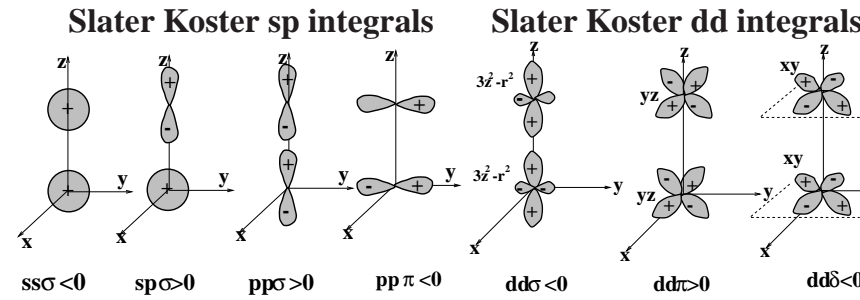
$$\begin{cases} \tilde{C}_p^\alpha(\mathbf{k}) = \{c_{\tau_p\lambda}^\alpha(\mathbf{k})\}_{(\lambda=1,l)} = \langle k\tau_p\lambda | \psi_\alpha(\mathbf{k}) \rangle \\ \tilde{H}_{pq}(\mathbf{k}) = \{H_{pq}^{\lambda\mu}(\mathbf{k})\}_{(\lambda=1,l,\mu=1,l)} \end{cases}$$

$$H_{pq}^{\lambda\mu} = \langle k\tau_p\lambda | H | k\tau_q\mu \rangle = \sum_j e^{i\mathbf{k}\cdot(\mathbf{R}_j + \boldsymbol{\tau}_q - \boldsymbol{\tau}_p)} H^{\lambda\mu}(\mathbf{R}_j + \boldsymbol{\tau}_q - \boldsymbol{\tau}_p)$$

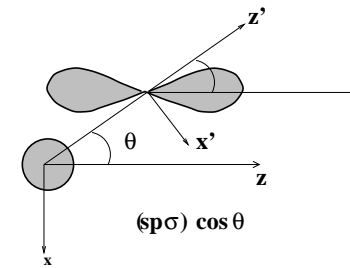
Eigenvalue matrix equation of size $(N_c \times N_c)$

d) Slater Koster parameters

definition of some hopping integrals



angular dependance of hopping integrals



$$\tilde{\beta}(\mathbf{R}) = \tilde{T}^{-1}(u, v, w) \tilde{\beta}(0, 0, 1) \tilde{T}(u, v, w)$$

$$\begin{pmatrix} ss\sigma & 0 & 0 & sp\sigma & 0 & 0 & 0 & 0 & sd\sigma \\ 0 & pp\pi & 0 & 0 & 0 & 0 & pd\pi & 0 & 0 \\ 0 & 0 & pp\pi & 0 & 0 & pd\pi & 0 & 0 & 0 \\ -sp\sigma & 0 & 0 & pp\sigma & 0 & 0 & 0 & 0 & pd\sigma \\ 0 & 0 & 0 & 0 & dd\delta & 0 & 0 & 0 & 0 \\ 0 & 0 & -pd\pi & 0 & 0 & dd\pi & 0 & 0 & 0 \\ 0 & -pd\pi & 0 & 0 & 0 & 0 & dd\pi & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & dd\delta & 0 \\ sd\sigma & 0 & 0 & -pd\sigma & 0 & 0 & 0 & 0 & dd\sigma \end{pmatrix}$$

$\tilde{\beta}(001)$

SOME IMPORTANT QUANTITIES

a) 2 fundamental operators

Green operator : G(z)

By definition we have :

$$G(z) = (z - H)^{-1} \quad z \in \mathbb{C}$$

In distribution theory we have the well known identity :

$$\delta(x) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \left(\frac{1}{x + i\epsilon} \right)$$

Therefore we can write :

$$\delta(E - H) = -\frac{1}{\pi} \text{Im} G(E^+) \quad \text{where} \quad G(E^+) = \lim_{\epsilon \rightarrow 0^+} G(z = E + i\epsilon)$$

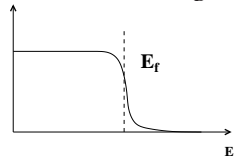
density operator : ρ

By definition we have :

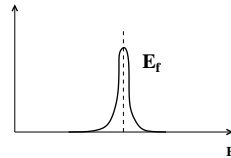
$$\rho = f(H)$$

where f is the Fermi function :

$$f(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - \mu}{k_B T}\right)}$$



$$-\frac{df(\epsilon)}{d\epsilon} \approx \delta(\epsilon - \mu)$$



$\rho(\mathbf{r})$ is the charge density : $\rho(\mathbf{r}) = \langle \mathbf{r} | \rho | \mathbf{r} \rangle$

Decay properties of the density matrix :

$$\langle \mathbf{r} | \rho | \mathbf{r}' \rangle \begin{cases} k_F \frac{\cos(k_F |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} & \text{metal OK} \\ k_F \frac{\cos(k_F |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} \exp(-c \frac{k_B T}{k_F} |\mathbf{r} - \mathbf{r}'|) & \text{metal temp T} \\ \exp(-\gamma \epsilon_{gap} |\mathbf{r} - \mathbf{r}'|) & \text{semi conductor} \end{cases}$$

Both operators have a very simple expression in the eigenfunction basis set $|\alpha\rangle$ of the Hamiltonian ($H|\alpha\rangle = \epsilon_\alpha|\alpha\rangle$) :

$$G(z) = \sum_{\alpha} |\alpha\rangle (z - \epsilon_\alpha)^{-1} \langle \alpha|$$

$$\rho = \sum_{\alpha} |\alpha\rangle f(\epsilon_\alpha) \langle \alpha|$$

b) density of states and local quantities

Total density of states

$$n(E) = \sum_{\alpha} \delta(E - \epsilon_\alpha) = \text{Tr} \delta(E - H)$$

It follows that :

$$n(E) = -\frac{\text{Im}}{\pi} \text{Tr} [G(E^+)]$$

Local density of states

$$n_{n\lambda}(E) = \langle n\lambda | \delta(E - H) | n\lambda \rangle = -\frac{\text{Im}}{\pi} \langle n\lambda | [G(E^+)] | n\lambda \rangle$$

$$= \sum_{\alpha} |\langle n\lambda | \alpha \rangle|^2 \delta(E - \epsilon_\alpha)$$

The total charge

$$N_{el} = \text{Tr} [\rho] = \sum_{\alpha} f(\epsilon_\alpha)$$

Local charge

$$q_{n\lambda} = \langle n\lambda | \rho | n\lambda \rangle = \sum_{\alpha} |\langle n\lambda | \alpha \rangle|^2 f(\epsilon_\alpha)$$

Obviously we have the relation :

$$q_{n\lambda} = \int f(E) n_{n\lambda}(E) dE$$

and

$$n(E) = \sum_{n\lambda} n_{n\lambda}(E) \quad , \quad N_{el} = \sum_{n\lambda} q_{n\lambda}$$

Local density of states (and local charges) are very useful too have a description at the atomic level : for example it can give insight in reactivity mechanisms, understanding of STM images in magnetism (interfaces etc..) which are extremely dependant of local electronic structure.

c) Moments

It is often not necessary to know all the details of the band structure of the Hamiltonian. One possibility is to use an integrated quantity such as the moments of the density of states.

pth moment

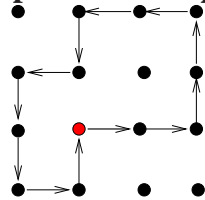
Let $\mu_n^{(p)}$ be the p th moment of the local density of states n_n (let's forget about the orbitals for the sake of simplicity) :

$$\mu_n^{(p)} = \int E^p n_n(E) dE = \int E^p \langle n | \delta(E - H) | n \rangle$$

It comes that :

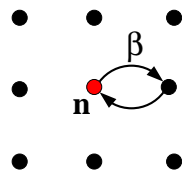
$$\mu_n^{(p)} = \langle n | H^p | n \rangle = \sum_{n_1, n_2, \dots, n_{p-1}} \langle n | H | n_1 \rangle \langle n_1 | H | n_2 \rangle \dots \langle n_{p-1} | H | n \rangle$$

closed path in real space



Second Moment

$$\mu_n^{(2)} = \langle n | H^2 | n \rangle = \sum_m \beta^2(\mathbf{m}) = Z_n \beta^2$$



rectangular lattice

$$\mu_n^{(2)} = 4 \beta^2$$

Width of the density of states :

$$W_n = \sqrt{\mu_n^{(2)}} = \sqrt{Z_n} |\beta|$$

The width of the local density of states depends on the hopping integrals and on the square root of the number of neighbours.

A SIMPLE EXAMPLE

Let us consider the simple-cubic s band lattice with hopping integrals only between first neighbours (we will omit λ index).

$$H = \sum_n |n\rangle \varepsilon^0 \langle n| + \sum_{n,m}' |n\rangle \beta \langle m|$$

a) Volume

Bloch States :

$$|k\rangle = \frac{1}{\sqrt{N_{at}}} \sum_n' e^{i\mathbf{k}\cdot\mathbf{n}} |n\rangle$$

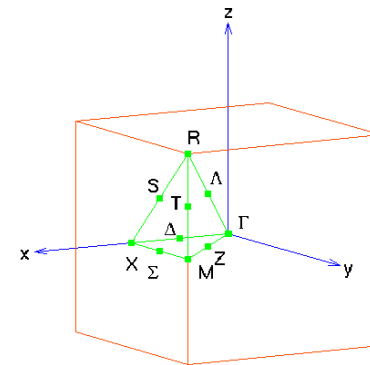
A standard calculation then yields :

$$H|k\rangle = \varepsilon(\mathbf{k})|k\rangle \quad \text{with} \quad \varepsilon(\mathbf{k}) = E^0 + \beta \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}$$

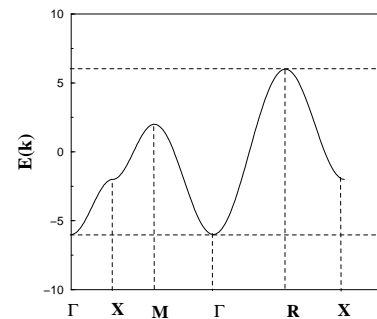
\mathbf{R} : 1st neighbours vector. ($\mathbf{R} = \pm a(1, 0, 0), \pm a(0, 1, 0), \pm a(0, 0, 1)$)

$$\varepsilon(\mathbf{k}) = \varepsilon^0 + 2\beta(\cos k_x a + \cos k_y a + \cos k_z a)$$

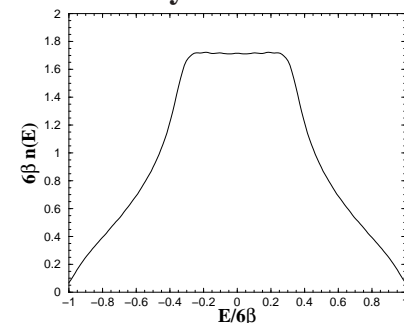
Brillouin zone



band structure

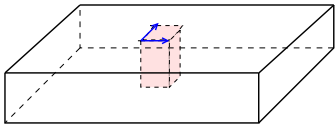


density of states

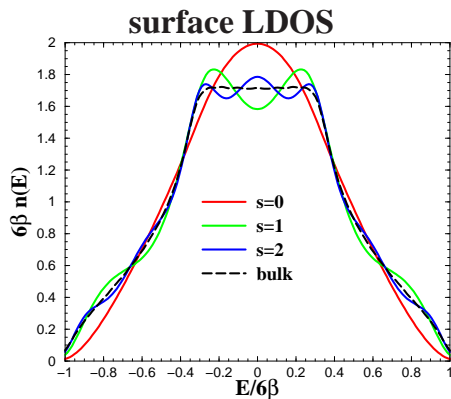
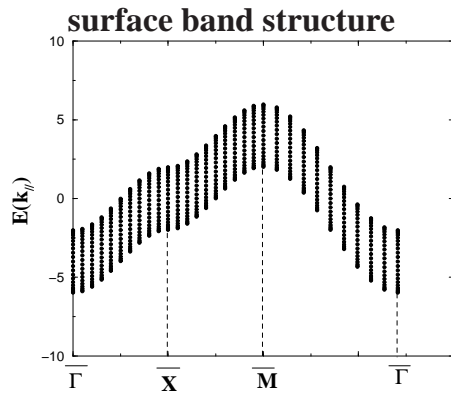
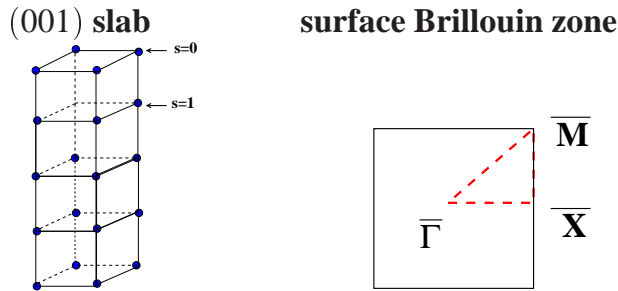


b) Surface

Slab geometry : P infinite atomic planes with two dimensional periodicity \Rightarrow Eigenvalue matrix equation of size : $(Pl \times Pl)$.



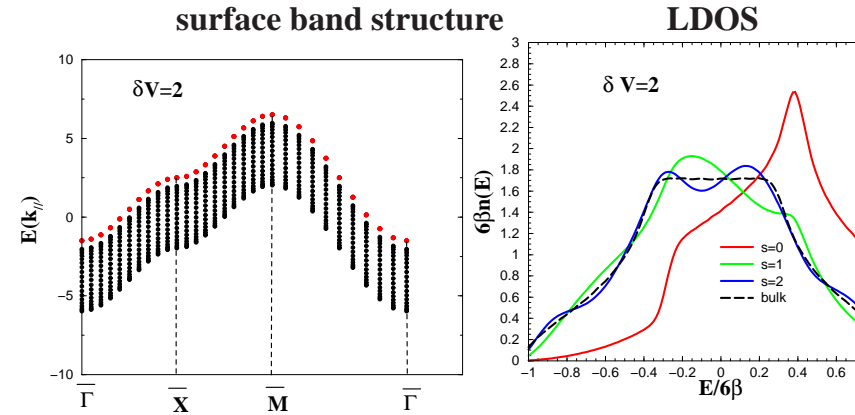
(001) surface of the simple cubic s-band lattice.



c) Surface States

Perturbation potential :

$$\delta V = |n_s = 0\rangle \delta V_s \langle n_s = 0|$$



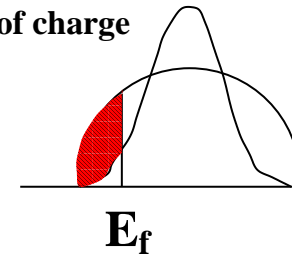
d) general trends

- Total range of the spectrum : same as in the bulk (if no surface states)
- LDOS of the surface plane is narrower ($W_s = \sqrt{Z_s}\beta$).
- Rapid recovery of the bulk LDOS on going into the crystal.
- van-Hove singularities smoother than in the bulk.
- Surface states : not if $\delta V_s = 0$ but possible if δV_s large enough.

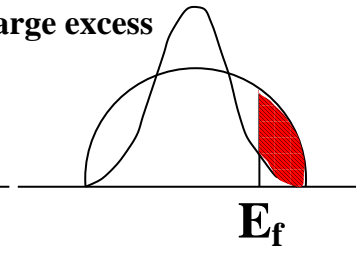
e) problems of charges

There is a charge transfer at the surface.

lack of charge



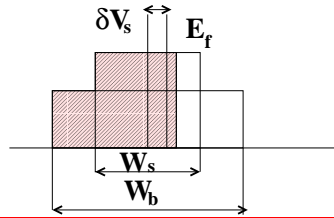
charge excess



Self consistent tight-binding

a) Local Charge Neutrality (LCN)

In metals and also semi-conductors there is an efficient screening and each atom remains almost neutral. We introduce a local potential which is diagonal and therefore modifies the intra-atomic levels.



The shifts δV_s of the intra-atomic levels are determined self-consistently in order to impose a strict local charge neutrality.

$$\int f(E) n_s(E, \delta V_s) = q_b \quad , \quad q_b = \text{bulk number of electron}$$

b) Hubbard U model

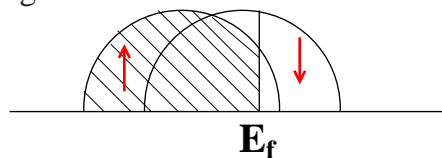
In situation where it may not be appropriate to ensure a strict LCN, because charge transfert are significant, but bonding is still covalent the simplest approximation is the Hubbard U model.

$$\delta V_n = U \times (q_n - q_b)$$

U : Hubbard U , q_n : charge of atom n , q_b : reference charge.

c) magnetism

The Hubbard U model can be extended by making the U term spin dependant, modifying the on-site elements of the Hamiltonian :



$$\begin{aligned} \varepsilon_{\uparrow} &= \varepsilon^0 + U(q_{\downarrow} - q^{para}) \\ \varepsilon_{\downarrow} &= \varepsilon^0 + U(q_{\uparrow} - q^{para}) \end{aligned}$$

Doing tight-binding

a) the TB parameters

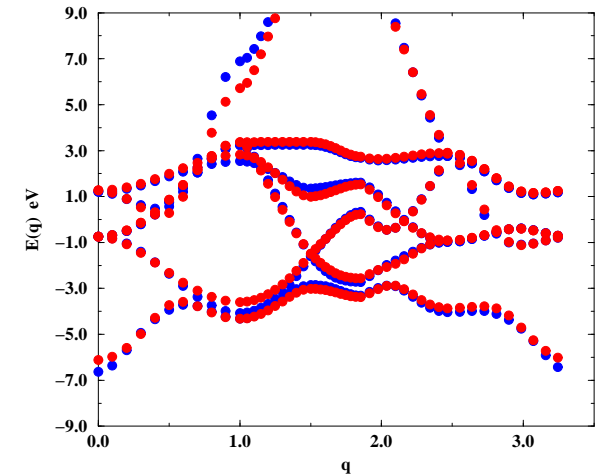
parameters of the model :

- intra-atomic levels ε_{λ}^0 ,
- Slater Koster parameters $\beta_{\lambda\mu}$
($ss\sigma$, $sp\sigma$, $sd\sigma$, $pp\sigma$, $pp\pi$, $pd\sigma$ $pd\pi$, $dd\sigma$, $dd\pi$, $dd\delta$)

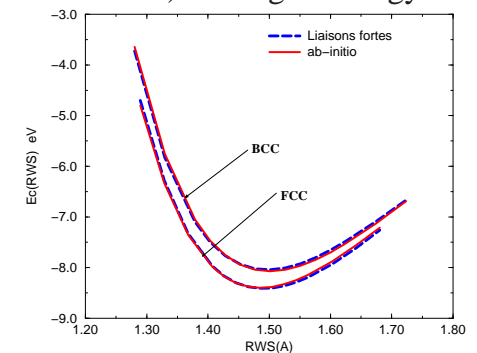
Distance dependance of hopping integrals : exponential decay...

$$\beta_{\lambda\mu}(R) = \beta_{\lambda\mu}^0 \exp[-q_{\lambda\mu}(\frac{R}{R_0} - 1)]$$

parameters fitted on *ab-initio* results for simple bulk systems, or molecules, depending on the type of system one wants to study.



Total energy (see next section) : fitting of energy curves.



b) Some refinements

- non-orthogonal tight-binding.

General eigenvalue problem :

$$\tilde{H}\tilde{C}^\alpha = \epsilon_\alpha \tilde{S}\tilde{C}^\alpha$$

There are several ways to proceed :

- * working with $\tilde{S}^{-1}\tilde{H}$ (not hermitian)

In general it is useful to define a conjuguate basis (not unique) :

$$|\tilde{m}\rangle = \sum_n [S^{-1}]_{nm} |n\rangle$$

The closure relation becomes :

$$\sum_n |\tilde{n}\rangle \langle n| = \sum_{nm} |n\rangle [S^{-1}]_{nm} \langle n| = Id$$

Local quantities are no longer defined in a unique manner.

$$q_n = \langle \tilde{n} | \rho | n \rangle = \sum_m \underbrace{\langle m | \rho | n \rangle}_{\rho_{mn}} S_{nm} = \sum_\alpha \sum_m \langle m | \alpha \rangle f(\epsilon_\alpha) \langle \alpha | n \rangle S_{nm}$$

- * using Lowdin or Cholesky decomposition ($\tilde{S} = \tilde{U}^\dagger \tilde{U}$) and solving :

$$\tilde{H}\tilde{C}^\alpha = \epsilon_\alpha \tilde{C}^\alpha$$

$$\tilde{H} = \tilde{U}^\dagger^{-1} \tilde{H} \tilde{U}^{-1} \quad \text{and} \quad \tilde{C}^\alpha = \tilde{U} \tilde{C}^\alpha$$

- environment dependance of some parameters.

- * hopping integrals.

Dorantes-Davila and Pastor, PRB **51**, 16 627 (1995)

Tang *et al.*, PRB **53**, 979 (1996)

Nguyen-Manh, Pettifor and Vitek, PRL **85**, 4136 (2000)

- * on-site levels.

Mehl and Papaconstantopoulos, PRB **54**, 4519 (1996).

- ab-initio tight-binding.

- * using pseudo-atomic orbitals but fitting total energy.

Porezag *et al.*, PRB **51**, 12947 (1995)

- * DFT-tight-binding with some approximations.

Sankey and Niklewsky, PRB **40**, 3979 (1989)

c) Direct Diagonalization

Standard diagonalization scheme : N^3 algorithm allowing to handle system size around $N = 5000$, on good work stations :

sp systems : $N = 4 \times N_{at}$, therefore $N_{at}^{max} \simeq 1250$

spd systems : $N = 9 \times N_{at}$, therefore $N_{at}^{max} \simeq 550$

N_{at}^{max} also depends on the physics : if self-consistent scheme needed, these atomic sizes can become prohibitive.

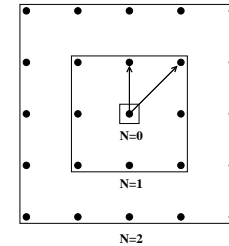
d) Order-N methods

Recursion methods : The Green function is back.

Expansion of diagonal elements of $G(z)$ in continued fraction :

$$\langle n | G | n \rangle = \frac{1}{z - a_1^n - \frac{b_1^n}{z - a_2^n - \frac{b_2^n}{\ddots \frac{b_N^n}{z - a_N^n - b_N^n \Sigma(z)}}}}$$

a_i^n, b_i^n coefficients of the continued fraction. Calculated by a recursion technic involving the building of “growing” clusters which size depends on the number of coefficients.



$\Sigma(z)$ terminating function to simulate the infinite system : related to the width of the electronic spectrum.

The recursion method is an efficient technic in some cases (it needs a good LDOS) but it suffers of several “drawbacks”, in particular the calculation of forces, which implies the calculation of off-diagonal elements of $G(z)$ that are difficult to evaluate.

Decomposition of the energy

Fermi Operator expansion : The density operator is back.

- Chebyshev expansion

Fermi function in a Chebyshev polynomial expansion :

$$\rho = f(H) \simeq p(H) = \frac{c_0}{2}I + \sum_{j=1}^{n_{pl}} c_j T_j(H)$$

matrix recursion relations :

$$\begin{cases} T_0(\tilde{H}) = \tilde{I}, \\ T_1(\tilde{H}) = \tilde{H}, \\ T_{j+1}(\tilde{H}) = 2\tilde{H}T_j(\tilde{H}) - T_{j-1}(\tilde{H}) \end{cases}$$

- rational representation

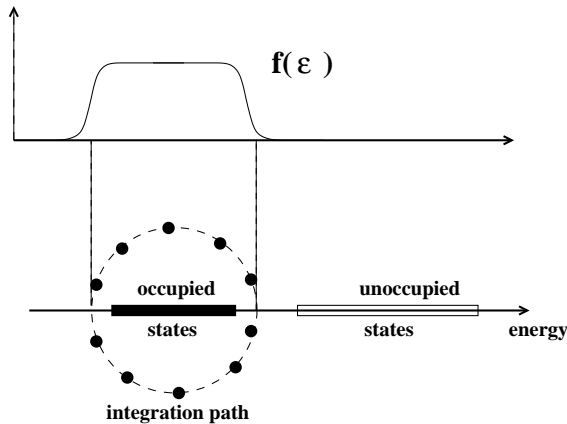
$$F = \sum_v \frac{w_v}{H - z_v}$$

Contour integral :

$$f(\varepsilon) = \frac{1}{2i\pi} \oint \frac{dz}{\varepsilon - z}$$

The discretization of this integral leads to :

$$f(\varepsilon) = \sum_{v=1}^{n_{pd}} \frac{w_v}{\varepsilon - z_v}$$

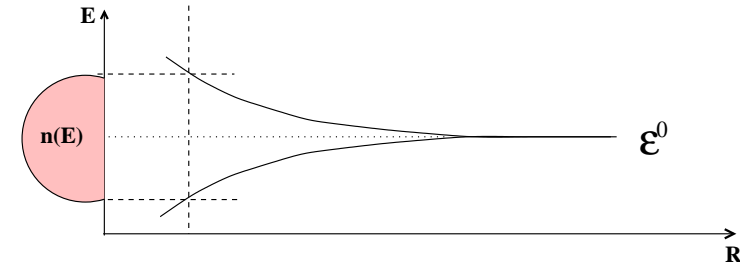


a) The band (bond) term

One important part of the total energy is the band energy term.

$$E_{band} = 2 \sum_{\alpha} f(\varepsilon_{\alpha}) \varepsilon_{\alpha} = \int E f(E) n(E) dE = Tr(\rho H)$$

$$E_{bond} = 2 \sum_n \int (E - \varepsilon_n^0) f(E) n_n(E) dE$$

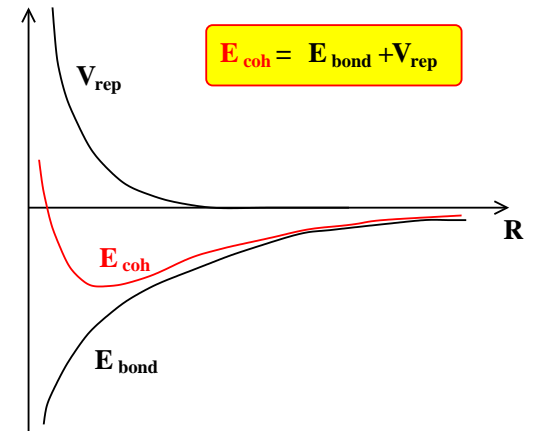


E_{bond} is an attractive term.

b) The repulsive term

Repulsive pairwise “empirical” potential :

$$V_{rep} = \sum_n \sum_{m \text{ neighbour of } n} A_{nm} e^{-p(\frac{R_{nm}}{R_0} - 1)}$$



Double counting terms to be subtracted : $E_{dc} = \sum_n q_n \delta V_n$

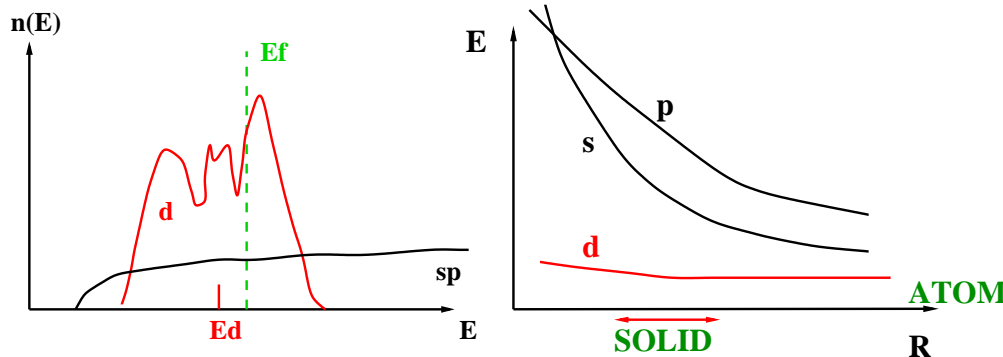
$$E_{coh} = E_{bond} + V_{rep} - \sum_n q_n \delta V_n$$

c) A different approach

FORCES

a problem of energy reference

Raising of the on-site levels in a “non-rigid” manner.



The “bonding” contribution of *s* and *p* electron is “unphysical”.

passing round the problem

Onsite levels are shifted in such a way that the cohesive energy is only given by a band term : the repulsive term is “hidden” in the raising of on site levels.

$$E_{coh} = \sum_{\alpha} \epsilon'_{\alpha}$$

On site levels are environment dependant :

$$\epsilon_{i\lambda}^0 = a_{\lambda} + b_{\lambda} g_i^{2/3} + c_{\lambda} g_i^{4/3} + d_{\lambda} g_i^2$$

$$g_i = \sum_{j \neq i} \exp(-p(R_{ij}/R_0 - 1)) f_c(R_{ij})$$

fitting the parameters

Parameters are obtained by a simultaneous fitting of band-structure and total energy.

a) Derivative of the band term

$$E_{band} = 2Tr[\rho H] = 2 \sum_{nm} \rho_{nm} H_{mn}$$

Derivation of E_{band} with respect to a displacement $\delta \mathbf{r}_k$:

$$\frac{dE_{band}}{d\mathbf{r}_k} = 2 \left(Tr \left[\frac{d\rho}{d\mathbf{r}_k} H \right] + Tr \left[\rho \frac{dH}{d\mathbf{r}_k} \right] \right)$$

Or more explicitly :

$$\frac{dE_{band}}{d\mathbf{r}_k} = 2 \left(\sum_{nm} \frac{d\rho_{nm}}{d\mathbf{r}_k} H_{mn} + \sum_{nm} \rho_{nm} \frac{dH_{mn}}{d\mathbf{r}_k} \right)$$

The first term is very small :

$$\frac{dE_{band}}{d\mathbf{r}_k} = 2Tr \left[\rho \frac{dH}{d\mathbf{r}_k} \right]$$

b) Local charge neutrality is not a problem !

$$\text{Local potential : } \delta V = \sum_n |n\rangle \delta V_n \langle n|$$

$$E_{band} = Tr[(H_0 + \delta V)\rho(H_0 + \delta V)] - \underbrace{\sum_n q_n \delta V_n}_{Tr[\rho(H_0 + \delta V)\delta V]} = Tr[H_0 \rho(H_0 + \delta V)]$$

the LCN potential δV does not appear explicitly. Therefore we have

$$\frac{dE_{band}}{d\mathbf{r}_k} = 2Tr \left[\rho \frac{dH_0}{d\mathbf{r}_k} \right]$$

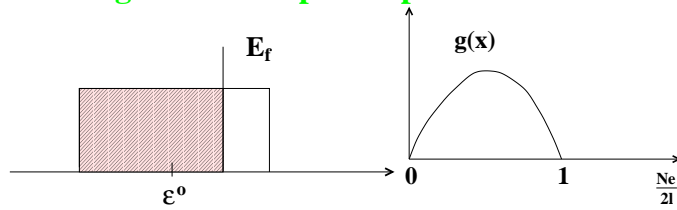
c) Derivative of the repulsive term

The repulsive potential is a simple pair-interaction it is therefore straightforward to derive analytically.

All terms of the Hamiltonian H_{nm} have an analytical expression and the forces are straightforward to calculate.

Empirical Potentials

a) Tight-Binding derived empirical potential



$$E_{bond} \propto W g(N_e) \quad \text{with} \quad W \propto \sqrt{\mu^{(2)}}$$

$g(x)$ parabolic-like function (whatever the DOS).

Second Moment potential :

$$E_{bond} = \sum_n E_{bond}^n$$

Second moment approximation

$$E_{bond}^n \propto \sqrt{\mu_n^{(2)}}$$

It leads to a potential of the form :

$$E_{tot} = - \sum_n \sqrt{\sum_{m \neq n} \xi_{nm}^2 e^{-2q(\frac{R_{nm}}{R_0}-1)}} + \sum_n \sum_{m \neq n} A_{nm}^2 e^{-p(\frac{R_{nm}}{R_0}-1)}$$

b) Embedded Atom Potentials

$$E_{tot} = \sum_n F(\rho_n(r)) + V_{pair}(r)$$

Second moment potential is very similar to embedded atom potential (EAM) even though its justification is very different.

$$\rho_n(r) = \sum_{m \neq n} \xi_{nm}^2 e^{-2q(\frac{R_{nm}}{R_0}-1)}$$

$$F(\rho) = \sqrt{\bar{\rho}}$$

DFT justification

a) The DFT energy

$$E[\rho] = \underbrace{\sum_{\alpha} f_{\alpha} \epsilon_{\alpha}}_{Tr(\rho H)} - \int V_{eff}(\mathbf{r}) \rho(\mathbf{r}) d^3 \mathbf{r} + F[\rho]$$

$$\left\{ \begin{array}{l} V_{eff}(\mathbf{r}) = V_N(\mathbf{r}) + \underbrace{\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r}'}_{V_H(\mathbf{r})} + \underbrace{\mu_{xc}(\mathbf{r})}_{\frac{d}{d\rho}[\rho \epsilon_{xc}(\rho)]} \\ F[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' + \int V_N(\mathbf{r}) \rho(\mathbf{r}) d^3 \mathbf{r} + \underbrace{\int \epsilon_{xc}(\rho(\mathbf{r})) \rho(\mathbf{r}) d^3 \mathbf{r}}_{E_{xc}[\rho]} \end{array} \right.$$

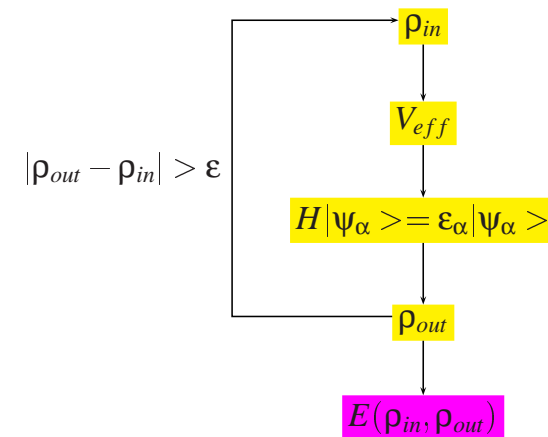
Therefore it comes that :

$$E[\rho] = \sum_{\alpha} f_{\alpha} \epsilon_{\alpha} - \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' + \int (\epsilon^{xc}(\mathbf{r}) - \mu^{xc}(\mathbf{r})) \rho(\mathbf{r}) d^3 \mathbf{r} + E_{N,N}$$

Which can be written in a “condensed manner” :

$$E[\rho] = Tr[\rho H] - Tr[\rho(1/2V_H + \mu^{xc})] + E_{xc}[\rho] + E_{NN}$$

b) Kohn Sham algorithm



c) Kohn-Sham and Harris energy

$$E^{KS}[\rho_{in}, \rho_{out}] = Tr[\rho_{out}H] - Tr\left[\rho_{out}\left(1/2V_H^{in} + \mu_{xc}(\rho_{in})\right)\right] + E_{xc}[\rho_{out}] + E_{NN}$$

$$E^{Har}[\rho_{in}, \rho_{out}] = Tr[\rho_{out}H] - Tr\left[\rho_{in}\left(1/2V_H^{in} + \mu_{xc}(\rho_{in})\right)\right] + E_{xc}[\rho_{in}] + E_{NN}$$

At self consistency we have

$$\rho_{in} = \rho_{out} = \rho \text{ and } E^{KS}[\rho] = E^{Harris}[\rho] = E[\rho]$$

d) the right input density

$$\rho_{in}(\mathbf{r}) = \sum_n \rho_n^{at}(\mathbf{r}) \quad \text{with} \quad \rho_n^{at}(\mathbf{r}) = \rho_{at}(\mathbf{r} - \mathbf{n})$$

Which can be written as an operator :

$$\rho_{in} = \sum_n |n\lambda\rangle q_{n\lambda}^{at} \langle n\lambda|$$

Where $q_{n\lambda}^{at}$ is the atomic occupation of the orbital λ at site n .

Ionic and Hartree potentials are also superposition of atomic contributions :

$$V_N = \sum_m V_N^m \quad ; \quad V_H = \sum_n V_H^n = \sum_n \int \frac{\rho_{at}(\mathbf{r}' - \mathbf{n})}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

The energy can be decomposed in the following way :

$$\begin{aligned} E &= Tr[(\rho_{out} - \rho_{in})H] && \rightarrow \text{bond energy} \\ &+ Tr \sum_n \rho_n^{at} \left(\sum_{m \neq n} 1/2V_H^m + V_N^m \right) + E_{NN} && \rightarrow E_{es} \\ &+ \left(E_{xc}[\rho_{in}] - \sum_n E_{xc}[\rho_n^{at}] \right) && \rightarrow \Delta E_{xc} \\ &+ \sum_n \left\{ Tr \rho_n^{at} (T + 1/2V_H^n + V_N^n) + E_{xc}[\rho_n^{at}] \right\} && \rightarrow \text{atomic energy} \end{aligned}$$

E_{es} electrostatic interaction between neutral atoms.

E_{es} EXACTLY PAIR INTERACTION

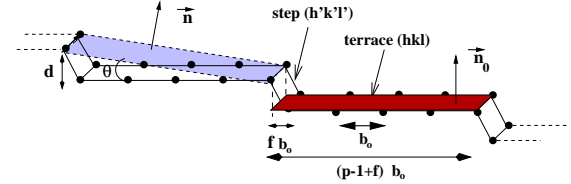
ΔE_{xc} variation of exchange correlation energy from atom to solid.

ΔE_{xc} APPROXIMATELY PAIR INTERACTION

$$E_{coh} \approx E_{bond} + V_{rep}$$

Step energies and step-step interactions

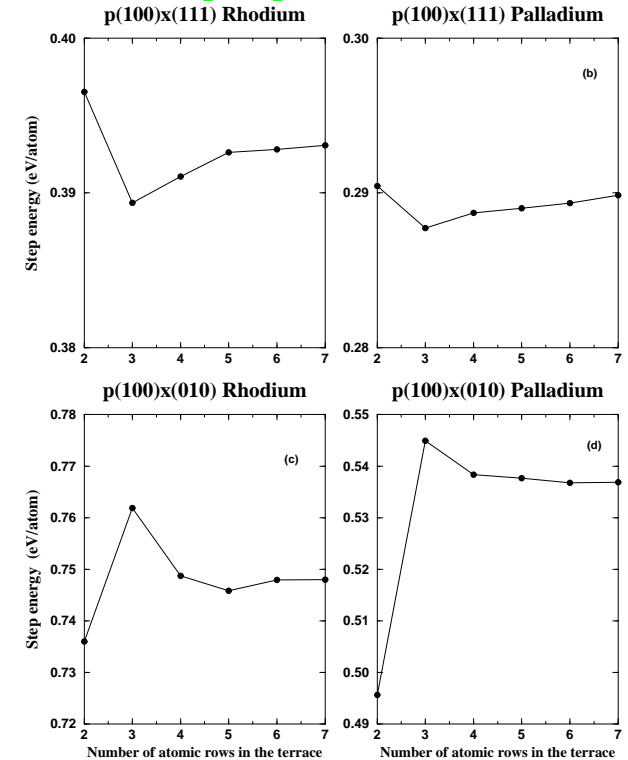
F. Raouafi, C. Barreateau, D. Spanjaard, M.C. Desjonquères, To be published in Surf. Science (2001).



Step energies of 5 different geometries

Somorjai notations	Miller indices	f	Edge geometry	2D unit cell
p(111)x(100) step A	(p+1,p-1,p-1)	2/3	nn	p odd : PR p even : CR
p(111)x(111) step B	(p-2,p,p)	1/3	nn	p odd : CR p even :PR
p(100)x(111)	(1,1,2p-1)	1/2	nn	CR
p(100)x(010)	(0,1,p-1)	0	n nn	p odd : CR p even :PR
p(110)x(111)	(2p-1,2p-1,1)	1/2	nn	CR

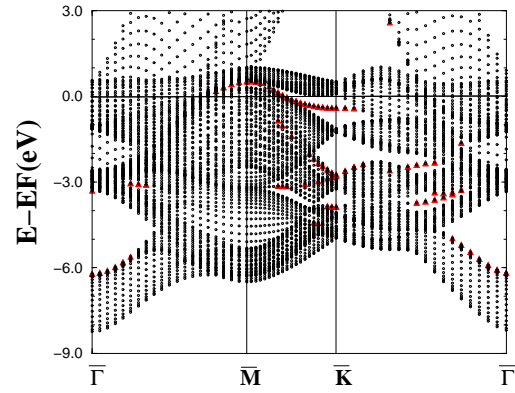
Step-step interaction



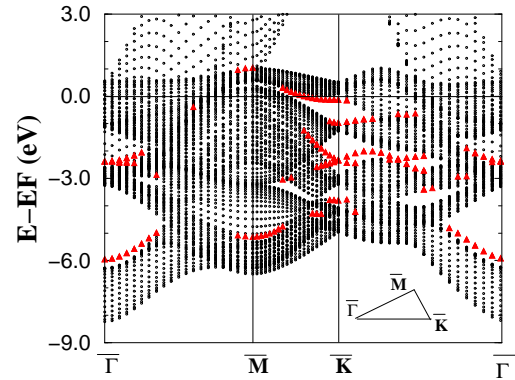
spd tight-binding for transition metals
Application to surfaces and clusters

C. Barreteau, D. Spanjaard, M.C. Desjonquères, PRB **58**, 9721 (1998).

$\delta V = 0$ (no Local Charge Neutrality)

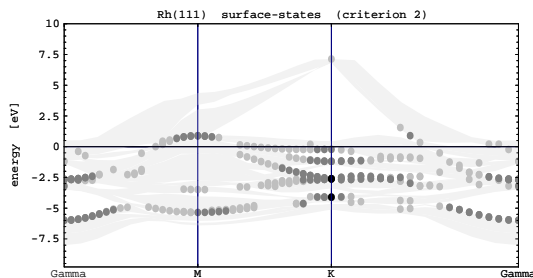


δV with Local Charge Neutrality



ab-initio Plane waves

A. Eichler, J. Hafner, J. Furthmüller G.Kresse, Surf. Sci. **346**,300 (1996).



Coalescence of Single-Walled Carbon Nanotubes

M. Terrones, H. Terrones, F. Banhart, J.-C. Charlier, and P. M. Ajayan, Science May 19 2000 : 1226-1229.

