# Ab-initio simulations

Mini course on DFT for PhD
March 2024

(many slides are adapted by M. Peressi from S. Baroni, P. Giannozzi)

# Ab-initio simulations

**To summarize the first lecture:**

- need of **transferable methods**
- **at the atomistic level**
- giving **results with predictive capabilities**

**=> ab-initio methods:**

- ingredients: nuclei, electrons, interactions

=> many-body Schroedinger equation: **how to solve it?**

# How to solve the many-body Schr. eq.?

**A first physical approximation**

- the adiabatic (Born-Oppenheimer) approx. (M>>m): decouples electronic and nuclear problems

**Density Functional Theory (DFT)** for the electronic problem: from a many-body wave function (3N variables) to the electron density n(**r**) (3 variables):

- use of the variational principle: ok for occupied states (not excited)
- map the interacting system into a non-interacting system and factorize => **one-electron** Scr. eq.

**The formal derivation is exact, but approximations are necessary for the practical implementation of the theory:**

- choice of **approximate exchange-correlation (*xc*) functionals**
- use of **pseudopotentials**
- use of **k-point** discrete meshes for numerical integration in k-space
- use of **periodic boundary conditions and plane-waves** for wavefunction expansion (ok for perfectly periodic extended systems; for others? problem of cell size *[today]*)

Not only…

# How to solve the one-electron Schr. eq.?

Given the one-electron Schroedinger equation (i.e., the Kohn-Sham eq.) how to proceed to really solve it?

$$\boxed{H_{KS}\psi_i \equiv \left(T + V + V_H[n] + V_{xc}[n]\right)\psi_i = \epsilon_i\psi_i}$$

the choice of pseudop and xc functional enters here

where

- $n(\mathbf{r}) = \sum_i f_i|\psi_i(\mathbf{r})|^2$ is the charge density, $f_i$ are occupation numbers
- $V$ is the nuclear (pseudo-)potential acting on electrons (may be nonlocal)
- $V_H[n]$ is the Hartree potential, $V_H(\mathbf{r}) = e^2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$
- $V_{xc}[n]$ is the exchange-correlation potential. For the simplest case, LDA, $V_{xc}[n]$ is a *function* of the charge density at point $\mathbf{r}$: $V_{xc}(\mathbf{r}) \equiv \mu_{xc}(n(\mathbf{r}))$

Orthonormality constraints $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ automatically hold.

# Self-consistent cycle - 1

By *constrained global minimization* of the energy functional

$$E[\psi] = \sum_i f_i \langle \psi_i | T + V | \psi_i \rangle + E_H[n] + E_{xc}[n]$$

under orthonormality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, i.e. minimize:

$$\widetilde{E}[\psi, \Lambda] = E[\psi] - \sum_{ij} \Lambda_{ij} \left( \langle \psi_i | \psi_j \rangle - \delta_{ij} \right)$$

where

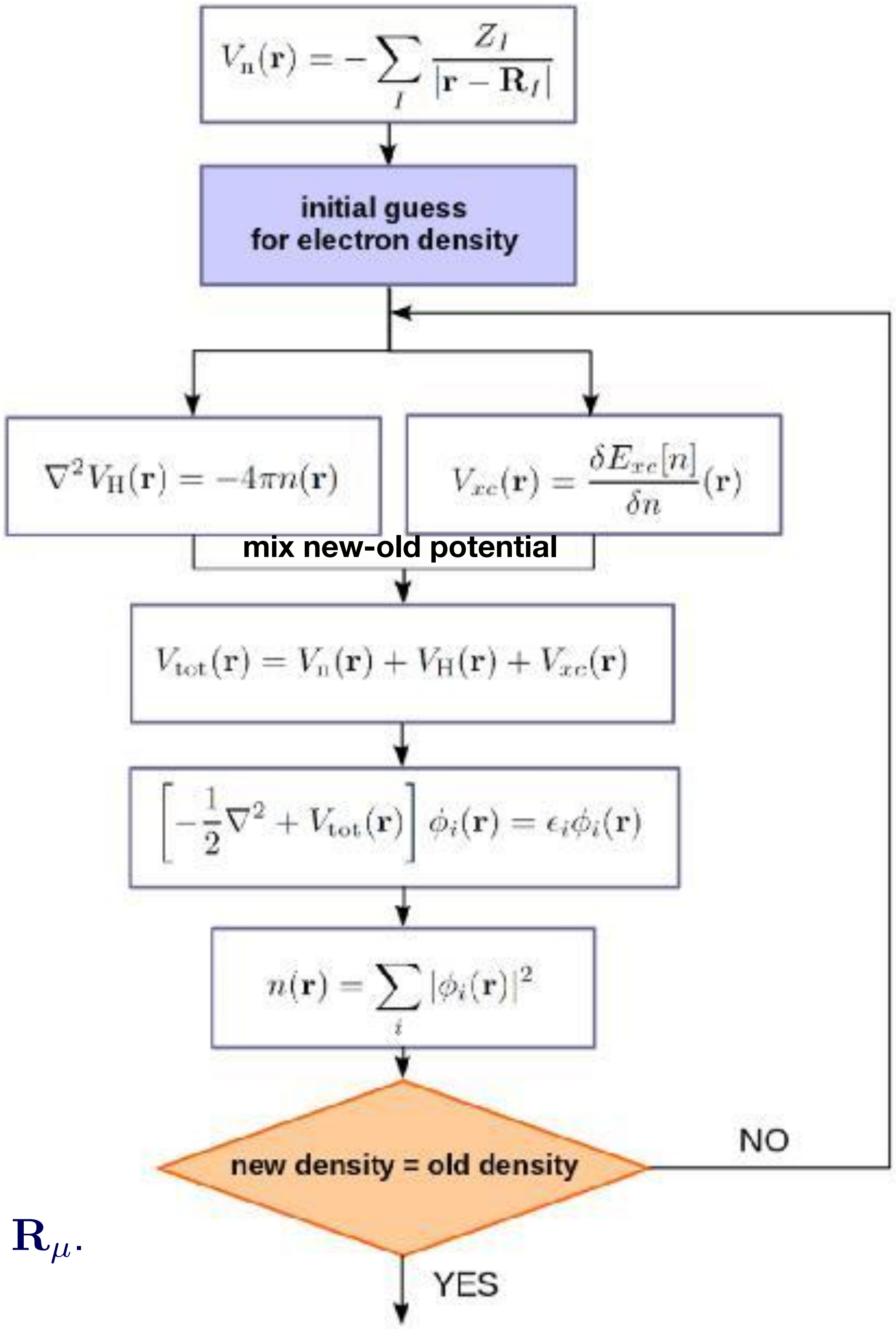
- $V$, $n(\mathbf{r})$ are defined as before, $\psi \equiv$ all occupied Kohn-Sham orbitals
- $\Lambda_{ij}$ are Lagrange multipliers, $\Lambda \equiv$ all of them
- $E_H[n]$ is the Hartree energy, $E_H = \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$
- $E_{xc}[n]$ is the exchange-correlation energy. For the simplest case, LDA, $E_{xc} = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}$ where $\epsilon_{xc}$ is a function of $n(\mathbf{r})$.

# Self-consistent cycle - 2

In a self-consistent approach, we need to find the self-consistent charge density (or potential), performing the following operations:

- Calculate the potential from the charge density
- Solve (*diagonalize*) the Kohn-Sham equations at fixed potential
- Calculate the charge density from Kohn-Sham orbitals

The total energy depends upon all atomic positions $\mathbf{R}_\mu$.



# running the pw.x code:

## In the input:

```
…
/
&electrons
   …
   mixing_beta     =  0.5
   conv_thr        =  1D-10
   electron_maxstep =  100
/
```

## In the output:

```
Self-consistent Calculation

iteration #  1     ecut=    50.00 Ry     beta= 0.50
Davidson diagonalization with overlap
ethr =  1.00E-02,  avg # of iterations =  2.2

total cpu time spent up to now is       20.0 secs

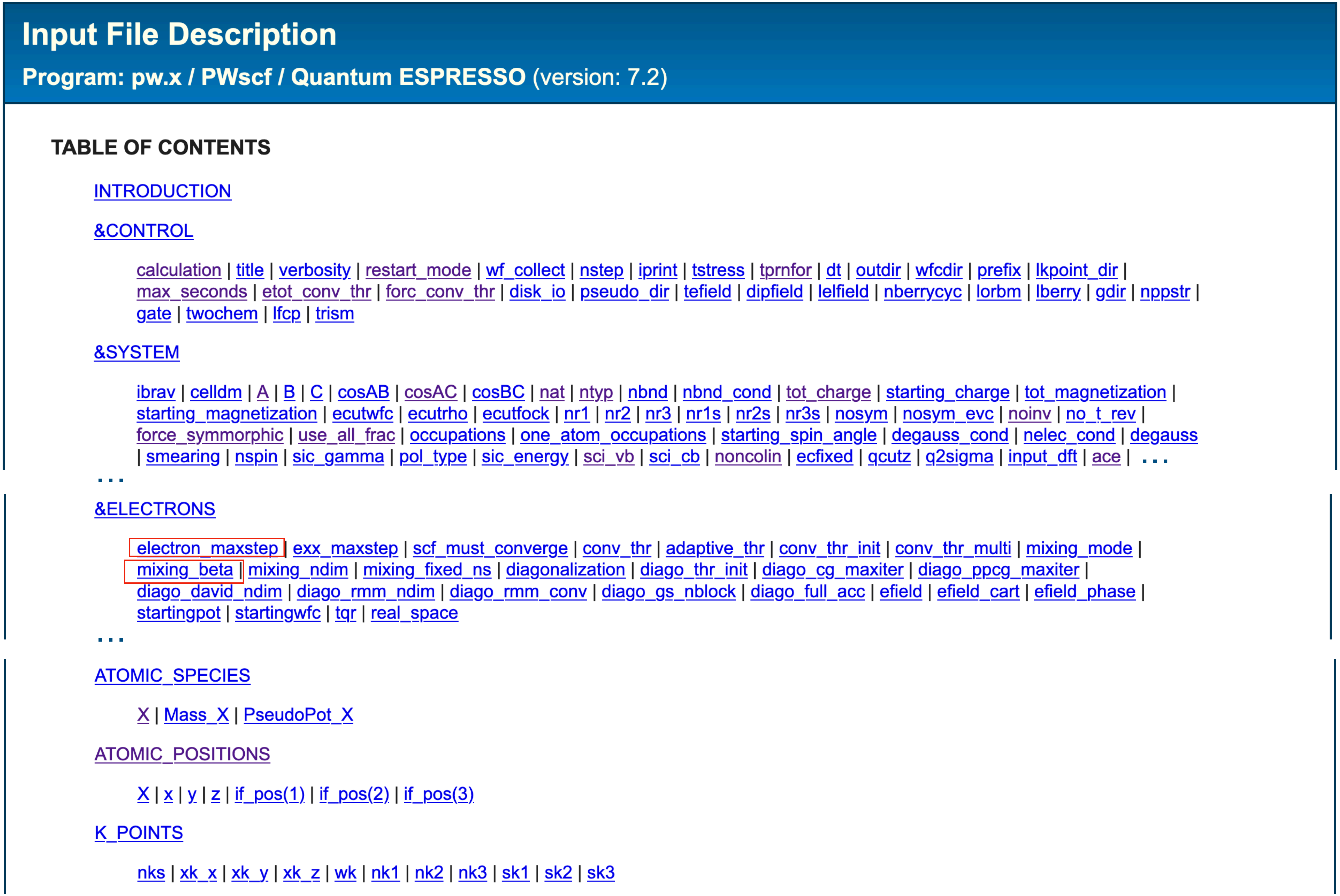
total energy              =    -202.68145378 Ry
estimated scf accuracy    <       0.45007650 Ry

iteration #  2     ecut=    50.00 Ry     beta= 0.50
….
….

End of self-consistent calculation

convergence has been achieved in  13 iterations
```

https://www.quantum-espresso.org/Doc/INPUT_PW.html



# Input File Description

**Program: pw.x / PWscf / Quantum ESPRESSO** (version: 7.2)

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INTRODUCTION

&CONTROL

calculation | title | verbosity | restart_mode | wf_collect | nstep | iprint | tstress | tprnfor | dt | outdir | wfcdir | prefix | lkpoint_dir | max_seconds | etot_conv_thr | forc_conv_thr | disk_io | pseudo_dir | tefield | dipfield | lelfield | nberrycyc | lorbm | lberry | gdir | nppstr | gate | twochem | lfcp | trism

&SYSTEM

ibrav | celldm | A | B | C | cosAB | cosAC | cosBC | nat | ntyp | nbnd | nbnd_cond | tot_charge | starting_charge | tot_magnetization | starting_magnetization | ecutwfc | ecutrho | ecutfock | nr1 | nr2 | nr3 | nr1s | nr2s | nr3s | nosym | nosym_evc | noinv | no_t_rev | force_symmorphic | use_all_frac | occupations | one_atom_occupations | starting_spin_angle | degauss_cond | nelec_cond | degauss | smearing | nspin | sic_gamma | pol_type | sic_energy | sci_vb | sci_cb | noncolin | ecfixed | qcutz | q2sigma | input_dft | ace | ...

...

&ELECTRONS

electron_maxstep | exx_maxstep | scf_must_converge | conv_thr | adaptive_thr | conv_thr_init | conv_thr_multi | mixing_mode | mixing_beta | mixing_ndim | mixing_fixed_ns | diagonalization | diago_thr_init | diago_cg_maxiter | diago_ppcg_maxiter | diago_david_ndim | diago_rmm_ndim | diago_rmm_conv | diago_gs_nblock | diago_full_acc | efield | efield_cart | efield_phase | startingpot | startingwfc | tqr | real_space

...

ATOMIC_SPECIES

X | Mass_X | PseudoPot_X

ATOMIC_POSITIONS

X | x | y | z | if_pos(1) | if_pos(2) | if_pos(3)

K_POINTS

nks | xk_x | xk_y | xk_z | wk | nk1 | nk2 | nk3 | sk1 | sk2 | sk3

# running the pw.x code:

## In the input:

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….
….

End of self-consistent calculation

convergence has been achieved in  13 iterations
```

?

# How to solve the one-electron Schr. eq.?

The solution of the Kohn-Sham problem $H_{KS}\psi = \epsilon\psi$ at fixed potential is (usually) the toughest problem. How to proceed? By expanding $\psi$ into some suitable **basis set** $\{\phi_i\}$ as

$$\psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r}).$$

For an orthonormal basis set, we solve the secular equations

$$\sum_j (H_{ij} - \epsilon\delta_{ij})c_j = 0$$

If we expand the unknown ψ
onto a basis set,
we transform the problem
into one of linear algebra

where $H_{ij} = \langle\phi_i|H_{KS}|\phi_j\rangle$ are the *matrix elements* of the Hamiltonian.
For a non-orthonormal basis set, we solve the generalized problem:

$$\sum_j (H_{ij} - \epsilon S_{ij})c_j = 0$$

where $S_{ij} = \langle\phi_i|\phi_j\rangle$ is the *overlap matrix*.

Diagonalization algorithms are well known in linear algebra, but in practice, one has to resort to smarter *iterative* algorithms, allowing *not* to store those matrices.

# Plane-wave basis set - 1

A PW basis set for states of wave vector $\mathbf{k}$ is defined as

$$\phi_{\mathbf{k+G}}(\mathbf{r}) = \langle \mathbf{r}|\mathbf{k}+\mathbf{G}\rangle = \frac{1}{\sqrt{\mathcal{N}\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \qquad \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 \le E_{cut}$$

$\Omega =$ unit cell volume, $\mathcal{N}\Omega =$ crystal volume, $E_{cut} =$ cutoff on the kinetic energy of PWs (in order to have a finite number of PWs!). The PW basis set is *complete* for $E_{cut} \to \infty$ and *orthonormal*: $\langle \mathbf{k}+\mathbf{G}|\mathbf{k}+\mathbf{G}'\rangle = \delta_{\mathbf{G}\mathbf{G}'}$

In a PW basis set one works with *Fourier components* ($c_{i,\mathbf{k}+\mathbf{G}}$ below):

$$|\psi_i\rangle = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} |\mathbf{k}+\mathbf{G}\rangle$$

$$c_{i,\mathbf{k}+\mathbf{G}} = \langle \mathbf{k}+\mathbf{G}|\psi_i\rangle = \frac{1}{\sqrt{\mathcal{N}\Omega}} \int \psi_i(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} d\mathbf{r} = \widetilde{\psi}_i(\mathbf{k}+\mathbf{G}).$$

Real-space quantities can be obtained on a grid using Fast Fourier Transform.

# Plane-wave basis set - 2

- Plane Waves:
  - – slow convergence with respect to basis set size (many more PWs than localized functions needed)
  - – require periodicity: in finite systems, *supercells* must be introduced
  - \+ easy to evaluate convergence quality (just increase a single parameter, the *cutoff*)
  - \+ easy to use (Fourier transform)

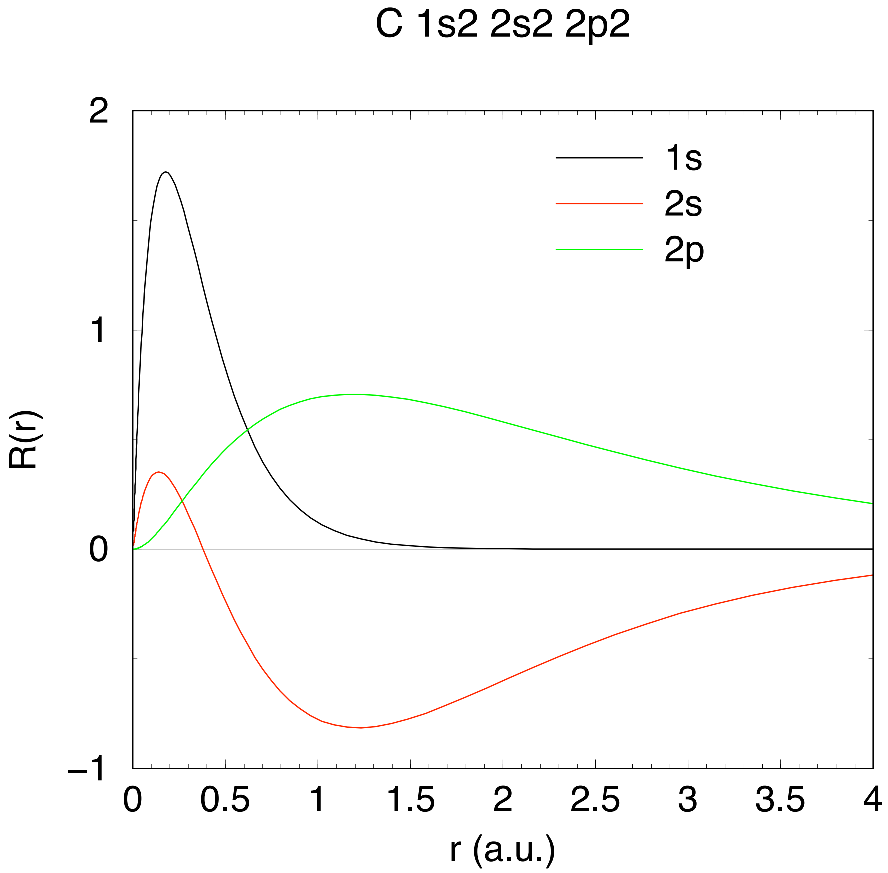
**Periodicity needed !**

# Pseudopotentials - 0

From simple Fourier analysis: length scale $\delta \longrightarrow$ Fourier components up to $q \sim 2\pi/\delta$. In a solid, this means $\sim 4\pi(2\pi/\delta)^3/3\Omega_{BZ}$ PWs (volume of the sphere of radius $q$ divided by $\Omega_{BZ} = 8\pi^3/\Omega$, volume of the Brillouin Zone).

Estimate for diamond: $1s$ wavefunction has $\delta \simeq 0.1$ a.u., $\Omega = (2\pi)^3/(a_0^3/4)$ with lattice parameter $a_0 = 6.74$ a.u. $\longrightarrow 250,000$ PWs! We need to:

- get rid of core states
- get rid of orthogonality wiggles close to the nucleus

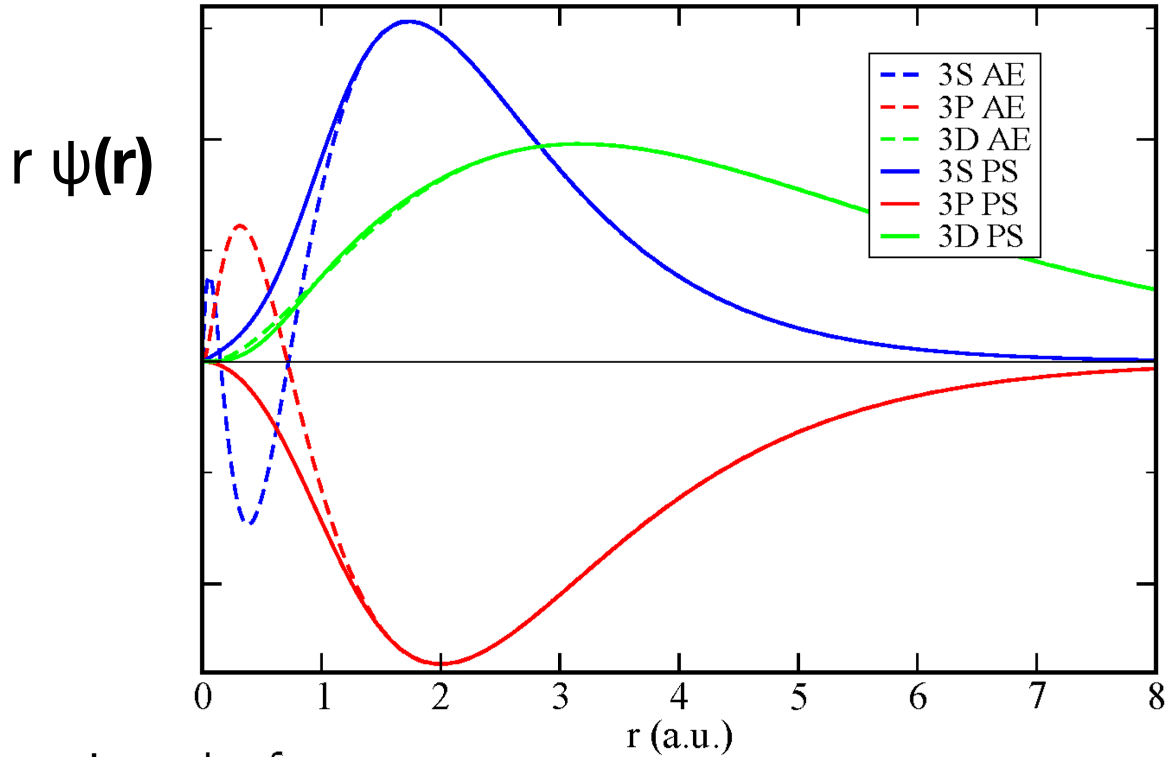


Solution: **Pseudopotentials** (PP). A smooth effective potential that reproduces the effect of the nucleus plus core electrons on valence electrons.

# Pseudopotentials - 1

**Norm-Conserving Pseudopotentials**

Electron-ionic core interactions are typically represented by a nonlocal *Norm-Conserving Pseudopotential* (NCPP): a soft potential, no core states, no orthonormality wiggles.



AE="all electron"
(i.e. calculations including also core electrons)

PS="pseudopotential"

One pseudo potential for each angular momentum :

$$V_l^{ps} = V_{loc}(r) + V_l(r)P_l = V\ (r) + \sum_m Y_{lm}(\mathbf{r})V(r)\delta(r-r')Y^*_{lm}(\mathbf{r}')$$

with $V_{loc}(r) = -Z_v\, e^2 / r$

In many systems, NCPP's allow accurate calculations with moderate-size $(E_c \sim 10-20Ry)$ plane-wave basis sets (explained in the following)

# Pseudopotentials - 2

**Norm-Conserving Pseudopotentials (continued)**

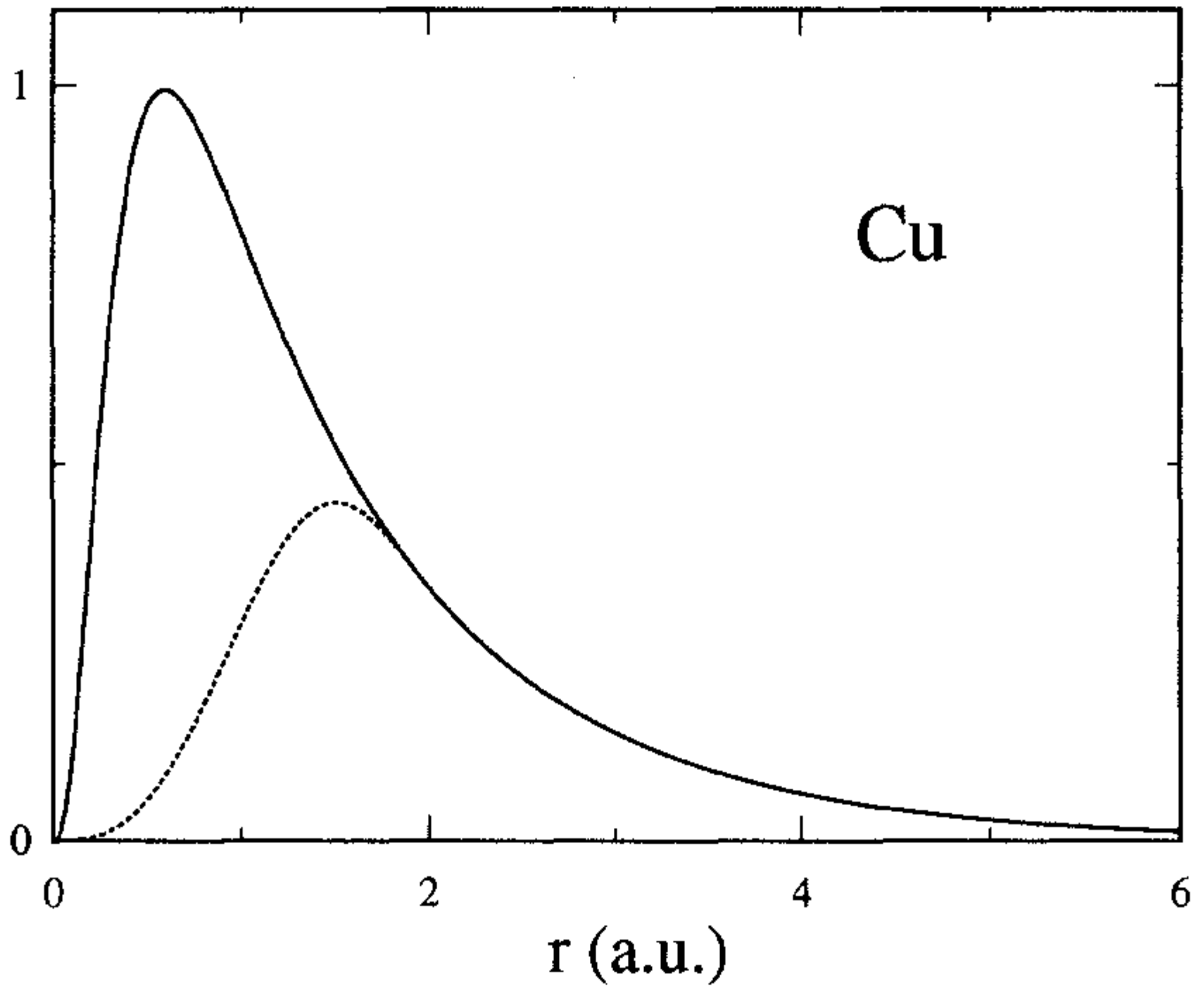
NCPP's based on atomic DFT calculations, were introduced by Hamann, Schlüter, Chiang in 1979. For a given reference atomic configuration, they must meet the following conditions:

- $\epsilon_l^{ps} = \epsilon_l^{ae}$ **<= atomic energy levels must be reproduced**
- $\phi_l^{ps}(r)$ is nodeless
- $\phi_l^{ps}(r) = \phi_l^{ae}(r)$ for $r > r_c$ **<= coincidence between the "true" and "pseudo" wfc in the external region**
- $\int_{r<r_c} |\phi_l^{ps}(r)|^2 r^2 dr = \int_{r<r_c} |\phi_l^{ae}(r)|^2 r^2 dr$ **<= norm-conserving**

where $\phi_l^{ae}(r)$ is the radial part of the atomic valence wavefunction with $l$ angular momentum, $\epsilon_l^{ae}$ its orbital energy. The *core radius* $r_c$ is approximately at the outermost maximum of the wavefunction.

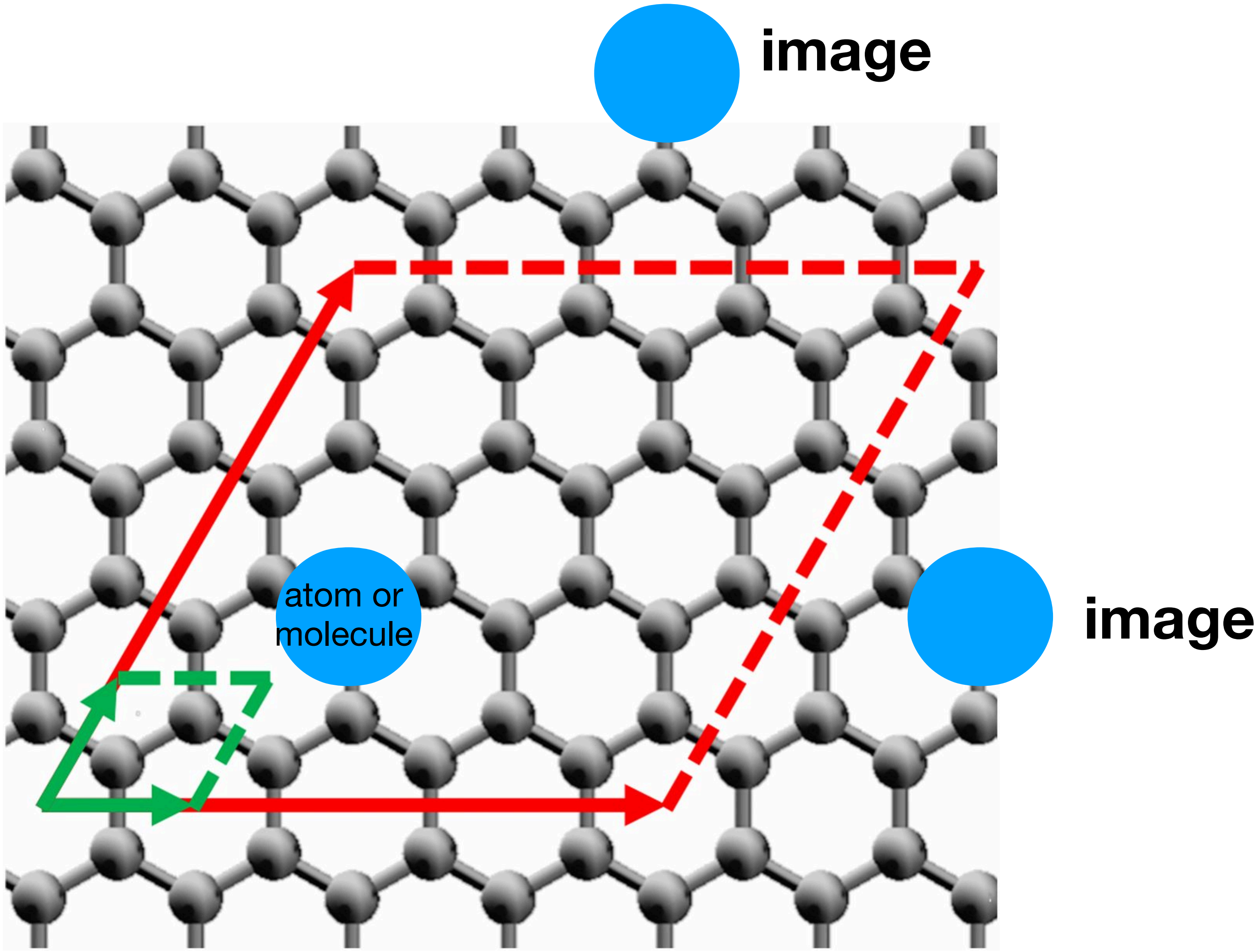
# Pseudopotentials - 3

“soft” or “ultrasoft” pseudopotentials: release the condition of norm-conserving => Smoother potentials => smoother wfc => less plane waves to describe them (see later)



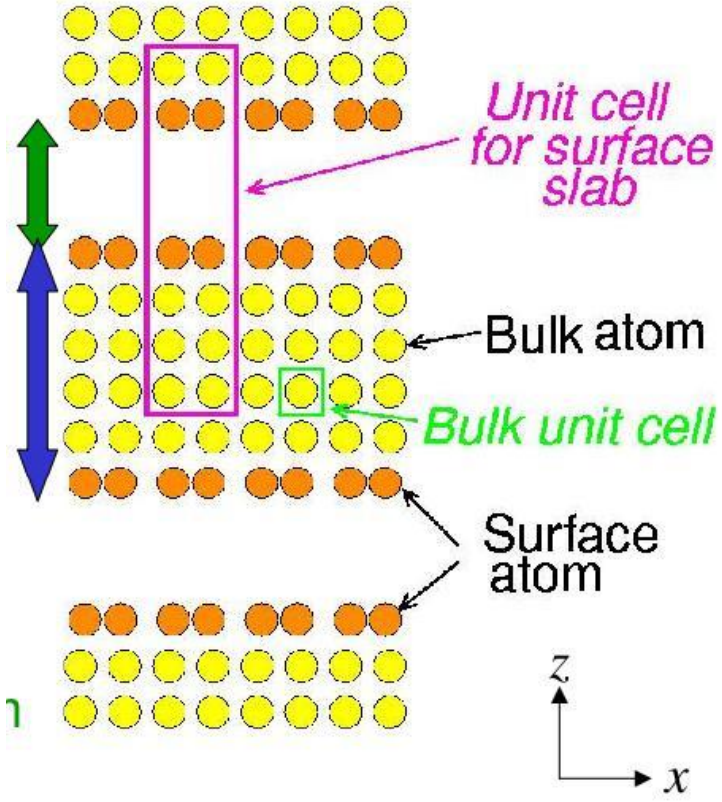
# Non-periodic systems: supercells - 1

Imposing Periodic Boundary Conditions (which allows for a Fourier transform treatment)
=> **Artificial repetition** of a “building block”
but “supercells” (cells larger than the normal size of bulk periodic systems) allows to reasonably describe even **non periodic systems provided that images from adjacent cells are separated enough not to interact each other**

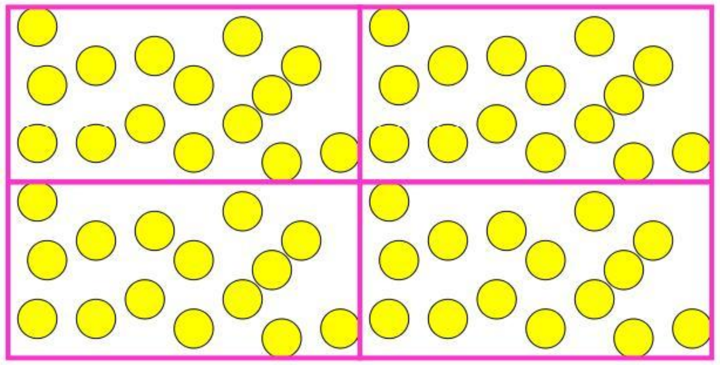


# Non-periodic systems: supercells - 2

- Surfaces:
  *slab geometry*. The number of layers of the materials must be "big enough" to have "bulk behaviour" in the furthest layer from the surface. The number of empty layers must be "big enough" to have minimal interactions between layers in different regions.



- Alloys, amorphous materials, liquids:
  the supercell must be "big enough" to give a reasonable description of physical properties.

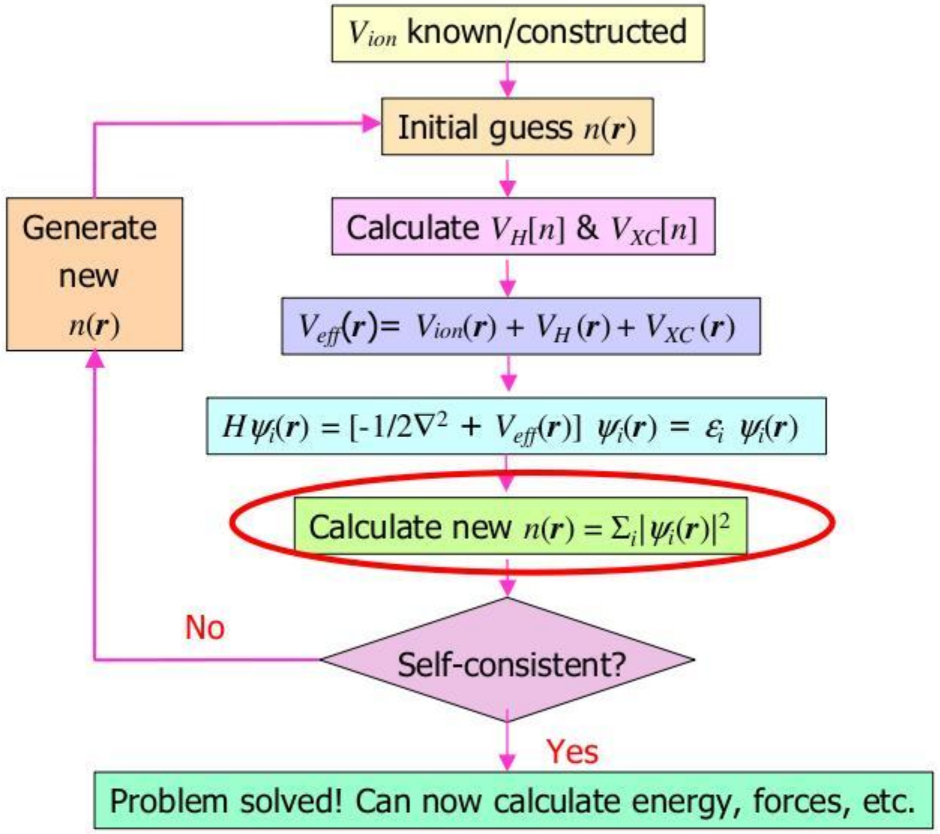


# Brillouin zone sampling

$$n(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{i} |\psi_{\mathbf{k},i}(\mathbf{r})|^2$$

- The calculation of the charge density (and of many other quantities) requires sums over all **k**-points in the Brillouin Zone (BZ); in practice, some form of *BZ sampling* is needed. Convergence wrt **k**-point sampling *must be tested*!

- For insulators in large supercells, amorphous systems, liquids, molecules, sampling with $\Gamma$ ($\mathbf{k} = 0$) only is fine. For other insulators, a small number of **k**-points is usually sufficient.



$V_{ion}$ known/constructed

Initial guess $n(\mathbf{r})$

Calculate $V_H[n]$ & $V_{XC}[n]$

$V_{eff}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$

$H\psi_i(\mathbf{r}) = [-1/2\nabla^2 + V_{eff}(\mathbf{r})]\ \psi_i(\mathbf{r}) = \varepsilon_i\ \psi_i(\mathbf{r})$

Calculate new $n(\mathbf{r}) = \Sigma_i|\psi_i(\mathbf{r})|^2$

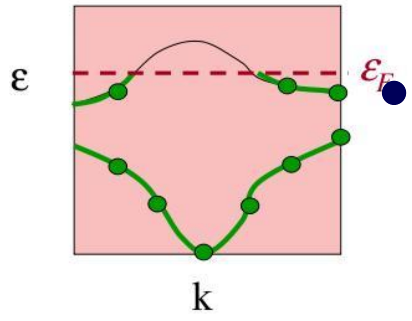
Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

Problem solved! Can now calculate energy, forces, etc.



- For metals, a very fine sampling of the *Fermi surface*, together with some *broadening*, or *smearing*, technique, is needed. One could in principle use Fermi-Dirac occupations at finite $T$, but this would require either very high $T$ or too fine sampling

# Grids of k-points for Brillouin Zone sampling

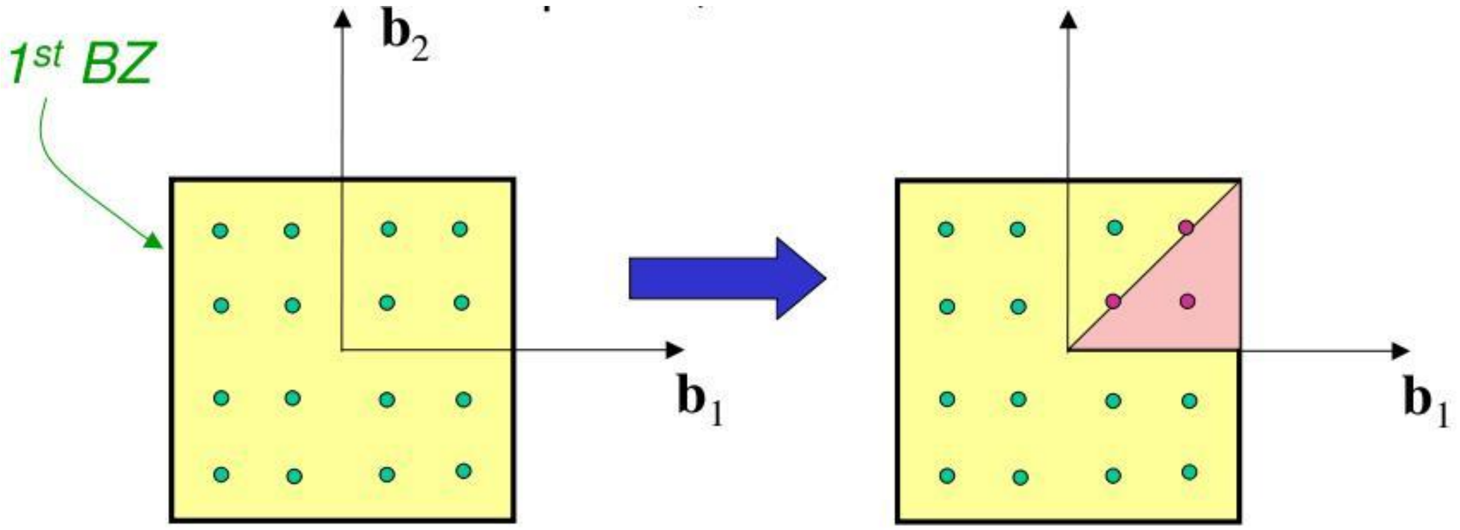
Typical ways of sampling the Brillouin Zone (BZ):

- **Special Points** (e.g. Baldereschi, Chadi and Cohen)
  Points designed to give quick convergence for particular crystal structures.

- **Uniform Grids** (e.g. Monkhorst-Pack)
  Equally spaced in reciprocal space. May be centred on origin (“non-shifted”) or not (“shifted”).

$$\frac{1}{L}\sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) \longrightarrow \sum_{i} w_i f_{\mathbf{k}_i}(\mathbf{r}).$$

In presence of *symmetry*, only **k**-points in the *Irreducible* BZ, or IBZ, need to be computed: the charge density is reconstructed using symmetry. Appropriate *weights* for **k**-points must be specified (or can be calculated).



# Numerical approximations

- finiteness of: basis set
- Integration in reciprocal space (“special” k-point)
- discretized meshes for differentiation (FFT grid)
- …

**we need to study convergence !!!**

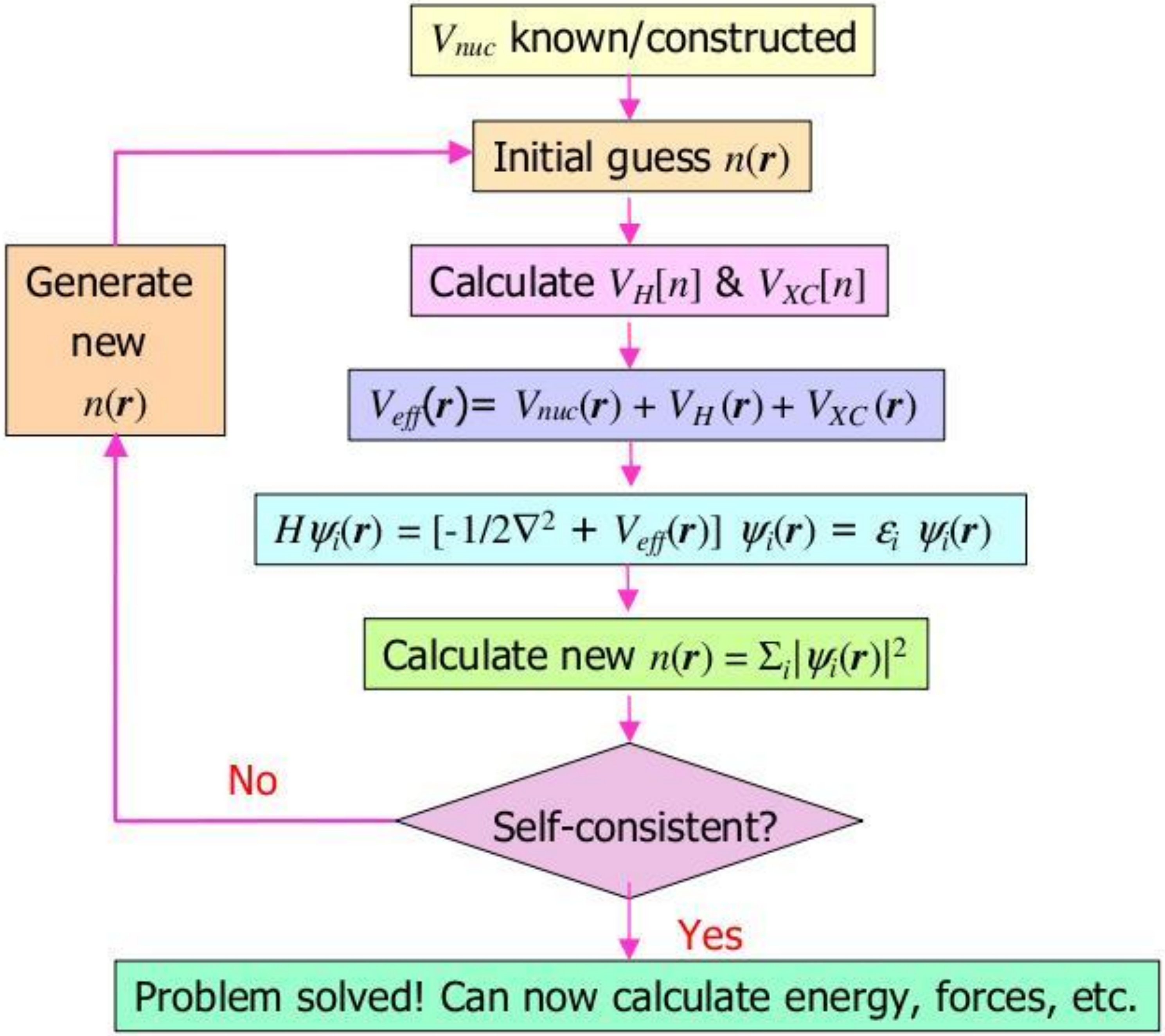
# Plane-Wave Pseudopotential method, summary

- Supercell geometry: lattice vectors + atoms in the unit cell

- Plane-wave basis set, determined by the lattice and by a single parameter (*cutoff*)

- Atom-based pseudopotentials representing the electron-nuclei potential ($V_{nuc}$ in the figure)

- Charge density computed with valence electrons only, on a suitable grid of **k**-points.



$V_{nuc}$ known/constructed

Initial guess $n(\mathbf{r})$

Calculate $V_H[n]$ & $V_{XC}[n]$

$V_{eff}(\mathbf{r}) = V_{nuc}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$

$H\psi_i(\mathbf{r}) = [-1/2\nabla^2 + V_{eff}(\mathbf{r})]\ \psi_i(\mathbf{r}) = \varepsilon_i\ \psi_i(\mathbf{r})$

Calculate new $n(\mathbf{r}) = \Sigma_i|\psi_i(\mathbf{r})|^2$

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

Problem solved! Can now calculate energy, forces, etc.

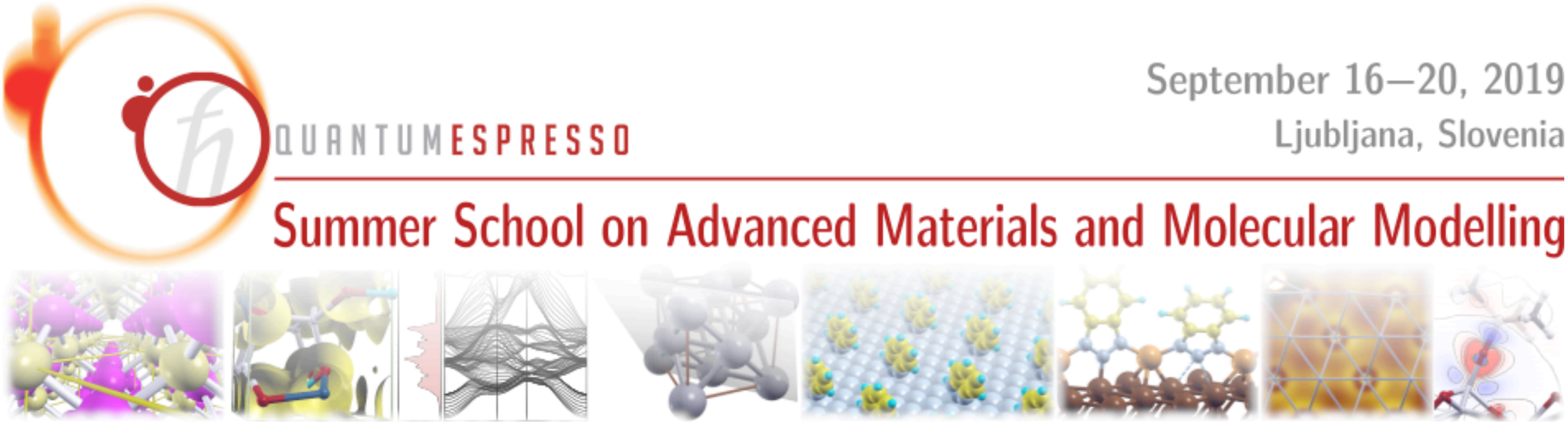
# What can I do with “standard” DFT?

**Electronic structure:** SCF diagonalization (Kohn-Sham eqs., electronic energy minimization)

**Geometry optimization:** calculation of forces acting on atoms via Helmann-Feynman theorem and consequent optimization of nuclear positions => also calculations of energy barrier for reactions

**Dynamics:** Born-Oppenheimer

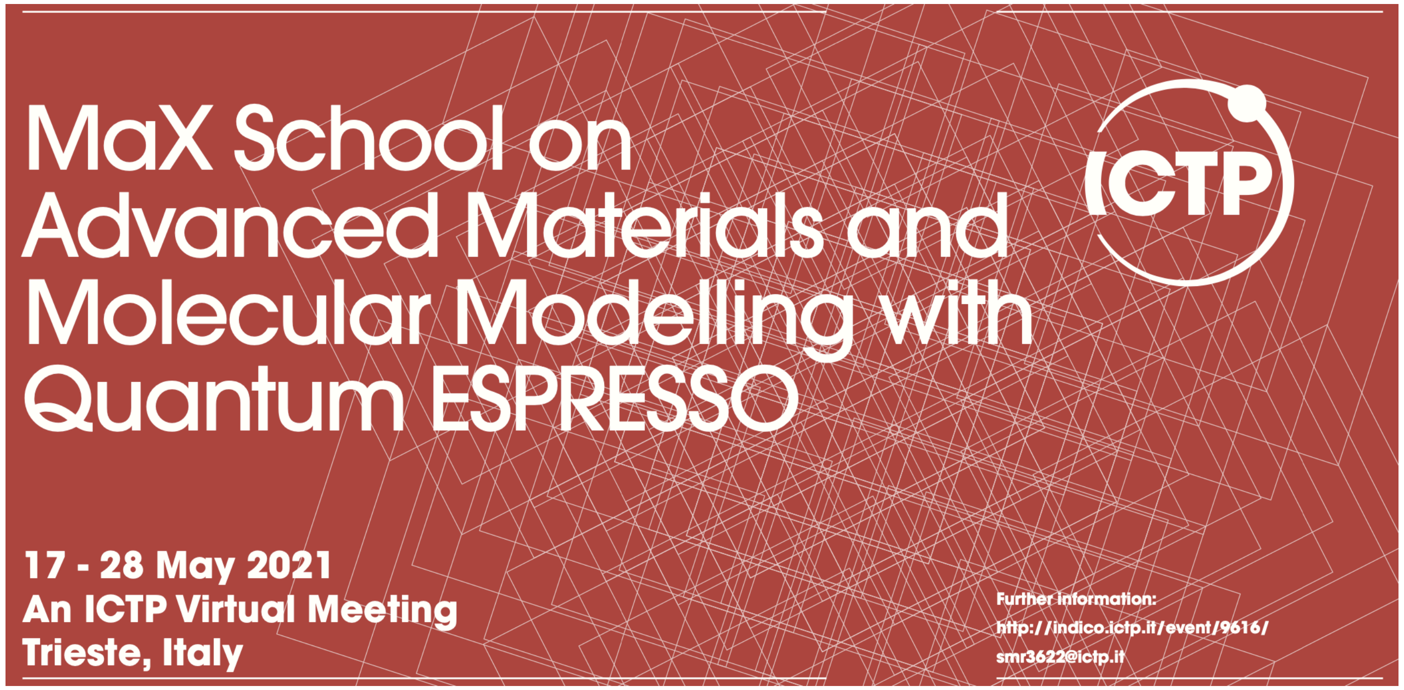
# Recent QE tutorials


QUANTUMESPRESSO

September 16—20, 2019
Ljubljana, Slovenia

Summer School on Advanced Materials and Molecular Modelling

http://qe2019.ijs.si/program.html


MaX School on Advanced Materials and Molecular Modelling with Quantum ESPRESSO

ICTP

17 - 28 May 2021
An ICTP Virtual Meeting
Trieste, Italy

Further information:
http://indico.ictp.it/event/9616/
smr3622@ictp.it

https://indico.ictp.it/event/9616/other-view?view=ictptimetable

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*Thermal Contraction and Disordering of the Al(110) Surface*,
Phys. Rev. Lett. **82**, 3296 (1999)

# Structural optimization

# Forces on the atoms - I

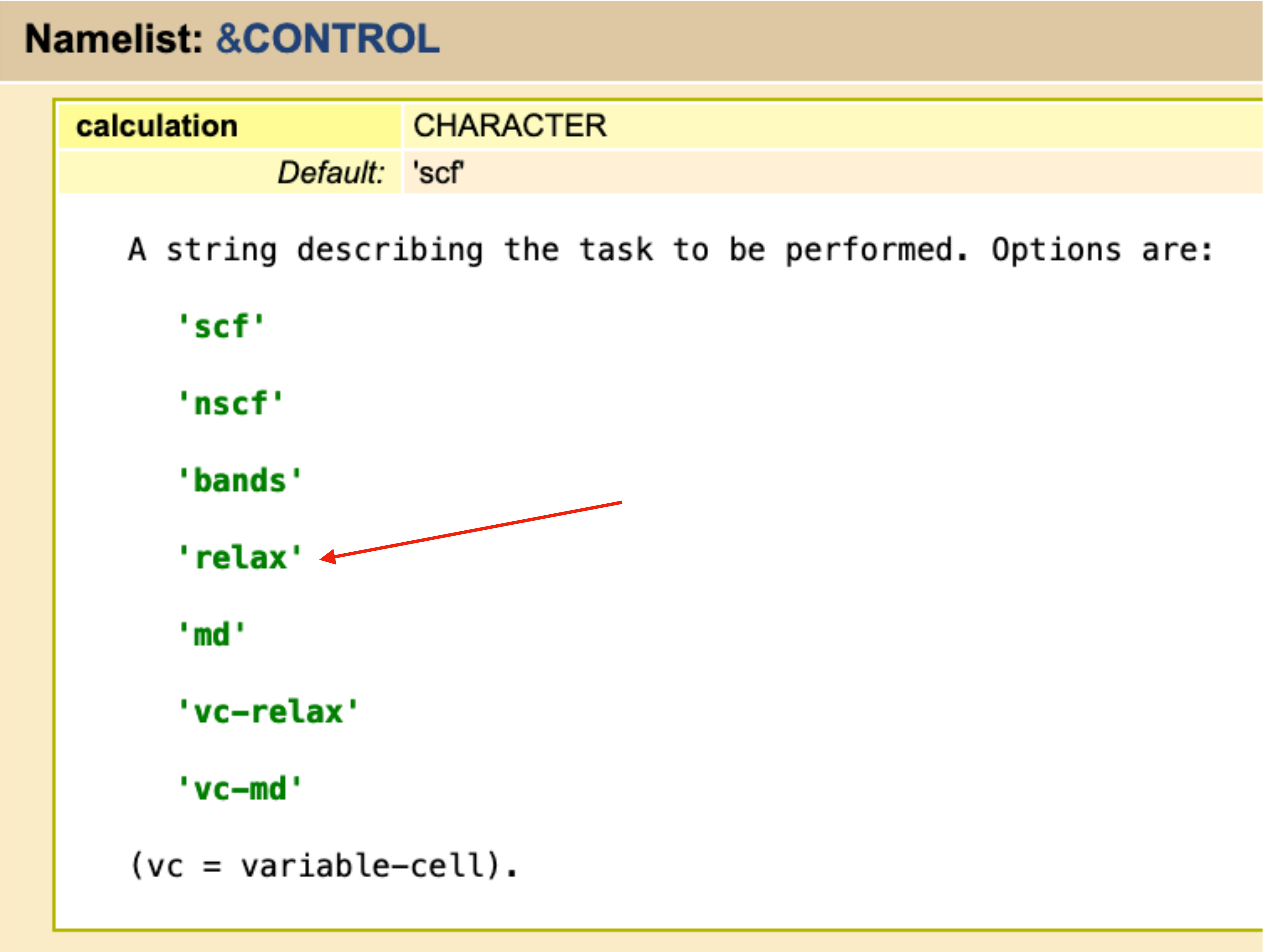
Forces on atoms are the derivatives of the total energy wrt atomic positions. The *Hellmann-Feynman theorem* tells us that forces are the expectation value of the derivative of the external potential only:

$$\mathbf{F}_\mu = -\frac{\partial E}{\partial \mathbf{R}_\mu} = -\sum_i f_i \langle \psi_i | \frac{\partial V}{\partial \mathbf{R}_\mu} | \psi_i \rangle = -\int n(\mathbf{r}) \frac{\partial V}{\partial \mathbf{R}_\mu} d\mathbf{r}$$

This last “=“ in particular is
valid only for *local* potentials,

The calculation of the Hellmann-Feynman forces is **in principle** straightforward

# Forces on the atoms - II



**Namelist: &CONTROL**

| **calculation** | CHARACTER |
|---|---|
| *Default:* | 'scf' |

A string describing the task to be performed. Options are:

`'scf'`

`'nscf'`

`'bands'`

`'relax'`

`'md'`

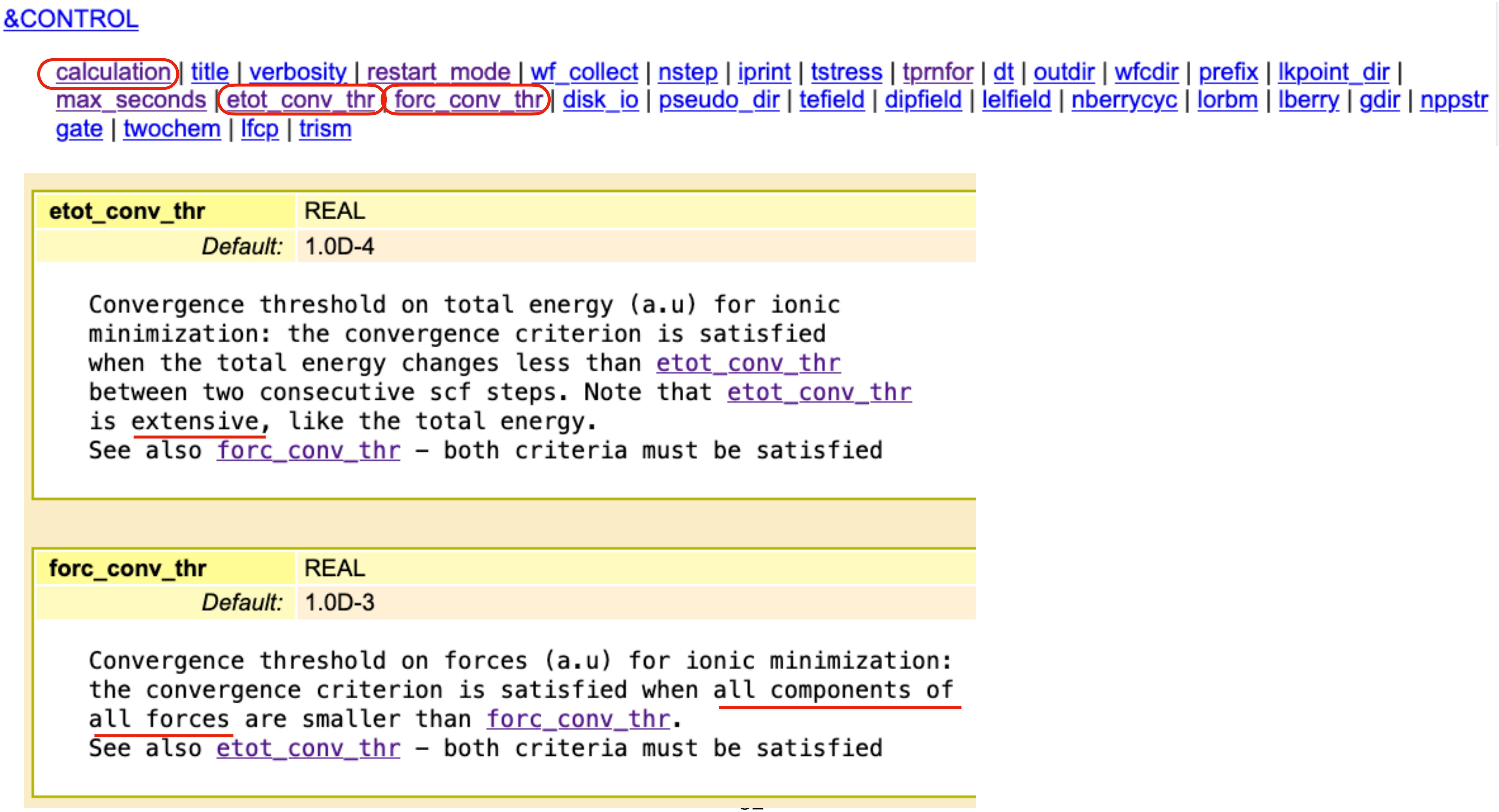
`'vc-relax'`

`'vc-md'`

(vc = variable-cell).

# Forces on the atoms - II

**calculation = ‘relax’**



&CONTROL

calculation | title | verbosity | restart_mode | wf_collect | nstep | iprint | tstress | tprnfor | dt | outdir | wfcdir | prefix | lkpoint_dir | max_seconds | etot_conv_thr | forc_conv_thr | disk_io | pseudo_dir | tefield | dipfield | lelfield | nberrycyc | lorbm | lberry | gdir | nppstr | gate | twochem | lfcp | trism

| | |
|---|---|
| **etot_conv_thr** | REAL |
| *Default:* | 1.0D-4 |

Convergence threshold on total energy (a.u) for ionic minimization: the convergence criterion is satisfied when the total energy changes less than etot_conv_thr between two consecutive scf steps. Note that etot_conv_thr is extensive, like the total energy.
See also forc_conv_thr - both criteria must be satisfied

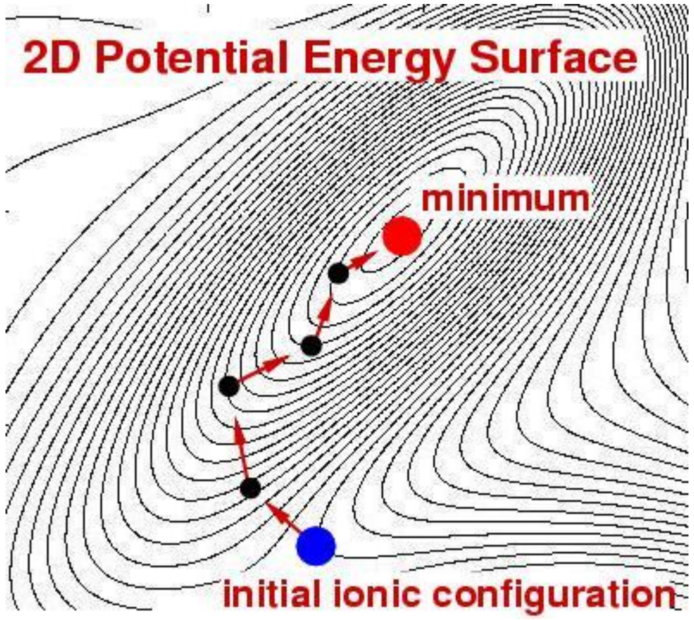
| | |
|---|---|
| **forc_conv_thr** | REAL |
| *Default:* | 1.0D-3 |

Convergence threshold on forces (a.u) for ionic minimization: the convergence criterion is satisfied when all components of all forces are smaller than forc_conv_thr.
See also etot_conv_thr - both criteria must be satisfied

# Structural Optimization and Molecular Dynamics

Within the *Born-Oppenheimer*, or *adiabatic* approximation, the total energy as a function of atomic positions, or *Potential Energy Surface* (PES), determines the behaviour of nuclei.

The *global* ground state can be found by minimizing the function $E(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)$, depending upon the $3N$ atomic coordinates for a system of $N$ atoms. This is a "standard" mathematical problem: finding the minimum of a function, knowing its derivatives, that is, the Hellmann-Feynman forces (in the picture, a cartoon of a PES in two dimensions with the path to the minimum).



Once forces are calculated, one can perform not only structural optimization, but also *molecular dynamics*. If a classical behaviour of the nuclei is assumed, all the machinery of classical MD can be recycled, with forces calculated from *first principles*.

Courtesy of P Giannozzi