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Density Functional Theory : Implementation in ABINIT

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Overview

Introduction
A. Density Functional Theory : our starting point
B. The plane wave basis set
C. Iterative algorithms. Data flow.

D. Brillouin zone integration
E. Pseudopotentials
F. Computing the forces

G. ABINIT
H. The band gap problem

Density Functional Theory : our starting point

Our starting point : DFT (I)

Non-interacting electrons in the Kohn-Sham potential :

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

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

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

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

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

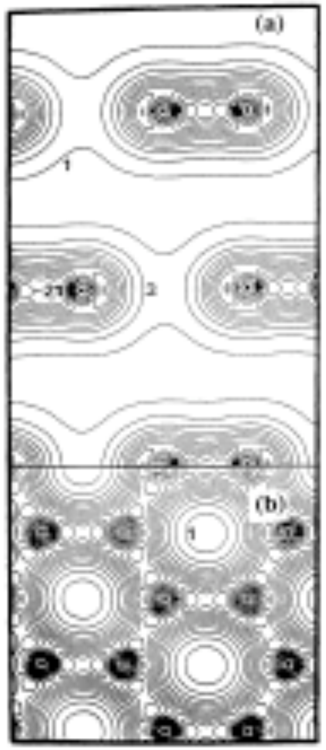
with $n(\mathbf{r}) = \sum_i^{occ} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$

under constraints of orthonormalization $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

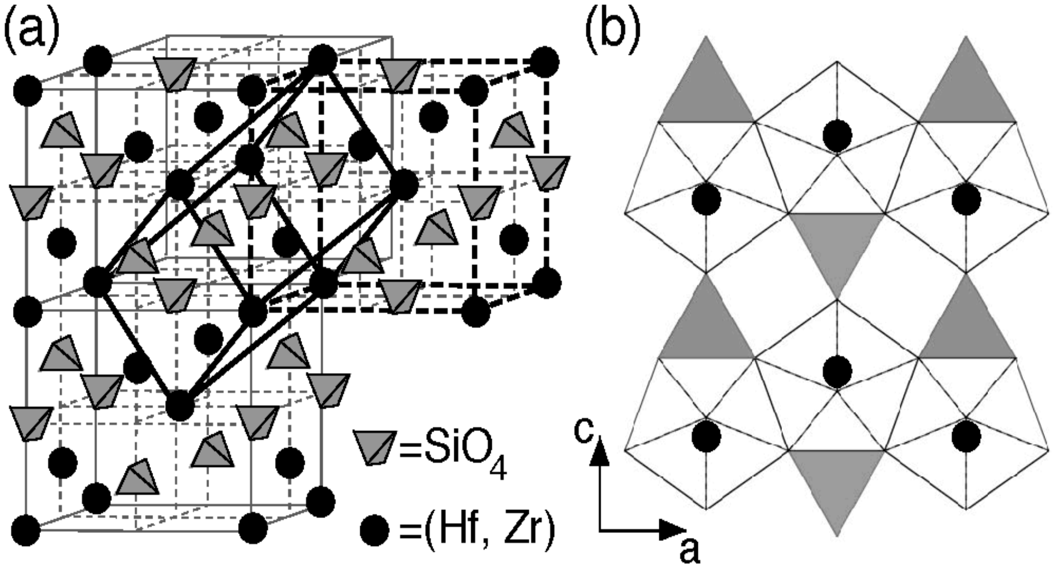
for the occupied orbitals.

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

Example



Charge density of graphite



	$HfSiO_4$		$ZrSiO_4$	
	Th.	Expt.	Th.	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
d(Si-O)	1.62	1.61	1.61	1.62
d(M-O)	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
∠(O-Si-O)	97°	97°	97°	97°
	116°	117°	116°	116°

Accuracy, typical usage.

If covalent bonds, metallic bonds, ionic bonds :

2-3% for the geometry (bond lengths, cell parameters)
0.2 eV for the bonding energies (GGA)
problem with the band gap

Worse for weak bonding situations (Hydrogen bonding, van der Waals).
Also problematic for strongly correlated systems : electronic structure.

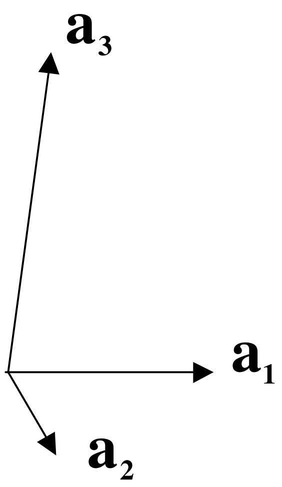
Treatment of a few hundred atoms is OK on powerful parallel computers
Up to 50-100 atoms is OK on a PC.

The plane wave basis set

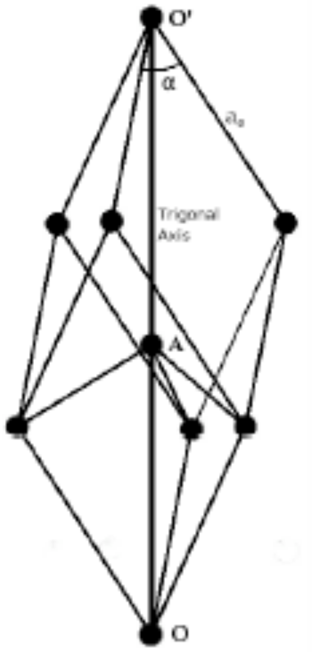
Prerequisites of plane waves

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

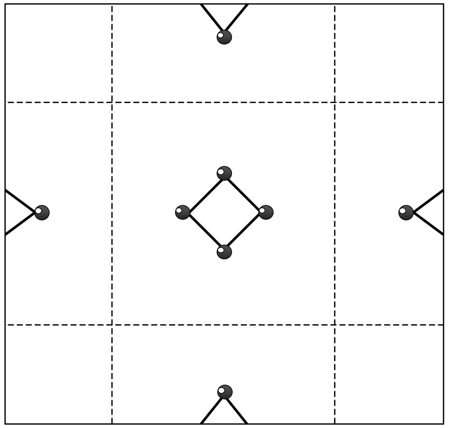
One cannot use a finite set of planewaves for a finite system !
Need periodic boundary conditions.
Primitive vectors $\mathbf{a}_i$, primitive cell volume Ω_0



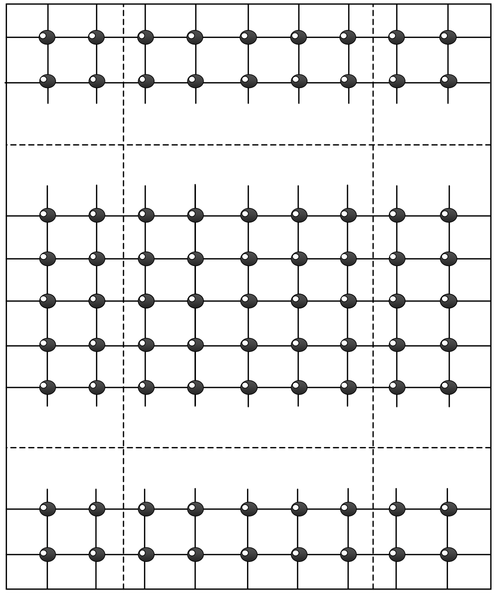
OK for crystalline solids
But : finite systems, surfaces,
defects, polymers, ... ?



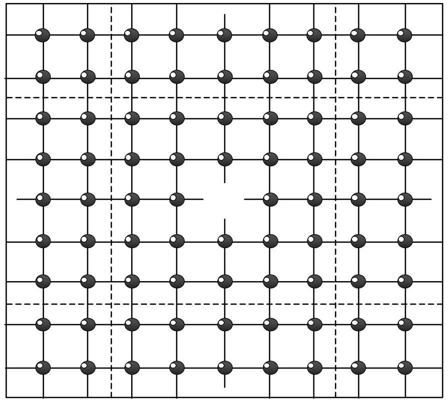
The supercell technique



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 $\psi_{m,\mathbf{k}}(\mathbf{r}+\mathbf{a}_i) = e^{i\mathbf{k}.\mathbf{a}_i}\psi_{m,\mathbf{k}}(\mathbf{r})$

Normalization of wavefunctions ?

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

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

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

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

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{u}_{\mathbf{k}}(\mathbf{G})\, e^{i\mathbf{G}\mathbf{r}} \qquad \psi_{\mathbf{k}}(\mathbf{r}) = \left(N\Omega_0\right)^{-1/2} \sum_{\mathbf{G}} \tilde{u}_{\mathbf{k}}(\mathbf{G})\, e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

$$\tilde{u}_{\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega_o} \int_{\Omega_o} e^{-i\mathbf{G}\mathbf{r}}\, u_{\mathbf{k}}(\mathbf{r})\, d\mathbf{r}$$ (Fourier transform)

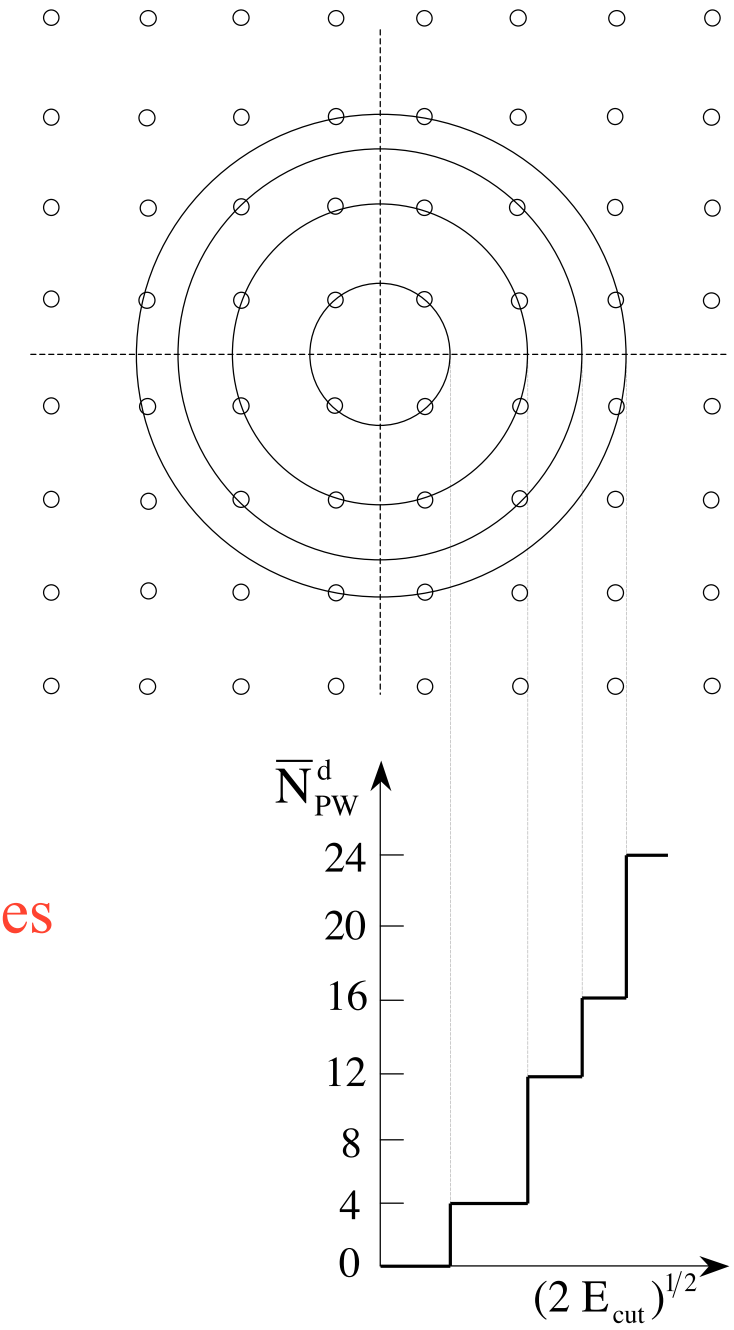
Kinetic energy of a plane wave $-\frac{\nabla^2}{2} \rightarrow \frac{(\mathbf{k}+\mathbf{G})^2}{2}$

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

Selection of plane waves determined by a <u>cut-off energy</u> E_{cut}

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

⚠ Discontinuous increase of the number of the plane waves N_{pw}



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

Plane wave representation of the density and potential

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

$$\tilde{f}(\mathbf{G}) = \frac{1}{\Omega_{o\vec{r}}} \int_{\Omega_{o\vec{r}}} e^{-i\mathbf{G}\mathbf{r}} \; f(\mathbf{r}) \, d\mathbf{r} \qquad\qquad f(\mathbf{r}) = \sum_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} \; \tilde{f}(\mathbf{G})$$

Poisson's equation $\Rightarrow \tilde{n}\,(\mathbf{G})$ and $\tilde{V}_H\,(\mathbf{G})$

$$V_H\,(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}' \;\Leftrightarrow\; \nabla^2 V_H\big|_{\mathbf{r}} = -4\pi \; n(\mathbf{r})$$

Relation between Fourier coefficients:

$$G^2 \; \tilde{V}_H(\mathbf{G}) = 4\pi \; \tilde{n}(\mathbf{G}) \qquad\qquad \tilde{V}_H(\mathbf{G}) = \frac{4\pi}{G^2} \; \tilde{n}(\mathbf{G})$$

For $G^2 = 0$ ($\mathbf{G}=0$) divergence of V_H ($\mathbf{G}=0$)

$$\tilde{n}(\mathbf{G}=0) = \frac{1}{\Omega_{o\mathbf{r}}} \int_{\Omega_{o\mathbf{r}}} n(\mathbf{r}) \; d\mathbf{r}$$

Average

Representation of the density

Density associated with one eigenfunction :

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

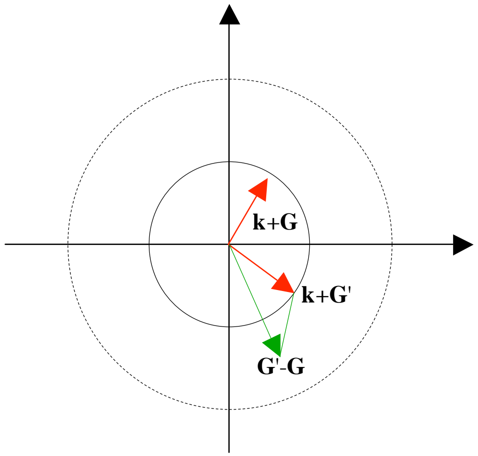
Computation of $u^*_{n\mathbf{k}}(\mathbf{r})\, u_{n\mathbf{k}}(\mathbf{r})$

$$= \left(\sum_{\mathbf{G}} \tilde{u}^*_{n\mathbf{k}}(\mathbf{G})\, e^{-i\mathbf{G}\mathbf{r}}\right)\left(\sum_{\mathbf{G}'} \tilde{u}_{n\mathbf{k}}(\mathbf{G}')\, e^{-i\mathbf{G}'\mathbf{r}}\right)$$

$$= \sum_{\mathbf{G}\mathbf{G}'} \left[\tilde{u}^*_{n\mathbf{k}}(\mathbf{G})\, \tilde{u}_{n\mathbf{k}}(\mathbf{G}')\right] e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}$$

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

$\mathbf{k+G'} \in$ sphere



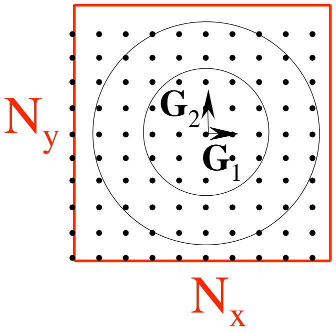
The sphere for $\tilde{n}(\mathbf{G})$ has a double radius

Going from the real space to the reciprocal space

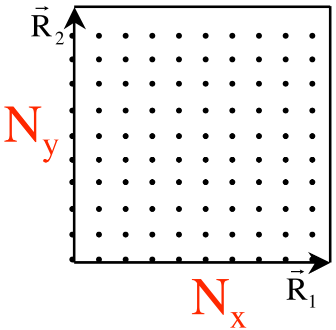
$$n(\mathbf{r}) = \sum_{\mathbf{G} \in \mathrm{sphere}(2)} \tilde{n}(\mathbf{G})\, e^{i\mathbf{G}\mathbf{r}}$$

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

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



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

$$\frac{(\mathbf{k}+\mathbf{G})^2}{2} < E_{\mathrm{cut}}$$

Sphere of plane waves

Discontinuous increase of the number of plane waves ?

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

-> Progressive incorporation of new **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

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

Iterative algorithms
Data flow

Algorithmics : problems to be solved

(1) Kohn - Sham equation $$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

Representation of V and ψ_i : real space $\{\mathbf{r}_j\}$, planewaves $\{\mathbf{G}_j\}$, localised functions ..

$$\boxed{\underline{\underline{A}}\;\underline{x}_i = \lambda_i\,\underline{x}_i}$$

Size of the system	[2 atoms…	600 atoms…]	+ vacuum ?
Dimension of the vectors $\underline{x}_i$	300…	100 000…	(if planewaves)
# of (occupied) eigenvectors	4…	1200…	

(2) Self-consistency

$$\begin{tikzcd} V_{KS}(\mathbf{r}) \arrow[rr, bend left] & & \psi_i(\mathbf{r}) \arrow[dl, bend left] \\ & n(\mathbf{r}) \arrow[ul, bend left] & \end{tikzcd}$$

(3) Geometry optimization

Find the positions $\{\mathbf{R}_\kappa\}$ of ions such that the forces $\{\mathbf{F}_\kappa\}$ vanish

[= Minimization of energy]

Current practice : iterative approaches

Analysis of self-consistency

$$\begin{tikzcd}
V_{KS}(\mathbf{r}) \arrow[rr, bend left] & & \psi_i(\mathbf{r}) \arrow[dl, bend left] \\
& n(\mathbf{r}) \arrow[ul, bend left] &
\end{tikzcd}$$

Natural iterative methodology (KS : in => out) :

$$V_{in}(\mathbf{r}) \rightarrow \psi_i(\mathbf{r}) \rightarrow n(\mathbf{r}) \rightarrow V_{out}(\mathbf{r})$$

Which quantity should vanish at the solution ?

The difference $\mathrm{V}_{out}(\mathbf{r}) - \mathrm{V}_{in}(\mathbf{r})$ (generic name : a "residual")

Simple mixing algorithm
(≈ steepest - descent)

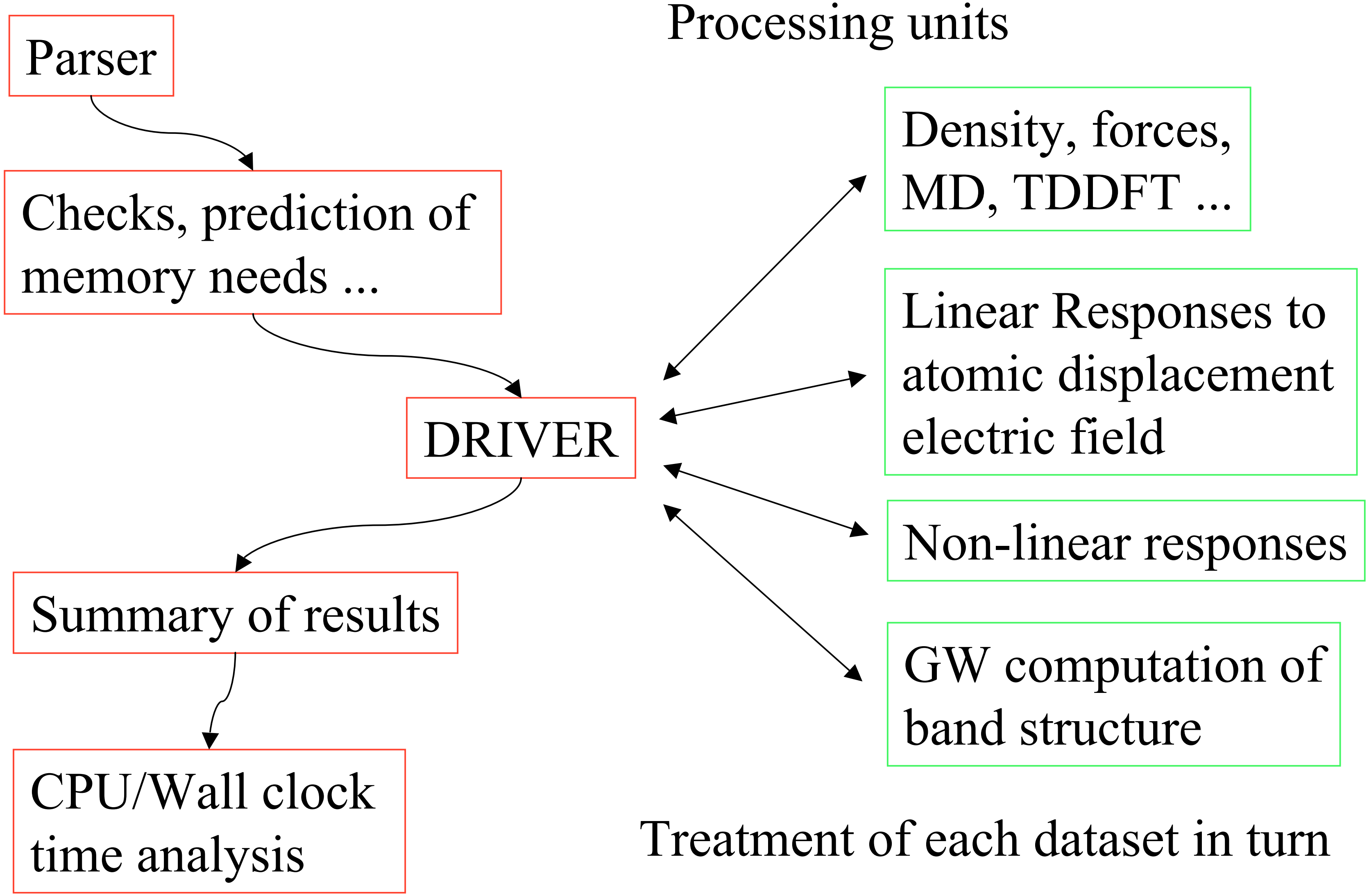
$$\boxed{\underline{\mathrm{v}}_{in}^{(n+1)} = \underline{\mathrm{v}}_{in}^{(n)} + \lambda\left(\underline{\mathrm{v}}_{out}^{(n)} - \underline{\mathrm{v}}_{in}^{(n)}\right)}$$

Analysis ... $\underline{\mathrm{v}}_{out}\left[\underline{\mathrm{v}}_{in}\right] = \underline{\mathrm{v}}_{out}\left[\underline{\mathrm{v}}^{*}\right] + \dfrac{\delta \underline{\mathrm{v}}_{out}}{\delta \underline{\mathrm{v}}_{in}}\left(\underline{\mathrm{v}}_{in} - \underline{\mathrm{v}}^{*}\right)$

$$\searrow \underline{\underline{\mathrm{H}}}$$

This leads to the requirement to minimize $|1-\lambda h_i|$ where h_i are eigenvalues of $\dfrac{\delta \underline{\mathrm{v}}_{out}}{\delta \underline{\mathrm{v}}_{in}}$ (actually, the dielectric matrix)

ABINIT : the pipeline and the driver



Parser

Checks, prediction of memory needs ...

DRIVER

Summary of results

CPU/Wall clock time analysis

Processing units

Density, forces, MD, TDDFT ...

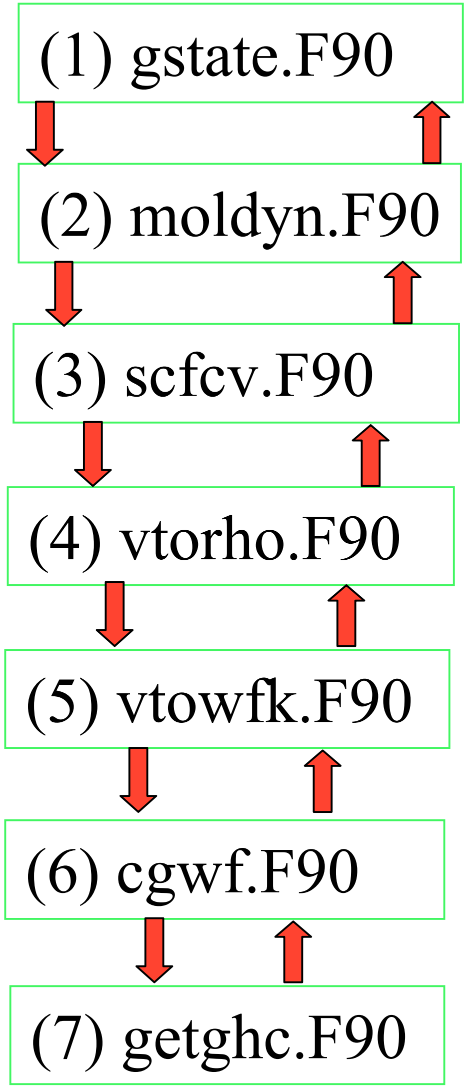
Linear Responses to atomic displacement electric field

Non-linear responses

GW computation of band structure

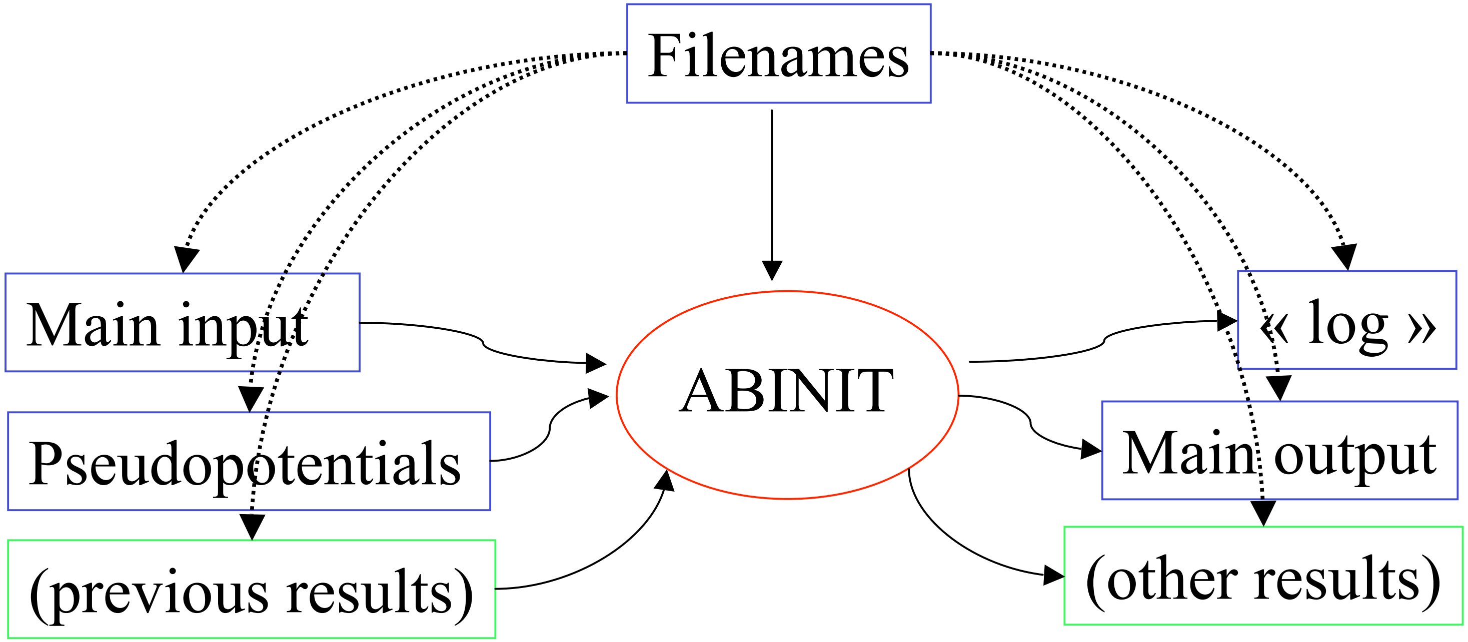
Treatment of each dataset in turn

Stages in the main processing unit



(1) gstate.F90	Ground-state
(2) moldyn.F90	Molecular dynamics
(3) scfcv.F90	Self-consistent field convergence
(4) vtorho.F90	From a potential (v) to a density (rho)
(5) vtowfk.F90	From a potential (v) to a wavefunction at some k-point
(6) cgwf.F90	Conjugate-gradient on one wavefunction
(7) getghc.F90	Get the application of the Hamiltonian

External files in a ABINIT run



Results : density (_DEN), potential (_POT),
wavefunctions (_WFK), ...

Brillouin zone integration

From discrete states to the Brillouin zone

Discrete summations over states :

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

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

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

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

How to treat $\frac{1}{\Omega_{o\mathbf{k}}} \int_{\Omega_{o\mathbf{k}}} \mathrm{X}_{\mathbf{k}} \, \mathbf{dk}$?

Brillouin zone integration

$$\frac{1}{\Omega_{o\mathbf{k}}} \int_{\Omega_{o\mathbf{k}}} X_{\mathbf{k}}\ d\mathbf{k} \ \Rightarrow \ \sum_{\{\mathbf{k}\}} w_{\mathbf{k}} X_{\mathbf{k}} \qquad \left[\text{ with } \sum_{\{\mathbf{k}\}} w_{\mathbf{k}} = 1 \ \right]$$

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

Special points

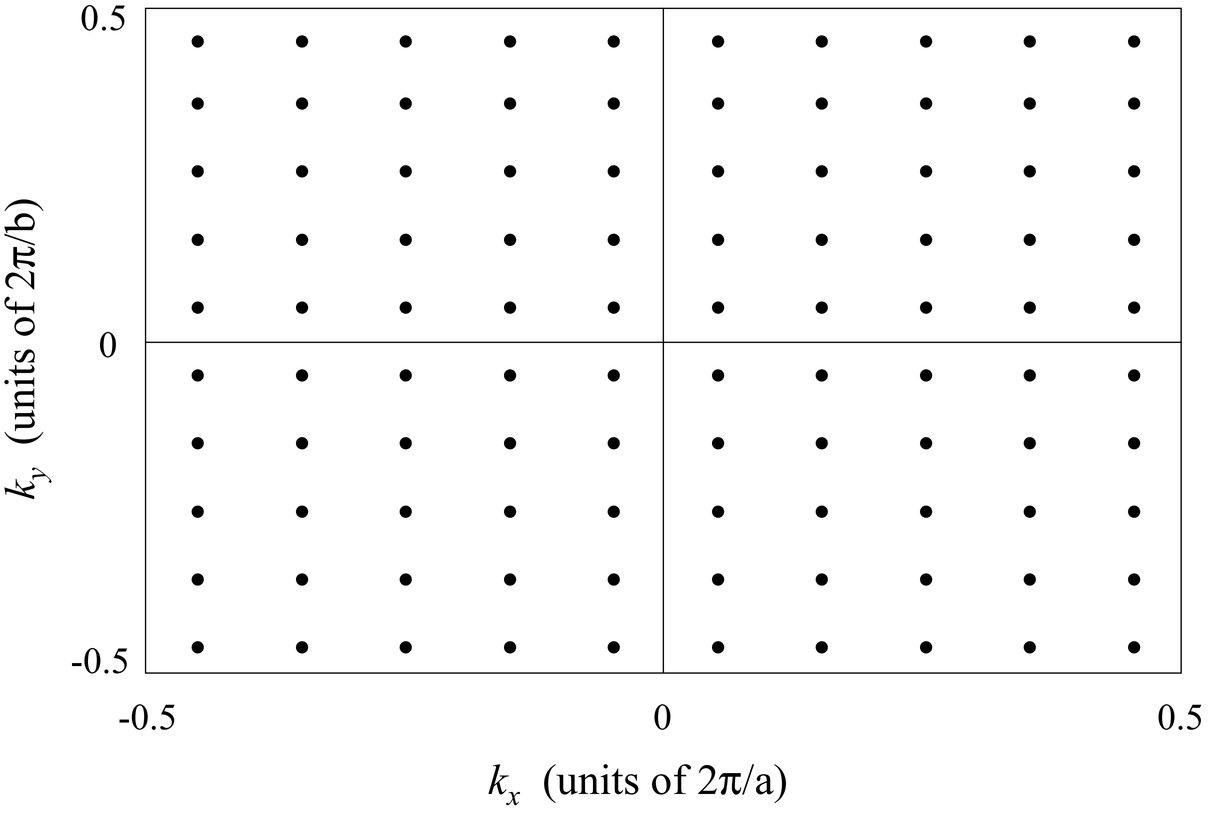
Weights

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

Then exponential convergence, with respect to Δk

- OK for semiconductors/insulators where the occupation number is independent of k within a band
- Convergence : one ought to test several grids with different Δk
- 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)

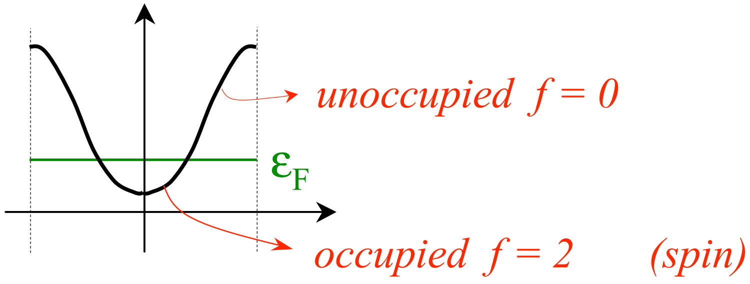
Homogeneous sampling of the Brillouin zone



Treatment of metals (I)

Behaviour of $f(\varepsilon_F - \varepsilon_{n\mathbf{k}})$?

Discontinuity of the integrand at the Fermi level



Smearing technique

First trial : generalisation of DFT to finite temperature

- $f(\varepsilon_{n\mathbf{k}}) = \dfrac{1}{1+e^{(\varepsilon_{n\mathbf{k}}-\varepsilon_F)/kT}}$

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

- $E(T) \cong E(T=0) + \alpha T^2 + \ldots$

  $F(T) = E - TS$

Problem : the T needed to recover the same convergence as for semiconductors is very high (>> 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 σ is similar to a temperature

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

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

$$f_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}) = s \,.\, \int_{t=\frac{\varepsilon_{n\mathbf{k}}-\varepsilon_F}{\sigma}}^{\infty} \tilde{\delta}(t)\,dt \qquad \left[\text{ with } \int_{-\infty}^{\infty} \tilde{\delta}(t)\,dt = 1 \right]$$

Spin factor

Gaussian smearing $\tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} e^{-x^2}$ ⇨ α small

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

⇨ $n = 4$ but occupations can be negatives

…

'Cold Smearing' (Marzari)

How many k points ? Smearing width ?

Semiconductors - Insulators

k x N_{atoms} *50 ... 500*

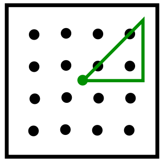
⇩

lattice parameter converged better than 0.5 %

Metals # **k** x N_{atoms} → *1000 ... 2000*

⚠ Use symmetries ⇨ integration in the irreducible Brillouin zone

2D Example



grid 4 x 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 ...) ~ 0.04 Ha

d Metal (Cu, Ag...) ~ 0.01 Ha

⚠ magnetism needs small σ

Pseudopotentials

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
(will be the subject of a later section)

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...

$$n(\mathbf{r}) = \sum_{i}^{occ} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$$= \sum_{i \in core}^{N_{core}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + \sum_{i \in val}^{N_{val}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = n_{core}(\mathbf{r}) + n_{val}(\mathbf{r})$$

« 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.

F atom : $\boxed{(1s)^2} + (2s)^2(2p)^5$

IP 1keV 10-100 eV

Ti atom : $\boxed{(1s)^2(2s)^2(2p)^6}(3s)^2(3p)^6(4s)^2(3d)^2$ small core

$\boxed{(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6}(4s)^2(3d)^2$ large core

IP 99.2 eV 43.3eV

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 ...

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

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

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 κ is screened by the core electrons

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

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

The total energy becomes

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

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

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

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 $\left(-\frac{1}{2}\nabla^2 + \mathrm{v}\right) | \psi_i > = \varepsilon_i \; | \psi_i >$

To $\left(-\frac{1}{2}\nabla^2 + \mathrm{v}_{ps}\right) | \psi_{ps,i} > = \varepsilon_{ps,i} \; | \psi_{ps,i} >$

Possible set of conditions (norm-conserving pseudopotentials) :

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

$$\varepsilon_i = \varepsilon_{ps,i}$$

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

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

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

Forms of pseudopotentials

Must be a linear, hermitian operator

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

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

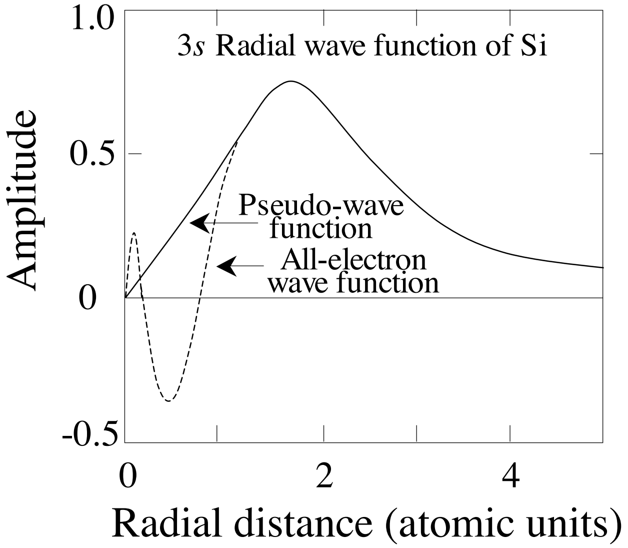
Non-local part $V_{nloc}(\mathbf{r},\mathbf{r}') = \sum_{\ell m} Y_{\ell m}^{*}(\theta,\varphi)V_{\ell}(r,r')Y_{\ell m}(\theta',\varphi')$

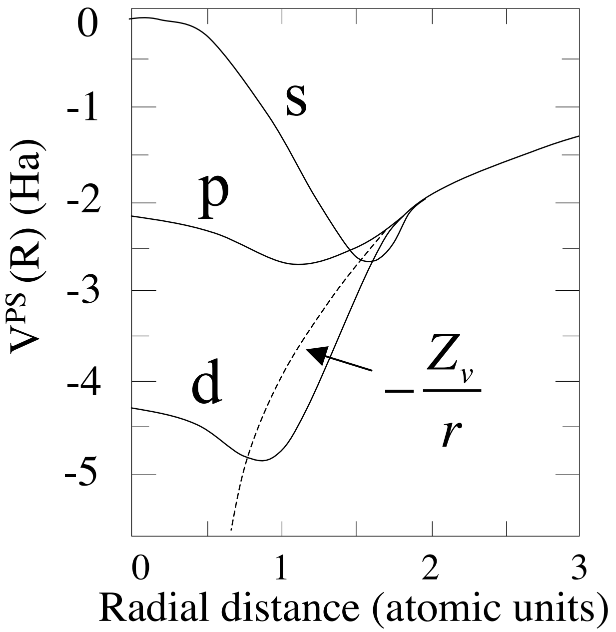
Semi-local psp $V_{\ell}(r,r') = V_{\ell}(r)\delta(r-r')$

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)


3*s* Radial wave function of Si
Pseudo-wave function
All-electron wave function
Amplitude
1.0
0.5
0
-0.5
0
2
4
Radial distance (atomic units)


s
p
d
$-\frac{Z_v}{r}$
V^{PS} (R) (Ha)
0
-1
-2
-3
-4
-5
0
1
2
3
Radial distance (atomic units)

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 Ψ

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

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

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

$\Psi = T\tilde{\Psi}$ with $T = 1 + \sum_R S_R$ (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 : $|\phi_i\rangle = (1 + S_R)|\tilde{\phi}_i\rangle$

The projector functions

Inside each atom sphere

$$\Psi(\vec{r}) = \sum_{i\in R} \phi_i(\vec{r}) c_i \qquad \tilde{\Psi}(\vec{r}) = \sum_{i\in R} \tilde{\phi}_i(\vec{r}) c_i$$

How to compute the coefficients of this expansion ?

Definition of the projector functions, dual of the pseudo partial waves : $\sum_i |\tilde{\phi}_i\rangle\langle\tilde{p}_i| = 1$ within the sphere, with $\langle\tilde{p}_i|\tilde{\phi}_j\rangle = \delta_{ij}$

Inside the atomic sphere R $\quad \tilde{\Psi}(\vec{r}) = \sum_{i\in R} \tilde{\phi}_i(\vec{r}) \langle\tilde{p}_i|\tilde{\Psi}\rangle$

Combining the different definitions :

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

Representation of the wavefunctions

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

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

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

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

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

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

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

is only approximately true !

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

Expectation values of the set of occupied WFs (1)

$$\langle A\rangle = \sum_{\mathrm{n}} f_{\mathrm{n}} \langle \Psi_{\mathrm{n}} | A | \Psi_{\mathrm{n}} \rangle + \sum_{\mathrm{n}=1}^{\mathrm{N_{core}}} \langle \phi_{\mathrm{n}}^{\mathrm{c}} | A | \phi_{\mathrm{n}}^{\mathrm{c}} \rangle = \sum_{\mathrm{n}} f_{\mathrm{n}} \langle \tilde{\Psi}_{\mathrm{n}} | T^{+} A T | \tilde{\Psi}_{\mathrm{n}} \rangle + \sum_{\mathrm{n}=1}^{\mathrm{N_{core}}} \langle \phi_{\mathrm{n}}^{\mathrm{c}} | A | \phi_{\mathrm{n}}^{\mathrm{c}} \rangle$$

Matrix elements, for local or semi-local operators

$$\langle \Psi | A | \Psi \rangle = \left\langle \left(\tilde{\Psi} + \sum_{R} \left(\Psi_{R}^{1} - \tilde{\Psi}_{R}^{1} \right) \right) \middle| A \middle| \left(\tilde{\Psi} + \sum_{R} \left(\Psi_{R}^{1} - \tilde{\Psi}_{R}^{1} \right) \right) \right\rangle$$

$$= \langle \tilde{\Psi} | A | \tilde{\Psi} \rangle + \sum_{R} \left(\langle \Psi_{R}^{1} | A | \Psi_{R}^{1} \rangle - \langle \tilde{\Psi}_{R}^{1} | A | \tilde{\Psi}_{R}^{1} \rangle \right) \qquad \text{(part 1)}$$

$$+ \sum_{R} \left(\langle \Psi_{R}^{1} - \tilde{\Psi}_{R}^{1} | A | \tilde{\Psi} - \tilde{\Psi}_{R}^{1} \rangle + (c.c) \right) \qquad \text{(part 2)}$$

$$+ \sum_{R \neq R'} \langle \Psi_{R}^{1} - \tilde{\Psi}_{R}^{1} | A | \Psi_{R}^{1} - \tilde{\Psi}_{R}^{1} \rangle \qquad \text{(part 3)}$$

Parts 2 and 3 would vanish if the partial wave expansion were complete. They are neglected in practice.

Expectation values of the set of occupied WFs (2)

$$\langle A\rangle = \sum_n f_n \left(\langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_R \left(\langle \Psi^1_{n,R} | A | \Psi^1_{n,R} \rangle - \langle \tilde{\Psi}^1_{n,R} | A | \tilde{\Psi}^1_{n,R} \rangle \right) \right) + \sum_{n=1}^{N_c} \langle \phi_n^c | A | \phi_n^c \rangle$$

Thanks to the explicit expressions for the radial parts of the wavefunction in terms of the projector functions, this gives :

$$\begin{aligned}
&= \sum_n f_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_{n=1}^{N_c} \langle \tilde{\phi}_n^c | A | \tilde{\phi}_n^c \rangle \\
&+ \sum_R \left(\sum_{i,j\in R} D_{i,j} \langle \phi_j | A | \phi_i \rangle + \sum_{n\in R}^{N_{c,R}} \langle \phi_n^c | A | \phi_n^c \rangle \right) \\
&- \sum_R \left(\sum_{i,j\in R} D_{i,j} \langle \tilde{\phi}_j | A | \tilde{\phi}_i \rangle + \sum_{n\in R}^{N_{c,R}} \langle \tilde{\phi}_n^c | A | \tilde{\phi}_n^c \rangle \right)
\end{aligned}$$

where $D_{i,j}$ is the one-center density matrix defined as

$$D_{i,j} = \sum_n \langle \tilde{p}_i | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi}_n | \tilde{p}_j \rangle$$

Example : the expression for the density

Sum of PW and atom-centered contributions

$$\mathrm{n}(\vec{\mathrm{r}}) = \tilde{\mathrm{n}}(\vec{\mathrm{r}}) + \sum_{R} \left(\mathrm{n}_{R}^{1}(\vec{\mathrm{r}}) - \tilde{\mathrm{n}}_{R}^{1}(\vec{\mathrm{r}}) \right)$$

with

$$\tilde{\mathrm{n}}(\vec{r}) = \sum_{n} f_n \tilde{\Psi}_n^{*}(\vec{\mathrm{r}}) \tilde{\Psi}_n(\vec{\mathrm{r}}) + \tilde{\mathrm{n}}_c$$

$$\mathrm{n}_{R}^{1}(\vec{\mathrm{r}}) = \sum_{i,j \in R} D_{i,j} \phi_j^{*}(\vec{\mathrm{r}}) \phi_i(\vec{\mathrm{r}}) + \mathrm{n}_{c,R}$$

$$\tilde{\mathrm{n}}_{R}^{1}(\vec{r}) = \sum_{i,j \in R} D_{i,j} \tilde{\phi}_j^{*}(\vec{r}) \tilde{\phi}_i(\vec{r}) + \tilde{\mathrm{n}}_{c,R}$$

Compare with norm-conserving and ultra-soft PPs ...

Computing the forces

Computing the forces (I)

Born - Oppenheimer approximation ⇨ 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.

$$F_{\kappa,\alpha} = - \left. \frac{\partial E}{\partial R_{\kappa,\alpha}} \right|_{\{\vec{R}_\kappa\}}$$

(principle of virtual works)

Forces can be computed by finite differences.
Better approach : compute the response to a perturbation

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

Small parameter

⇨ What is the energy change ?

Computing the forces (II)

Case of an electronic eigenvalue

Perturbation theory : Hellmann - Feynman theorem

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

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

Application to an atomic displacement :

$$\hat{H} = \hat{T} + \hat{V}_{ext}\{\hat{R}\} \Rightarrow \frac{\partial \hat{H}}{\partial R_{\kappa,\alpha}} = \frac{\partial \hat{V}_{ext}}{\partial R_{\kappa,\alpha}}$$

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

Computing the forces (III)

Generalisation to density functional theory

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

If change of atomic positions ...

$$V_{ext}(\vec{r}) = \sum_{k'} - \frac{Z_{k'}}{|\vec{r} - \vec{R}_{k'}|}$$

(can be generalized to pseudopotential case)

$$\frac{\partial V_{ext}(\vec{r})}{\partial R_{k,\alpha}} = + \frac{Z_{k'}}{|\vec{r} - \vec{R}_k|^2} \cdot \frac{\partial |\vec{r} - \vec{R}_k|}{\partial R_{k,\alpha}}$$

$$= - \frac{Z_{k'}}{|\vec{r} - \vec{R}_k|^3} \cdot (\vec{r} - \vec{R}_k)_\alpha$$

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

Computing the forces (IV)

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

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

ABINIT

ABINIT in brief

Chronology :

- Precursor : the Corning PW code (commercialized 1992-1995 by Biosym)
- 1997 : beginning of the ABINIT project
- Dec 2000 : release of ABINITv3 under the GNU General Public License (GPL)
- Nov 2002 : 1st int. ABINIT developer workshop - 40 participants
- May 2004 : 2nd int. ABINIT developer workshop
- Aug 2005 : Summer School Santa Barbara - 45 students + 18 instructors
- Dec 2006 : CECAM school "Electronic excitations" - 30 students
- Jan 2007 : 3rd int. ABINIT developer workshop
- As of March 2008 : about 1250 addresses in the main mailing list, and about 30 registered developers on the repository

The “Free” or “Open Source” software concept

Free for freedom, not price

- freedom 1 : unlimited use for any purpose
- freedom 2 : study and modify for your needs (need source access !)
- freedom 3 : copy
- freedom 4 : distribute modifications

From copyright to freedom (“copyleft”)

- copyright allows licensing
- licenses grants freedom

Terminology : Free software=Open source=Libre software

Free software licences ...

Many types

- GNU General Public Licence
- GNU Lesser General Public License (links are possible)
- BSD licence
- X11 license, Perl license, Python license...
- public domain release

GNU General Public License (GPL)

"The licences for most softwares are designed to take away your freedom to share and change it. By contrast, the GNU GPL is intended to guarantee your freedom to share and change free software - to make sure the software is free for all its users" (http://www.gnu.org/copyleft/gpl.html)

- grants four freedoms
- protection of freedom
- « vaccination »

ABINIT v5.5 capabilities (I)

Methodologies

Pseudopotentials/Plane Waves

+ Projector Augmented Waves (for selected capabilities)

Many pseudopotential types, different PAW generators

+ Wavelets (BIGDFT effort)

Density functionals : LDA, GGA (PBE and variations, HCTH),

LDA+U (or GGA+U)

+ some advanced functionals (exact exchange + RPA or ...)

LR-TDDFT for finite systems excitation energies (Casida)

GW for accurate electronic eigenenergies

(4 plasmon pole models or contour integration ; non-self-consistent / partly self-consistent / quasiparticle self-consistent ; spin-polarized)

ABINIT v5.5 capabilities (II)

Insulators/metals - smearings : Fermi, Gaussian, Gauss-Hermite ...

Collinear spin / non-collinear spin / spin-orbit coupling

Forces, stresses, automatic optimisation of atomic positions and unit cell parameters (Broyden and Molecular dynamics with damping)

Molecular dynamics (Verlet or Numerov), Nosé thermostat, Langevin dynamics

Susceptibility matrix by sum over states (Adler-Wiser)

Optical (linear + non-linear) spectra by sum over states

Electric field gradients

Symmetry analyser (database of the 230 spatial groups and the 1191 Shubnikov magnetic groups)

ABINIT v5.5 capabilities (III)

Density-Functional Perturbation Theory :

- Responses to atomic displacements, to static homogeneous electric field, to strain perturbations

↓

- Second-order derivatives of the energy, giving direct access to :
  dynamical matrices at any q, phonon frequencies, force constants ;
  phonon DOS, thermodynamic properties (quasi-harmonic approximation) ;
  dielectric tensor, Born effective charges ;
  elastic constants, internal strain ;
  piezoelectric tensor ...
- Matrix elements, giving direct access to :
  electron-phonon coupling, deformation potentials, superconductivity
- Non-linear responses thanks to the 2n+1 theorem - at present :
  non-linear dielectric susceptibility; Raman cross-section ;
  electro-optic tensor

The band gap problem

The DFT bandgap problem (I)

- DFT is a ground state theory

  $\Rightarrow$ no direct interpretation of Kohn-Sham eigenenergies ε_i in

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + V_{xc}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- However $\{\varepsilon_i\}$ are similar to quasi-particle band structure : LDA / GGA results for valence bands are accurate ... but

  NOT for the band gap $E_g^{KS} = \varepsilon_c - \varepsilon_v$

- The band gap can alternatively be obtained from total energy differences

  [correct expression !]

$$E_g = E(N+1) + E(N-1) - 2\,E(N) = \{E(N+1) - E(N)\} - \{E(N) - E(N-1)\}$$

  in the limit N → ∞

  (where E(N) is the total energy of the N - electron system)

The DFT bandgap problem (II)

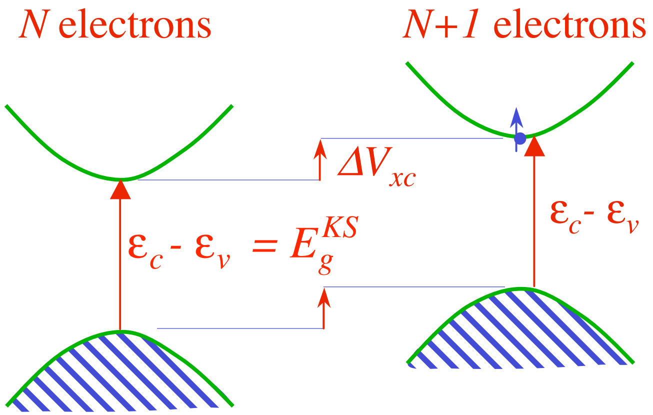
- For LDA & GGA, the *XC* potential is a continuous functional of the number of electrons

$$\varepsilon_i = \frac{\partial E}{\partial f_i} \qquad \text{[Janak's theorem]}$$

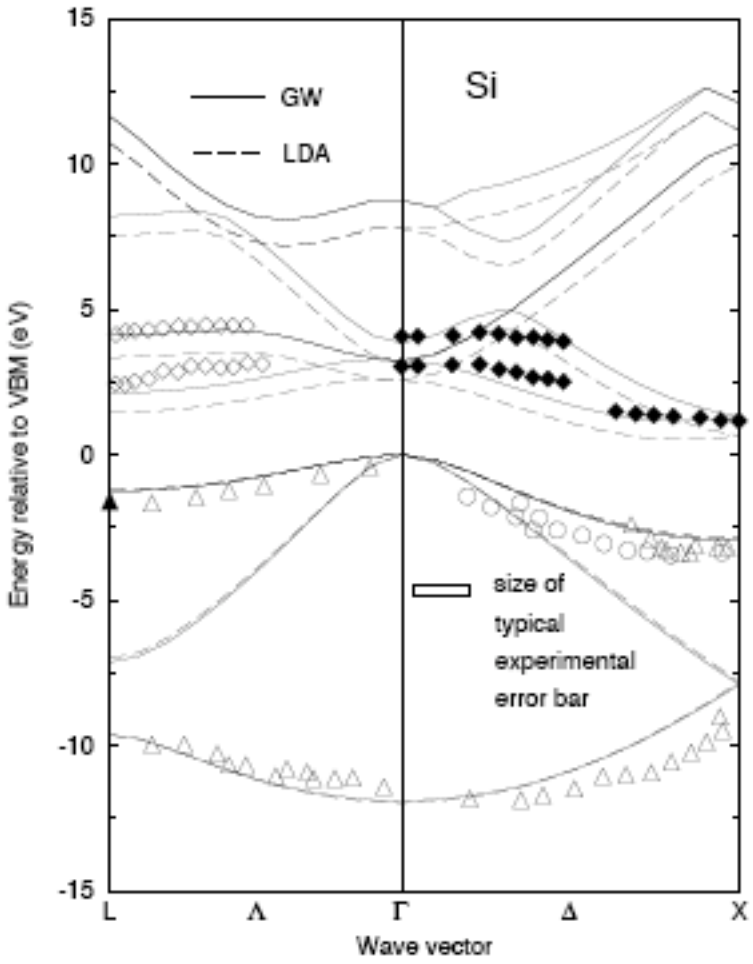
$$\Rightarrow \quad E_g^{KS} = \varepsilon_c - \varepsilon_v \underset{N \to \infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

- In general, the *XC* potential might be discontinuous with the number of particle

$$e.g. \quad xOEP \qquad\qquad E_g^{KS} \neq E_g$$



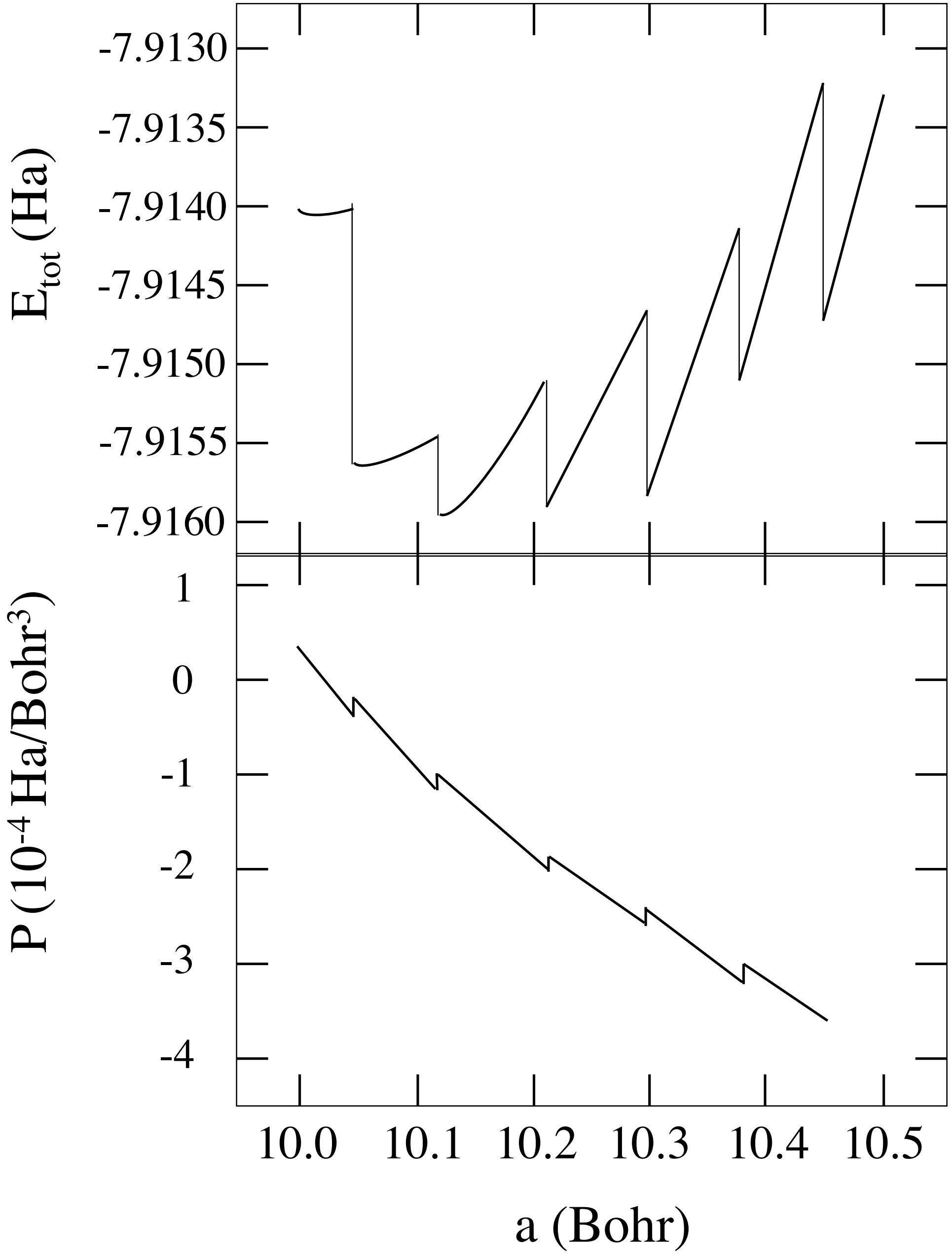
The DFT bandgap problem (III)



Comparison of LDA and GW band
Structures with photoemission and
Inverse photoemission experiments
for Silicon.

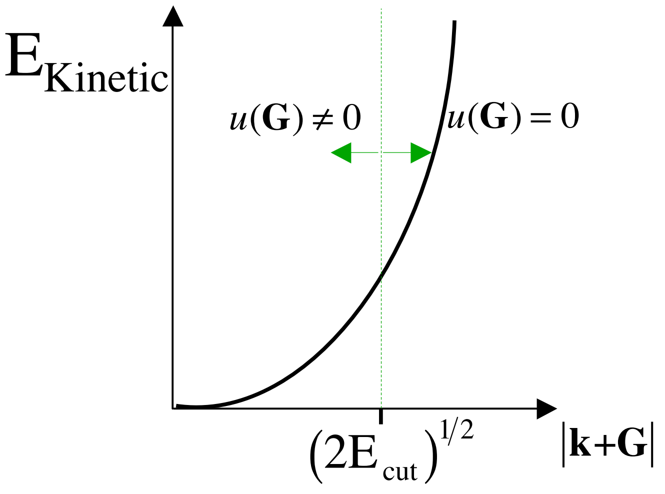
From "Quasiparticle calculations in solids",
by Aulbur WG, Jonsson L, Wilkins JW,
in Solid State Physics 54, 1-218 (2000)

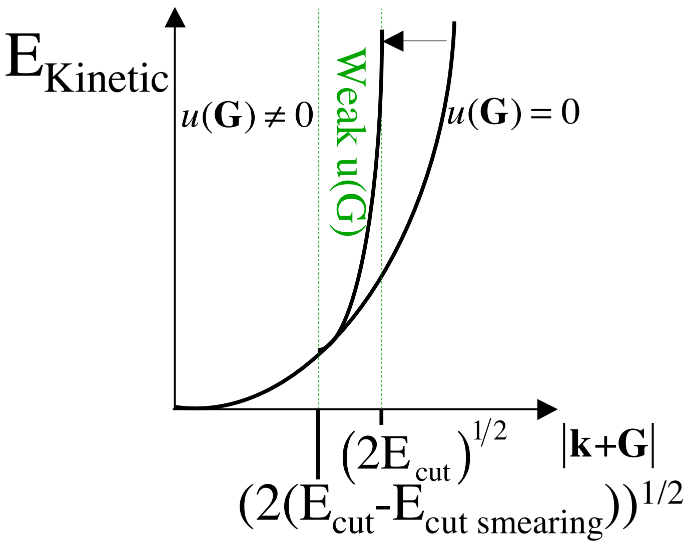
Discontinuities due to the sudden change of the number of plane waves



Note atomic units are used here :
1Ha = 2 Ry = 27.211 eV
1Bohr=0.529 angstrom
1 Ha/Bohr^3=21421 GPa

Removal of the discontinuities of the total energy





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

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

Sources and binaries

Numbering of version : x.y.z e.g. 5.5.3

Major version number (change each other year) → x

Minor version number (new capabilities, change every three months) → y

Debug status number (change during the life of a minor version number) → z

Usually, three « active » minor versions at all time.

Life of a minor version (usually one year) :

tests → availability for developers → production

↓

obsolete ← very robust ← robust