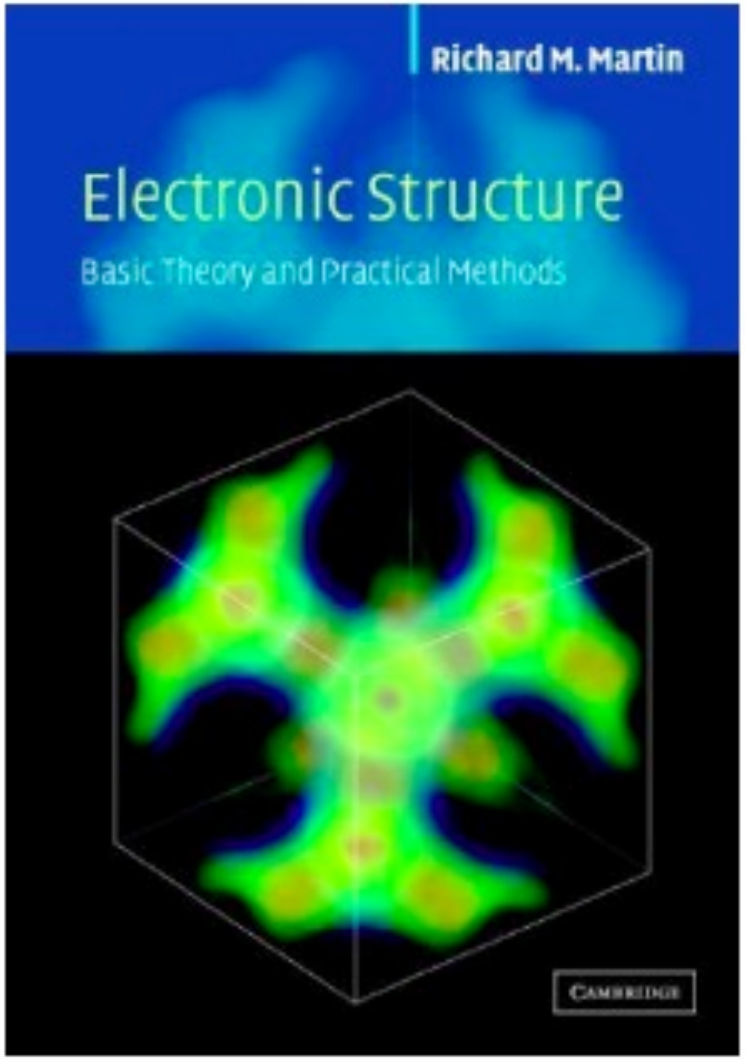
Advanced Materials Modeling
Advanced DFT 2

+ Reminder about implementation of DFT for simulation of materials
+ Pseudopotentials, Projector Augmented Waves
+ Introduction to Lab #1 : usage of ABINIT
+ Reminder about wavevector sampling
+ Launch of lab #1

Forthcoming lectures linked to the lab :
Advanced DFT3 (forces and perturbations, iterative techniques, spin+magnetism)
Then, linked to ABINIT, possibly for a project,
Beyond DFT 1 and **beyond DFT 2** :
- Accurate electronic structure (GW approximation)
- Optical properties (absorption, index of refraction, luminescence),

Finally, **vibrational properties (phonons) and transport properties (electron-phonon)**

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

Reminder : implementation of DFT for materials

Basic equations in DFT

Solve self-consistently the Kohn-Sham equation

$$\left\{\begin{array}{l} \hat{H}\left|\psi_n\right\rangle = \varepsilon_n\left|\psi_n\right\rangle \\[2ex] \hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[\mathrm{n}] \\[2ex] \mathrm{n}(\mathbf{r}) = \sum\limits_{\mathrm{n}}^{occ} \psi_{\mathrm{n}}^{*}(\mathbf{r})\psi_{\mathrm{n}}(\mathbf{r}) \end{array}\right.$$

$$\begin{tikzcd} \hat{H} \arrow[rr, bend left] & & \psi_n(\mathbf{r}) \arrow[dl, bend left] \\ & n(\mathbf{r}) \arrow[ul, bend left] & \end{tikzcd}$$

$$\delta_{\mathrm{mn}} = \left\langle \psi_{\mathrm{m}} \middle| \psi_{\mathrm{n}} \right\rangle \text{for m,n} \in \text{occupied set}$$

or minimize

$$E_{el}\{\psi\} = \sum_{\mathrm{n}}^{occ} \left\langle \psi_{\mathrm{n}} \middle| \hat{T} + \hat{V} \middle| \psi_{\mathrm{n}} \right\rangle + E_{Hxc}[\mathrm{n}]$$

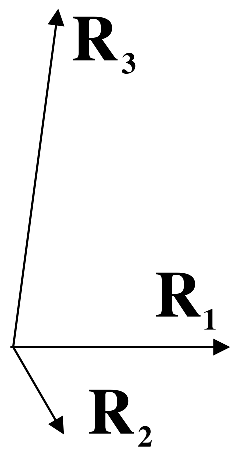
with

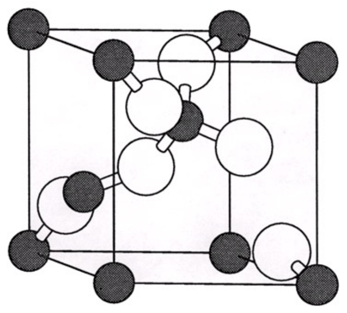
$$\hat{V}(\mathbf{r}) = \sum_{\kappa} -\frac{Z_{\kappa}}{\left|\mathbf{r} - \mathbf{R}_{\kappa}\right|}$$

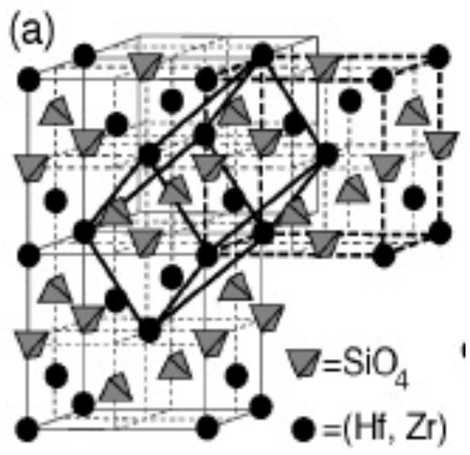
Exchange-correlation functional might be LDA, GGA (e.g. PBE, PBESol), or hybrids, van der waals, etc

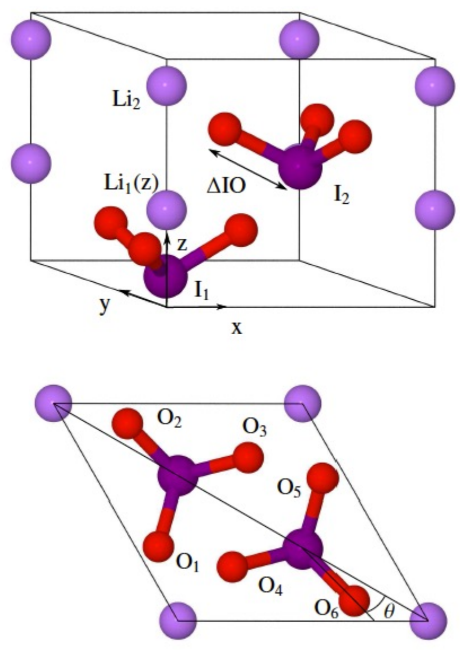
Materials : infinite extent, periodicity

Need periodic boundary conditions.
Primitive vectors $\mathbf{R}_j$, primitive cell volume Ω_0



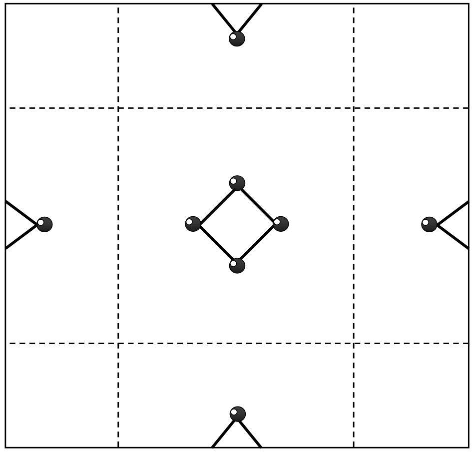




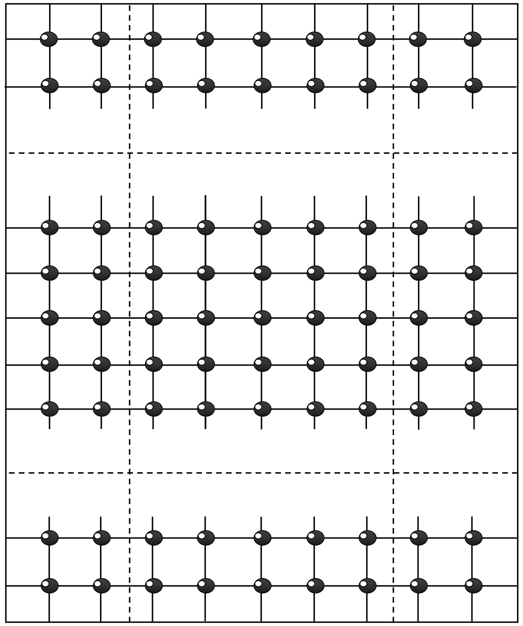


OK for crystalline solids
But : finite systems, surfaces, defects, polymers, nanosystems ... ?

Solution : the supercell technique

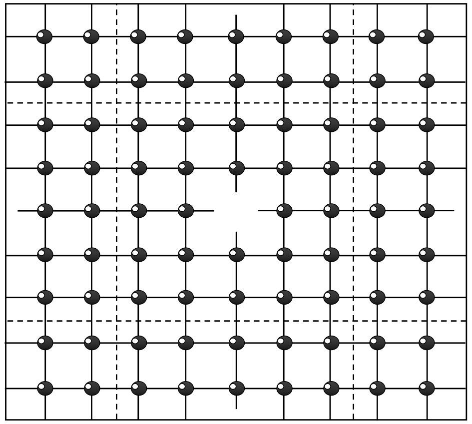


Molecule,
cluster



Surface : treatment of a slab

Interface

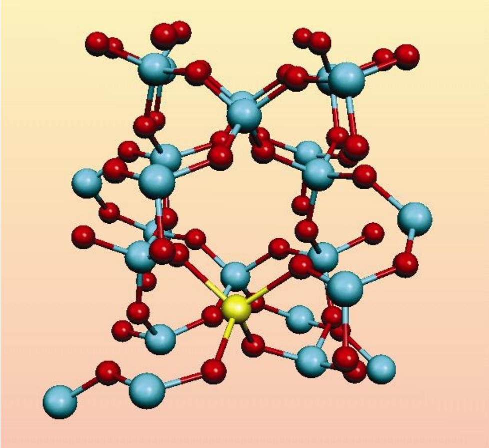


Point defect in a bulk solid

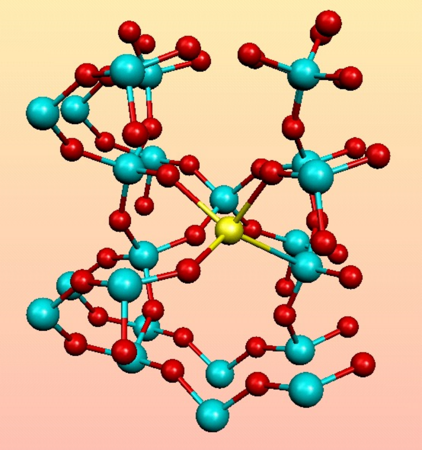
The supercell must be sufficiently big : convergence study

Examples of defects SiO_2-quartz : Pb

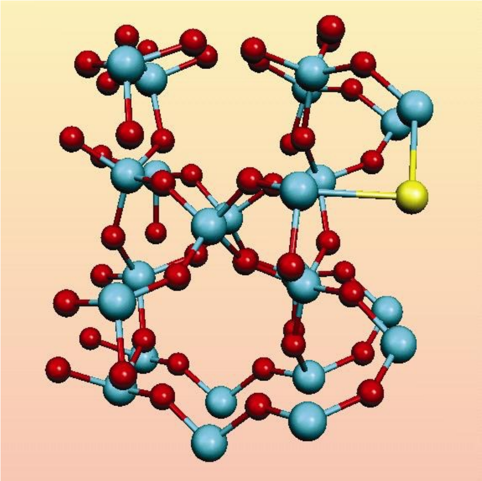
72-atom supercell of quartz



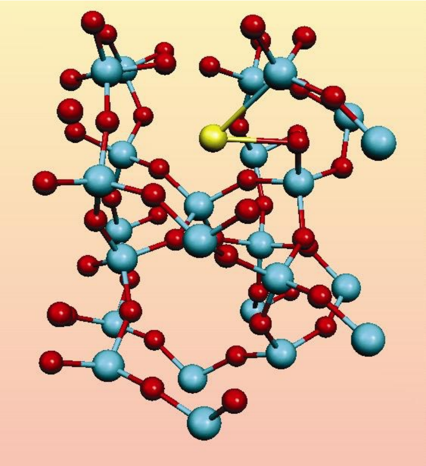
Pb^{Si}



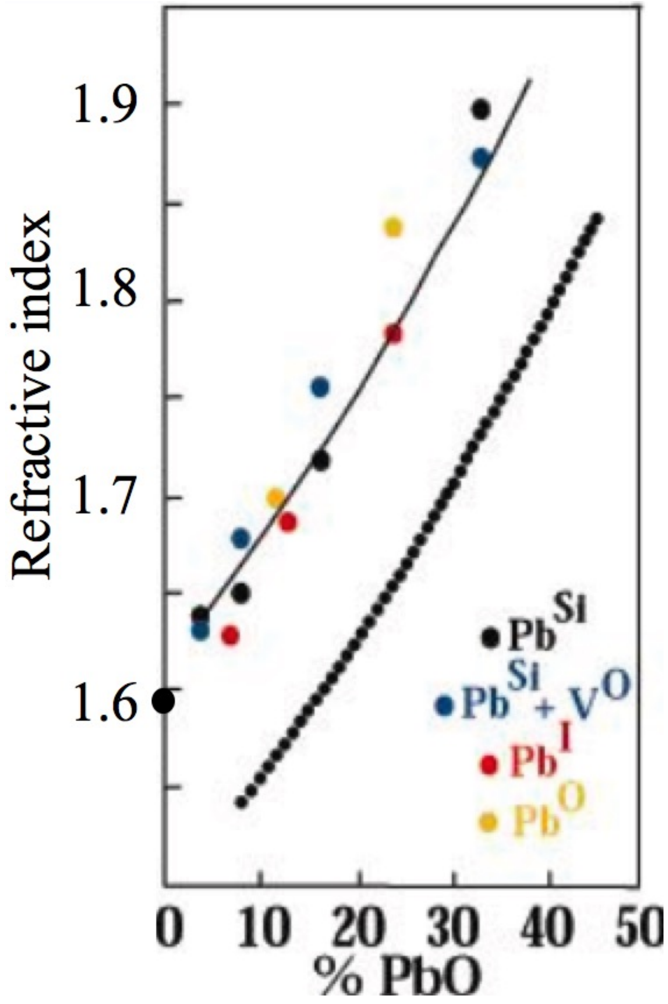
$Pb^{Si} + V^{O}$



Pb^{O}



Pb^{I}



Comparison with amorphous SiO_2

Periodic system : wavevectors

For a periodic Hamiltonian : wavefunctions characterized by a wavevector $\mathbf{k}$ (crystal momentum) in Brillouin Zone

Bloch theorem $\psi_{m,\mathbf{k}}(\mathbf{r}+\mathbf{R}_j) = e^{i\mathbf{k}.\mathbf{R}_j}\psi_{m,\mathbf{k}}(\mathbf{r})$

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

Plane waves $e^{i\mathbf{K}\mathbf{r}}$: particularly simple and efficient (when used with pseudopotentials), infinite spatial extent.

Planewave basis set

Reciprocal lattice : set of $\mathbf{G}$ vectors such that $\mathrm{e}^{\mathrm{i}\mathbf{G}\mathbf{R}_j} = 1$

$\mathrm{e}^{\mathrm{i}\mathbf{G}\mathbf{r}}$ has the periodicity of the real lattice

$$\mathrm{u}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} \mathrm{u}_{\mathbf{k}}(\mathbf{G})\, \mathrm{e}^{\mathrm{i}\mathbf{G}\mathbf{r}}$$

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

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

(Fourier transform)

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

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

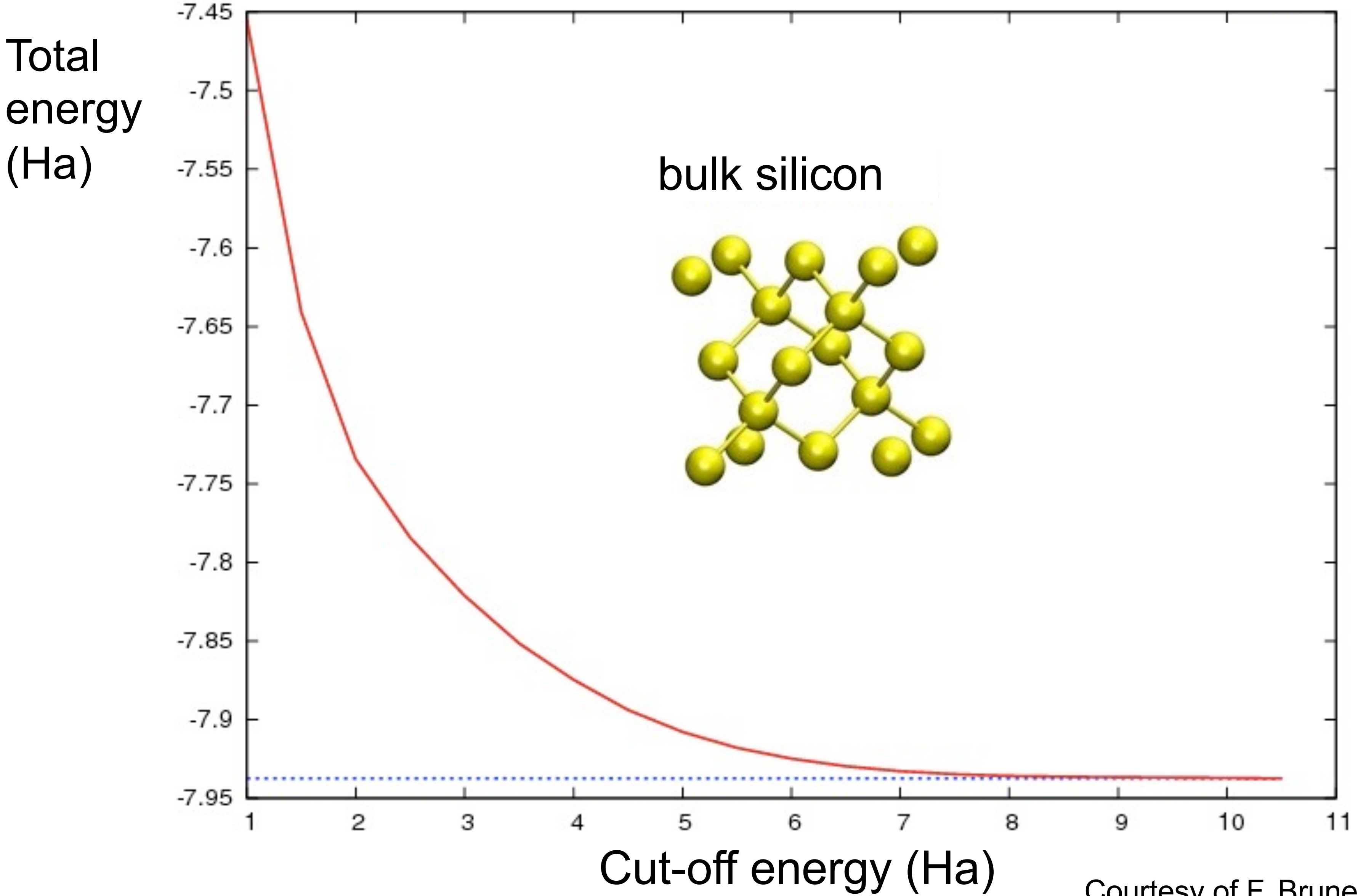
Selection of plane waves determined by a <u>cut-off energy</u> $\mathrm{E}_{\mathrm{cut}}$

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

Plane wave sphere

`ecut`

Convergence wrt to kinetic energy cutoff



Courtesy of F. Bruneval

Plane waves : the density and potential

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

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

Poisson equation

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

Relation between Fourier coefficients: $\Rightarrow\ n\ (\mathbf{G})$ and $V_H\ (\mathbf{G})$

$$V_H(\mathbf{G}) = \frac{4\pi}{G^2}\ n(\mathbf{G}) \qquad G^2\ V_H(\mathbf{G}) = 4\pi\ n(\mathbf{G})$$

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

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

Average

Representation of the density

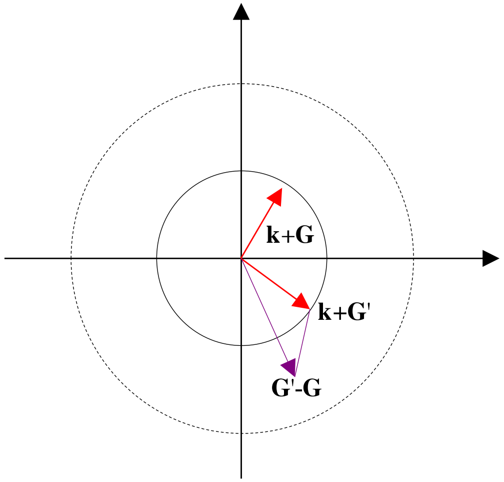
Density associated with one eigenfunction :

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

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

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

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



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

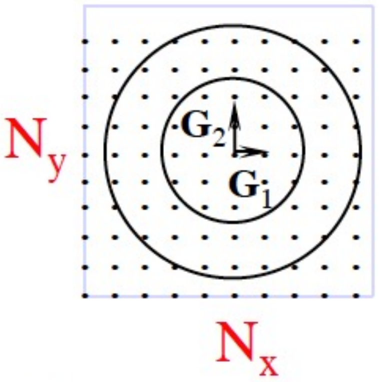
$\mathbf{k}+\mathbf{G}' \in$ sphere

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

From real space to reciprocal space

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

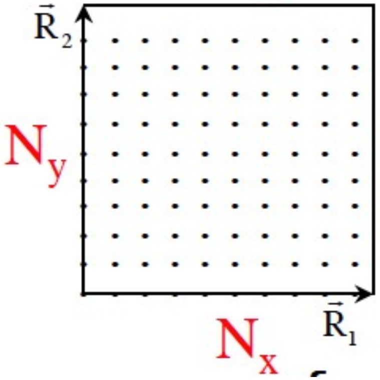
Use of the discrete Fourier transform $\{\mathbf{r}_i\} \leftrightarrow \{\mathbf{G}\}$



Reciprocal lattice

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

Fast Fourier Transform algorithm



Real lattice: original cell

Representation : wrap-up

- Choice of a basis (e.g. Plane waves)
- Truncation of the basis : finite basis

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

- 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

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

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...

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

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

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

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 ...

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

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

$$+ \sum_{i\in val}^{N_{val}} \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle + \int V_{ext}(\mathbf{r}) n_{val}(\mathbf{r}) \mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n_{val}(\mathbf{r}_1) n_{val}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

$$+ \int \frac{n_{core}(\mathbf{r}_1) n_{val}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

$$V_{ion} = V_{ext} + n_{core}$$

$$+ \boxed{E_{\mathrm{xc}}\left[n_{core} + n_{val}\right]}$$

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

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

Possible set of conditions (norm-conserving pseudopotentials)

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

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

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

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

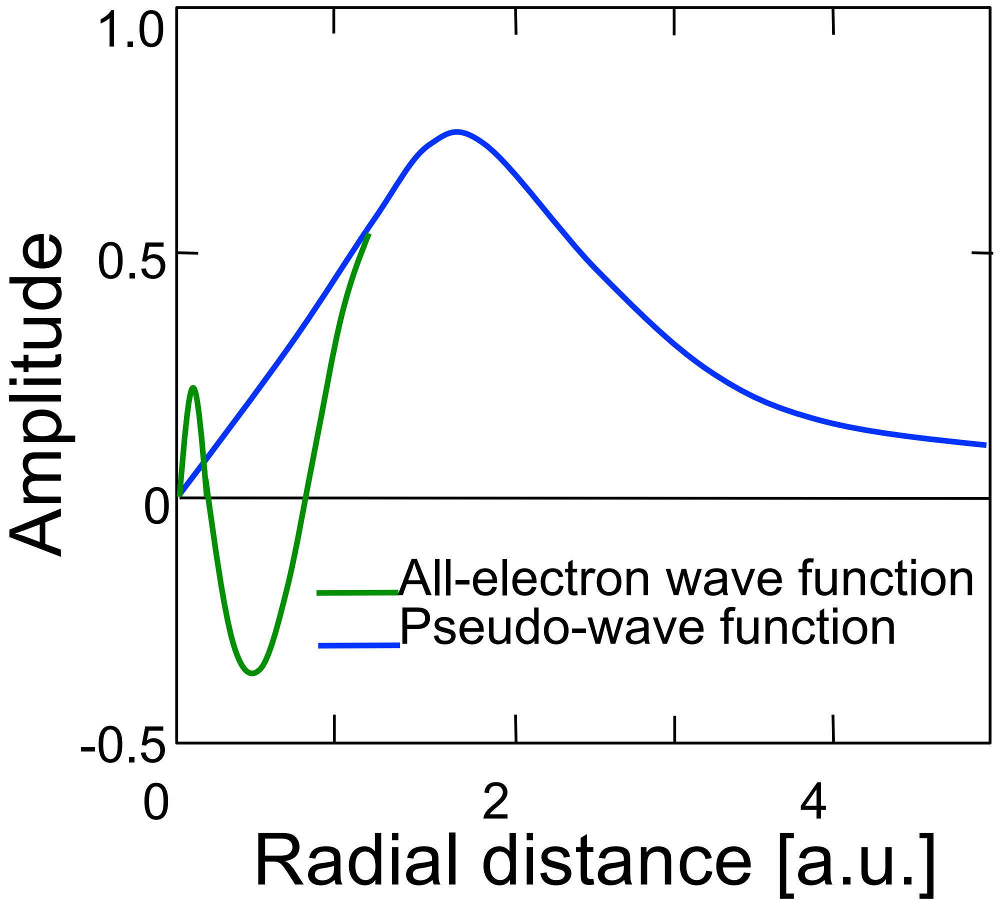
For the lowest angular momentum channels (s + p ... d ...f)

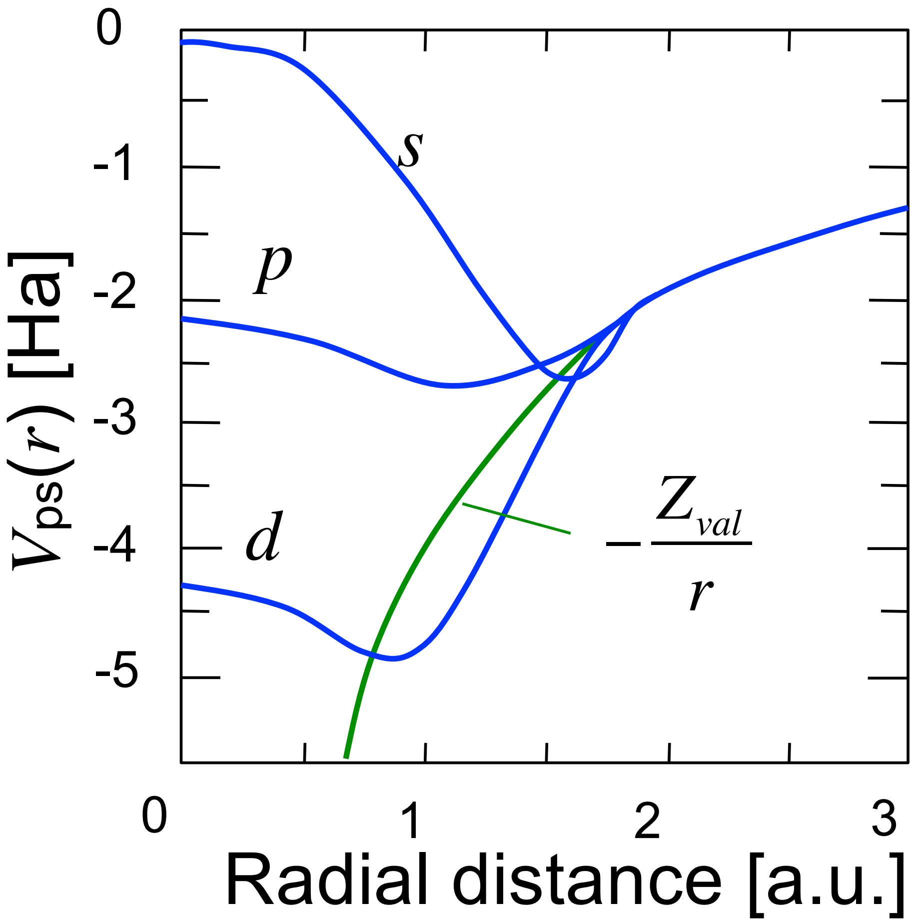
Generalisation : ultra-soft pseudopotentials (USPP), projector-augmented plane waves (PAW)

Warning : be it NCPP, USPP or PAW, regions within cut-off spheres of different atoms forming solid or molecule should not overlap. Uncontrolled approximation !

Example of pseudopotential

3*s* Radial wave function of Si





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 $V_{nloc}(\mathbf{r},\mathbf{r}') = \sum_{\ell m} Y_{\ell m}^{*}\left(\theta,\varphi\right)V_{\ell}(r,r')Y_{\ell m}\left(\theta',\varphi'\right)$

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

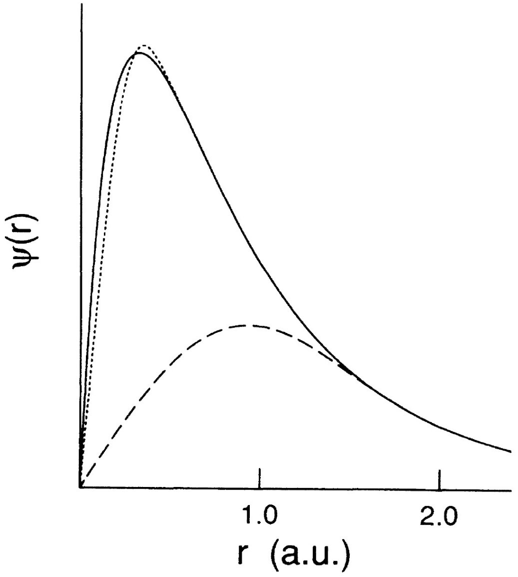
see Bachelet, Hamann and Schlüter, Phys.Rev.B 26, 4199 (1982)

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)

Ultrasoft Pseudopotentials and Projector-Augmented Waves (PAW)

Ultra-soft pseudopotentials : the idea



Problem with NC pseudopotentials :
Norm-conservation limits the softness !
When orbitals without nodes (1s, 2p, 3d, 4f)
treated as valence => small characteristic length
energy cut-off large.

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

Suppress norm-conservation condition :
- modify normalization, to keep correct scattering properties
- introduce charge density corrections.

For selected elements, can decrease number of PW/FFT Grid points by a factor of two or three, with even larger speed up.
More difficult to implement than norm-conserving PPs.

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

Projector-Augmented Waves : the idea

Idea P. Blöchl Phys. Rev. B 50, 17953 (1994)

The true wavefunction and a well-behaving pseudo-wavefunction are linked by a linear transformation

Strong oscillations near the nucleus

$$\Psi = \hat{T}\,\tilde{\Psi}$$

No oscillation near the nucleus

True wavefunction (all electron)

Auxiliary wavefunction (soft pseudofunction)

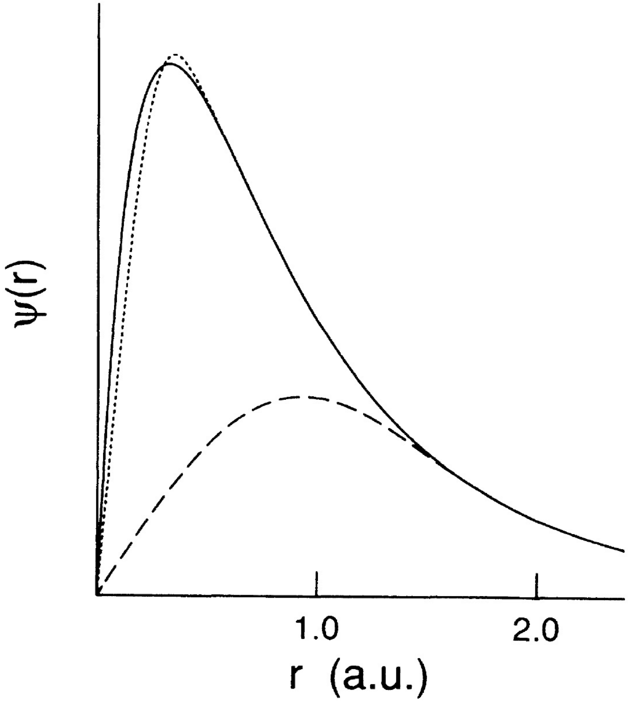
More rigorous than USPP

USPP and PAW : common features

Generalized Schrödinger Eq., with overlap operator S.

$$\left[-\frac{\nabla^2}{2}+\mathrm{v}_{ps}\right]\psi_{ps,i}=\varepsilon_i\hat{S}\psi_{ps,i}$$

Charge density
of each state
to be corrected
for the missing norm.



Projector-Augmented Waves : the math

True wave-function Ψ

Well-behaving pseudo-wavefunction $\tilde{\Psi}$

Linked by a linear transformation $\Psi = \hat{T}\tilde{\Psi}$

Physical quantities like $\langle \Psi | \hat{A} | \Psi \rangle$

computed in the pseudo representation $\langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle$

with $\tilde{A} = T^{+}\hat{A}T$

Similarly, variational principle for total energy gives

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

Equivalent to Kohn-Sham eq., for pseudowavefunctions.
Search for ground state done in the pseudo space.

Transformation operator

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

→ Identity + sum of atomic contributions

$\Psi = \hat{T}\tilde{\Psi}$ with $\hat{T} = 1 + \sum_R \hat{S}_R$ (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, but smoother inside

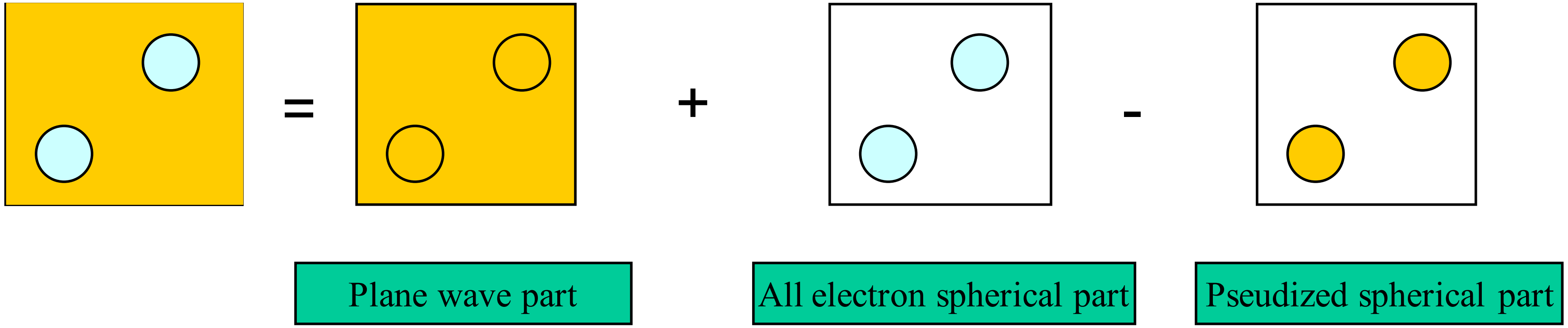
Define S such as : $|\phi_i\rangle = (1 + \hat{S}_R)|\tilde{\phi}_i\rangle$

Representation of the wavefunctions

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

Explicitly,

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



Plane wave part

All electron spherical part

Pseudized spherical part

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

Warning : be it NCPP, USPP or PAW, regions within cut-off spheres of different atoms forming solid or molecule should not overlap. Uncontrolled approximation !

Wavefunctions, density, energy

$\tilde{\Psi}$ 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, times spherical harmonics

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

Density:

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_R \left(n_R^1(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) \right)$$

Energy:

$$E = \tilde{E} + \sum_R \left(E_R^1 - \tilde{E}_R^1 \right)$$

Approximations

(1) Core electrons : usually treated in the frozen-core approximation, and treated on radial grid (spherical harmonics).

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

is only approximately true !

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

Other basis sets than plane waves ?

(1) Without pseudopotentials : All-electron approach
- Linear combination of atomic-centered functions
  (e.g. FHI-AIMS)
- Augmented plane waves
  (Linear APW approach e.g. WIEN2k, EXCITING, FLEUR)
- Wavelets
  (e.g. BigDFT)
- Green’s function based – Korringa, Kohn, Rostoker (KKR)
- …

(2) With pseudopotentials
- Atomic-centered function (e.g. SIESTA)
- psinc functions, for O(N) scaling (e.g. ONETEP)
- …

Advantages of PW+PP or PAW method ?

(1) 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.

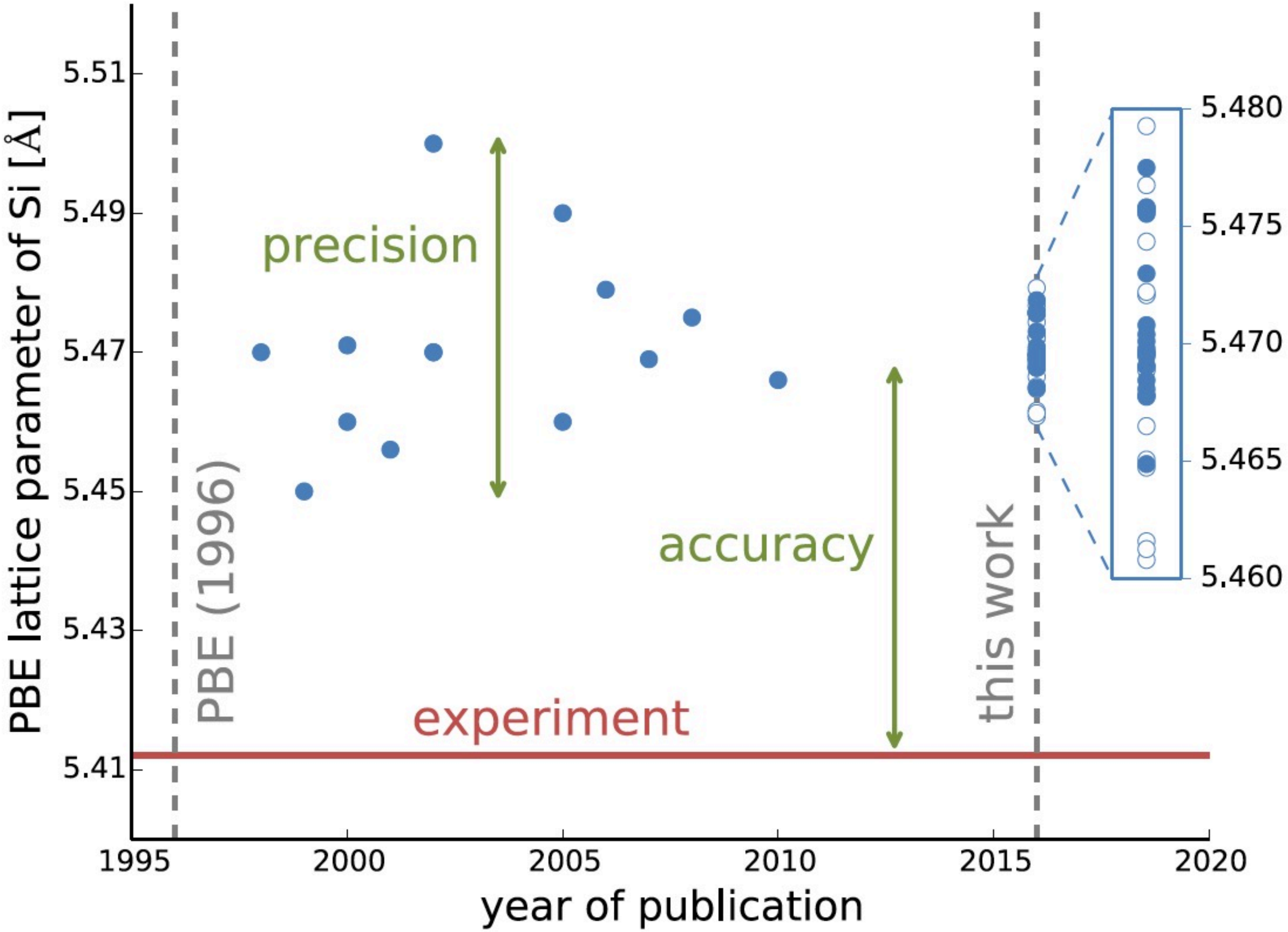
(2) Systematic way to complete the basis set

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

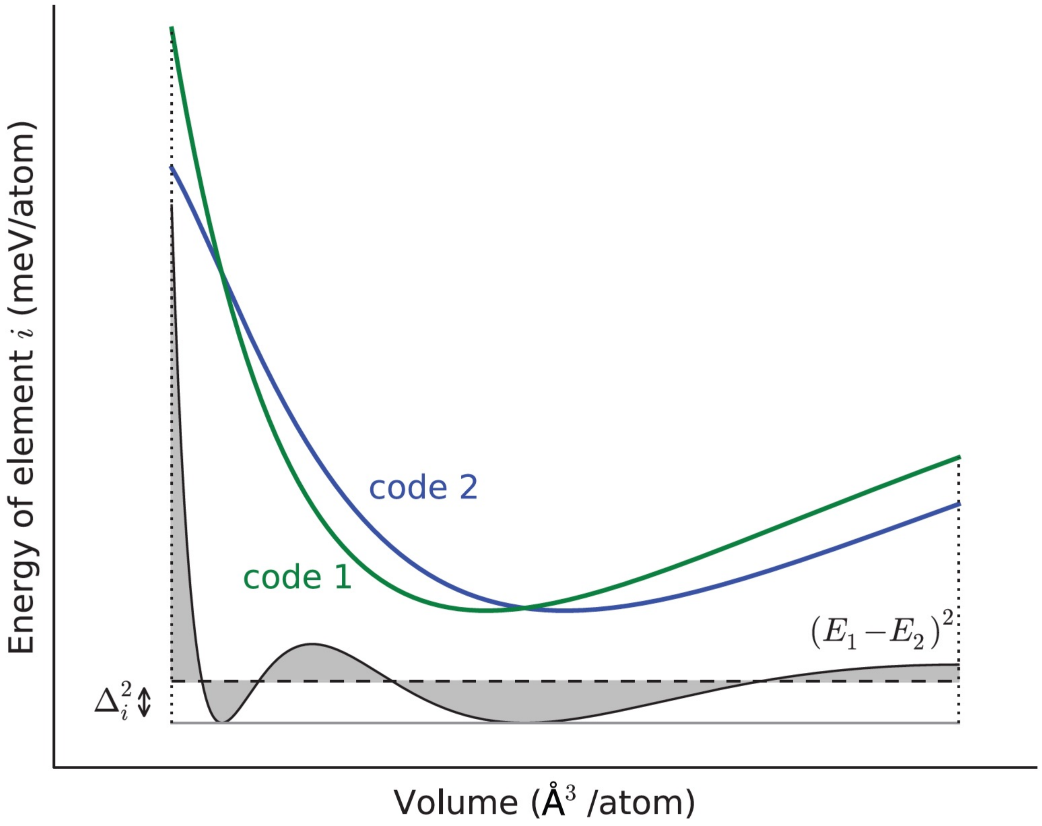
Disadvantages : cannot lead to Order(N) implementation,
does not treat efficiently finite systems (vacuum !).
Higher lying states (very high in energy) cannot be trusted...

Testing pseudopotentials

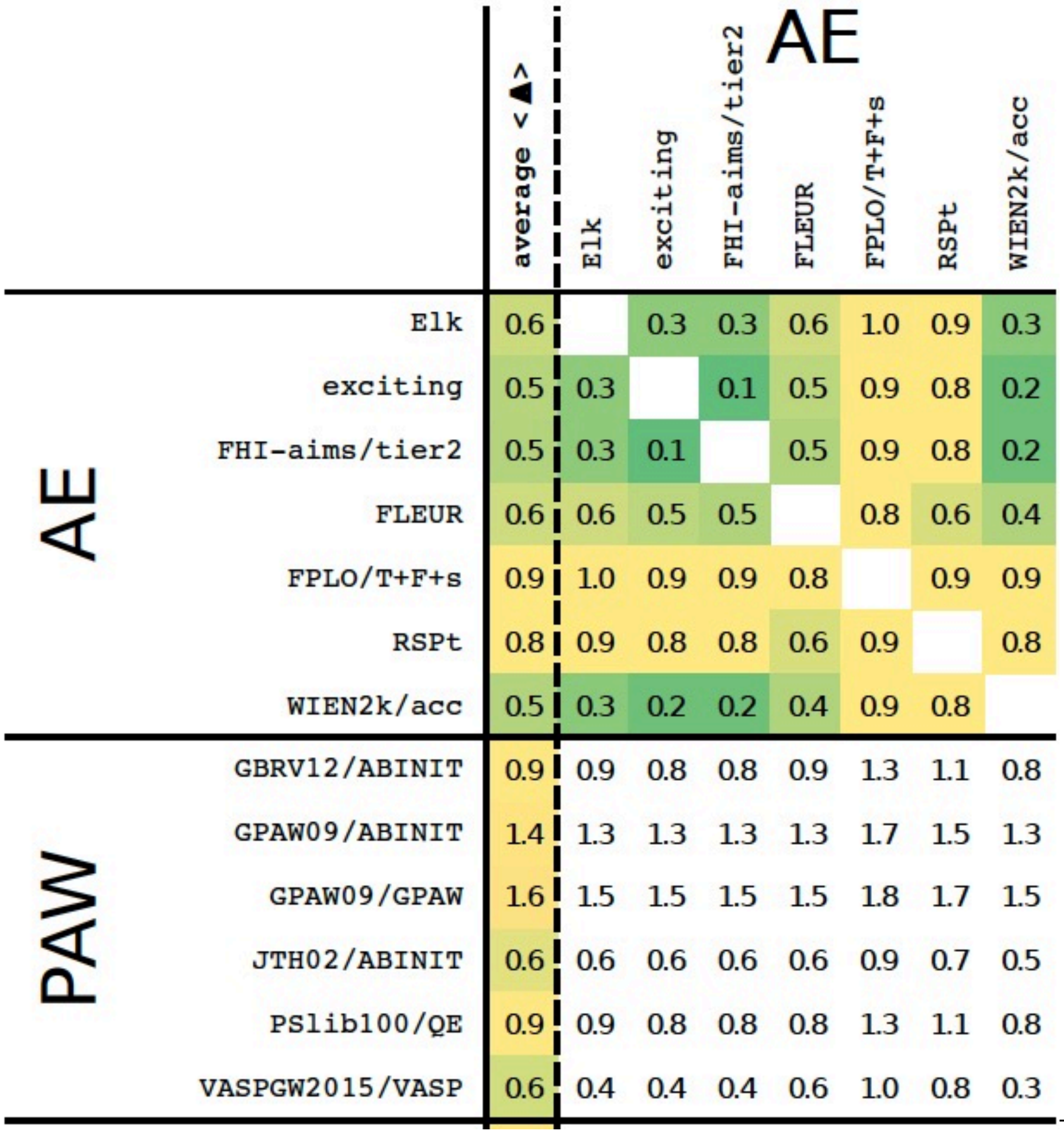


Comparing code/pseudopotential

Recently, large effort to improve uncertainty related to psps :
« Delta-factor » collaboration
Lejaeghere ... Cottenier, Science 351, aad3000 (2016)
Specification of 71 elemental solids for different volumes.

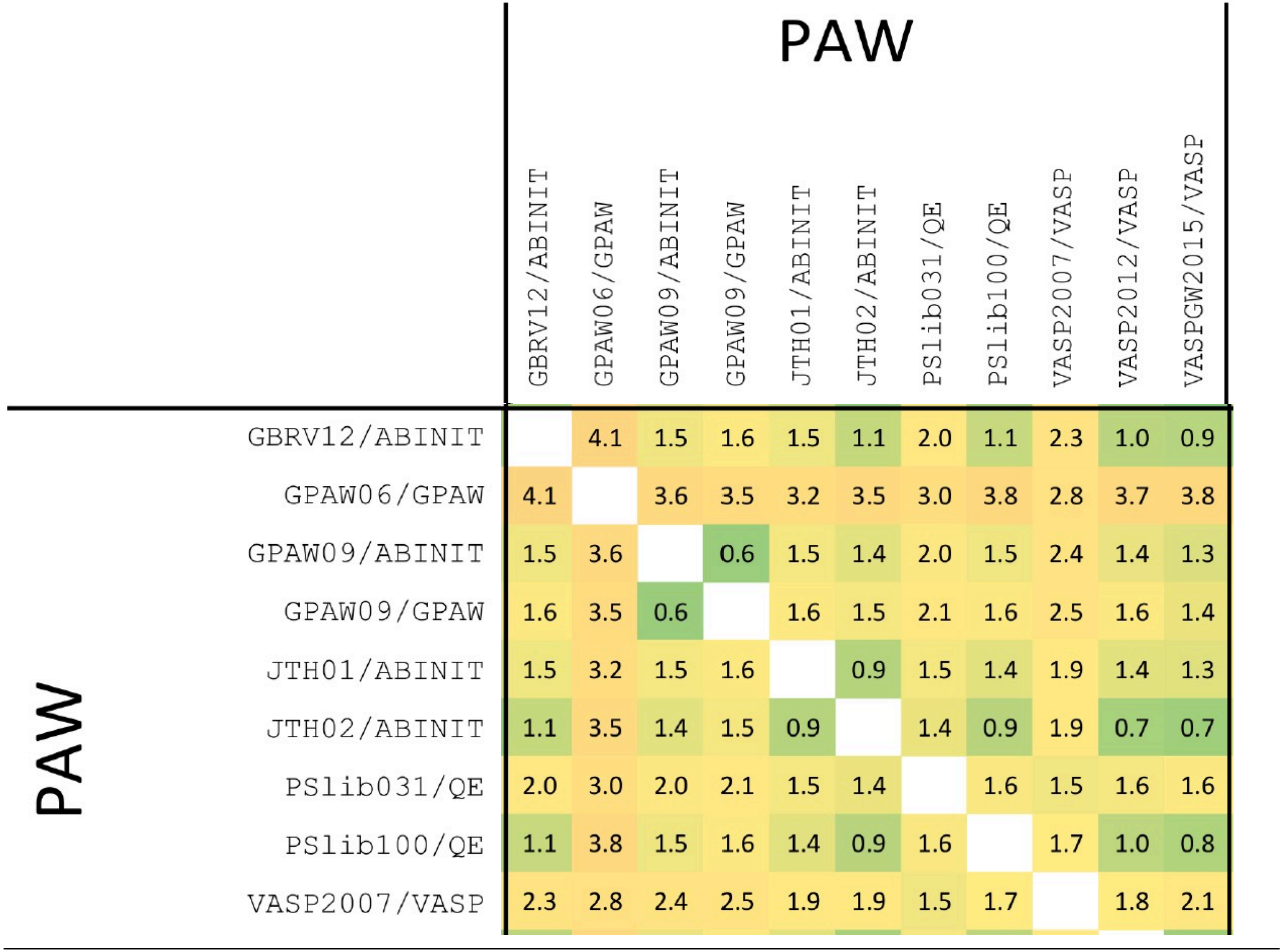


More about pseudopotentials / PAW datasets



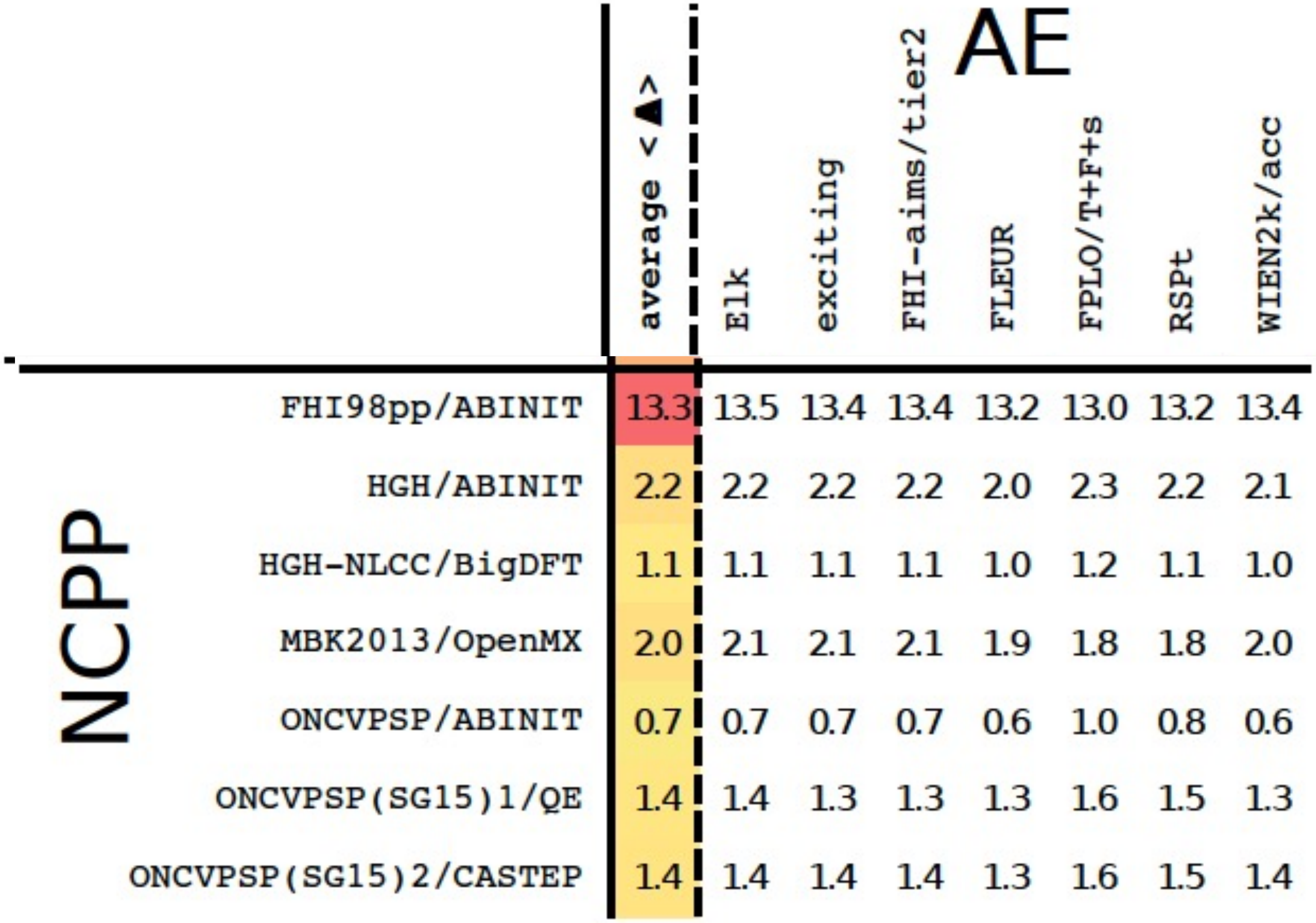
			AE						
		average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3

More about pseudopotentials / PAW datasets



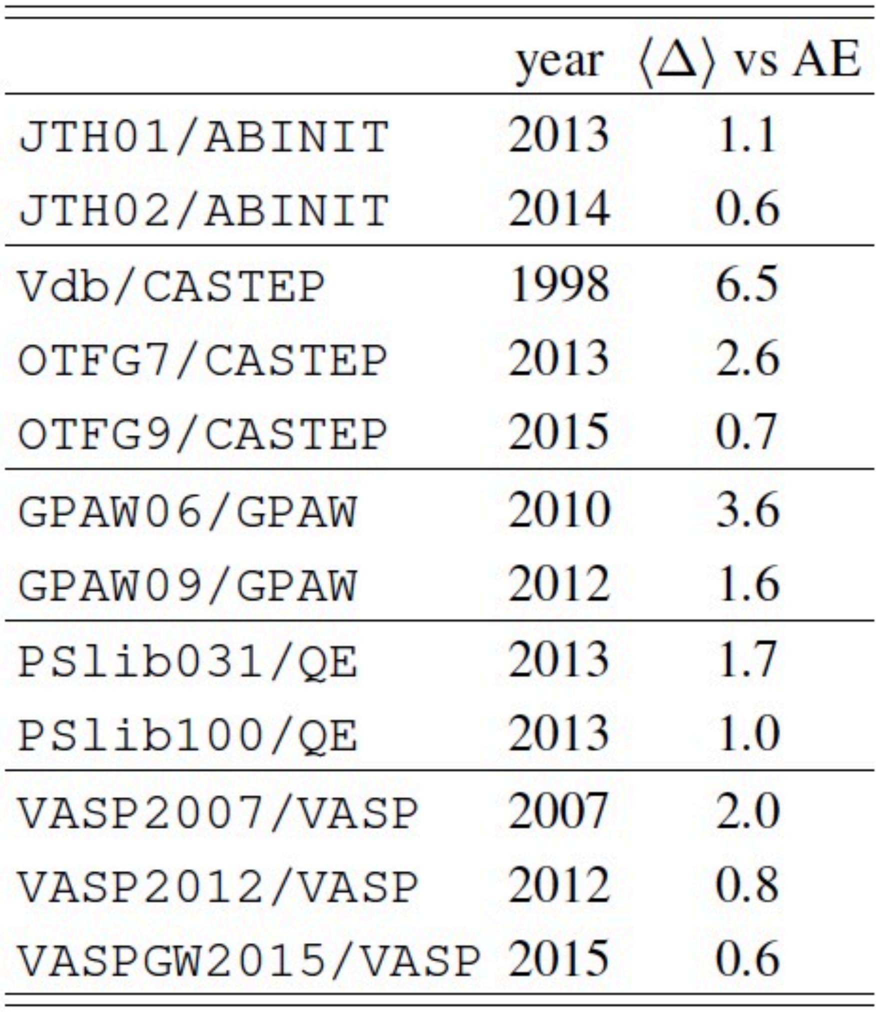
		PAW										
		GBRV12/ABINIT	GPAW06/GPAW	GPAW09/ABINIT	GPAW09/GPAW	JTH01/ABINIT	JTH02/ABINIT	PSlib031/QE	PSlib100/QE	VASP2007/VASP	VASP2012/VASP	VASPGW2015/VASP
PAW	GBRV12/ABINIT		4.1	1.5	1.6	1.5	1.1	2.0	1.1	2.3	1.0	0.9
	GPAW06/GPAW	4.1		3.6	3.5	3.2	3.5	3.0	3.8	2.8	3.7	3.8
	GPAW09/ABINIT	1.5	3.6		0.6	1.5	1.4	2.0	1.5	2.4	1.4	1.3
	GPAW09/GPAW	1.6	3.5	0.6		1.6	1.5	2.1	1.6	2.5	1.6	1.4
	JTH01/ABINIT	1.5	3.2	1.5	1.6		0.9	1.5	1.4	1.9	1.4	1.3
	JTH02/ABINIT	1.1	3.5	1.4	1.5	0.9		1.4	0.9	1.9	0.7	0.7
	PSlib031/QE	2.0	3.0	2.0	2.1	1.5	1.4		1.6	1.5	1.6	1.6
	PSlib100/QE	1.1	3.8	1.5	1.6	1.4	0.9	1.6		1.7	1.0	0.8
	VASP2007/VASP	2.3	2.8	2.4	2.5	1.9	1.9	1.5	1.7		1.8	2.1

More about pseudopotentials / PAW datasets



		AE						
NCPP	average < Δ >	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
ONCVPSP/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

Improvement with time



	year	$\langle\Delta\rangle$ vs AE
JTH01/ABINIT	2013	1.1
JTH02/ABINIT	2014	0.6
Vdb/CASTEP	1998	6.5
OTFG7/CASTEP	2013	2.6
OTFG9/CASTEP	2015	0.7
GPAW06/GPAW	2010	3.6
GPAW09/GPAW	2012	1.6
PSlib031/QE	2013	1.7
PSlib100/QE	2013	1.0
VASP2007/VASP	2007	2.0
VASP2012/VASP	2012	0.8
VASPGW2015/VASP	2015	0.6

Now :
JTH 1.0 => 0.4 meV

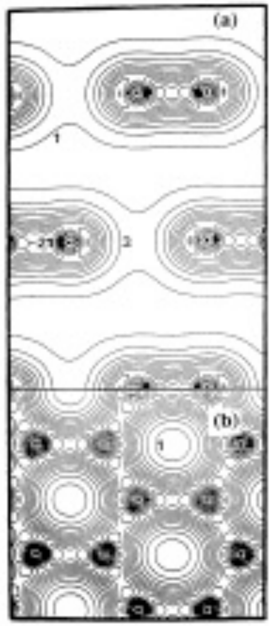
For norm-conserving
Pseudo-dojo 0.1
=> 0.6 meV

Updated information on : https://molmod.ugent.be/deltacodesdft

Going beyond basic properties:

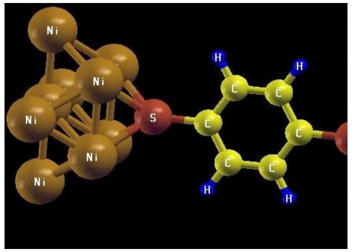
Advanced Material Property lab

Properties from DFT+MBPT+ …



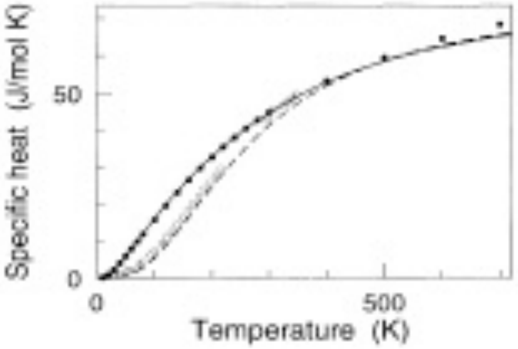
Computation of ...

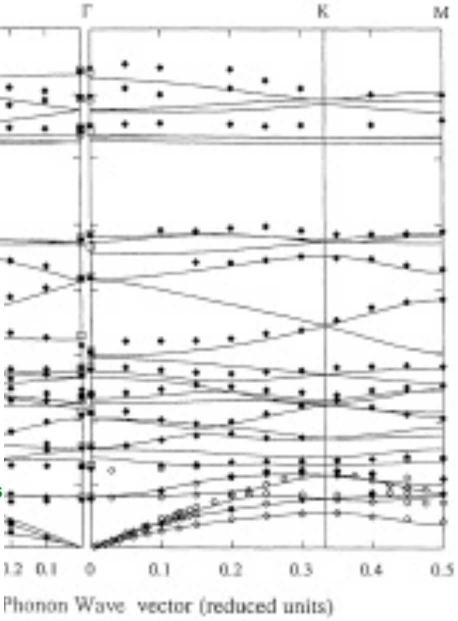
- interatomic distances, angles, total energies
- electronic charge densities, electronic energies

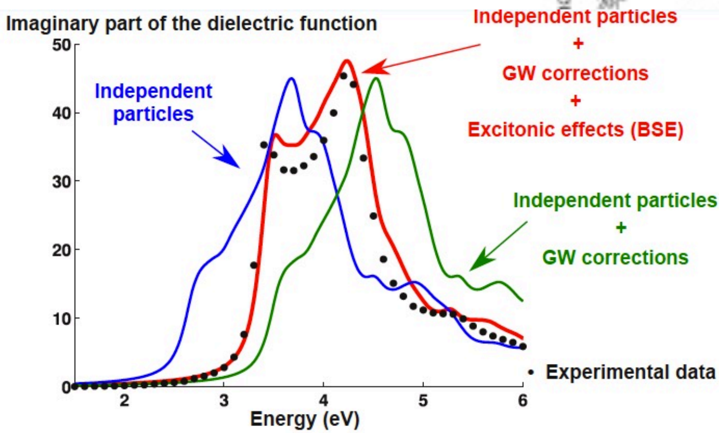


A basis for the computation of ...

- chemical reactions
- electronic transport
- vibrational properties
- thermal capacity
- dielectric behaviour
- optical response
- superconductivity
- surface properties
- spectroscopic responses
- ...







Objectives

Familiarization with more than one software application :

In this lab, ABINIT http://www.abinit.org instead of VASP

Last release v9.4 Available freely (GPL, like Linux).

Familiarization with the Materials Project (MP) http://www.materialsproject.org

The student should (see detailed description in document available on Web)

- Choose a materials from the MP, and sent the MP ID to Ch. Tantardini
- Compute energy & lattice parameter, as function of ecut and k-point grid
- Prove that the result is numerically converged
- Compute band structure (in GGA-PBE and TB09)
- Compare with literature and MP results.

Tutorial available on the Web.

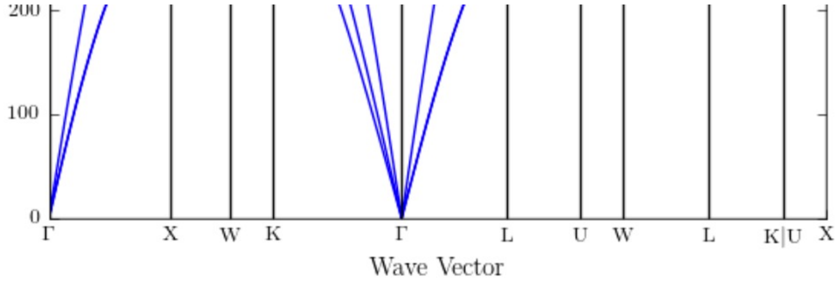
Resources are described in the document available on Web.

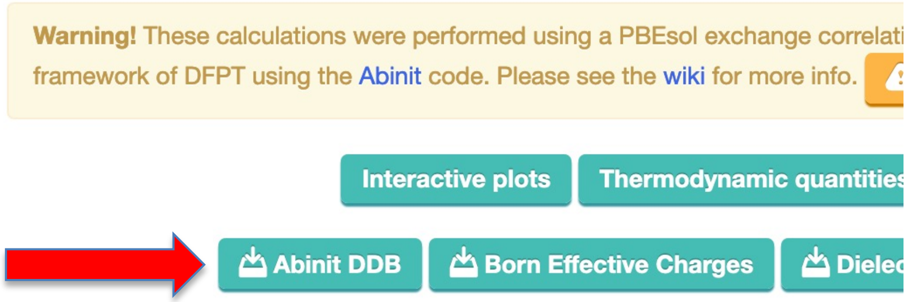
For band structure using TB09, use HGH pseudopotentials, fix the geometry at the GGA-PBE relaxed geometry, and use `ixc -12209 usekden 1`

The Materials Project

Short Demo (https://materialsproject.org/)

- Crystalline structure : CIF file, visualisation
- A reference electronic band structure (in the GGA PBE approximation)
- A reference phonon band structure, and the Abinit DDB
  (in the GGA PBEsol approximation).




Warning! These calculations were performed using a PBEsol exchange correlati
framework of DFPT using the Abinit code. Please see the wiki for more info.

Give references for :

`rprim (+acell), xred, …`
`ecut, nkpt, …`

See later !

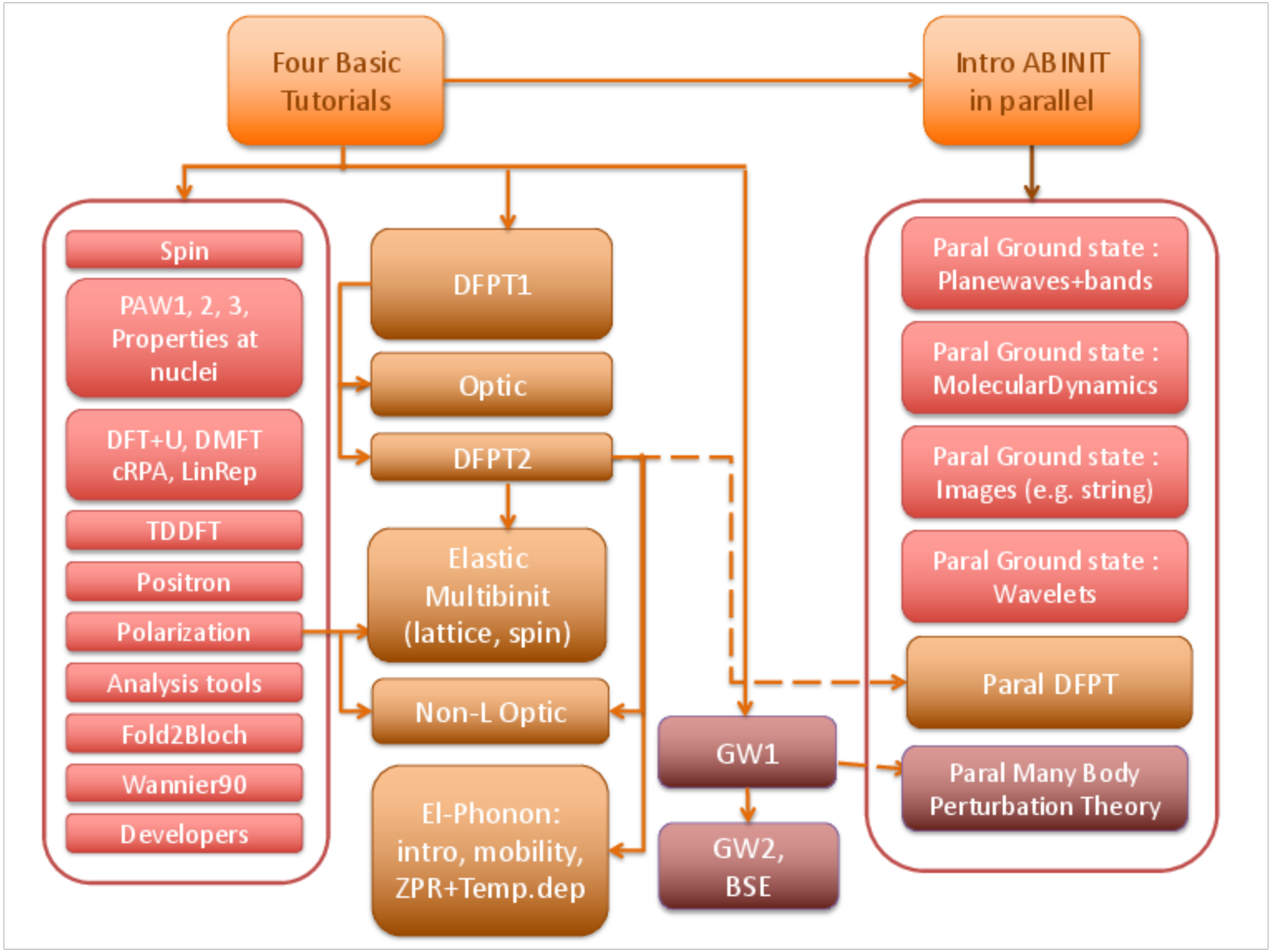
Basic Documentation

Web site http://www.abinit.org ; http://docs.abinit.org

- User's guides
- Installations notes
- List of input variables + description
- List of topics = a hub to input variables, files, tutorial, bibrefs
- over 800 example input files
- >30 tutorial lessons (each 1-2 hours)
  https://docs.abinit.org/tutorial

+ Forum Web site http://forum.abinit.org

ABINIT tutorial : layout + dependencies



Skoltech

Running ABINIT

Density Functional Theory calculations

In ABINIT …

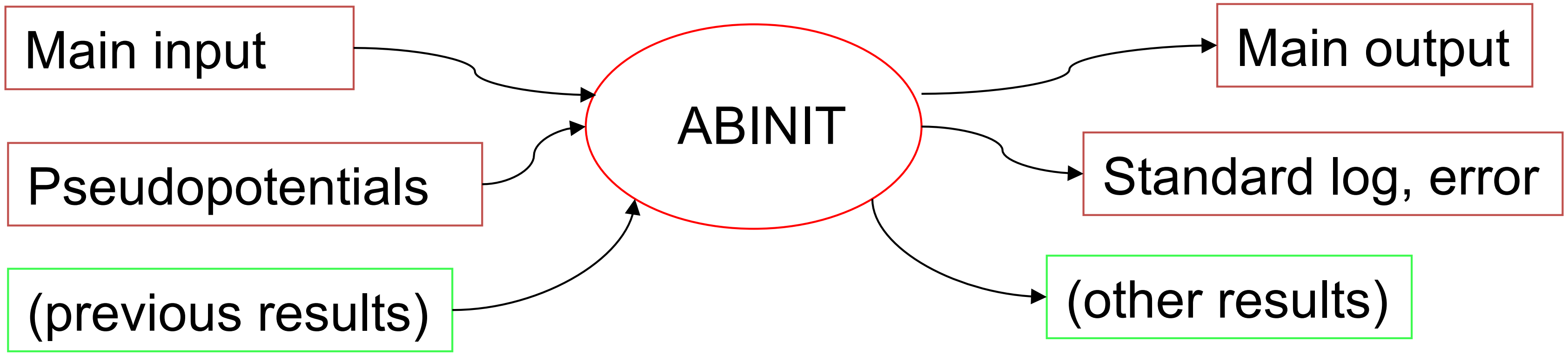
Representation of mathematical formalism
with a Plane Wave basis set :
- wavefunctions
- density, potential

Periodic boundary conditions
=> wavefunctions characterized by a wavevector (k-vector)

PseudoPotentials (or Projector Augmented Waves – PAW)

Iterative techniques to solve the equations
(Schrödinger equation ; DFT Self-consistency ; optimisation of atomic positions)

External files in a ABINIT run



Results :
log, main output, energy derivatives (_DDB), ... – text files
density (_DEN), potential (_POT), wavefunctions (_WFK), ... – binary F90 files
or similar files in netCDF (_DEN.nc, _POT.nc, _WFK.nc)

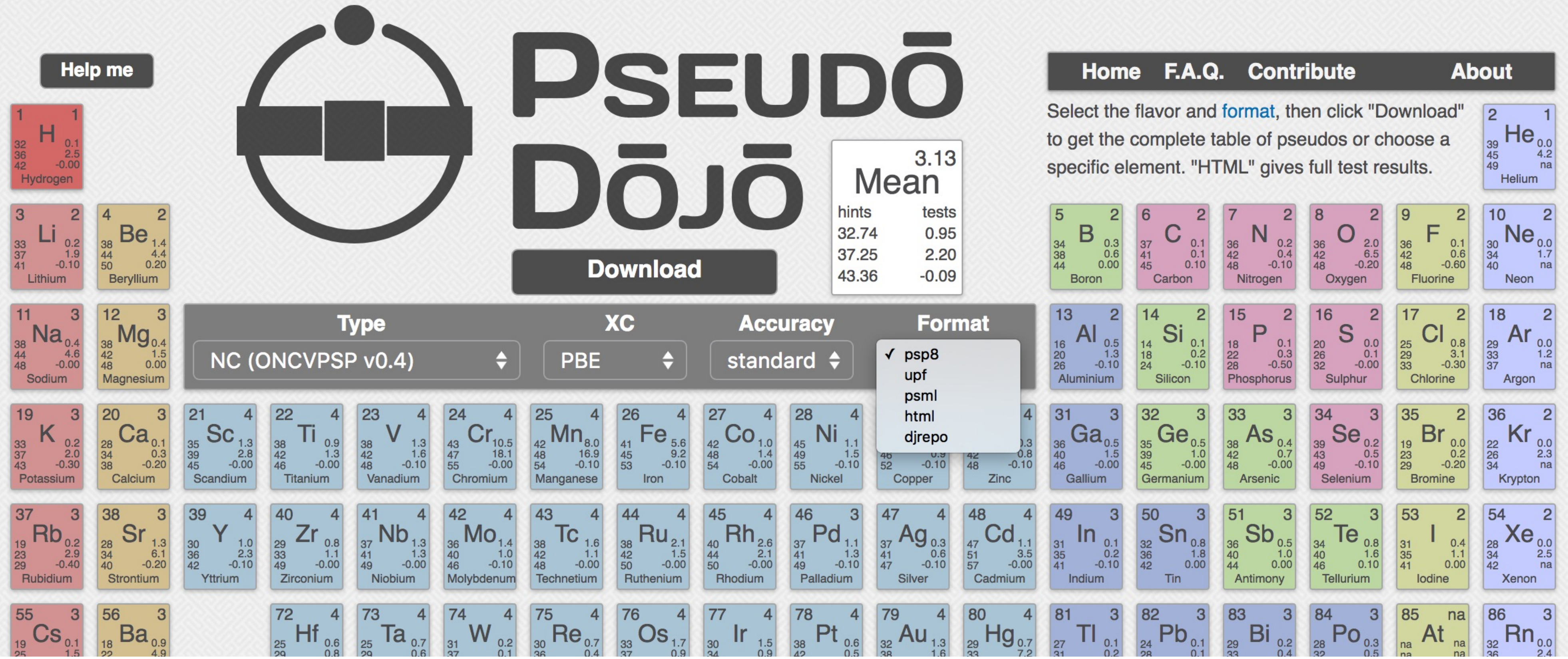
Advantage of netCDF : portable, addressed by content, extensible, Python-friendly

Pseudopotentials/PAW data in ABINIT

- Norm-conserving pseudos : pseudo-dojo approach

  Van Setten et al , Computer Physics Comm. 226, 39 (2018)

  https://www.pseudo-dojo.org

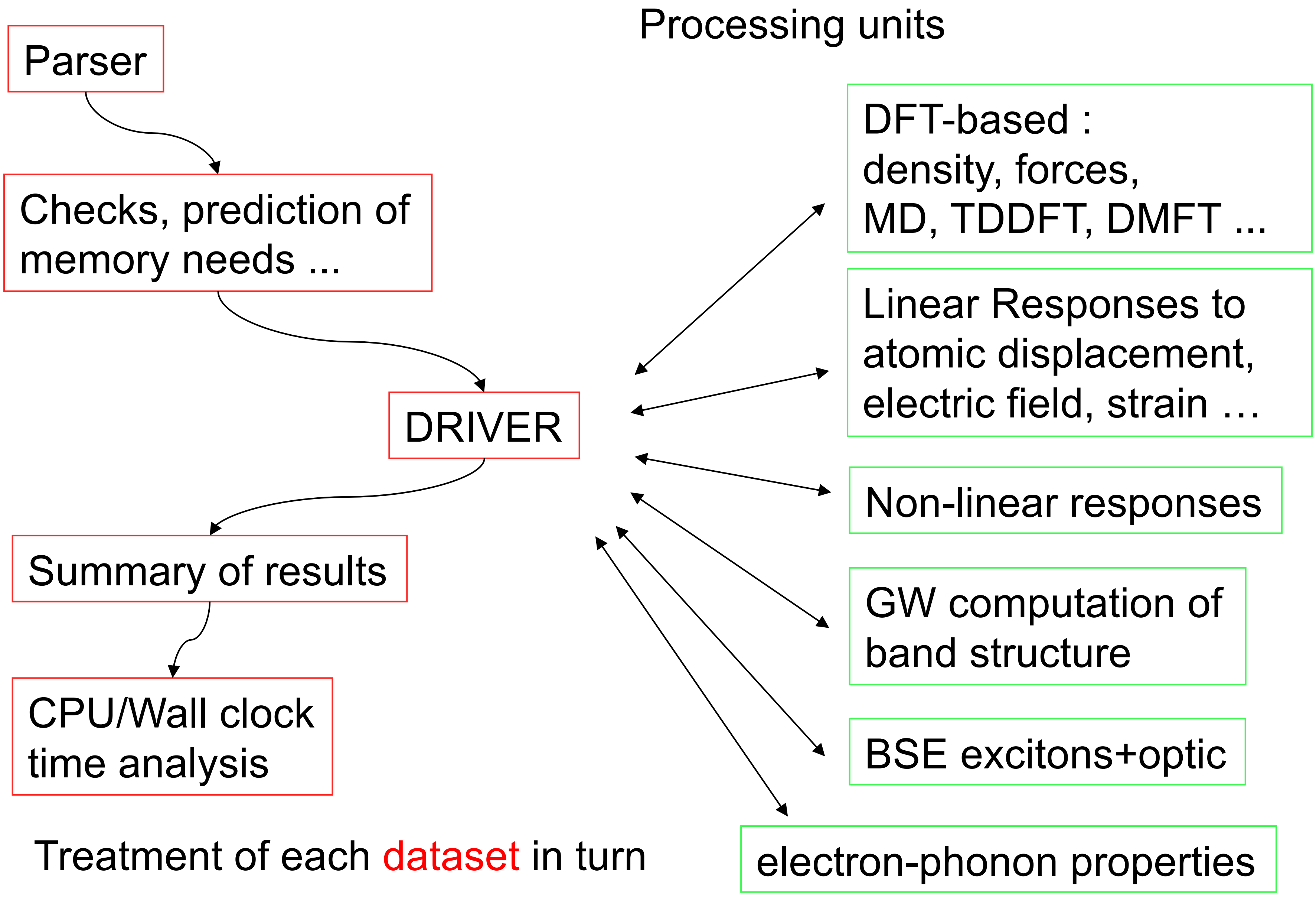


Select the flavor and format, then click "Download" to get the complete table of pseudos or choose a specific element. "HTML" gives full test results.

	3.13
	Mean
hints	tests
32.74	0.95
37.25	2.20
43.36	-0.09

Type: NC (ONCVPSP v0.4)
XC: PBE
Accuracy: standard
Format: ✓ psp8

ABINIT : the pipeline and the driver



Processing units

Parser

Checks, prediction of memory needs ...

DRIVER

Summary of results

CPU/Wall clock time analysis

DFT-based : density, forces, MD, TDDFT, DMFT ...

Linear Responses to atomic displacement, electric field, strain …

Non-linear responses

GW computation of band structure

BSE excitons+optic

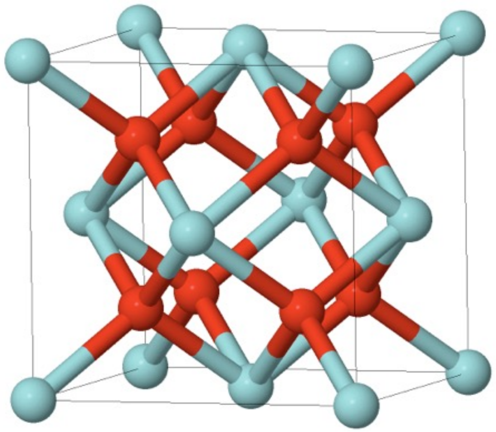
electron-phonon properties

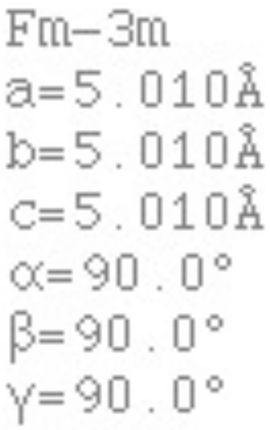
Treatment of each dataset in turn

Main input file : input variable flexibility

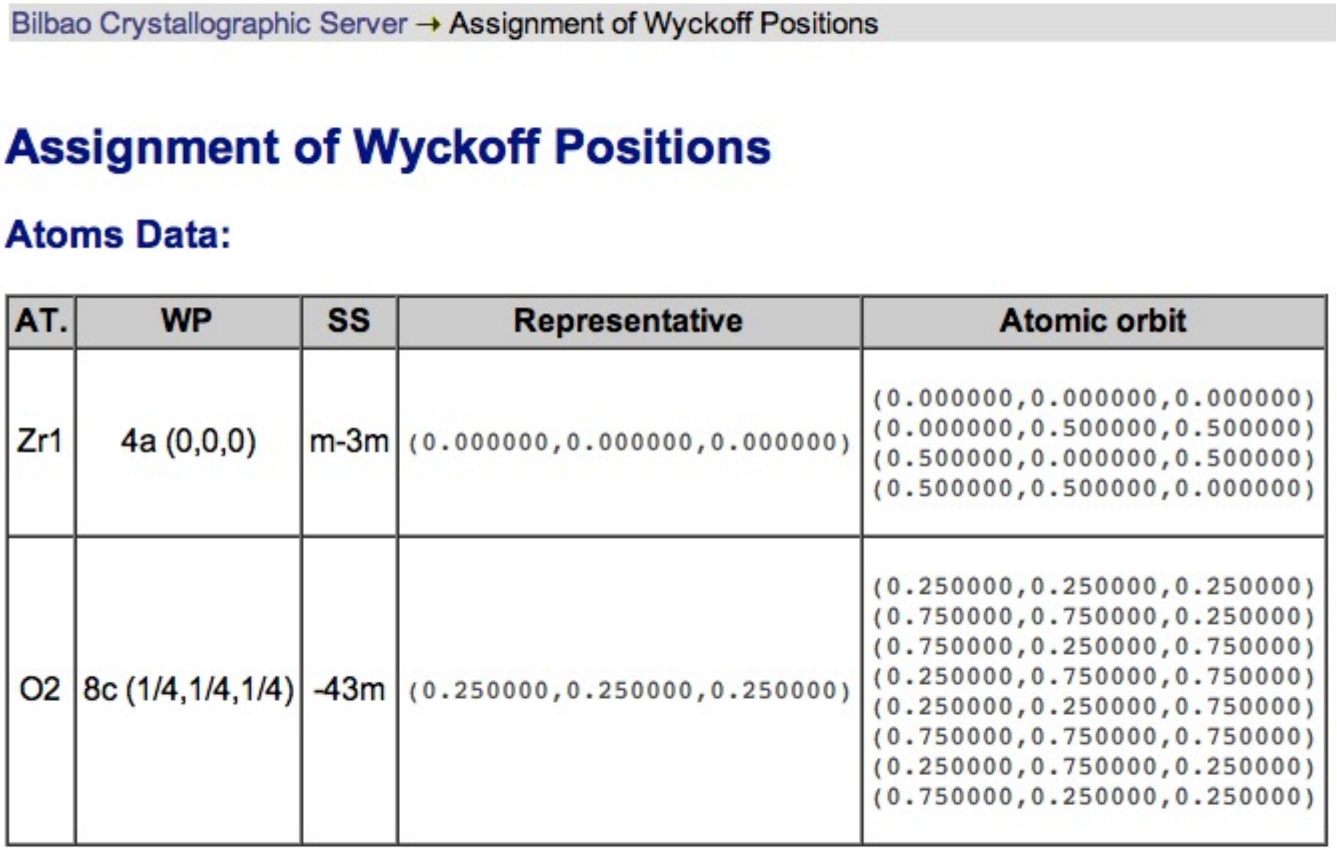
- by default : atomic units (Bohr, electron mass, Planck's constant, Hartree)
  but eV, Angst, nm ... are recognized in the input file
- cell primitive vectors → rprim
  … or angle (degrees) between primitive vectors → angdeg
  + scale cell vector lengths → acell
  + scale cartesian coordinates → scalecart
- number of atoms → natom
- reduced coordinates → xred (initial guess …)
  … or cartesian coordinates → xcart (in Bohr) / xangst (in Å)
- type of atoms → typat
- space group → spgroup + natrd
  … or number of symmetries → nsym
  + symmetry operations → symrel + tnons

Example : cubic zirconium dioxide





Fm-3m
a=5.010Å
b=5.010Å
c=5.010Å
α=90.0°
β=90.0°
γ=90.0°



Bilbao Crystallographic Server → Assignment of Wyckoff Positions

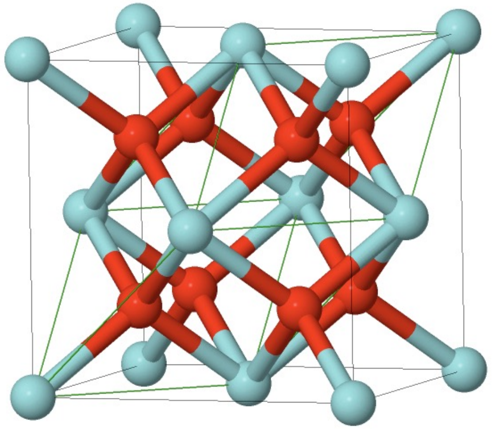
Assignment of Wyckoff Positions

Atoms Data:

AT.	WP	SS	Representative	Atomic orbit
Zr1	4a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000) (0.000000,0.500000,0.500000) (0.500000,0.000000,0.500000) (0.500000,0.500000,0.000000)
O2	8c (1/4,1/4,1/4)	-43m	(0.250000,0.250000,0.250000)	(0.250000,0.250000,0.250000) (0.750000,0.750000,0.250000) (0.750000,0.250000,0.750000) (0.250000,0.750000,0.750000) (0.250000,0.250000,0.750000) (0.750000,0.750000,0.750000) (0.250000,0.750000,0.250000) (0.750000,0.250000,0.250000)

Face-centered cubic, with three atoms per primitive cell

Example : cubic zirconium dioxide



```
natom 3
acell 3*5.01 Angst
rprim  0.0 0.5 0.5
       0.5 0.0 0.5
       0.5 0.5 0.0
typat 1 2 2
xred 3*0.0  3*0.25 3*0.75
```

NOTE “*” is a repeater

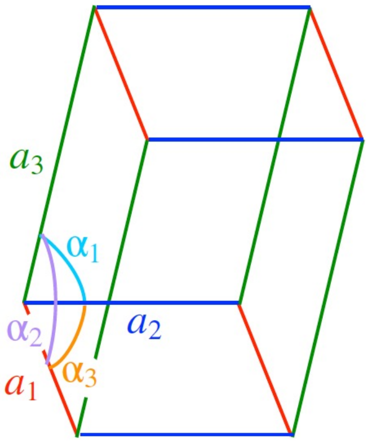
=> symmetries are found automatically

OR

```
natom 3
acell 3*5.01 Angst
rprim  0.0 0.5 0.5
       0.5 0.0 0.5
       0.5 0.5 0.0
typat 1 2 2
spgroup 225      natrd 2
xred 3*0.0  3*0.25
```

=> the set of atoms is completed automatically

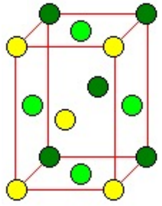
Primitive vectors in ABINIT (rprimd)



- $R_i(j) \rightarrow$ rprimd(j,i)=scalecart(j) × rprim(j,i) × acell(i)

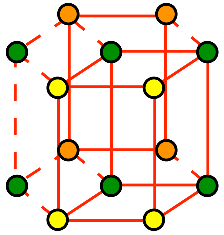
```
scalecart    9.5  9.8  10.0
    rprim    0.0  0.5  0.5
             0.5  0.0  0.5
             0.5  0.5  0.0
```

face-centered orthorhombic



```
acell    9.5  9.5  10.0
rprim    sqrt(0.75)  0.5  0.0
        -sqrt(0.75)  0.5  0.0
         0.0  0.0  1.0
```

hexagonal



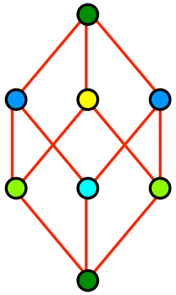
- $a_i \rightarrow$ acell(i) / $\alpha_i \rightarrow$ angdeg(i)

```
 acell    9.5  9.5  10.0
angdeg    120 90 90
```

hexagonal

```
 acell    9.0  9.0  9.0
angdeg    48 48 48
```

trigonal



A basic ‘input’ file : dihydrogen (I)

```
# H2 molecule in big cubic box
# Characters after  ’#’ or after ‘!’ are comments, will be ignored.
# Keywords followed by values. Order of keywords in file is not important.

# Definition of the unit cell
acell 10 10 10                  # Keyword "acell" refers to
                                #  lengths of primitive vectors (default in Bohr)
# Definition of the atom types
ntypat 1                        # Only one type of atom
znucl 1                         # Keyword "znucl" refers to atomic number of
                           # possible type(s) of atom. Pseudopotential(s)
                           # mentioned in "filenames" file must correspond
                           # to type(s) of atom. Here, the only type is Hydrogen.
pseudos "H.psp8”

# Definition of the atoms
natom 2                    # Two atoms
typat 1 1                       # Both are of type 1, that is, Hydrogen
xcart                      # This keyword indicate that location of the atoms
                           # will follow, one triplet of number for each atom
 -0.7 0.0 0.0              # Triplet giving cartesian coordinates of atom 1, in Bohr
  0.7 0.0 0.0              # Triplet giving cartesian coordinates of atom 2, in Bohr
```

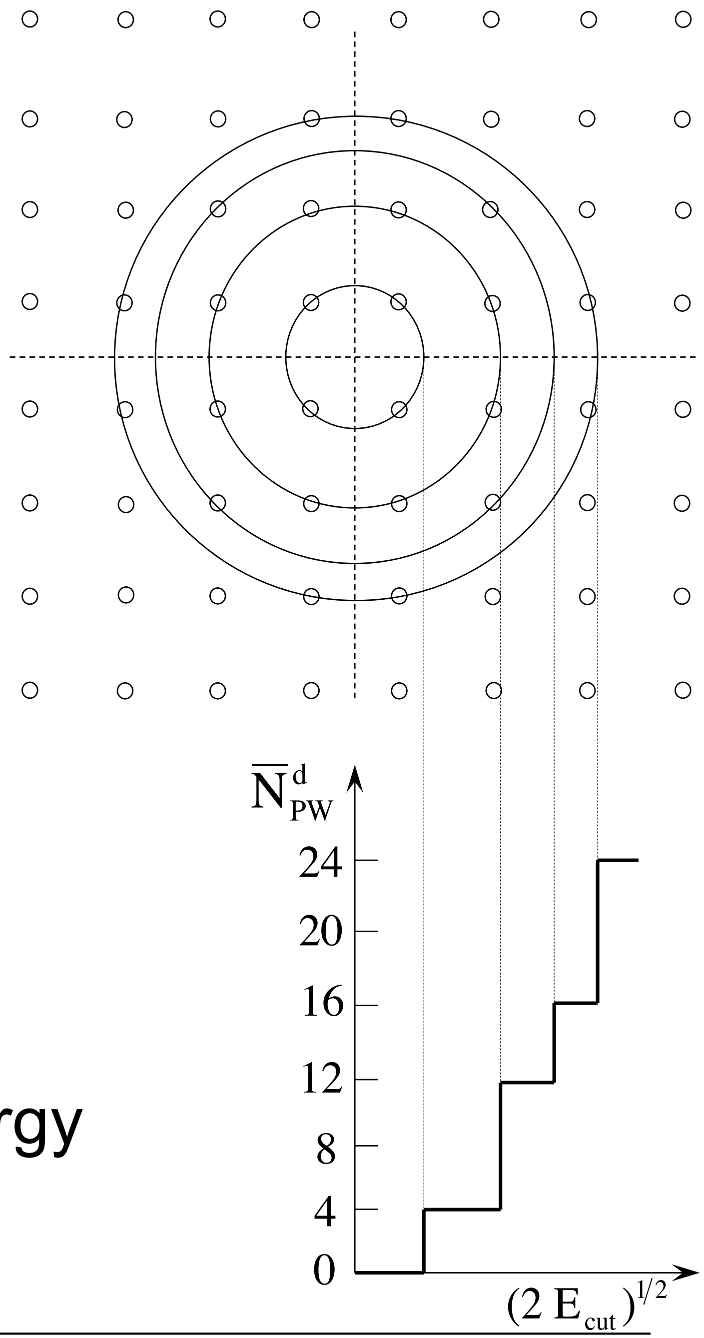
A basic input file : dihydrogen (II)

```
# Definition of planewave basis set
ecut 10.0          # Maximal plane-wave kinetic energy cut-off, in Hartree

# Definition of k-point grid
kptopt 0           # Enter k points manually
nkpt 1             # Only one k point is needed for isolated system,
                   # taken by default to be 0.0 0.0 0.0

#Definition of SCF (self-consistent field) procedure
nstep 10           # Maximal number of SCF cycles
toldfe 1.0d-6            # Will stop when, twice in a row, the difference
                         # between two consecutive evaluations of total energy
                         # differs by less than toldfe (default in Hartree)
diemac 2.0               # Although this is not mandatory, it is worth to precondition the
                   # SCF cycle. A model dielectric function, used as standard
                         # preconditioner, is described in "dielng" input variable section.
                         # Here, we follow prescriptions for molecules in a big box
## After modifying the following section, one might need to …
#%%<BEGIN TEST_INFO>            Metadata … to be ignored in the tutorial !
```

Number of planewaves

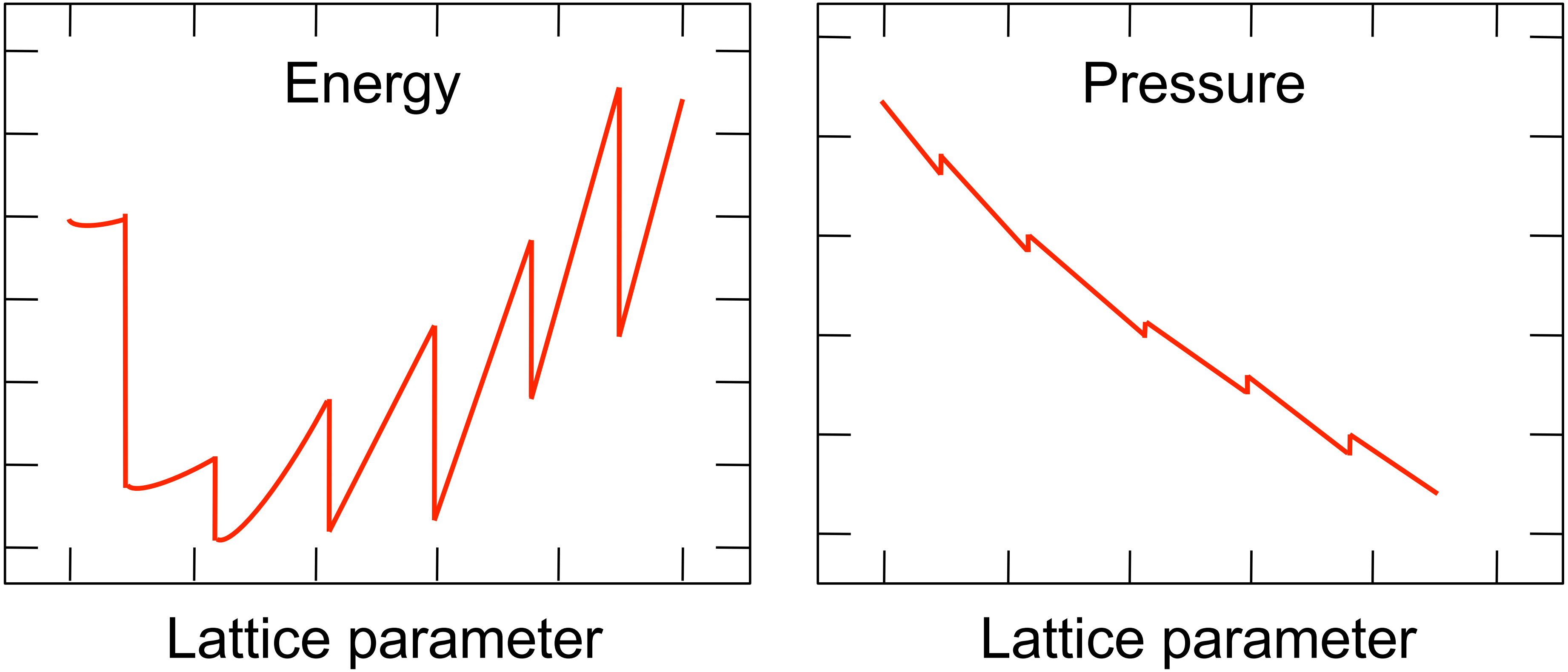


Number of plane waves
= function of the
kinetic energy cut-off
… not continuous

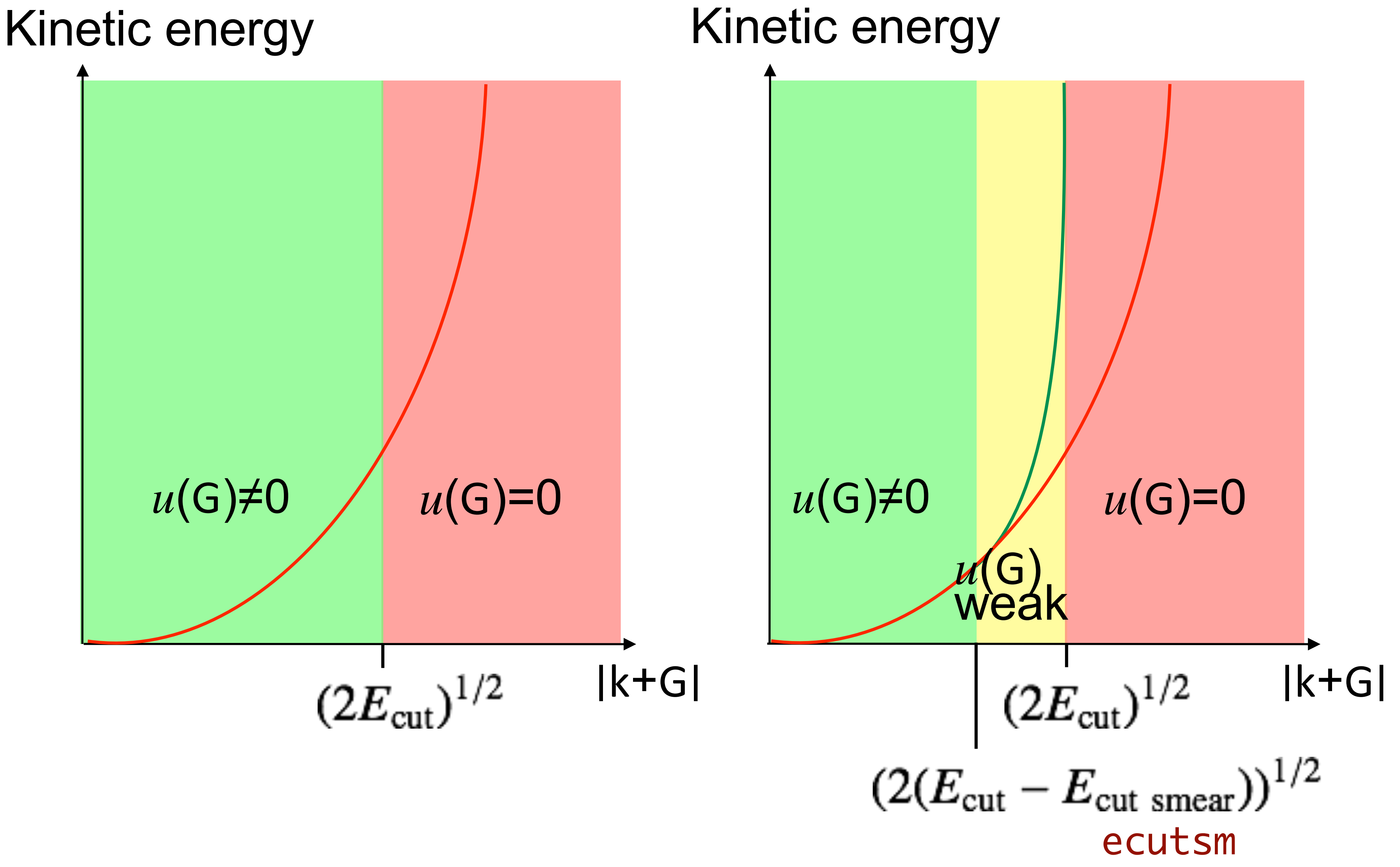
Also, a (discontinuous) function of lattice parameter at fixed kinetic energy

Discontinuities in energy and pressure

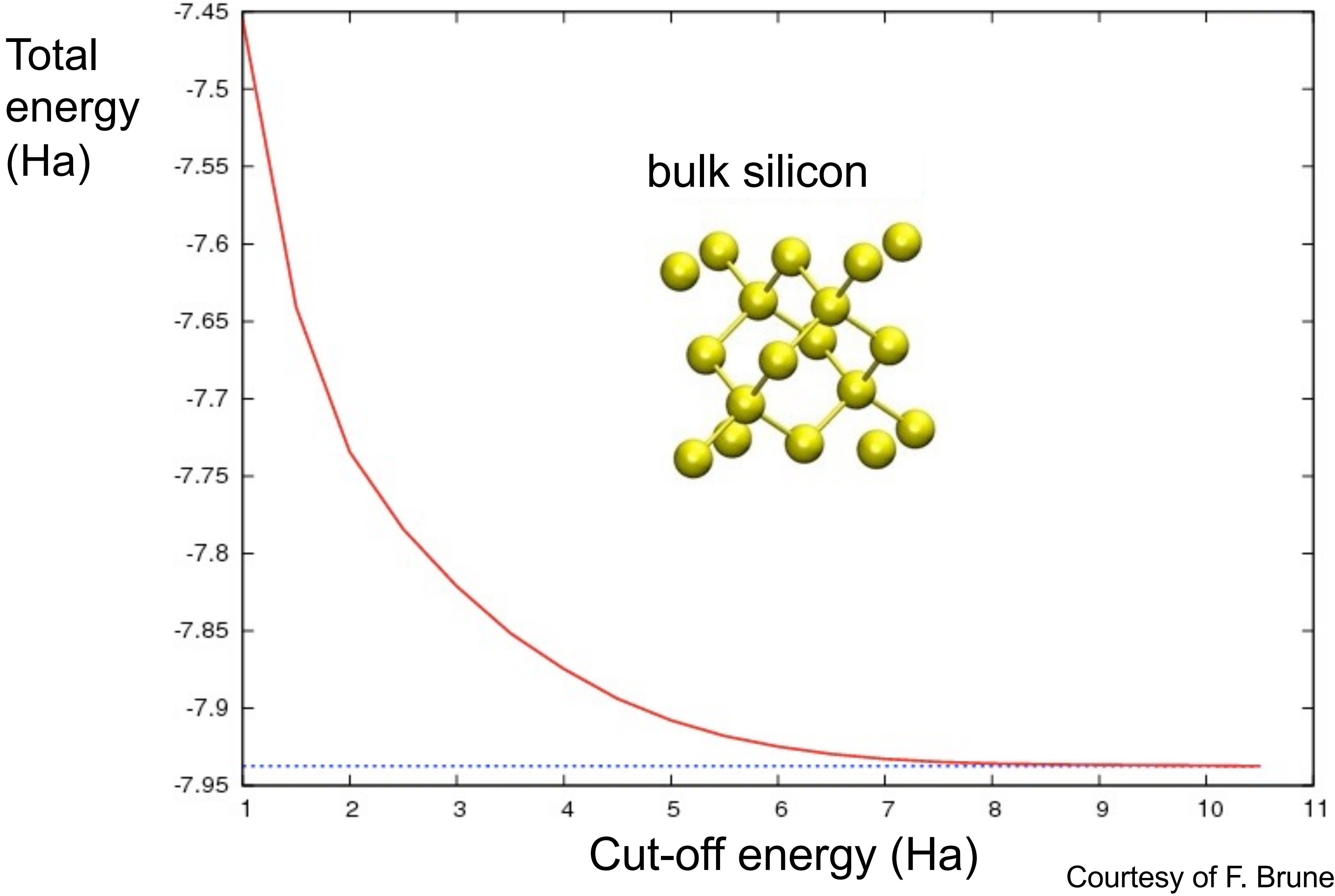
=> Energy (and pressure) also (discontinuous) functions of lattice parameter at fixed kinetic energy



Removing discontinuities (no need for Pulay stresses)



Convergence wrt to kinetic energy cutoff



Courtesy of F. Bruneval

Reminder
Brillouin zone, wavevectors and occupation numbers

From discrete states to Brillouin zone

Discrete summations over states :

Total kinetic energy $\sum_n \langle \psi_n | -\frac{1}{2}\nabla^2 | \psi_n \rangle$

Density $n(\mathbf{r}) = \sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})$

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

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

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

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

Skoltech

Brillouin zone integration

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

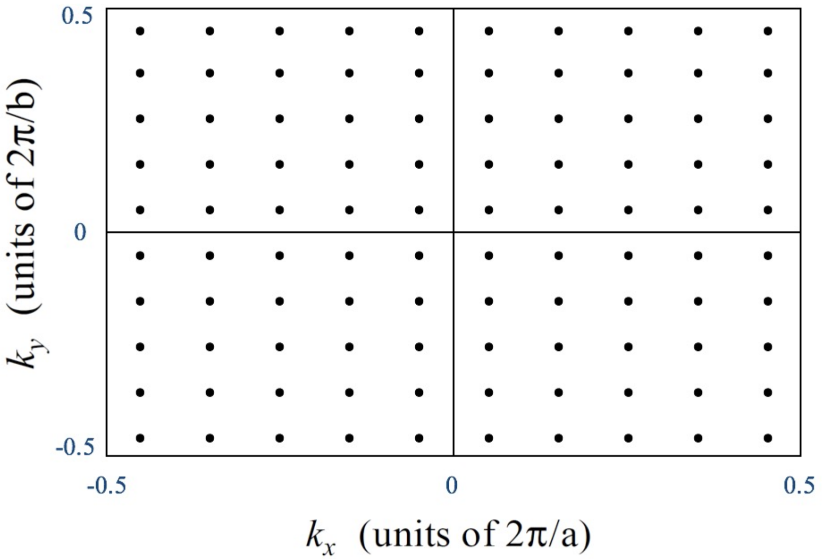
How to chose $\{\mathbf{k}\}$ and $\{w_{\mathbf{k}}\}$?

Special points

Weights

Simple answer : Homogeneous grid (1D - 2D - 3D) and equal weights

Homogeneous sampling of the Brillouin zone



Brillouin zone integration

Theorem :

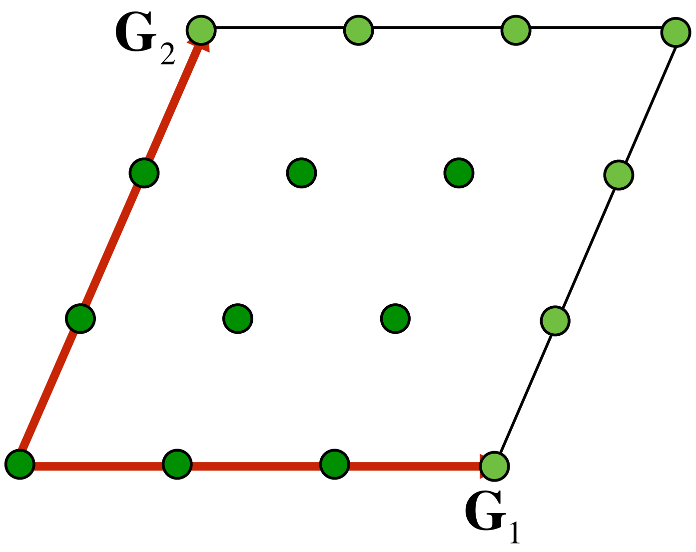
If
- the integrand is periodic
- the integrand is continuous + derivable at all orders $\left(C^\infty D^\infty\right)$
- $\{\mathbf{k}\}$ homogeneous grid (1D - 2D - 3D) and $w_\mathbf{k}$ all equal

Then exponential convergence, with respect to $\Delta\mathbf{k}$

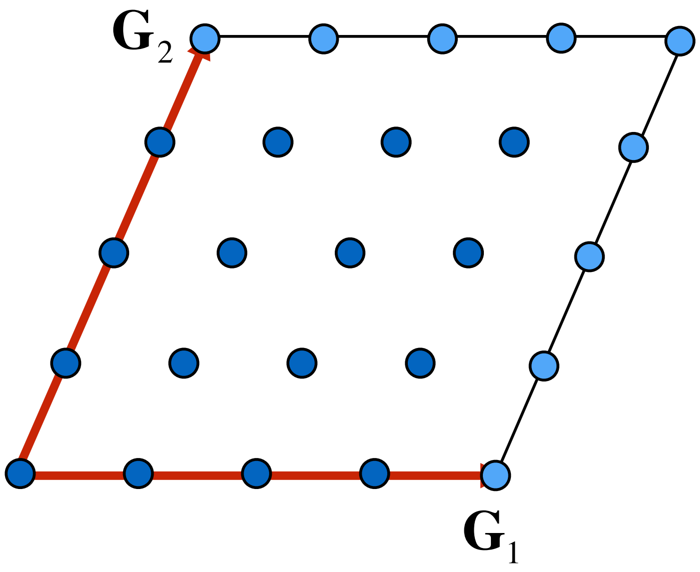
- OK for semiconductors/insulators where the occupation number is independent of k within a band
- Convergence : one ought to test several grids with different $\Delta\mathbf{k}$
- Monkhorst & Pack grids (Phys. Rev. B 13, 5188 (1976))
  k_1 x k_2 x k_3 points + simple cubic, FCC, BCC ...
- Other techniques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

BZ integration : Monkhorst-Pack grid

- Uniformly spaced grid of $n_{k1} \times n_{k2} \times n_{k3}$ points in the first Brillouin Zone [Monkhorst & Pack, Phys. Rev. B 13, 5188 (1976)]



$n_{k1} = n_{k2} = 3$

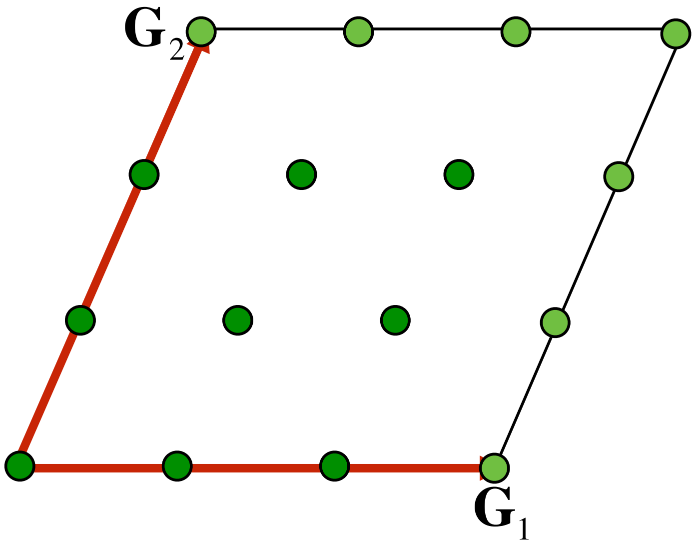


$n_{k1} = n_{k2} = 4$

```
ngkpt nk1 nk2 nk3
```

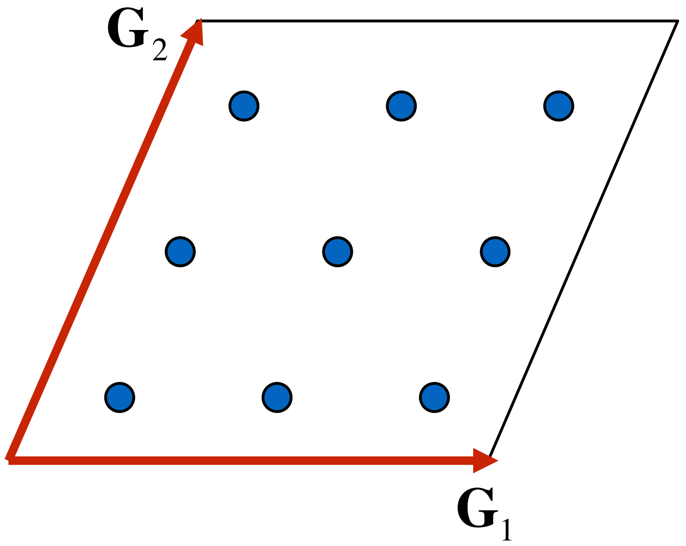
Unshifted and shifted grids

- k-points grid can be chosen to be shifted : not centered at Γ.
- Advantage : comparable accuracy can be obtained with fewer k-points in IBZ (especially for highly symmetric cases)



$n_{k1} = n_{k2} = 3$

unshifted



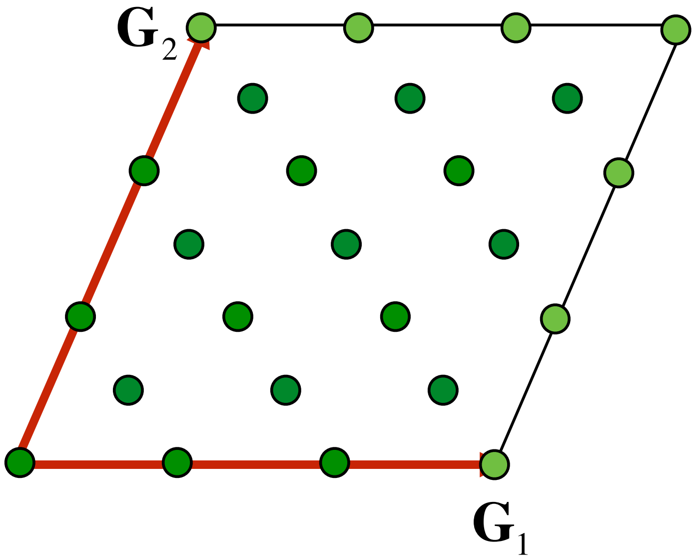
$n_{k1} = n_{k2} = 3$

shifted by (1/2,1/2)

```
ngkpt nk1 nk2 nk3
shiftk sk1 sk2 sk3   (defaut: 0.5 0.5 0.5)
```

Combining grids with various shifts

- k-points grid with various shifts can also be combined.



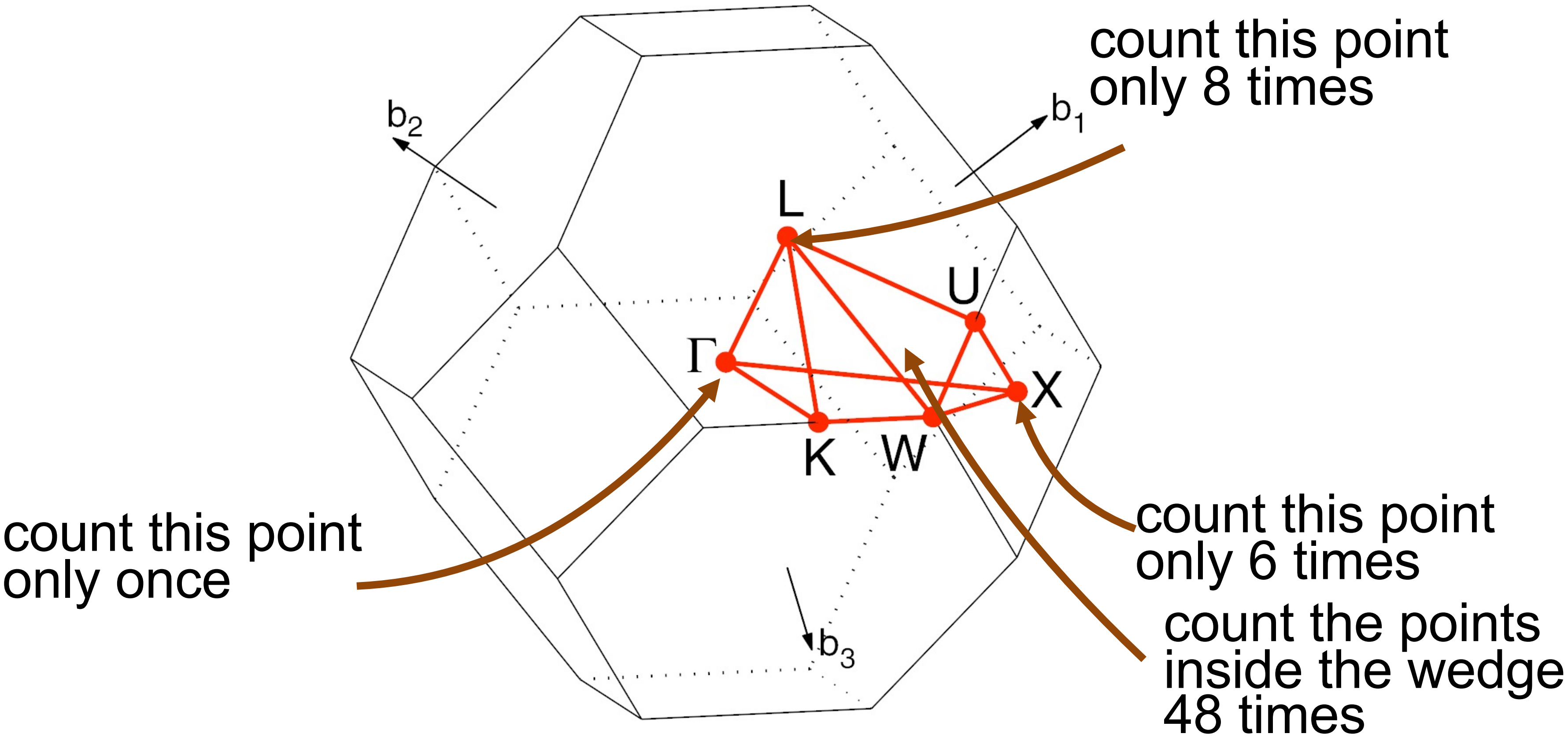
combining unshifted
and shifted by (1/2,1/2)
for $n_{k1} = n_{k2} = 3$

```
ngkpt nk1 nk2 nk3
nshiftk nsk
shiftk sk1(1)   sk2(1)   sk3(1)
       sk1(2)   sk2(2)   sk3(2)
       …        …        …
       sk1(nsk) sk2(nsk) sk3(nsk)
```

```
kptrlatt rl1_1 rl1_2 rl1_3
         rl2_1 rl2_2 rl2_3
         rl3_1 rl3_2 rl3_3
```

Irreducible wedge

- Using symmetries to avoid summing entire BZ :
- Restrict the sum to the Irreducible Brillouin zone (IBZ) provided that weights are adapted.



count this point only 8 times

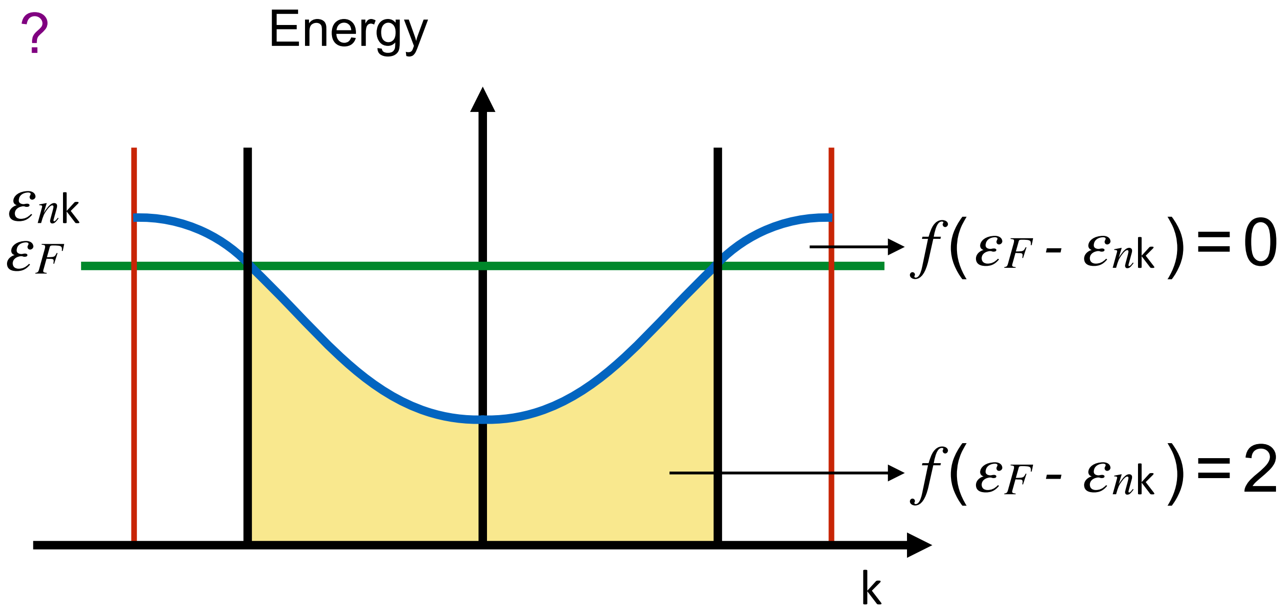
count this point only once

count this point only 6 times

count the points inside the wedge 48 times

Treatment of metals (I)

Behaviour of $f(\varepsilon_F - \varepsilon_{\mathrm{nk}})$?



Discontinuity of integrand at Fermi level

Smearing technique

First trial : generalisation of DFT to finite temperature

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

f goes from 0 to 2 in an energy range $\sigma = k_B T$

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

$$F(T) = E - TS$$

```
occopt 3
tsmear σ
```

Problem : T needed to recover the same convergence as for semiconductors is very high (>> 2000 K)

Treatment of metals (II)

Better technique : obtain $E(\sigma = 0)$ from total energy expression $E(\sigma)$ with modified occupation numbers, and σ similar to a temperature

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

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

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

Spin factor

Gaussian smearing $\tilde{\delta}(x) = \frac{1}{\sqrt{\pi}} e^{-x^2}$ ⇨ α small occopt 7

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

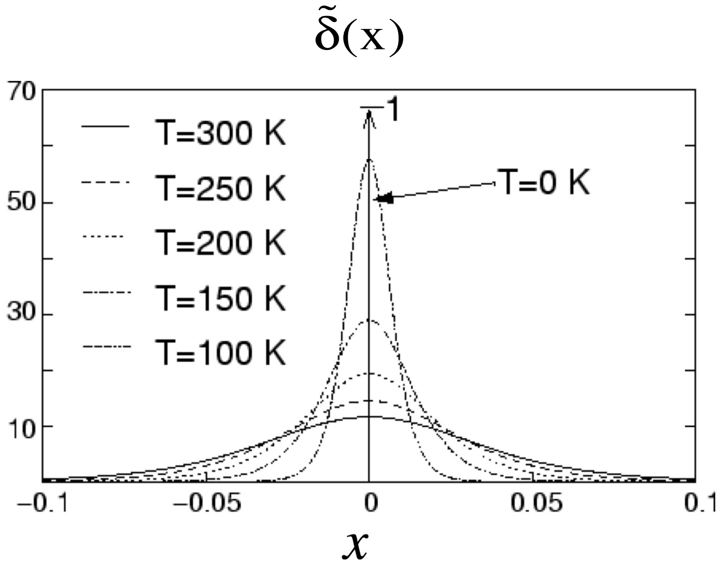
⇨ n = 4 but occupations can be negative

...

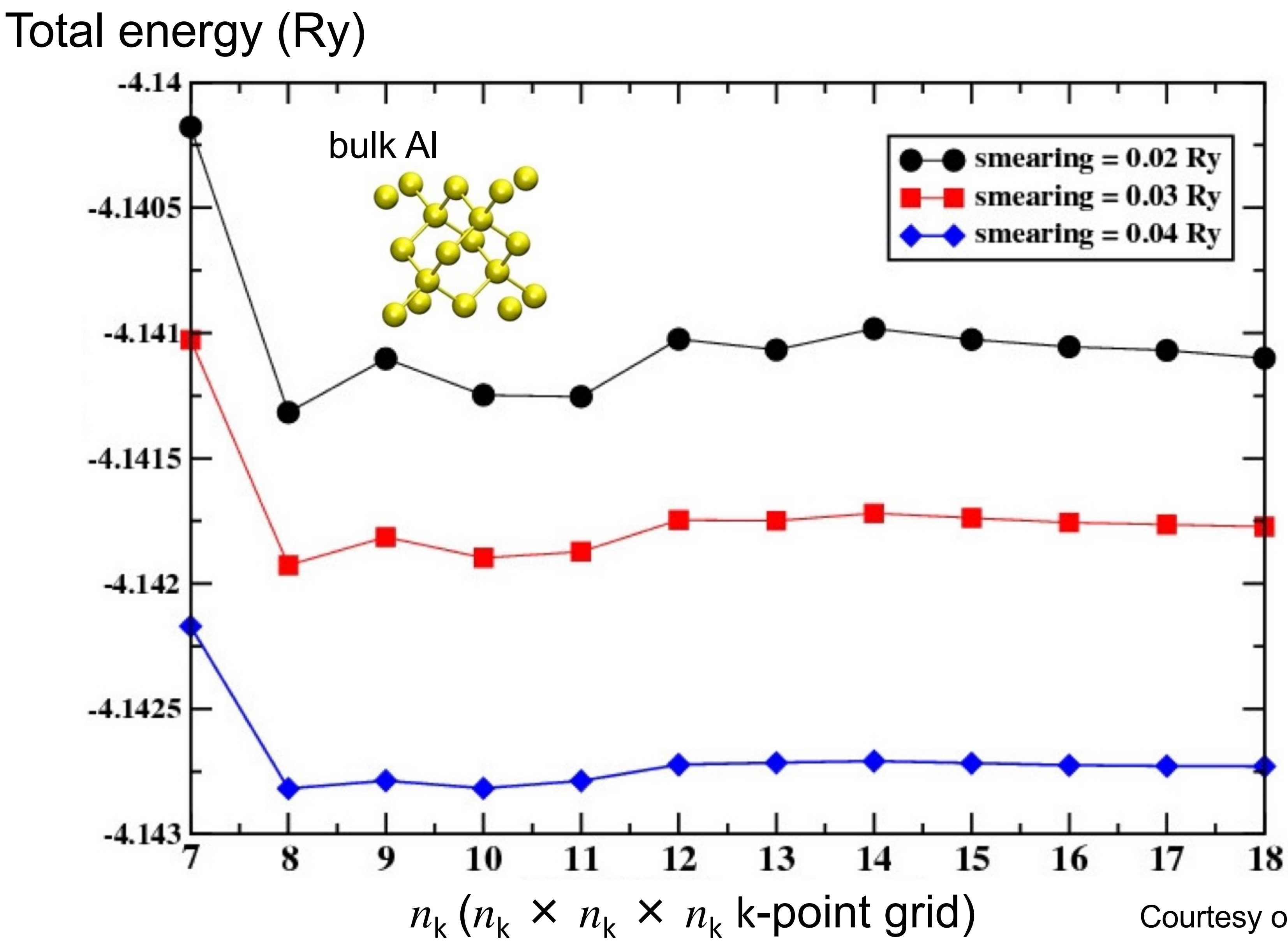
'Cold Smearing' occopt 4/5

(Marzari et al, Phys. Rev. Lett. 82, 3296 (1999))

⇨ n = 3 with positive occupations



Convergence wrt k-points and smearing



Courtesy of S. Narasimhan

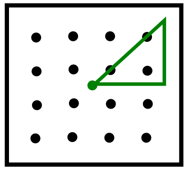
How many k points ? Smearing width ?

Rule of thumb ! Goal : lattice parameter converged better than 0.5 %

Semiconductors - Insulators	$\#\mathbf{k}\ \mathrm{x}\ N_{atoms}$	*50 ... 500*
Metals	$\#\mathbf{k}\ \mathrm{x}\ N_{atoms}$	*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