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# Plane waves and pseudopotentials : I. Formalism

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# Outline

## I. Formalism

(the PW basis set, Brillouin Zone integration, pseudopotentials, computing the forces, the PAW method)

## II. Iterative techniques

(the Kohn-Sham equation, the SCF convergence, optimization of the geometry)

## III. Applications

(the growth of Carbon nanotubes, the index of refraction of 'crystal')

## IV. The ABINIT software

(licence, structure, capabilities)

# A basic reference on DFT and applications to solids

Richard M. Martin

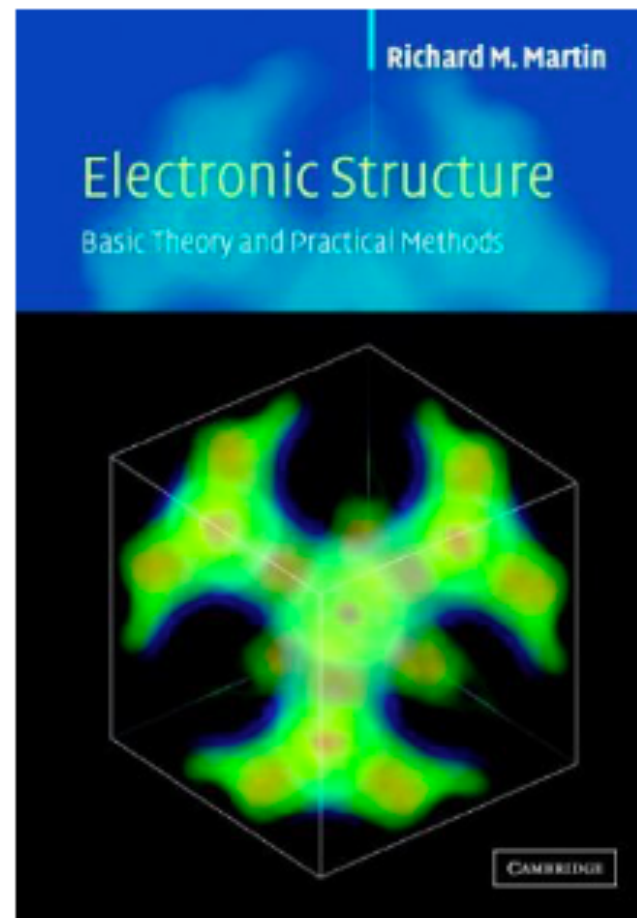
Cambridge University Press, 2004

Electronic Structure : Basic Theory and  
Practical Methods

(ISBN: 0521782856)

For details, see

[http : ///www.cambridge.org/uk/catalogue/catalogue.asp?isbn=0521782856](http://www.cambridge.org/uk/catalogue/catalogue.asp?isbn=0521782856)



# Our starting point : DFT (I)

Non-interacting electrons in the Kohn-Sham potential :

$$\left( -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Density  $n(\mathbf{r}) = \sum_i^{\text{occ}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

Hartree potential      Exchange-correlation potential

To be solved self-consistently !

## Our starting point : DFT (II)

The solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimisation of

$$E_{\text{KS}}[\{\psi_i\}] = \sum_i^{\text{occ}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

with 
$$n(\mathbf{r}) = \sum_i^{\text{occ}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

under constraints of orthonormalization  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$   
for the occupied orbitals.

How to represent all these quantities in a computer ?  
Only a finite set of numbers can be stored and treated ...

# The plane wave basis set

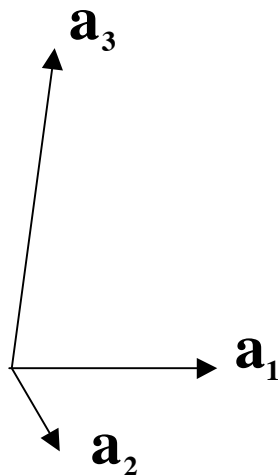


## Prerequisites of plane waves

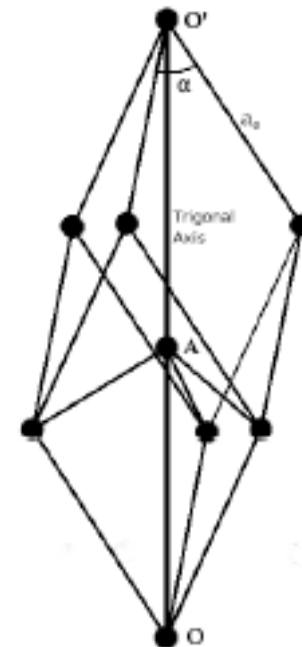
Plane waves  $e^{i\mathbf{K}\mathbf{r}}$  have infinite spatial extent.

One cannot use a finite set of planewaves for a finite system !  
Need periodic boundary conditions.

Primitive vectors  $\mathbf{a}_i$ , primitive cell volume  $\Omega_0$

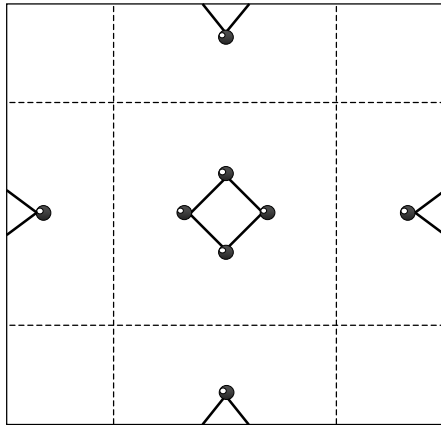


OK for crystalline solids  
But : finite systems, surfaces,  
defects, polymers, ... ?



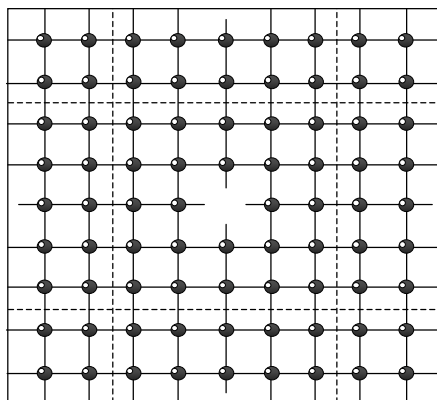
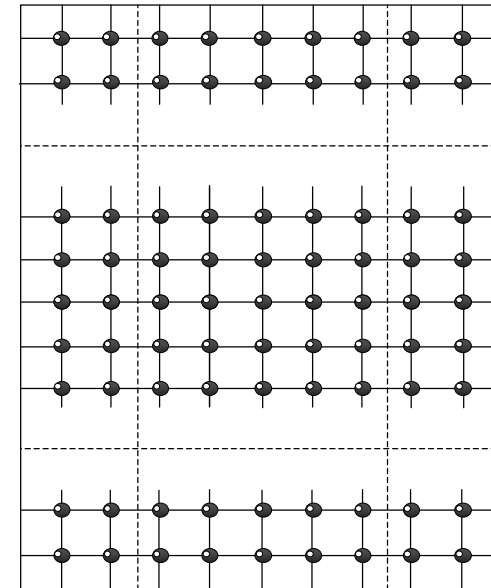


# The supercell technique



Molecule

Surface : treatment  
of a slab



Point defect in a bulk solid

The supercell must be sufficiently big : convergence study



## Treatment of a periodic system : wavevectors

For a **periodic** Hamiltonian : wavevector  $\mathbf{k}$  (crystal momentum)  
To be considered in the Brillouin Zone

Bloch's theorem 
$$\psi_{m,\mathbf{k}}(\mathbf{r}+\mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{a}_i} \psi_{m,\mathbf{k}}(\mathbf{r})$$

Normalization of wavefunctions ?

**Born-von Karman supercell** supercell vectors  $N_i\mathbf{a}_i$  with  $N=N_1N_2N_3$

$$\psi_{m,\mathbf{k}}(\mathbf{r}+N_i\mathbf{a}_i) = \psi_{m,\mathbf{k}}(\mathbf{r})$$

$$\psi_{m,\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u_{m,\mathbf{k}}(\mathbf{r}) \quad u_{m,\mathbf{k}}(\mathbf{r}+\mathbf{a}_i) = u_{m,\mathbf{k}}(\mathbf{r})$$



## Plane wave representation of wavefunctions

Reciprocal space lattice :  $\mathbf{G}$  such that  $e^{i\mathbf{G}\mathbf{r}}$  has the periodicity of the real space lattice

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} \quad \psi_{\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} \sum_{\mathbf{G}} u_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

$$u_{\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} e^{-i\mathbf{G}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) d\mathbf{r} \quad (\text{Fourier transform})$$

Kinetic energy of a plane wave  $-\frac{\nabla^2}{2} \rightarrow \frac{(\mathbf{k}+\mathbf{G})^2}{2}$

The coefficients  $u_{\mathbf{k}}(\mathbf{G})$  for the lowest eigenvectors decrease exponentially with the kinetic energy  $\frac{(\mathbf{k}+\mathbf{G})^2}{2}$

Selection of plane waves determined by a cut-off energy  $E_{\text{cut}}$

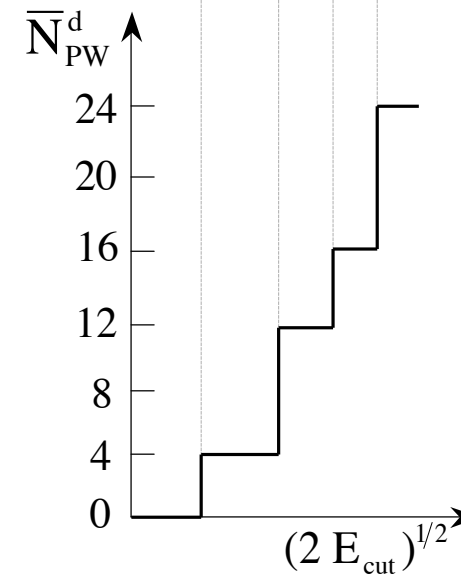
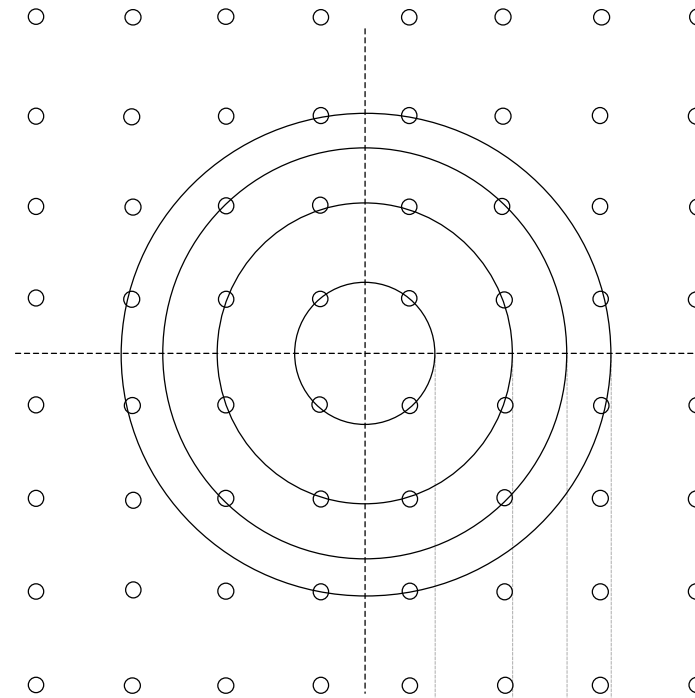
$$\frac{(\mathbf{k} + \mathbf{G})^2}{2} < E_{\text{cut}} \quad \text{Plane wave sphere}$$



Discontinuous increase of the number of the plane waves  $N_{\text{pw}}$



The number of plane waves  
as a function of the  
kinetic energy cut-off





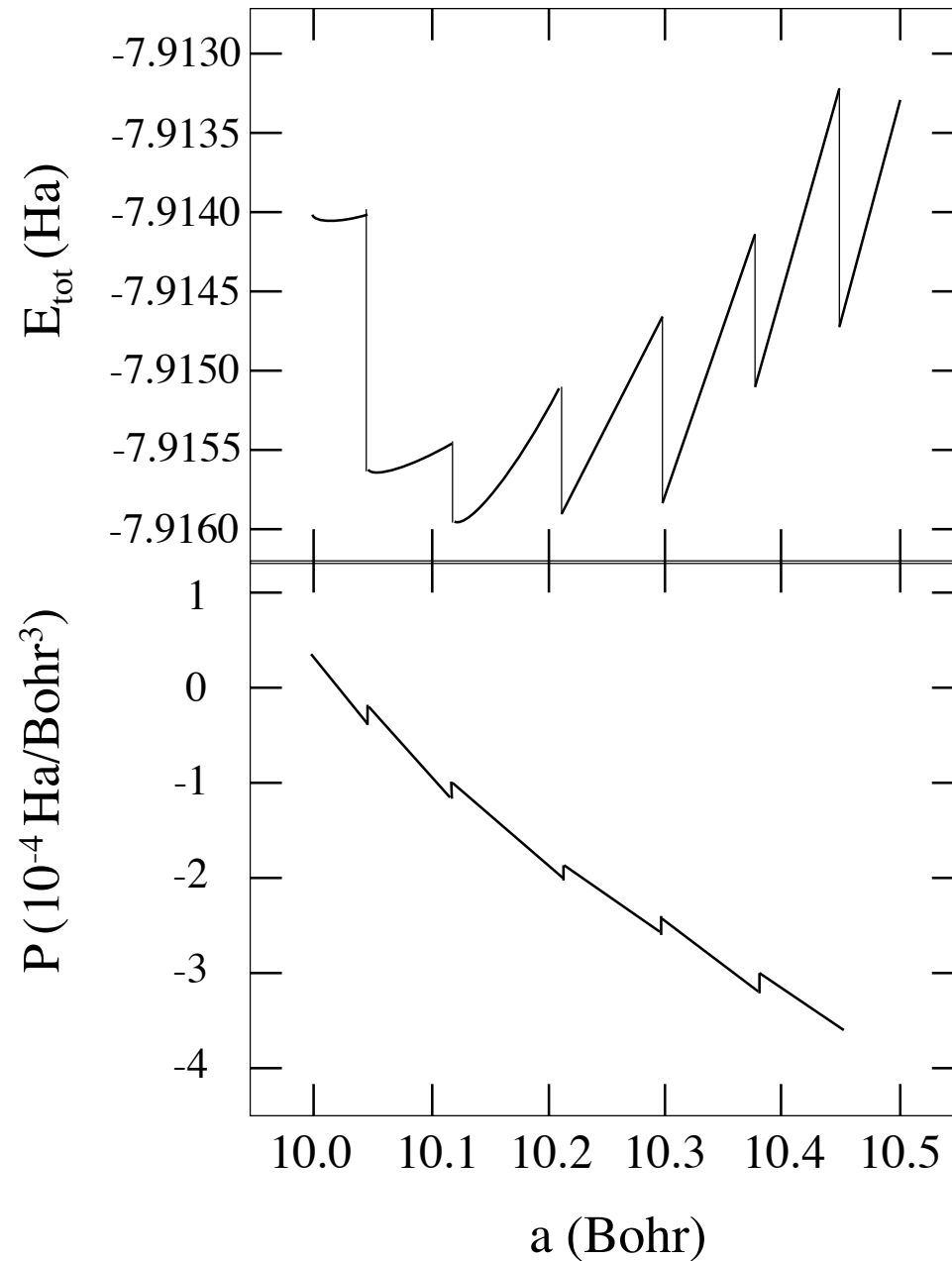
## Discontinuities due to the sudden change of the number of plane waves

Note atomic units are used here :

1Ha = 2 Ry = 27.211 eV

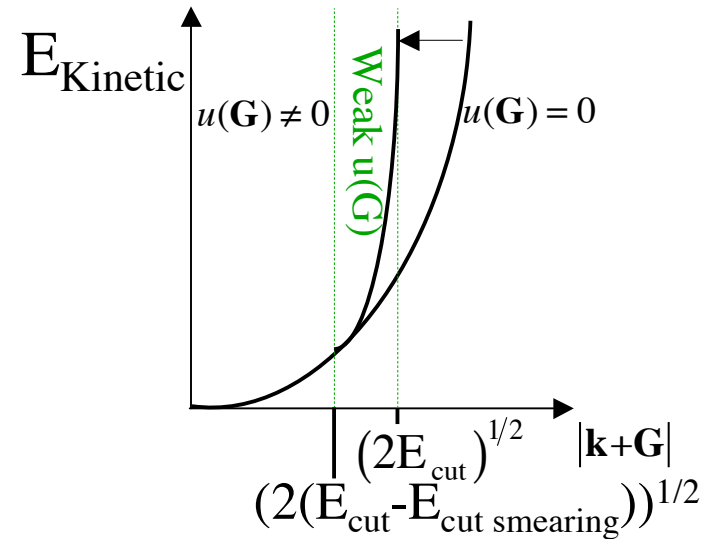
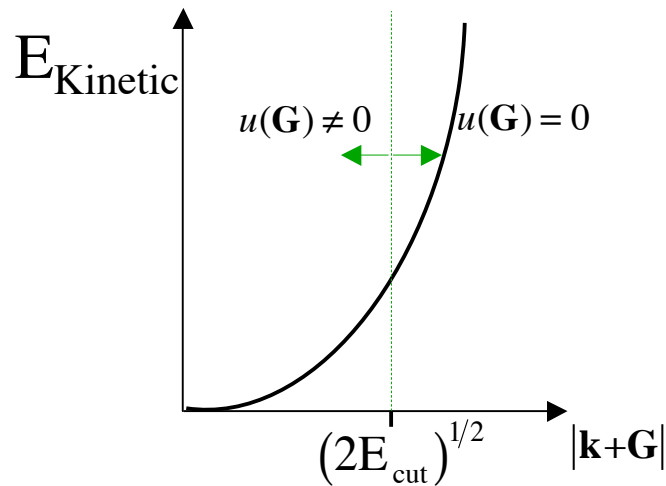
1Bohr=0.529 angstrom

1 Ha/Bohr<sup>3</sup>=21421 GPa





# Removal of the discontinuities of the total energy



Smearing of  $u(\mathbf{G})$

Damping of the  $u(\mathbf{G}) \Rightarrow$  progressive enlargement of the  $\mathbf{G}$  set  
 $\Rightarrow$  removal of the discontinuities

# Plane wave representation of the density and potential

Fourier transform of a periodic function  $f(\mathbf{r})$

$$f(\mathbf{G}) = \frac{1}{\Omega_{\text{or}\bar{\mathbf{r}}}} \int_{\Omega_{\text{or}\bar{\mathbf{r}}}} e^{-i\mathbf{G}\mathbf{r}} f(\mathbf{r}) d\mathbf{r} \quad f(\mathbf{r}) = \sum_{\bar{\mathbf{G}}} e^{-i\mathbf{G}\mathbf{r}} f(\mathbf{G})$$

Poisson's equation  $\Rightarrow n(\mathbf{G})$  and  $V_{\text{H}}(\mathbf{G})$

$$V_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \Leftrightarrow \nabla^2 V_{\text{H}}|_{\mathbf{r}} = -4\pi n(\mathbf{r})$$

Relation between Fourier coefficients:

$$\mathbf{G}^2 V_{\text{H}}(\mathbf{G}) = 4\pi n(\mathbf{G}) \quad V_{\text{H}}(\mathbf{G}) = \frac{4\pi}{\mathbf{G}^2} n(\mathbf{G})$$

For  $\mathbf{G}^2 = 0$  ( $\mathbf{G} = 0$ ) divergence of  $V_{\text{H}}(\mathbf{G} = 0)$

$$n(\mathbf{G} = 0) = \frac{1}{\Omega_{\text{or}}} \int_{\Omega_{\text{or}}} n(\mathbf{r}) d\mathbf{r} \quad \text{Average}$$



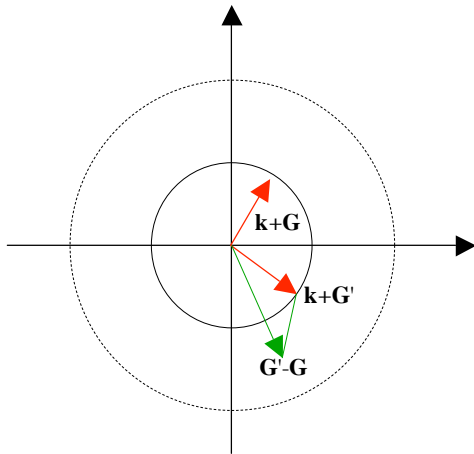
## Representation of the density

Density associated with one eigenfunction :

$$n_{\mathbf{n}\mathbf{k}}(\mathbf{r}) = u_{\mathbf{n}\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{n}\mathbf{k}}(\mathbf{r})$$

Computation of  $u_{\mathbf{n}\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{n}\mathbf{k}}(\mathbf{r})$

$$\begin{aligned} &= \left( \sum_{\mathbf{G}} u_{\mathbf{n}\mathbf{k}}^*(\mathbf{G}) e^{-i\mathbf{G}\mathbf{r}} \right) \left( \sum_{\mathbf{G}'} u_{\mathbf{n}\mathbf{k}}(\mathbf{G}') e^{-i\mathbf{G}'\mathbf{r}} \right) \\ &= \sum_{\mathbf{G}\mathbf{G}'} \left[ u_{\mathbf{n}\mathbf{k}}^*(\mathbf{G}) u_{\mathbf{n}\mathbf{k}}(\mathbf{G}') \right] e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \end{aligned}$$



Non-zero coefficients for  $\mathbf{k}+\mathbf{G} \in \text{sphere}$   
 $\mathbf{k}+\mathbf{G}' \in \text{sphere}$

The sphere for  $n(\mathbf{G})$  has a double radius

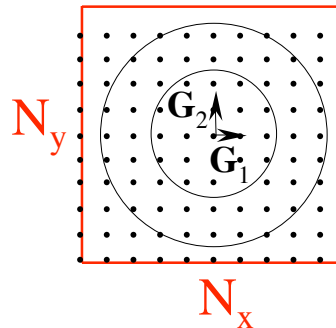


# Going from the real space to the reciprocal space

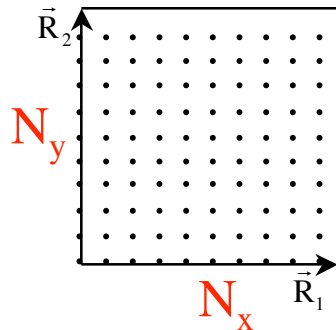
$$n(\mathbf{r}) = \sum_{\mathbf{G} \in \text{sphere}(2)} n(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$$

Use of the discrete Fourier transform  $\{\mathbf{r}_i\} \leftrightarrow \{\mathbf{G}\}$

$$n(\mathbf{G}) = \frac{1}{N_{\mathbf{r}_i}} \sum_{\{\mathbf{r}_i\}} n(\mathbf{r}_i) e^{-i\mathbf{G}\mathbf{r}_i}$$



Reciprocal lattice



Real lattice: original cell

Fast transform  $\{\mathbf{r}_i\} \leftrightarrow \{\mathbf{G}\}$ : algorithm Fast Fourier Transform





# Treatment of the continuity of space

Choice of a basis (e.g. Plane waves)

Truncating of the basis -> finite basis

$$\frac{(\mathbf{k}+\mathbf{G})^2}{2} < E_{\text{cut}} \quad \text{Sphere of plane waves}$$

Discontinuous increase of the number of plane waves ?

Smearing of  $u(\mathbf{G})$

-> Progressive incorporation of new  $\mathbf{G}$  vectors

Representation of the density

Sphere with a double radius in the reciprocal space

Going from the real space to reciprocal space

Discrete Fourier transform

Grid of points + Fast Fourier Transform

$$\{\mathbf{r}_i\} \leftrightarrow \{\mathbf{G}\}$$



## Simplicity of PW basis, but need for pseudopotentials

### The Fourier transform theory teaches us :

- details in real space are described if their characteristic length is larger than the inverse of the largest wavevector norm (roughly speaking)
- quality of a plane wave basis set can be systematically increased by increasing the cut-off energy

Problem : huge number of PWs is required to describe localized features (core orbitals, oscillations of other orbitals close to the nucleus)



Pseudopotentials (or, in general, « pseudization »)  
to eliminate the undesirable small wavelength features

# Brillouin zone integration

# From discrete states to the Brillouin zone

Discrete summations over states :

$$\text{Total kinetic energy } T = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$

$$\text{Density } n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

In the periodic case : summation over energy bands and integration over the Brillouin zone

$$\text{Total kinetic energy } T = \sum_n \frac{1}{\Omega_{0\mathbf{k}}} \int_{\Omega_{0\mathbf{k}}} f(\varepsilon_F - \varepsilon_{\mathbf{n}\mathbf{k}}) \langle \psi_{\mathbf{n}\mathbf{k}} | -\frac{1}{2} \nabla^2 | \psi_{\mathbf{n}\mathbf{k}} \rangle d\mathbf{k}$$

$$\text{Density } n(\mathbf{r}) = \sum_n \frac{1}{\Omega_{0\mathbf{k}}} \int_{\Omega_{0\mathbf{k}}} f(\varepsilon_F - \varepsilon_{\mathbf{n}\mathbf{k}}) \psi_{\mathbf{n}\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{n}\mathbf{k}}(\mathbf{r}) d\mathbf{k}$$

How to treat  $\frac{1}{\Omega_{0\mathbf{k}}} \int_{\Omega_{0\mathbf{k}}} X_{\mathbf{k}} d\mathbf{k}$  ?

# Brillouin zone integration

$$\frac{1}{\Omega_{ok}} \int_{\Omega_{ok}} X_{\mathbf{k}} d\mathbf{k} \Rightarrow \sum_{\{\mathbf{k}\}} w_{\mathbf{k}} X_{\mathbf{k}} \quad [ \text{with } \sum_{\{\mathbf{k}\}} w_{\mathbf{k}} = 1 ]$$

How to chose  $\{\mathbf{k}\}$  and  $\{w_{\mathbf{k}}\}$  ?

Special points

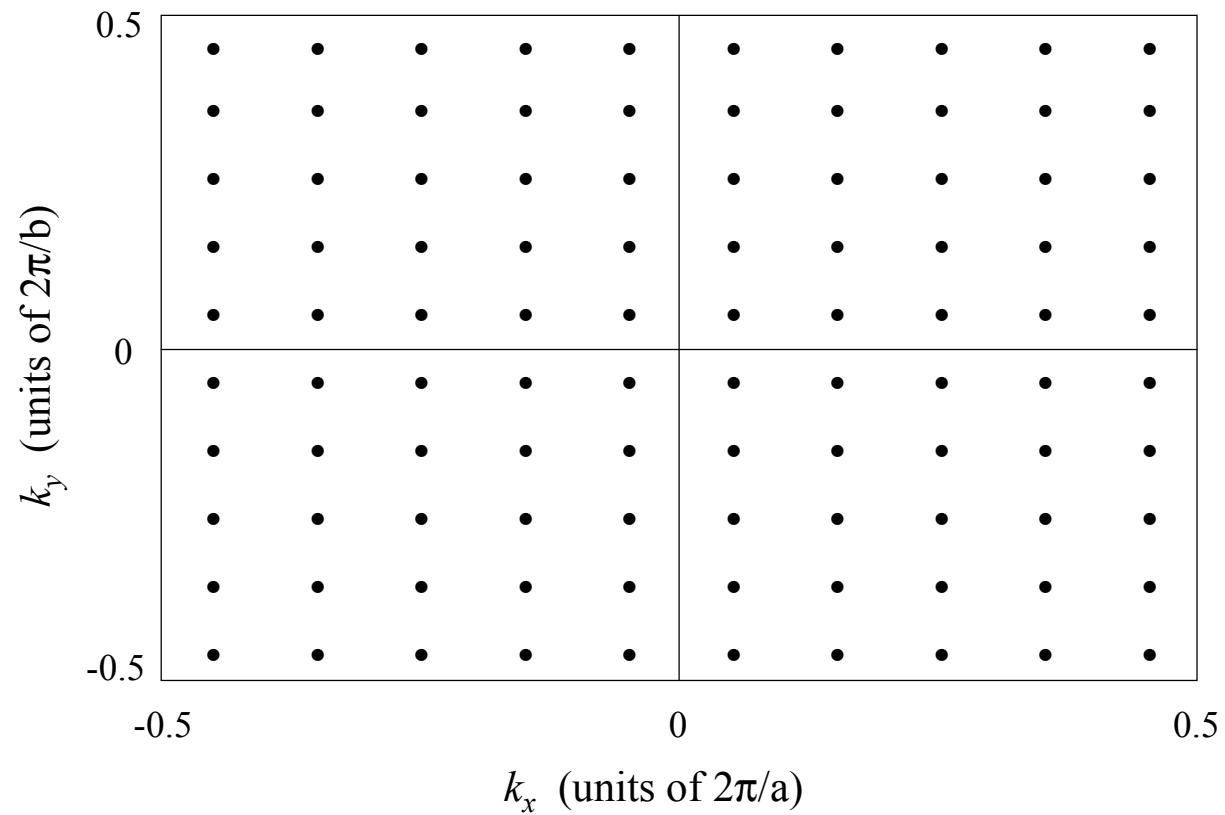
Weights

- If
- the integrand is periodic
  - the integrand is continuous + derivable at all orders (  $\mathcal{C}^\infty \mathcal{D}^\infty$  )
  - $\{\mathbf{k}\}$  homogeneous grid (1D - 2D - 3D) and  $w_{\mathbf{k}}$  all equal

Then exponential convergence, with respect to  $\Delta k$

- OK for semiconductors/insulators where the occupation number is independent of  $k$  within a band
- Convergence : one ought to test several grids with different  $\Delta k$
- Monkhorst & Pack grids (Phys. Rev. B 13, 5188 (1976))  
 $k_1 \times k_2 \times k_3$  points + simple cubic, FCC, BCC ...
- Other techniques ... (tetrahedron method)

*Homogeneous sampling of the Brillouin zone*

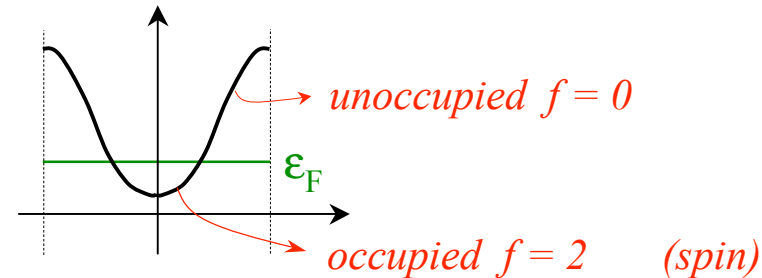




# Treatment of metals (I)

Behaviour of  $f(\epsilon_F - \epsilon_{nk})$  ?

Discontinuity of the integrand  
at the Fermi level



Smearing technique

First trial : generalisation of DFT to finite temperature

- $$f(\epsilon_{nk}) = \frac{1}{1 + e^{(\epsilon_{nk} - \epsilon_F)/kT}}$$

$f$  goes from 0 to 2 in an energy range of width  $kT$

- $$E(T) \cong E(T=0) + \alpha T^2 + \dots$$
$$F(T) = E - TS$$

**Problem :** the  $T$  needed to recover the same convergence  
as for semiconductors is very high ( $\gg 2000$  K)

# Treatment of metals (II)

Better technique : the goal is to obtain  $E(\sigma = 0)$

from a total energy expression  $E(\sigma)$  with modified occupation numbers, where  $\sigma$  is similar to a temperature

$$E(\sigma) \approx E(\sigma=0) + \alpha \sigma^2 + O(\sigma^3) \quad \text{with } \alpha \text{ small}$$

$$\text{or } E(\sigma) \approx E(\sigma=0) + \beta \sigma^n + O(\sigma^{n+1}) \quad \text{with } n > 2$$

$$f_{nk}(\epsilon_{nk}) = s \cdot \int_{t=\frac{\epsilon_{nk}-\epsilon_F}{\sigma}}^{\infty} \tilde{\delta}(t) dt \quad [ \text{with } \int_{-\infty}^{\infty} \tilde{\delta}(t) dt = 1 ]$$

*Spin factor*  $\nearrow$

$$\text{Gaussian smearing} \quad \tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} e^{-x^2} \quad \Rightarrow \quad \alpha \text{ small}$$

$$\text{Gauss - Hermite smearing} \quad \tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} \left( \frac{3}{2} - x^2 \right) e^{-x^2}$$

$$\Rightarrow n = 4 \quad \text{but occupations can be negatives}$$

...

'Cold Smearing' (Marzari)



# How many k points ? Smearing width ?

Semiconductors - Insulators

$$\# \mathbf{k} \times N_{atoms} \quad 50 \dots 500$$

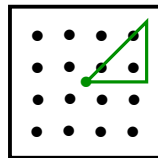


lattice parameter converged better than 0.5 %

Metals  $\# \mathbf{k} \times N_{atoms} \rightarrow 1000 \dots 2000$

⚠ Use symmetries  $\Leftrightarrow$  integration in the **irreducible** Brillouin zone

2D Example



grid  $4 \times 4 = 16$



3 points in the irreducible Brillouin Zone

Smearing : depends on the density of electronic states (DOS) at the Fermi level

s-p Metal (Al, Na ...)  $\sim 0.04$  Ha

d Metal (Cu, Ag...)  $\sim 0.01$  Ha

⚠ magnetism needs small  $\sigma$

# Pseudopotentials

## Core and valence electrons (I)

Core electrons occupy orbitals that are « the same » in the atomic environment or in the bonding environment

**It depends on the accuracy of the calculation !**

Separation between core and valence orbitals : the density...

$$\begin{aligned}n(\mathbf{r}) &= \sum_i^{occ} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \\ &= \sum_{i \in core}^{N_{core}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) + \sum_{i \in val}^{N_{val}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) = n_{core}(\mathbf{r}) + n_{val}(\mathbf{r})\end{aligned}$$

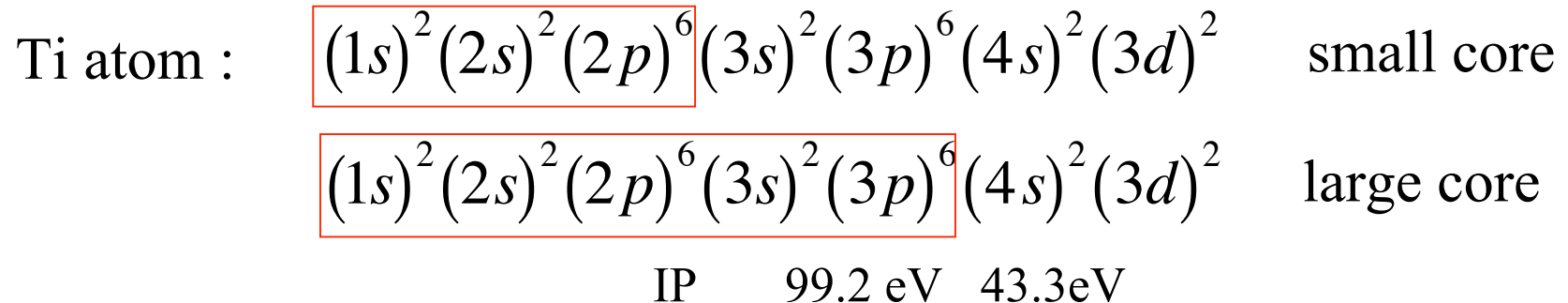
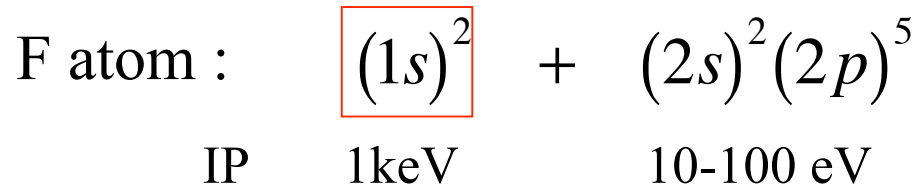
« Frozen core »     for  $i \in core$  :  $\psi_i = \psi_i^{atom}$

## Small core / Large core

It depends on the target accuracy of the calculation !

(remark also valid for pseudopotentials, with similar cores)

For some elements, the core/valence partitioning is obvious, for some others, it is not.



Gd atom : small core with n=1,2,3 shells , might include 4s, 4p, and 4d in the core. 4f partially filled

## Core and valence electrons (II)

Separation between core and valence orbitals : the energy ...

$$E_{\text{KS}}[\{\psi_i\}] = \sum_i^{\text{occ}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

$$\begin{aligned} E_{\text{KS}}[\{\psi_i\}] &= \sum_{i \in \text{core}}^{N_{\text{core}}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{core}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{core}}(\mathbf{r}_1) n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \sum_{i \in \text{val}}^{N_{\text{val}}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{val}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n_{\text{core}} + n_{\text{val}}] \end{aligned}$$

One would like to have an expression for the energy of the valence electrons ...

## Valence electrons in a screened potential

The potential of the nuclei  $\kappa$  is screened by the core electrons

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1$$

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\text{val},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \left( -\frac{Z_{\text{core},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 \right)$$

The total energy becomes

$$E = \left( E_{\text{val}} + \sum_{\kappa} E_{\text{core},\kappa} \right) + \frac{1}{2} \sum_{\substack{(\kappa,\kappa') \\ \kappa \neq \kappa'}} \frac{Z_{\text{val},\kappa} Z_{\text{val},\kappa'}}{|\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa'}|}$$

with  $E_{\text{val,KS}}[\{\psi_i\}] = \sum_{i \in \text{val}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int \left( \sum_{\kappa} V_{\text{ion},\kappa}(\mathbf{r}) \right) n_{\text{val}}(\mathbf{r}) d\mathbf{r}$

$$+ \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n_{\text{core}} + n_{\text{val}}]$$

Non-linear XC  
core correction

## Removing core electrons (I)

From the previous construction : valence orbitals must still be orthogonal to core orbitals  
( => oscillations, slope at the nucleus ...)

Pseudopotentials try to remove completely the core orbitals from the simulation

Problem with the number of nodes  
This is a strong modification of the system ...

Pseudopotentials confine the strong changes within a « cut-off radius »

## Removing core electrons (II)

Going from  $\left(-\frac{1}{2} \nabla^2 + v\right) |\psi_i\rangle = \epsilon_i |\psi_i\rangle$

To  $\left(-\frac{1}{2} \nabla^2 + v_{ps}\right) |\psi_{ps,i}\rangle = \epsilon_{ps,i} |\psi_{ps,i}\rangle$

**Possible** set of conditions (norm-conserving pseudopotentials) :

Hamann D.R., Schluter M., Chiang C, Phys.Rev.Lett. 43, 1494 (1979)

$$\epsilon_i = \epsilon_{ps,i}$$

$$\psi_i(\mathbf{r}) = \psi_{ps,i}(\mathbf{r}) \quad \text{for } r > r_c$$

$$\int_{r < r_c} |\psi_i(\mathbf{r})|^2 d\mathbf{r} = \int_{r < r_c} |\psi_{ps,i}(\mathbf{r})|^2 d\mathbf{r}$$

For the lowest  
angular momentum  
channels (s + p ... d ...f)



## Forms of pseudopotentials

Must be a linear, hermitian operator

$$\text{General form : } \left( \hat{V}_{ps} \psi \right) (\mathbf{r}) = \int V_{ps}^{kernel} (\mathbf{r}, \mathbf{r}') \psi (\mathbf{r}') d\mathbf{r}'$$

**Spherically symmetric !**  $V_{ps}^{kernel} (\mathbf{r}, \mathbf{r}') = V_{loc} (\mathbf{r}) \delta (\mathbf{r} - \mathbf{r}') + V_{nloc} (\mathbf{r}, \mathbf{r}')$

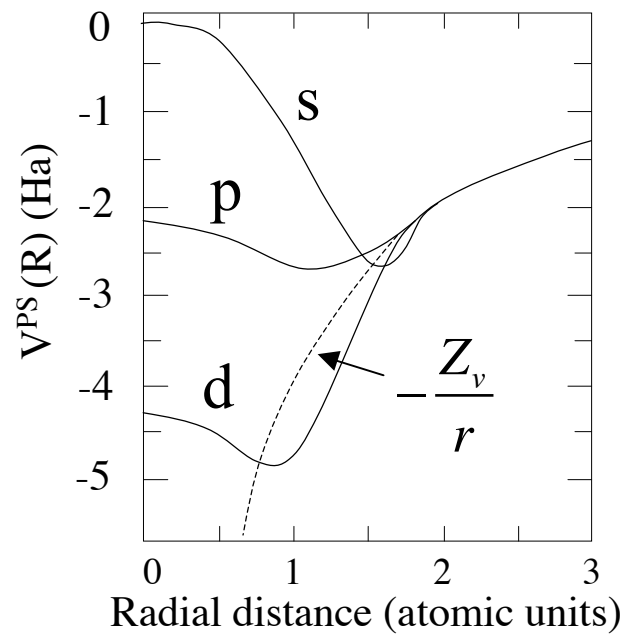
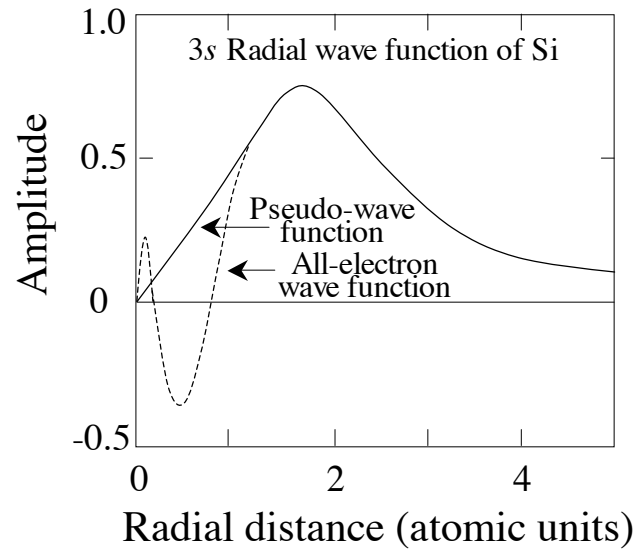
Non-local part  $V_{nloc} (\mathbf{r}, \mathbf{r}') = \sum_{\ell m} Y_{\ell m}^* (\theta, \varphi) V_{\ell} (r, r') Y_{\ell m} (\theta', \varphi')$

Semi-local psp  $V_{\ell} (r, r') = V_{\ell} (r) \delta (r - r')$

see the paper by Bachelet, Hamann and Schlüter, Phys.Rev.B 26, 4199 (1982)

Separable psp  $V_{\ell} (r, r') = \xi_{\ell}^* (r) f_{\ell} \xi_{\ell} (r')$

Kleinman L., Bylander D.M., Phys.Rev.Lett. 48, 1425 (1982)



# Computing the forces



# Computing the forces (I)

Born - Oppenheimer approximation  $\Rightarrow$  one finds the electronic ground state in the potential created by the nuclei.

Consider a given configuration of nuclei  $\{ R_{\kappa} \}$ .  
Usually it is NOT the equilibrium geometry.

$$F_{\kappa,\alpha} = - \left. \frac{\partial E}{\partial R_{\kappa,\alpha}} \right|_{\{ \bar{R}_{\kappa} \}} \quad (\text{principle of virtual works})$$

Forces can be computed by finite differences.

Better approach : compute the response to a perturbation

$$\{ R_{\kappa,\alpha} \} \rightarrow \{ R_{\kappa,\alpha} + \lambda \delta R_{\kappa,\alpha} \}$$

*Small parameter*

$\Rightarrow$  What is the energy change ?



# Computing the forces (II)

Case of an electronic eigenvalue

Perturbation theory : Hellmann - Feynman theorem

$$\frac{dE_n}{d\lambda} = \left\langle \psi_n^{(0)} \left| \frac{d\hat{H}}{d\lambda} \right| \psi_n^{(0)} \right\rangle$$

$$\frac{d\psi_n}{d\lambda} \text{ is not needed !}$$

Application to an atomic displacement :

$$\hat{H} = \hat{T} + \hat{V}_{ext} \{ \hat{\mathbf{R}} \} \Rightarrow \frac{\partial \hat{H}}{\partial \mathbf{R}_{\kappa, \alpha}} = \frac{\partial \hat{V}_{ext}}{\partial \mathbf{R}_{\kappa, \alpha}}$$
$$\mathbf{F}_{\kappa, \alpha} = - \frac{\partial E_n}{\partial \mathbf{R}_{\kappa, \alpha}} = - \left\langle \psi_n \left| \frac{\partial \hat{H}}{\partial \mathbf{R}_{\kappa, \alpha}} \right| \psi_n \right\rangle = - \int n(\mathbf{r}) \frac{\partial \hat{V}_{ext}(\mathbf{r})}{\partial \mathbf{R}_{\kappa, \alpha}} d\mathbf{r}$$

# Computing the forces (III)

## Generalisation to density functional theory

Reminder :  $E[\psi_i] = \sum_n \langle \psi_i | \hat{T} | \psi_i \rangle + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + E_{\text{Hxc}}[n]$

If change of atomic positions ...

$$V_{\text{ext}}(\vec{r}) = \sum_{k'} -\frac{Z_{k'}}{|\vec{r} - \vec{R}_{k'}|} \quad (\text{can be generalized to pseudopotential case})$$

$$\begin{aligned} \frac{\partial V_{\text{ext}}(\vec{r})}{\partial R_{k,\alpha}} &= +\frac{Z_{k'}}{|\vec{r} - \vec{R}_k|^2} \cdot \frac{\partial |\vec{r} - \vec{R}_k|}{\partial R_{k,\alpha}} \\ &= -\frac{Z_{k'}}{|\vec{r} - \vec{R}_k|^3} \cdot (\vec{r} - \vec{R}_k)_\alpha \end{aligned}$$

$$\frac{dE}{\partial R_{k,\alpha}} = \int n(\mathbf{r}') \frac{\partial V_{\text{ext}}(\mathbf{r}')}{\partial R_{k,\alpha}} d\mathbf{r}' = - \int \frac{n(\mathbf{r}')}{|\vec{r}' - \vec{R}_k|^3} \cdot (\vec{r}' - \vec{R}_k)_\alpha d\vec{r}'$$

# Computing the forces (IV)

$$\frac{dE}{\partial \mathbf{R}_{k,\alpha}} = \int n(\mathbf{r}') \frac{\partial V_{\text{ext}}(\mathbf{r}')}{\partial \mathbf{R}_{k,\alpha}} d\mathbf{r}' = - \int \frac{n(\mathbf{r}')}{|\vec{\mathbf{r}}' - \vec{\mathbf{R}}_k|^3} \cdot (\vec{\mathbf{r}}' - \vec{\mathbf{R}}_k)_\alpha d\vec{\mathbf{r}}'$$

Forces can be computed directly from the density !

No need for additional work (like solving the Kohn-Sham equation, or self-consistency) - at variance with finite-difference approach to forces.

Pseudopotentials instead of Coulomb potential ...

⇒ additional term, involving also wavefunctions ...

... Needed for PW/PP approach

If the basis set depends on the atomic positions, and is not complete ...

⇒ additional term (Pulay correction, or  
IBSC, incomplete basis set correction)

... Not needed for PW/PP approach

**Ultra-soft pseudopotentials,  
Projector Augmented Wave  
(PAW) method**



## Ultra-soft pseudopotentials : the idea

Problem with norm-conserving pseudopotentials :  
the norm conservation limits the softness !

When orbitals without nodes (1s, 2p, 3d, 4f) must be treated as valence, their characteristic wavelength is quite small, and the energy cut-off is large.

Idea (Vanderbilt, Phys. Rev. B 41, 7892 (1990))

Suppress the norm-conservation condition :

- modify the normalization, to keep correct scattering properties
- introduce charge density corrections,

For selected elements, can decrease the number of PW/Grid points by a factor of two or three.

More difficult to implement than norm-conserving PPs.

Can be obtained as a particular case of PAW construction ...

# Projector Augmented Waves (PAW)

Idea (P. Blöchl, PRB50, 17953 (1994)).

The true wave-function  $\Psi$   
 and a well-behaving pseudo-wavefunction  $\tilde{\Psi}$   
 can be linked by a linear transformation  $\Psi = T\tilde{\Psi}$   
 by which physical quantities like  $\langle \Psi | A | \Psi \rangle$   
 can be easily calculated in the  
 pseudo Hilbert space representation  $\langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle$  ,  
 with  $\tilde{A} = T^+ A T$ .

Similarly, the variational principle for the total energy

$$\frac{\partial E [T|\tilde{\Psi}\rangle]}{\partial \langle \tilde{\Psi} |} = \epsilon T^+ T |\tilde{\Psi}\rangle$$

gives an equivalent of the Kohn-Sham equation, for the pseudowavefunctions, and the search for the ground state can also be done in the pseudo Hilbert space.



# The transformation operator

The operator  $T$  has to modify the smooth pseudowavefunction in each atomic region, to give it the correct nodal structure.

➔ Identity + sum of atomic contributions

$$\Psi = T\tilde{\Psi} \quad \text{with} \quad T = 1 + \sum_R S_R \quad (\text{R=atomic site label})$$

Choose :

Partial waves  $|\phi_i\rangle$  = basis set, solutions of the Schrödinger Eq. for the isolated atoms within some cut-off radius  $r_{c,R}$

Pseudo partial waves  $|\tilde{\phi}_i\rangle$  , identical to the partial waves beyond the cut-off radius

Define  $S$  such as :  $|\phi_i\rangle = (1 + S_R)|\tilde{\phi}_i\rangle$

# Representation of the wavefunctions

$$\Psi = T\tilde{\Psi} \quad T = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle\tilde{p}_i|$$

Explicitely,  $\Psi = \tilde{\Psi} + \sum_R (|\Psi_R^1\rangle - |\tilde{\Psi}_R^1\rangle)$

with  $|\Psi_R^1\rangle = \sum_{i \in R} |\phi_i\rangle\langle\tilde{p}_i|\tilde{\Psi}\rangle$        $|\tilde{\Psi}_R^1\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle\langle\tilde{p}_i|\tilde{\Psi}\rangle$

$\tilde{\Psi}$  represented by **plane waves** (might use other representations)

$|\Psi_R^1\rangle$  and  $|\tilde{\Psi}_R^1\rangle$  represented on a **radial grid**, centered on R

Note :

$$\left\{ \begin{array}{l} \text{Outside of the spheres,} \\ \text{Inside one sphere,} \end{array} \right. \quad \begin{array}{l} |\Psi_R^1\rangle = |\tilde{\Psi}_R^1\rangle \\ \tilde{\Psi} = |\tilde{\Psi}_R^1\rangle \left( = \sum_{i \in R} |\tilde{\phi}_i\rangle\langle\tilde{p}_i|\tilde{\Psi}\rangle \right) \end{array}$$

# Approximations

- (1) Core electrons : usually treated in the frozen-core approximation, and treated separately (see later), without PW representation (same as PPs).
- (2) Finite PW basis set (same as PPs)
- (3) The partial wave expansion is truncated : only **one** or **two** partial wave(s), for each atom R, and each l,m channel

$$\sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i| \neq 1$$

**Inside** one sphere,  $\tilde{\Psi} = |\tilde{\Psi}_R^1\rangle \left( = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i| \tilde{\Psi} \right)$

is only **approximately true** !

$\tilde{\Psi}$  contributes inside the atomic spheres, and corrects for the missing terms due to truncation of partial wave expansion

## Why use the PW + PP or PAW methods ?

- (1) The basis set does not depend on atomic coordinates :  
easy computation of forces as numerically exact derivatives  
of the total energy with respect to atomic coordinates  
(no Pulay forces). Easy structural optimisation, or MD.  
This leads also to Car-Parrinello technique.
- (2) Systematic way to complete the basis set

For PW-PP : simple implementation

For PW-PAW : can be a numerically accurate  
implementation of DFT, including properties  
related to cores ; usually faster than PW-PP

Disadvantages : cannot lead to Order(N) implementation,  
does not treat efficiently finite systems (vacuum !).