First-principles molecular dynamics

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Outline

1. First-principles molecular dynamics: when and what?

2. A quick look at the theoretical basis, with emphasis on Density-Functional Theory

3. Born-Oppenheimer and Car-Parrinello Molecular Dynamics

4. Technicalites you should be aware on: plane waves, pseudopotentials

5. Software and needed hardware

# 1. What is First-Principles Molecular Dynamics?

In First-Principles Molecular Dynamics (FPMD) the forces acting on nuclei are computed from the *electronic states*, i.e. by solving, in principle *exactly*, the many-body Schrödinger equation for electrons (nuclei are approximated by classical particles).

FPMD is the method of choice whenever "force fields" do not give a sufficiently accurate or reliable description of the system under study, or of a specific phenomenon: typically, whenever bonds are broken or formed, or in presence of complex bonding, e.g.: transition metals.

With FPMD, all techniques used in classical (with force fields) MD can be used; *moreover*, one has access to the electronic structure and charge density, can in principle compute excitation spectra: *however*, the heavy computational load of FPMD, *in spite* of available efficient implementations, limits its range of application to systems containing $\mathcal{O}(1000)$ atoms max, for rather short times (tens of ps).

An example of application

Below, the simplest model for the myoglobin active site: iron-porphyrin-imidazole complex. Yellow: Fe. Dark Gray: C. Blue: N. Light gray: H.
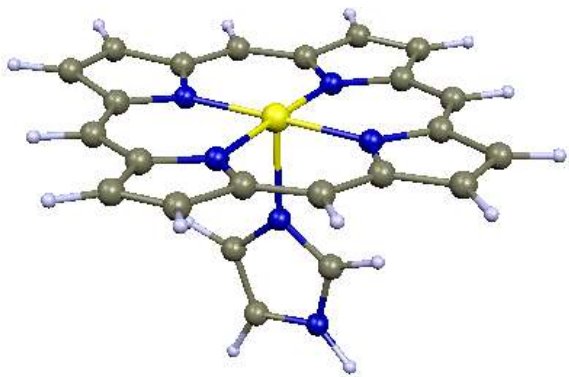
To the right: extended model of the myoglobin active site (including the 13 residues in a 8A sphere centered on Fe, terminated with NH_2 groups, containing 332 atoms, 902 electrons). Red: O, all other atoms as in the above picture.
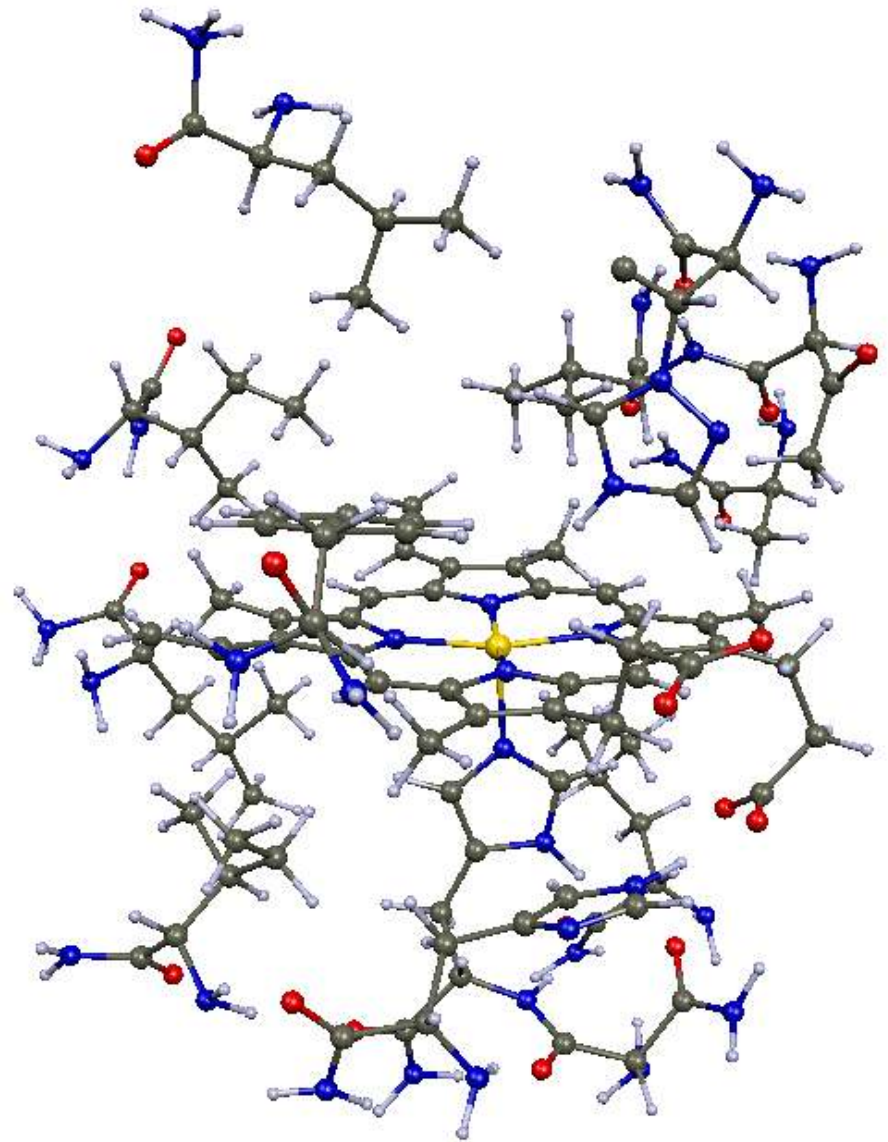
The need for first-principles MD

- *High-level theoretical description* needed, due to the presence of transition metal atoms

- *Complex energy landscape*: many possible spin states and local minima, not easy to guess from static (single-point) calculations − Molecular Dynamics may be better suited.

Interest: respiration, photosynthesis, enzymatic catalysis...
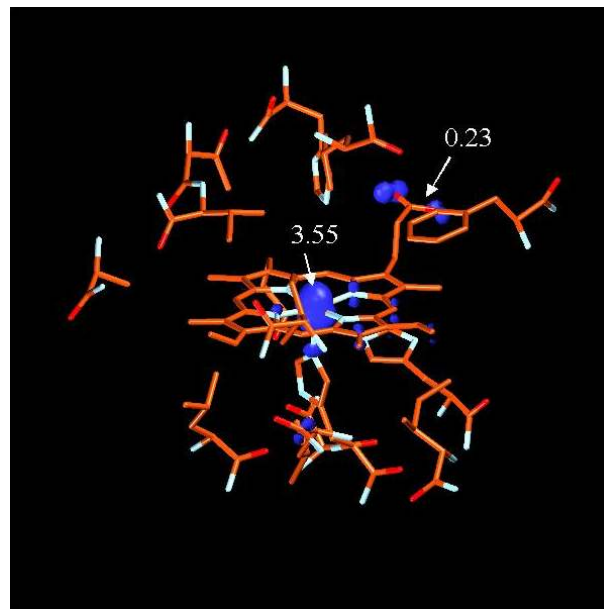
Note however that sizable systems (hundreds of atoms in this case) are needed in order to accurately describe the effect of surrounding environment: *efficient* first-principles techniques are needed (P. Giannozzi, F. de Angelis, and R. Car, J. Chem. Phys. **120**, 5903 (2004); D. Marx and J. Hutter, *Modern Methods and Algorithms of Quantum Chemistry*, John von Neumann Institute for Computing, Jülich, NIC Series, Vol.3, pp. 329-477 (2000) http://juser.fz-juelich.de/record/152459/files/FZJ-2014-02061.pdf)

2. The basics: Born-Oppenheimer approximation

The behavior of a system of interacting electrons $\mathbf{r}$ and nuclei $\mathbf{R}$ is determined by the solutions of the *time-dependent Schrödinger equation*:

$$i\hbar\frac{\partial\hat{\Phi}(\mathbf{r},\mathbf{R};t)}{\partial t} = \left(-\sum_{\mu}\frac{\hbar^2}{2M_\mu}\frac{\partial^2}{\partial\mathbf{R}_\mu^2} - \sum_{i}\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}_i^2} + V(\mathbf{r},\mathbf{R})\right)\hat{\Phi}(\mathbf{r},\mathbf{R};t)$$

where $V(\mathbf{r},\mathbf{R})$ is the potential describing the coulombian interactions:

$$
\begin{aligned}
V(\mathbf{r},\mathbf{R}) &= \sum_{\mu>\nu}\frac{Z_\mu Z_\nu e^2}{|\mathbf{R}_\mu-\mathbf{R}_\nu|} - \sum_{i,\mu}\frac{Z_\mu e^2}{|\mathbf{r}_i-\mathbf{R}_\mu|} + \sum_{i>j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}\\
&\equiv V_{nn}(\mathbf{R}) + V_{ne}(\mathbf{r},\mathbf{R}) + V_{ee}(\mathbf{r})
\end{aligned}
$$

Born-Oppenheimer (or *adiabatic*) approximation (valid for $M_\mu >> m$):

$$\hat{\Phi}(\mathbf{r},\mathbf{R};t) \simeq \Phi(\mathbf{R})\Psi(\mathbf{r}|\mathbf{R})e^{-i\hat{E}t/\hbar}$$

NB: in order to keep the notation simple: $\mathbf{r}\equiv(\mathbf{r}_1,..,\mathbf{r}_N)$, $\mathbf{R}\equiv(\mathbf{R}_1,..,\mathbf{R}_n)$; spin and relativistic effects are not included

Potential Energy Surface

The Born-Oppenheimer approximation allows to split the original problem into an *electronic problem depending upon nuclear positions*:

$$\left(-\sum_i \frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathbf{r}, \mathbf{R}) \right) \Psi(\mathbf{r}|\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}|\mathbf{R})$$

and a *nuclear problem under an effective interatomic potential*, determined by the electrons:

$$\left(-\sum_\mu \frac{\hbar^2}{2M_\mu}\frac{\partial^2}{\partial \mathbf{R}_\mu^2} + E(\mathbf{R}) \right) \Phi(\mathbf{R}) = \hat{E}\Phi(\mathbf{R})$$

$E(\mathbf{R})$ defines the *Potential Energy Surface* (PES). The PES determines the motion of atomic nuclei and the equilibrium geometry: the forces $\mathbf{F}_\mu$ on nuclei, defined as

$$\mathbf{F}_\mu = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_\mu},$$

vanish at equilibrium: $\mathbf{F}_\mu = 0$.

Solving the electronic problem: Hartree-Fock

Let us write the many-body electronic wave-function as a *Slater determinant*:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & ... & \psi_1(N) \\ . & . & . \\ . & . & . \\ \psi_N(1) & ... & \psi_N(N) \end{vmatrix}$$

for N electrons, where $(i) \equiv (\mathbf{r}_i, \sigma_i)$, σ_i is the spin of the $i-$th electron, the ψ_i states are all different. Minimization of E yields the *Hartree-Fock equations*.

For the "restricted" case (pairs of states with opposite spin):

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) + V_H(\mathbf{r})\psi_i(\mathbf{r}) + (\hat{V}_x\psi_i)(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where $i = 1, ..., N/2$, $V(\mathbf{r})$ is the external (nuclear) potential acting on each electron:

$$V(\mathbf{r}) = -\sum_\mu \frac{Z_\mu e^2}{|\mathbf{r} - \mathbf{R}_\mu|},$$

V_H is the *Hartree* potential:

$$V_H(\mathbf{r}) = 2 \sum_j \int |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$\hat{V}_x$ is the (nonlocal) *exchange* potential:

$$(\hat{V}_x \psi_i)(\mathbf{r}) = - \sum_j \int \psi_j(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') d\mathbf{r}'.$$

These are integro-differential equations that must be solved *self-consistently*.

In practice, HF is not a very good approximation. More accurate results require perturbative corrections (Møller-Plesset) or to add more Slater determinants (Configuration Interaction) in order to find more of the *correlation energy*, defined as "the difference between the true and the Hartree-Fock energy".

Solving HF and post-HF equations is the "traditional" approach of Quantum Chemistry. An alternative approach, based on the *charge density*, is provided by *Density-Functional Theory* (DFT)

Solving the electronic problem: Hohenberg-Kohn theorem

Let us introduce the ground-state *charge density* $n(\mathbf{r})$. For N electrons:

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, ...\mathbf{r}_N)|^2 d\mathbf{r}_2 ... d\mathbf{r}_N.$$

The *Hohenberg-Kohn theorem* (1964) can be demonstrated: there is a *unique* potential $V(\mathbf{r}, \mathbf{R})$ having $n(\mathbf{r})$ as ground-state charge density. Consequences:

• The energy can be written as a *functional* of $n(\mathbf{r})$:

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

where $F[n(\mathbf{r})]$ is a *universal* functional of the density, $V(\mathbf{r})$ is the external (nuclear) potential acting on each electron:

$$V(\mathbf{r}) = -\sum_\mu \frac{Z_\mu e^2}{|\mathbf{r} - \mathbf{R}_\mu|}.$$

• $E[n(\mathbf{r})]$ is *minimized* by the ground-state charge density $n(\mathbf{r})$.

Note: the energy E defined above does not include nuclear-nuclear interaction terms

Density-Functional Theory: Kohn-Sham approach

Let us introduce the orbitals ψ_i for an auxiliary set of *non-interacting electrons* whose charge density is the same as that of the true system:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2, \qquad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Let us rewrite the energy functional in a more manageable way as:

$$E = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

where $T_s[n(\mathbf{r})]$ is the kinetic energy of the non-interacting electrons:

$$T_s[n(\mathbf{r})] = -\frac{\hbar^2}{2m}\sum_i \int \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})d\mathbf{r},$$

$E_H[n(\mathbf{r})]$ is the *Hartree energy*, due to electrostatic interactions:

$$E_H[n(\mathbf{r})] = \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}',$$

$E_{xc}[n(\mathbf{r})]$ is called *exchange-correlation energy* (a reminiscence from the Hartree-Fock theory) and includes all the remaining (unknown!) energy terms.

Minimization of the energy with respect to ψ_i yields the *Kohn-Sham* (KS) equations:

$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right)}_{H_{KS}} \psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}),$$

where the Hartree and exchange-correlation potentials:

$$V_H(\mathbf{r}) = \frac{\delta E_H[n(\mathbf{r})]}{\delta n(\mathbf{r})} = e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

depend self-consistently upon the ψ_i via the charge density.

The energy can be rewritten in an alternative form using the KS eigenvalues ϵ_i:

$$E = \sum_i \epsilon_i - E_H[n(\mathbf{r})] - \int n(\mathbf{r})V_{xc}(\mathbf{r})d\mathbf{r} + E_{xc}[n(\mathbf{r})]$$

Exchange-correlation functionals: simple approximations

What is $E_{xc}[n(\mathbf{r})]$? Viable approximations needed to turn DFT into a useful tool. The first, "historical" approach (1965) is the *Local Density Approximation* (LDA): replace the energy functional with a *function* of the local density $n(\mathbf{r})$,

$$E_{xc} = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))d\mathbf{r}, \qquad V_{xc}(\mathbf{r}) = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r})\left.\frac{d\epsilon_{xc}(n)}{dn}\right|_{n=n(\mathbf{r})}$$

where $\epsilon_{xc}(n)$ is calculated for the homogeneous electron gas of uniform density n (e.g. using Quantum Monte Carlo) and parameterized.

Generalized Gradient Approximation (GGA): A more recent class of functionals depending upon the local density and its *local gradient* $|\nabla n(\mathbf{r})|$,

$$E_{xc} = \int n(\mathbf{r})\epsilon_{GGA}\left(n(\mathbf{r}), |\nabla n(\mathbf{r})|\right)d\mathbf{r}$$

There are many flavors of GGA, yielding similar (but slightly different) results. GGA is the "standard" functional in most FPMD calculations, with excellent price-to-performance ratio, but some noticeable shortcomings.

Spin-polarized extension: LSDA

Simplest case: assume a unique quantization axis for spin. Energy functional:

$$E \equiv E[n_+(\mathbf{r}), n_-(\mathbf{r})] = T_s + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_H + E_{xc}[n_+(\mathbf{r}), n_-(\mathbf{r})]$$

$n_\sigma(\mathbf{r})$ = charge density with spin polarization σ
$n(\mathbf{r}) = n_+(\mathbf{r}) + n_-(\mathbf{r})$ total charge density.

Minimization of the above functional yields the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + V_{xc}^\sigma(\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \psi_i^\sigma(\mathbf{r})$$

Exchange-correlation potential and charge density:

$$V_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_\sigma(\mathbf{r})}, \qquad n_\sigma(\mathbf{r}) = \sum_i f_i^\sigma |\psi_i^\sigma(\mathbf{r})|^2$$

Note the extension to *fractional occupancies* (i.e. metallic systems): $0 \leq f_i^\sigma \leq 1$.
Noncolinear magnetism (no fixed axis for magnetization) can also be described.

"Standard" DFT: advantages and shortcomings

+ **Computationally convenient**: calculations in relatively complex condensed-matter systems become affordable (GGA marginally more expensive than LDA)

+ **Excellent results** in terms of prediction of atomic structures, bond lengths, lattice parameters (within $1 \div 2\%$), binding and cohesive energies (5 to 10% GGA; LDA much worse, strongly overestimates), vibrational properties. Especially good for $sp-$bonded materials, may work well also in more "difficult" materials, such as transition metal compounds

− The infamous **band gap problem**: $\epsilon_c - \epsilon_v$ (or HOMO-LUMO in quantum chemistry parlance) wildly underestimates the true band gap (mostly due to missing discontinuity in V_{xc} for integer number of electrons)

− Serious trouble in dealing with **strongly correlated materials**, such as e.g. magnetic materials (trouble mostly arising from spurious self-interaction)

− **No van der Waals interactions** in any functional based on the local density and gradients: van der Waals is nonlocal, cannot depend upon charge overlap

Advanced DFT functionals

- **DFT+U**. LDA and GGA are often unable to find the correct occupancy of atomic-like electronic states, leading to *qualitatively* wrong results – but when occupancy is correct, results are not bad. DFT+U adds a Hubbard-like term, accounting for strong Coulomb correlations in systems with highly localized, atomic-like states:

$$E_{DFT+U}[n(\mathbf{r})] = E_{DFT}[n(\mathbf{r})] + E_U[n(\mathbf{r})],$$

where (simplified, rotationally invariant form):

$$E_U[n(\mathbf{r})] = \frac{U}{2} \sum_\sigma \mathrm{Tr}[\mathbf{n}^\sigma (1 - \mathbf{n}^\sigma)],$$

U being a (system-dependent) Coulomb repulsion (typically a few eV) and $\mathbf{n}^\sigma$ is the matrix of orbital occupancies for a set of atomic-like states ϕ_m:

$$\mathbf{n}^\sigma_{mm'} = \sum_\sigma \sum_i f_i^\sigma \langle \psi_i^\sigma | P_{mm'} | \psi_i^\sigma \rangle, \qquad P_{mm'} = |\phi_m\rangle\langle\phi_{m'}|$$

DFT+U is a "quick-and-dirty" but effective solution for a deep problem of DFT: the lack of discontinuity in approximated functionals, due to incomplete self-interactions cancellation, favors fractionary occupancy. DFT+U also improves the gap and level alignement in heterostructures, at the price of introducing an adjustable parameter U
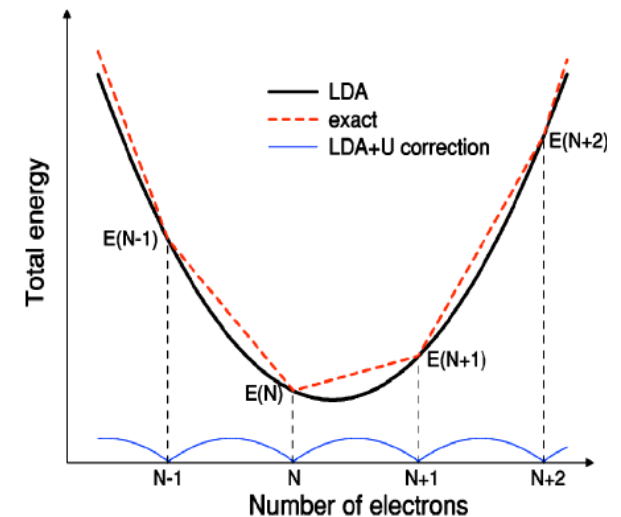
figure: Cococcioni&de Gironcoli, PRB **71**, 035105 (2005)

- **Meta-GGA**. Has a further dependence upon the *non-interacting kinetic energy density* $\tau_s(\mathbf{r})$:

$$E_{xc} = \int \epsilon_{mGGA}\left(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \tau_s(\mathbf{r})\right) d\mathbf{r}$$

where

$$\tau_s(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla^2 \psi_i(\mathbf{r})|^2$$

Meta-GGA may yield very good results and is not in principle much more expensive than GGA but it is numerically very nasty (at least in my experience)

- **Hybrid functionals**, such as B3LYP or PBE0, containing some amount of *exact* exchange, as in Hartree-Fock theory (spin-restricted):

$$E = T_s + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_H \underbrace{- \frac{e^2}{2}\sum_{i,j}\int \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'}_{E_x^{HF}}$$

In Hybrid DFT:

$$E = T_s + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_H + \overbrace{\alpha_x E_x^{HF} + (1-\alpha_x)E_x^{DFT} + E_c^{DFT}}^{E_{xc}^{hyb}},$$

with $\alpha_x = 20 \div 30\%$. This is the method of choice in Quantum Chemistry, yielding very accurate results and correcting most GGA errors.

In FPMD, however, hybrid functionals are computationally very heavy (due to usage of plane waves). Moreover, an adjustable parameter is introduced.

- **Nonlocal vdW functionals**, accounting for van der Waals (dispersive) forces, with a reasonable computational overhead.

Towards electronic ground state (fixed nuclei)

Possible methods to find the DFT ground state:

1. By the *self-consistent* solution of the Kohn-Sham equations

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

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, $V_H(\mathbf{r}) = e^2 \int \dfrac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}'$
- $V_{xc}[n]$ 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.

2. 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
- Λ_{ij} are Lagrange multipliers, $\Lambda \equiv$ all of them
- $E_H[n]$ is the Hartree energy, $E_H = \dfrac{e^2}{2} \displaystyle\int \dfrac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$
- $E_{xc}[n]$ is the exchange-correlation energy. For the simplest case, LDA, $E_{xc} = \displaystyle\int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))d\mathbf{r}$ where ϵ_{xc} is a function of $n(\mathbf{r})$.

Towards electronic ground state II

In the global-minimization approach, we need to compute the *gradients* of the energy functional, that is, $H_{KS}\psi$ products:

$$\frac{\delta \widetilde{E}[\psi, \Lambda]}{\delta \psi_i^*} = H_{KS}\psi_i - \sum_j \Lambda_{ij}\psi_j$$

In the self-consistent approach with *iterative* diagonalization, the basic ingredient is the same: $H_{KS}\psi$ products.

We further need to compute

1. the charge density from the ψ_i's, and

2. the potential from the charge density.

Typically, constrained global minimization is the preferred technique for FPMD.

Calculation of the total energy

Once the electronic ground state is reached, the **total energy** of the system can be calculated:

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

where E_{nn} is the repulsive contribution from nuclei to the energy:

$$E_{nn} = \frac{e^2}{2} \sum_{\mu \neq \nu} \frac{Z_\mu Z_\nu}{| \mathbf{R}_\mu - \mathbf{R}_\nu |}$$

Equivalent expression for the energy, using Kohn–Sham eigenvalues:

$$E = \sum_i f_i \epsilon_i - E_H[n] + E_{xc}[n(\mathbf{r})] - \int n(\mathbf{r}) V_{xc}[n(\mathbf{r})] d\mathbf{r} + E_{nn}$$

The total energy depends upon all atomic positions $\mathbf{R}_\mu$ (the PES is nothing but the total energy for all $\mathbf{R}_\mu$).

Hellmann-Feynman Forces

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:

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

the rightmost expression being valid only for *local* potentials, $V \equiv V(\mathbf{r})$ (the one at the left is more general, being valid also for nonlocal potentials $V \equiv V(\mathbf{r}, \mathbf{r}')$).

Demonstration (simplified). In addition to the explicit derivative of the external potential (first term), there is an implicit dependency via the derivative of the charge density:

$$\frac{\partial E}{\partial \mathbf{R}_\mu} = \int n(\mathbf{r}) \frac{\partial V}{\partial \mathbf{R}_\mu} d\mathbf{r} + \int \frac{\delta E}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \mathbf{R}_\mu} d\mathbf{r}$$

The green term cancels due to the *variational character* of DFT: $\delta E/\delta n(\mathbf{r}) = \mu$, constant.

The calculation of the Hellmann-Feynman forces is straightforward (in principle, not necessarily in practice!) once the ground-state electronic structure is available.

3.1 Born-Oppenheimer Molecular Dynamics

Let us assume classical behavior for the nuclei and electrons in the ground state. We introduce a classical Lagrangian:

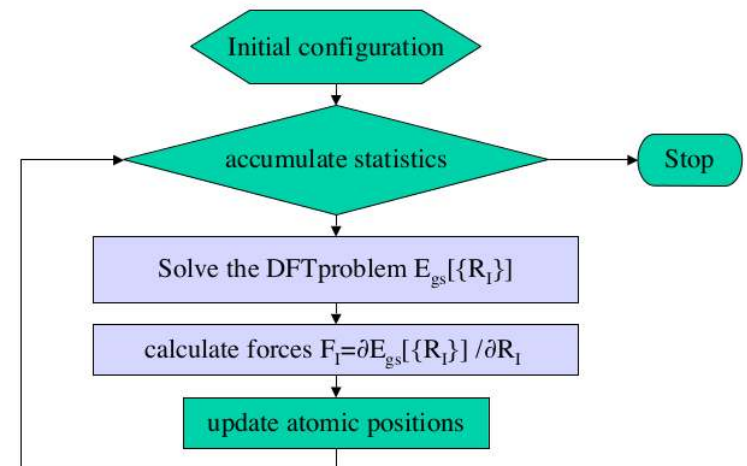$$L = \frac{1}{2}\sum_\mu M_\mu \dot{\mathbf{R}}_\mu^2 - E(\mathbf{R})$$

describing the motion of nuclei. The equations of motion:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{R}}_\mu} - \frac{\partial L}{\partial \mathbf{R}_\mu} = 0, \qquad \mathbf{P}_\mu = \frac{\partial L}{\partial \dot{\mathbf{R}}_\mu}$$

are nothing but usual Newton's equations:

$$\mathbf{P}_\mu \equiv M_\mu \mathbf{V}_\mu, \qquad M_\mu \dot{\mathbf{V}}_\mu = \mathbf{F}_\mu,$$

that can be discretized and solved by integration. This procedure defines Molecular Dynamics "on the Born-Oppenheimer surface", with electrons always at their instantaneous ground state.

Initial configuration

accumulate statistics → Stop

Solve the DFT problem $E_{gs}[\{R_I\}]$

calculate forces $F_I = \partial E_{gs}[\{R_I\}]/\partial R_I$

update atomic positions

Discretization of the equation of motion

Like in classical MD, the equation of motions can be discretized using the *Verlet algorithm*:

$$\mathbf{R}_\mu(t + \delta t) = 2\mathbf{R}_\mu(t) - \mathbf{R}_\mu(t - \delta t) + \frac{\delta t^2}{M_\mu}\mathbf{F}_\mu(t) + \mathcal{O}(\delta t^4)$$

$$\mathbf{V}_\mu(t) = \frac{1}{2\delta t}\left[\mathbf{R}_\mu(t + \delta t) - \mathbf{R}_\mu(t - \delta t)\right] + \mathcal{O}(\delta t^3).$$

or the *Velocity Verlet*:

$$\mathbf{V}_\mu(t + \delta t) = \mathbf{V}_\mu(t) + \frac{\delta t}{2M_\mu}\left[\mathbf{F}_\mu(t) + \mathbf{F}_\mu(t + \delta t)\right]$$

$$\mathbf{R}_\mu(t + \delta t) = \mathbf{R}_\mu(t) + \delta t\mathbf{V}_\mu(t) + \frac{\delta t^2}{2M_\mu}\mathbf{F}_\mu(t).$$

Both sample the *microcanonical ensemble*, or NVE: the energy (mechanical energy: kinetic + potential) is conserved.

Thermodynamical averages

Averages (ρ = probability of a microscopic state):

$$\langle A \rangle = \int \rho(\mathbf{R}, \mathbf{P}) A(\mathbf{R}, \mathbf{P}) d\mathbf{R} d\mathbf{P}$$

are usually well approximated by averages over time:

$$\lim_{T \to \infty} A_T \to \langle A \rangle$$

and the latter by discrete average over a trajectory:

$$A_T = \frac{1}{T} \int_0^T A(\mathbf{R}(t), \mathbf{P}(t)) dt \simeq \frac{1}{M} \sum_{n=1}^{M} A(t_n), \quad t_n = n\delta t, \quad t_M = M\delta t = T.$$

Costant-Temperature and constant-pressure dynamics

- Molecular Dynamics with *Nosé Thermostats* samples the *canonical ensemble* (NVT): the average temperature

$$\langle \sum_{\mu=1}^{N} \frac{\mathbf{P}_\mu^2}{2M_\mu} \rangle_{NVT} = \frac{3}{2} N k_B T$$

  is fixed (the instantaneous value has wide oscillations around the desired value)

- Molecular Dynamics with *variable cell* samples the NPT ensemble: the average pressure is fixed

In both cases, additional (fictitious) degrees of freedom are added to the system

Technicalities

- time step as big as possible, but small enough to follow nuclear motion with little loss of accuracy. Rule of thumb: $\delta t \sim 0.01 - 0.1 \delta t_{max}$, where $\delta t_{max} = 1/\omega_{max} = $ period of the fastest phonon (vibrational) mode.

- calculations of forces must be *very well converged* (good self-consistency needed) at each time step or else a systematic *drift* of the conserved energy will appear

  Note that:

  - the error on DFT *energy* is a *quadratic* function of the self-consistency error of the charge density (because energy has a minimum in correspondence to the self-consistent charge)
  - the error for DFT *forces* is a *linear* function of the self-consistency error of the charge density

  As a consequence, Born-Oppenheimer MD is usually computationally heavy

3.2 Car-Parrinello Molecular Dynamics

The idea: introduce a *fictitious* electron dynamics that keeps the electrons close to the ground state. The electron dynamics is *faster* than the nuclear dynamics and averages out the error, but *not too fast* so that a reasonable time step can be used

Car-Parrinello Lagrangian:

$$L = \frac{m^*}{2}\sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2}\sum_\mu M_\mu \dot{\mathbf{R}}_\mu^2 - E[\mathbf{R},\psi] + \sum_{i,j}\Lambda_{ij}\left(\int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} - \delta_{ij}\right)$$
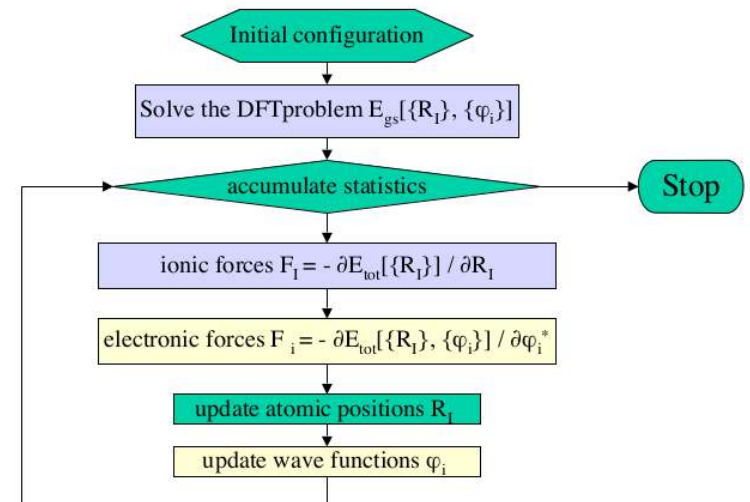
generates equations of motion:

CPMD Car-Parrinello Molecular Dynamics

$$m^*\ddot{\psi}_i = H\psi_i - \sum_j \Lambda_{ij}\psi_j, \quad M_\mu\ddot{\mathbf{R}}_\mu = \mathbf{F}_\mu \equiv -\frac{\partial E}{\partial \mathbf{R}_\mu}$$

m^* = fictitious electronic mass
Λ_{ij} = Lagrange multipliers, enforcing orthonormality constraints.
Very effective, but requires a judicious choice of simulation parameters.

Car-Parrinello Molecular Dynamics (2)

- electronic degrees of freedom ψ_i are the expansion coefficients of KS orbitals into a suitable basis set (typically Plane Waves for technical reasons)

- "forces" on electrons are determined by the KS Hamiltonian calculated from current values of ψ_i and of $\mathbf{R}_\mu$

- "forces" acting on nuclei have the Hellmann-Feynman form:

$$\frac{\partial E}{\partial \mathbf{R}_\mu} = \sum_i \langle \psi_i | \frac{\partial V}{\partial \mathbf{R}_\mu} | \psi_i \rangle$$

  but they slightly differ from "true" forces (ψ_i are not exact ground-state orbitals)

- The simulation is performed using classical MD technology (e.g. Verlet) on *both* nuclear positions *and* electronic degrees of freedom (Kohn-Sham orbitals)

- Orthonormality constraints are imposed *exactly at each time step*, using an iterative procedure

Car-Parrinello technicalities

- Starting point: bring the electrons to the ground state at fixed nuclear positions – this can be achieved using *damped* dynamics.

- Next step is often to bring the system to an equilibrium state – this can also be achieved using damped dynamics for both electrons and nuclei.

- The fictitious electronic mass m^* must be big enough to enable the use of a reasonable time step, but small enough to guarantee

  - *adiabaticity*, i.e. no energy transfer from nuclei to electrons, which always remain close to the ground state (no systematic increase of the fictitious "kinetic energy" of the electronic degrees of freedom)
  - *correctness* of the nuclear trajectory

  Typical values: $m^* \sim 100 \div 400$ electron masses

- The time step δt should be the largest value that yields a stable dynamics (no drifts, no loss of orthonormality). Typical values: $\delta t \sim 0.1 \div 0.3$ fs

Why (and when) Car-Parrinello works

The CP dynamics is *classical*, both for nuclei and electrons: the energy should equipartition!

Typical frequencies associated to electron dynamics: $\omega^{el} \sim \sqrt{(\epsilon_i - \epsilon_j)/m^*}$.
if there is a gap in the electronic spectrum, $\omega^{el}_{min} \sim \sqrt{\epsilon_{gap}/m^*}$

Typical frequencies associated to nuclear dynamics: phonon (vibrational) frequencies ω^{ph}

If $\omega^{ph}_{max} << \omega^{el}_{min}$ there is negligible energy transfer from nuclei to electrons

A fast electron dynamics keeps the electrons close to the ground state and averages out the error on the forces. The slow nuclear dynamics is very close to the correct one, i.e. with electrons in the ground state.

(G. Pastore, E. Smargiassi, F. Buda, Phys. Rev. A **44**, 6334 (1991)).

4.1 Choice of a basis set

The actual solution of the electronic problem requires to expand Kohn-Sham states into a sum over a suitable (finite!) set of *basis functions* $b_n(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_n c_n b_n(\mathbf{r})$$

Typical basis sets:

- *Localized* functions:
  atom-centred functions such as

  - Linear Combinations of Atomic Orbitals (LCAO)
  - Gaussian-type Orbitals (GTO)
  - Linearized Muffin-Tin Orbitals (LMTO)

- *Delocalized* functions:

  - Plane Waves (PW)

One could also consider *mixed* basis sets. The Linearized Augmented Plane Waves (LAPW) could be classified in this category.

Advantages and disadvantages of various basis sets

- Localized basis sets:

  + fast convergence with respect to basis set size: few functions per atom needed
  + can be used in finite as well as in periodic systems (as Bloch sums: $\phi_{\mathbf{k}} = \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R})$)
  − difficult to evaluate convergence quality (no systematic way to improve convergence)
  − difficult to use (two- and three-centre integrals)
  − difficult to calculate forces (*Pulay forces* if basis set is not complete)

- 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: there is a single convergence parameter, the *cutoff*)
  + easy to use (Fourier transform)
  + easy to calculate forces (no Pulay forces even if the basis set is incomplete)

Periodicity (or lack of it) and Supercells

Let us borrow some concepts from solid-state physics. A perfect crystal, having discrete translation symmetry, is described in terms of

- a periodically repeated **unit cell** and a **lattice** of translation vectors $\mathbf{R} = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3$, defined via three primitive vectors $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$ and integer coefficients n_1, n_2, n_3.
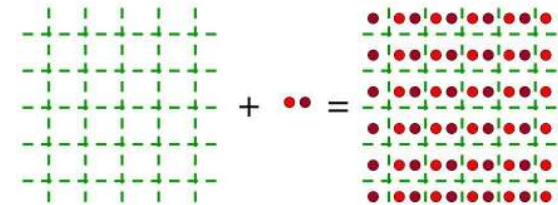
- a **basis** of atomic positions $\mathbf{d}_i$ into the unit cell

- a **reciprocal lattice** of vectors $\mathbf{G}$ such that $\mathbf{G} \cdot \mathbf{R} = 2\pi l$, with l integer: $\mathbf{G} = m_1\mathbf{G}_1 + m_2\mathbf{G}_2 + m_3\mathbf{G}_3$ with $\mathbf{G}_i \cdot \mathbf{R}_j = 2\pi\delta_{ij}$ and m_1, m_2, m_3 integer.
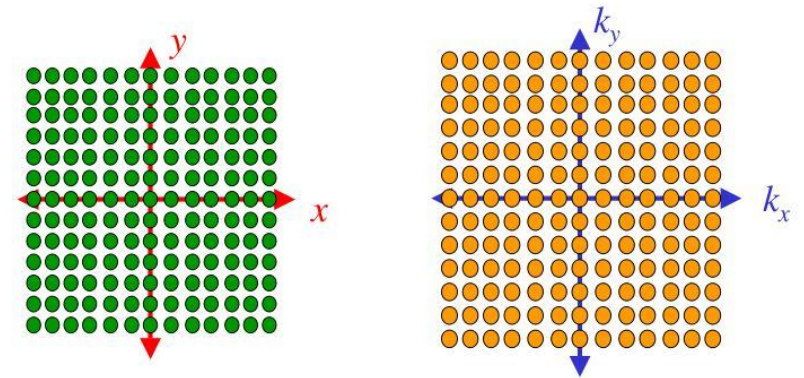
For non-periodic systems, as typically found in FPMD, the periodicity is artificial and it is defined by the simulation cell, or *supercell*.

Band Structure, Bloch states

The one-electron states $\psi(\mathbf{r})$ for a periodic system are classified by a **band index** i and a **wave vector** $\mathbf{k}$:

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r})$$

where $u_{i,\mathbf{k}}(\mathbf{r})$ is translationally invariant:

$$u_{i,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{i,\mathbf{k}}(\mathbf{r}).$$

For "true" periodic system, one has to deal with sums over $\mathbf{k}$-points.

In FPMD, it is usual to assume *Periodic Boundary Conditions* (PBC) on the simulation cell (defined by $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$) :

$$\psi(\mathbf{r} + \mathbf{R}_1) = \psi(\mathbf{r} + \mathbf{R}_2) = \psi(\mathbf{r} + \mathbf{R}_3) = \psi(\mathbf{r}).$$

This means that only states with $\mathbf{k} = 0$ ("Gamma point") are considered.

The simulation cell uniquely defines the PW basis set.

Plane-wave basis set

A PW basis set for states at $\mathbf{k} = 0$ is defined as

$$\langle \mathbf{r} | \mathbf{G} \rangle = \frac{1}{\sqrt{\mathcal{N}\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad \frac{\hbar^2}{2m} G^2 \leq E_{cut}$$

Ω = 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*: $\langle \mathbf{G} | \mathbf{G}' \rangle = \delta_{\mathbf{G}\mathbf{G}'}$

The components on a PW basis set are the *Fourier transform*:

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

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

Note that the larger the supercell, the larger the number of PW's for a given cutoff.

4.2 The need for Pseudopotentials

Are PWs a practical basis set for electronic structure calculations? Not really! Simple Fourier analysis shows that Fourier components up to $q \sim 2\pi/\delta$ are needed to reproduce a function that varies on a scale of length δ.

Since atoms have strongly localized core orbitals (e.g. $1s$ wavefunction for C has $\delta \simeq 0.1$ a.u.), millions of PW's would be needed even for simple crystals with small cells! We need to:

- get rid of core states

- get rid of orthogonality wiggles close to the nucleus

C 1s2 2s2 2p2
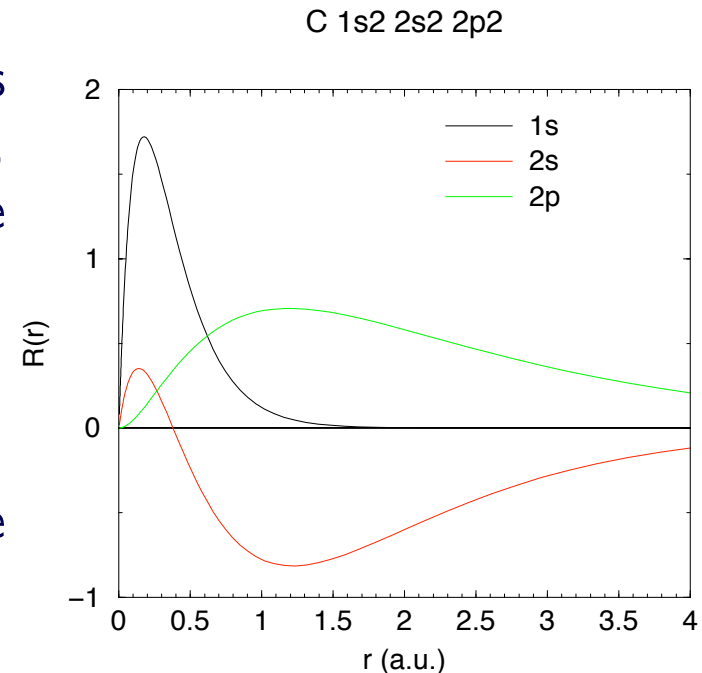
Solution: **Pseudopotentials** (PP). A smooth effective potential that reproduces the effect of the nucleus plus core electrons on valence electrons.

Understanding Pseudopotentials

Smoothness and *transferability* are the relevant keywords:

- We want our pseudopotential and pseudo-orbitals to be as *smooth* as possible so that expansion into plane waves is convenient (i.e. the required kinetic energy cutoff E_{cut} is small)

- We want our pseudopotential to produce pseudo-orbitals that are as close as possible to true ("all-electron") orbitals outside the core region, *for all systems containing a given atom* (in the figure: all-electron and pseudo-orbitals for Si)

Of course, the two goals are usually conflicting!

Pseudopotentials have a long story: let's start from the end.
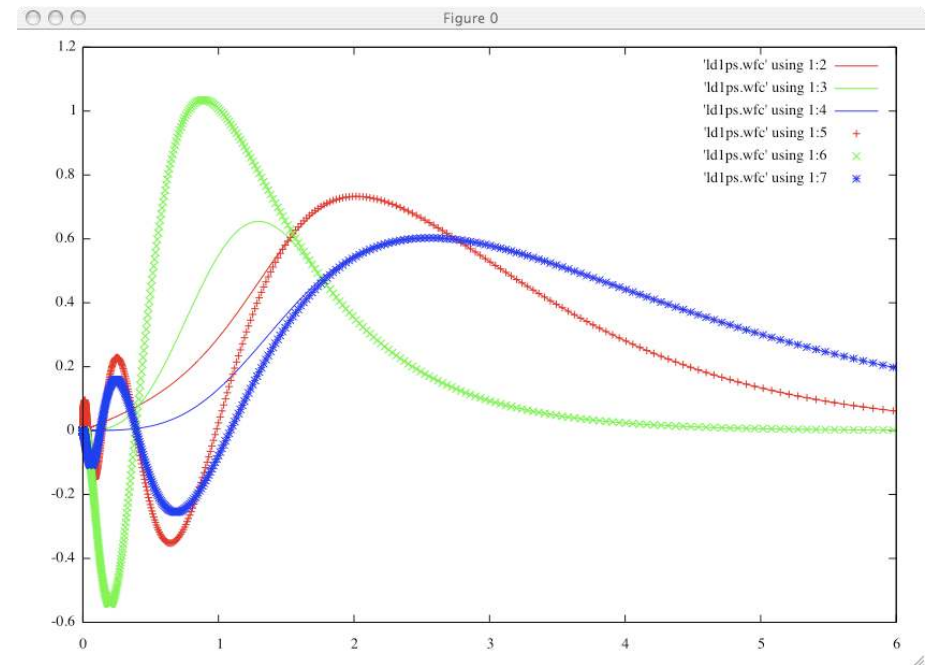
Understanding PP: Projector-Augmented Waves

Let us look for a linear operator $\widehat{T}$ connecting all-electron orbitals $|\psi_i\rangle$ to pseudo-orbitals $|\widetilde{\psi}_i\rangle$ as in: $|\psi_i\rangle = \widehat{T}|\widetilde{\psi}_i\rangle$. Pseudo-orbitals will be our variational parameters. We write the charge density, energy, etc. using pseudo-orbitals and $\widehat{T}$ instead of all-electron orbitals.

The operator $\widehat{T}$ can be defined in terms of its action on atomic waves (i.e. orbitals at a given energy, not necessarily bound states):

- $|\phi_l\rangle$: set of atomic all-electron waves (bound or unbound states)

- $|\widetilde{\phi}_l\rangle$: corresponding set of atomic pseudo-waves. Beyond some suitable "core radius" R_l, $\widetilde{\phi}_l(r) = \phi_l(r)$; for $r < R_l$, $\widetilde{\phi}_l(r)$ are smooth functions.
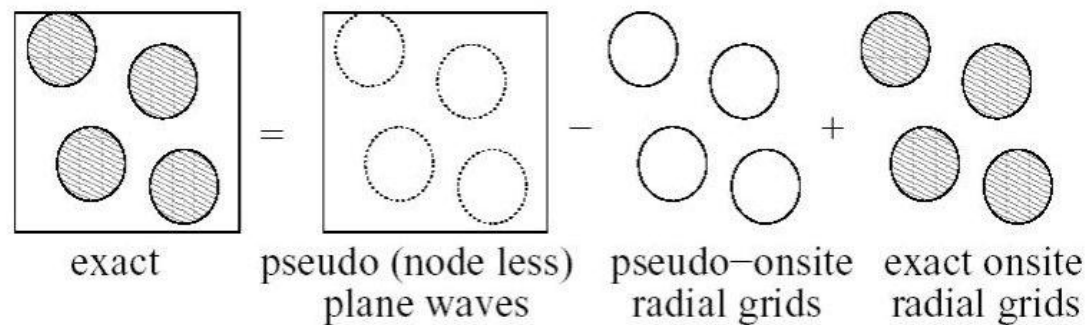
(P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994))

Understanding PP: the PAW transformation

If the above sets are complete in the core region, the operator $\widehat{T}$ can be written as

$$|\psi_i\rangle = \widehat{T}|\widetilde{\psi}_i\rangle = |\widetilde{\psi}_i\rangle + \sum_l \left(|\phi_l\rangle - |\widetilde{\phi}_l\rangle \right) \langle\beta_l|\widetilde{\psi}_i\rangle$$

where the β_l "projectors" are atomic functions, having the properties $\langle\beta_l|\widetilde{\phi}_m\rangle = \delta_{lm}$ and $\beta_l(r) = 0$ for $r > R_l$. The logic is described in the picture below:

exact   pseudo (node less)   pseudo−onsite   exact onsite
plane waves   radial grids   radial grids

The pseudopotential itself is written as a *nonlocal* operator, $\hat{V}$, in terms of the β_l projectors:

$$\hat{V} \equiv V_{loc}(r) + \sum_{lm} |\beta_l\rangle D_{lm} \langle\beta_m|$$

(V_{loc} contains the long-range Coulomb part $-Ze^2/r$)

Understanding PP: Charge in PAW

The (valence) charge density is no longer the simple sum of $|\psi_i|^2$:

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 + \sum_i f_i \sum_{lm} \langle \psi_i | \beta_l \rangle Q_{lm}(\mathbf{r}) \langle \beta_m | \psi_i \rangle,$$

and

$$Q_{lm}(\mathbf{r}) = \phi_l^*(\mathbf{r})\phi_m(\mathbf{r}) - \widetilde{\phi}_l^*(\mathbf{r})\widetilde{\phi}_m(\mathbf{r}).$$

The *augmentation charges* $Q_{lm}(\mathbf{r})$ are zero for $r > R_l$. A generalized orthonormality relation holds for pseudo-orbitals:

$$\langle \psi_i | S | \psi_j \rangle = \int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} + \sum_{lm} \langle \psi_i | \beta_l \rangle q_{lm} \langle \beta_m | \psi_j \rangle = \delta_{ij}$$

where $q_{lm} = \int Q_{lm}(\mathbf{r})d\mathbf{r}$. The D_{lm} quantites and β_l, Q_{lm} functions are atomic quantities that define the PP (or PAW set).

PP taxonomy: PAW, Ultrasoft, norm-conserving

- In the full PAW scheme, the augmentation functions are calculated and stored on a *radial grid*, centred at each atom. The charge density is composed by a "smooth" term expanded into plane waves, and an "augmentation" term calculated on the radial grid (Kresse and Joubert, Phys. Rev. B **59**, 1759 (1999))

- In the Ultrasoft PP scheme (D. Vanderbilt, B **41**, R7892 (1990)), the augmentation functions $Q_{lm}(r)$ are *pseudized*, i.e. made smoother: both "smooth" and "augmentation" terms can be calculated using FFT (see later), in either reciprocal or real space. The augmentation term usually requires a larger FFT grid in G-space than for the smooth term ("double grid")

- If we set $Q_{lm}(r) = 0$, we obtain good old norm-conserving PPs (Hamann, Schlüter, Chiang 1982) in the separable, nonlocal form.

Which pseudopotentials are good for me?

- **Norm-conserving**:

  + are simple to generate and to use. Theory and methodological improvements are invariably implemented first (and often only) for norm-conserving PPs
  − are relatively *hard*: core radii R_l cannot exceed by much the outermost maximum of the valence atomic orbitals, or else the loss of transferability is large. For some atoms: 2p elements C, N, O, F, 3d transition metals, 4f rare earths, this restriction may lead to very high plane-wave cutoffs (70 Ry and up)
  − do not give any sensible information about the orbitals close to the nucleus (all-electron orbitals can be "reconstructed" using the PAW transformation)

Unless too hard for practical usage, this is usually the first choice

Which pseudopotentials are good for me? (II)

- **Ultrasoft**:

  + can be made *smooth* with little loss of transferability: core radii R_l can be pushed to larger values, even for "difficult cases". Cutoffs of 25 to 35 Ry are usually good for most cases. Note that you may need a second FFT grid for augmentation charges, with typical cutoff $8 \div 12 \times$ orbital cutoff (instead of 4)
  - are not simple to generate: the pseudization of augmentation charges is often a source of trouble (e.g. negative charge)
  - some calculations not available for Ultrasoft PPs
  − give even less information about the orbitals close to the nucleus (all-electron orbitals can be "reconstructed")

Ultrasoft PPs are typically used in all cases where norm-conserving PPs are too hard: C, N, O, F, 3d elements, elements with "semicore" states
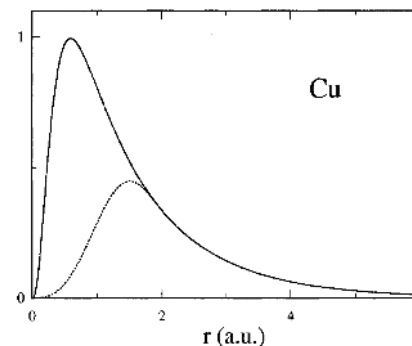
Which pseudopotentials are good for me? (III)

- **PAW**:

  + most transferrable, even for atoms that are "difficult" for Ultrasoft PPs (e.g. magnetic materials): accuracy is comparable to all-electron techniques (e.g. FLAPW)
  + give information about the orbital close to the nucleus
  - less well-known and used, less experience available
  - not all calculations are available for PAW

Which pseudopotentials are good for me? (IV)

There are a few more aspect to be considered in the choice of a pseudopotential:

- *PPs are bound to a specific XC functional*, at least in principle. xception: Hybrid and nonlocal (vdW-DF) functionals, for which very few (or no) PPs are available.

- The distinction between "core" and "valence" electrons is not always clear-cut. In some cases you may need to extend "valence" to include the so-called *semicore states* in order to achieve better (or less lousy) transferability. E.g.: 3d states in Zn and Ga; 3s and 3p states in 3d transition metals Fe, Co, Ni, ...

Inclusion of semicore states adds considerable complexity to both the generation and the practical usage of a PP: to be done only if needed.

Where do I find pseudopotentials?

There are many ready-to-use PPs tables around, and by now several papers containing extensive PP tables, e.g.:

- PSLib (US/PAW): A. Dal Corso, Comp. Material Science **95**, 337 (2014)

- PSLib tests: E. Kucukbenli *et al.*, http://arxiv.org/abs/1404.3015

- GRBV (US/PAW): K. F. Garrity *et al.*, Comput. Mater. Sci. **81**, 446 (2014)

- PAW: F. Jollet *et al.*, Comp. Phys. Commun. **185**, 1246 (2014)

- NC: A. Willand *et al.*, J. Chem. Phys. **138**, 104109, 2013

but *there is not a single standard PP file format*: each code has its own format.

Pseudopotential testing

PPs must be *always* tested to check for
— needed cutoff E_{cut} (plus augmentation charge cutoff for US PP)
— transferability to the expected chemical environment
— absence of *ghost states*: spurious unphysical states in the valence region of energies, or close to it. All nonlocal PPs can be affected

Testing can be performed

- in the single atom, using an atomic code or the PP generation code itself, by comparing *energy differences* between electronic configurations, and verifying that *logarithmic derivatives* are well reproduced;

- in simple molecular or solid-state systems, *ideally* by comparing with accurate all-electron results; less ideally, with other PP results, or with experimental data
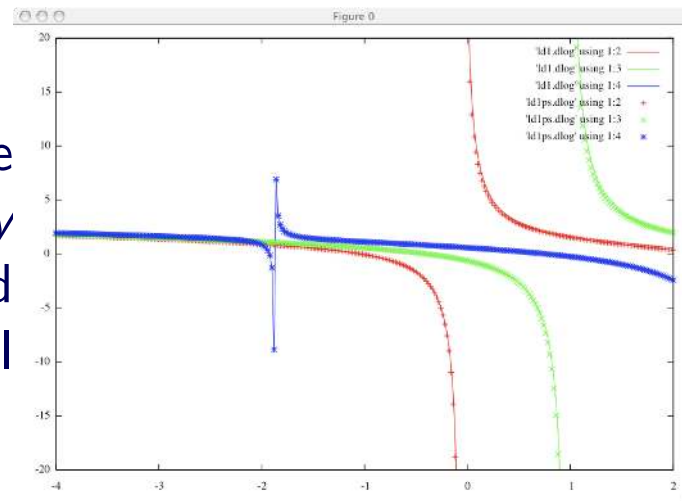
5. Software: Quantum ESPRESSO

Car-Parrinello simulations can be performed using the CP package of QUANTUM ESPRESSO: *Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization*.

QUANTUM ESPRESSO is a *distribution* of software for atomistic calculations based on electronic structure, using density-functional theory, a plane-wave basis set, pseudopotentials. Freely available under the terms of the GNU General Public License.

Main goals of QUANTUM ESPRESSO are *innovation* in methods and algorithms; *efficiency* on modern computer architectures.

QUANTUM ESPRESSO implements *multiple parallelization levels*

See: `http://www.quantum-espresso.org` for more info, in particular `http://www.quantum-espresso.org/pseudopotentials/` for available PP's.

www.quantum-espresso.org

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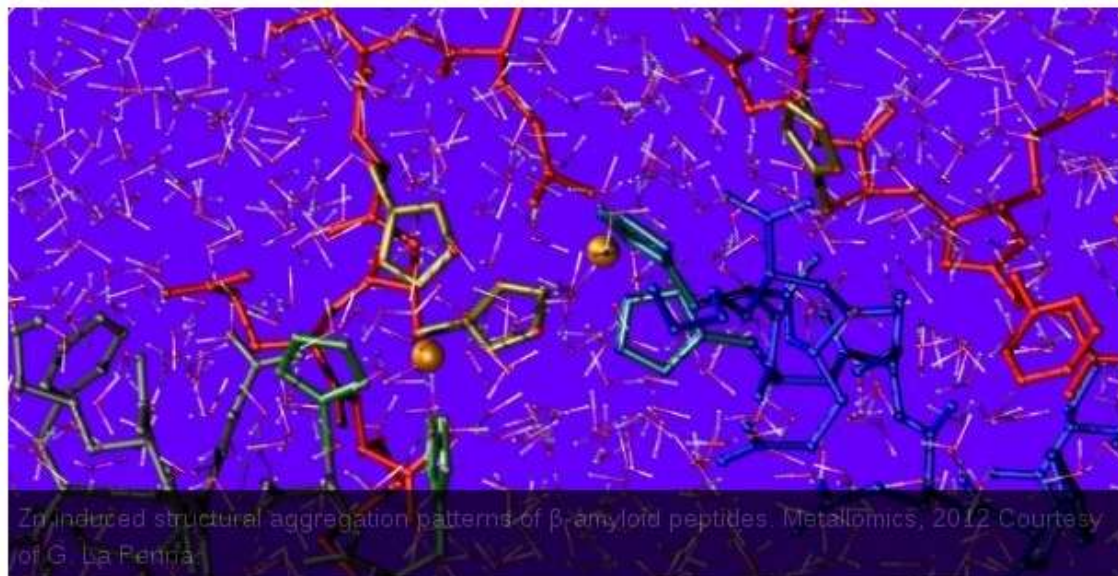## NEWS

22.01.15
2015 DEVELOPERS' MEETING

Program of the 2015 developers meeting, held
on 14th January 2014 in ICTP. (more...)

18.11.14

Zn induced structural aggregation patterns of β-amyloid peptides. Metallomics, 2012 Courtesy of G. La Penna.

CP package

Car-Parrinello variable-cell molecular dynamics for norm-conserving or ultrasoft PPs, Γ point ($\mathbf{k} = 0$) only. Originaly developed by A. Pasquarello (EPF Lausanne), K. Laasonen (Oulu), A. Trave (LLNL), R. Car (Princeton), P. Giannozzi (Udine), N. Marzari (EPF Lausanne); C. Cavazzoni (CINECA), S. Scandolo (ICTP), and many others.

- Electronic and ionic minimization schemes: damped dynamics, conjugate gradient

- Verlet dynamics with mass preconditioning

- Constrained dynamics

- Nosé thermostat for both electrons and nuclei, velocity rescaling

- Fast treatment ("grid box") of augmentation terms in Ultrasoft PPs

- Parallelization levels: on plane-wave and real-space grids; on Kohn-Sham states; on FFT's in $H\psi_i$ products ("task groups"); OpenMP

CP package, advanced features

- Nonlocal van-der-Waals functionals, or semiempirical corrections

- DFT+U and metaGGA functionals

- Fast implementation of hybrid functionals with Wannier functions

- Modified kinetic functional for constant-pressure calculations

- Metallic systems: variable-occupancy (ensemble) dynamics

- Self-Interaction Correction for systems with one unpaired electron

- Dynamics with Wannier functions under an external electric field

- Finite electric fields with Berry's phase

- With `plumed` plugin: metadynamics (Laio-Parrinello)

Some words on computer requirements

Quantum simulations are both CPU *and* RAM-intensive.
Actual CPU time and RAM requirements depend upon:

- *size of the system under examination:* As a rule of thumb, CPU $\propto N^{2\div3}$, RAM $\propto N^2$, where $N =$ number of atoms

- *kind of system:* type and arrangement of atoms, influencing the number of plane waves, of electronic states, of **k**-points needed...

- *desired results:* computational effort increases from simple self-consistent (single-point) calculation to structural optimization to reaction pathways, molecular-dynamics simulations, ...

CPU time mostly spent in FFT and linear algebra.
RAM mostly needed to store Kohn-Sham orbitals.

Typical computational requirements

For typical biological systems ($\mathcal{O}(1000)$ atoms): days to weeks of CPU, or more, tens to hundreds Gb RAM. *Massively parallel machines* are needed, together with effective, memory-distributing algorithms.
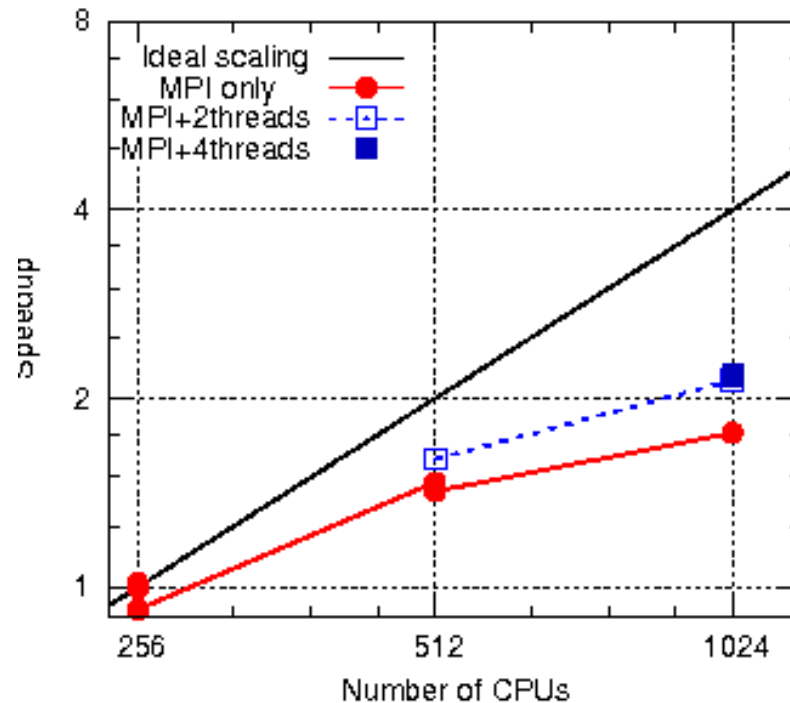
Fragment of an Aβ-peptide in water containing 838 atoms and 2312 electrons in a 22.1×22.9×19.9 A^3 cell, Γ-point. CP code on BlueGene/P, 4 processes per computing node.

Very Technical Appendix:
Fast Fourier Transforms, Dual-space technique

Let us consider first the simple case of a periodical function $f(x)$, with period L. Its Fourier components:

$$\widetilde{f}(q) = \frac{1}{L} \int f(x) e^{-iqx} dx$$

are nonzero over an *infinite* set of *discrete* values of q:

$$q_n = n\frac{2\pi}{L}, \qquad -\infty < n < \infty$$

The Fourier components decay to 0 for large q. The inverse Fourier transform has the form

$$f(x) = \sum_n \widetilde{f}(q_n) e^{iq_n x} = \sum_n \widetilde{f}_n e^{in(2\pi x/L)}$$

Our functions are however defined over a discrete but *finite* grid of q. How are they represented in x space?

Discrete Fourier Transform

We assume *both* x and q grids to be discrete, finite, and periodically repeated, and we write, for N large enough to accommodate all q components:

$$f(x) \quad \rightarrow \quad f_m = f(x_m), \qquad x_m = m\frac{L}{N}, \qquad m = 0, .., N-1$$

$$\widetilde{f}(q) \quad \rightarrow \quad \widetilde{f}_n = \widetilde{f}(q_n), \qquad q_n = n\frac{2\pi}{L}, \qquad n = 0, .., N-1$$

(q components of negative value refold into those at the end of the box). The *Discrete Fourier Transform* can be written as

$$f_m \quad = \quad \sum_{n=0}^{N-1} \widetilde{f}_n e^{i(2\pi nm/N)} \qquad (x - \text{space})$$

$$\widetilde{f}_n \quad = \quad \frac{1}{N} \sum_{m=0}^{N-1} f_m e^{-i(2\pi nm/N)} \qquad (q - \text{space})$$

Discrete Fourier Transform in 3D

Generalization of the Discrete Fourier Transform to 3 dimensions:

$$\mathbf{G} = n_1' \mathbf{G}_1 + n_2' \mathbf{G}_2 + n_3' \mathbf{G}_3$$

with $n_1 = 0, .., N_1 - 1$, $n_2 = 0, .., N_2 - 1$, $n_3 = 0, .., N_3 - 1$, and n_1', n_2', n_3' are n_1, n_2, n_3 refolded so that they are centered around the origin (remember: the $\mathbf{G}-$space grid is also periodic!). $\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3$ are the primitive translations of the unit cell of the reciprocal lattice.

$$\mathbf{r} = m_1 \frac{\mathbf{R}_1}{N_1} + m_2 \frac{\mathbf{R}_2}{N_2} + m_3 \frac{\mathbf{R}_3}{N_3}$$

with $m_1 = 0, .., N_1 - 1$, $m_2 = 0, .., N_2 - 1$, $m_3 = 0, .., N_3 - 1$. $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$ are the primitive translations of the unit cell. This grid spans the unit cell.

N_1, N_2, N_3 define the *FFT grid*.

Discrete Fourier Transform in 3D (2)

Original Fourier transform:

$$f(\mathbf{r}) = \sum_{\mathbf{G}} \widetilde{f}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \rightarrow f(m_1, m_2, m_3)$$

$$\widetilde{f}(\mathbf{G}) = \frac{1}{\Omega} \int f(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r} \rightarrow \widetilde{f}(n_1, n_2, n_3)$$

Discretized Fourier Transform:

$$f(m_1, m_2, m_3) = \sum_{n_1, n_2, n_3} \widetilde{f}(n_1, n_2, n_3) e^{i(2\pi n_1 m_1/N_1)} e^{i(2\pi n_2 m_2/N_2)} e^{i(2\pi n_3 m_3/N_3)}$$

$$\widetilde{f}(n_1, n_2, n_3) = \frac{1}{N} \sum_{m_1, m_2, m_3} \widetilde{f}(m_1, m_2, m_3) e^{-i(2\pi n_1 m_1/N_1)} e^{-i(2\pi n_2 m_2/N_2)} e^{-i(2\pi n_3 m_3/N_3)}$$

where $N = N_1 N_2 N_3$. Remember that $\mathbf{G}_i \cdot \mathbf{R}_j = 2\pi\delta_{ij}$.

PW-PP calculations and Discrete Fourier Transform

$$\psi_i(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \qquad \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 \le E_{cut}$$

Which grid in **G**-space? Need to calculate the charge density. From its **G**-space expression:

$$n(\mathbf{G}') = \sum_{\mathbf{G}} \sum_{i,\mathbf{k}} f_{i,\mathbf{k}} c_{i,\mathbf{k}+\mathbf{G}}^* c_{i,\mathbf{k}+\mathbf{G}+\mathbf{G}'}$$

one can see that Fourier components $\mathbf{G}'$ up to $\max(|\mathbf{G}'|) = 2\max(|\mathbf{G}|)$ appear. Or we need the product of the potential time a wavefunction:

$$(V\psi)(\mathbf{G}) = \sum_{\mathbf{G}'} V(\mathbf{G} - \mathbf{G}') c_{i,\mathbf{k}+\mathbf{G}'}$$

Again, $\max(|\mathbf{G} - \mathbf{G}'|) = 2\max(|\mathbf{G}|)$. We need a kinetic energy cutoff for the Fourier components of the charge and potentials that is four time larger as the cutoff for the PW basis set:

$$\frac{\hbar^2}{2m}|\mathbf{G}|^2 \le 4E_{cut}$$

In practice such condition may occasionally be relaxed. **Important:** for *ultrasoft* pseudopotentials, a different (larger) cutoff for augmentation charges may be needed!

The Fourier Transform grid is thus

$$\mathbf{G} = n_1'\mathbf{G}_1 + n_2'\mathbf{G}_2 + n_3'\mathbf{G}_3$$

with $n_1 = 0, .., N_1 - 1$, $n_2 = 0, .., N_2 - 1$, $n_3 = 0, .., N_3 - 1$. This grid must be big enough to include all $\mathbf{G}-$vectors up to a cutoff

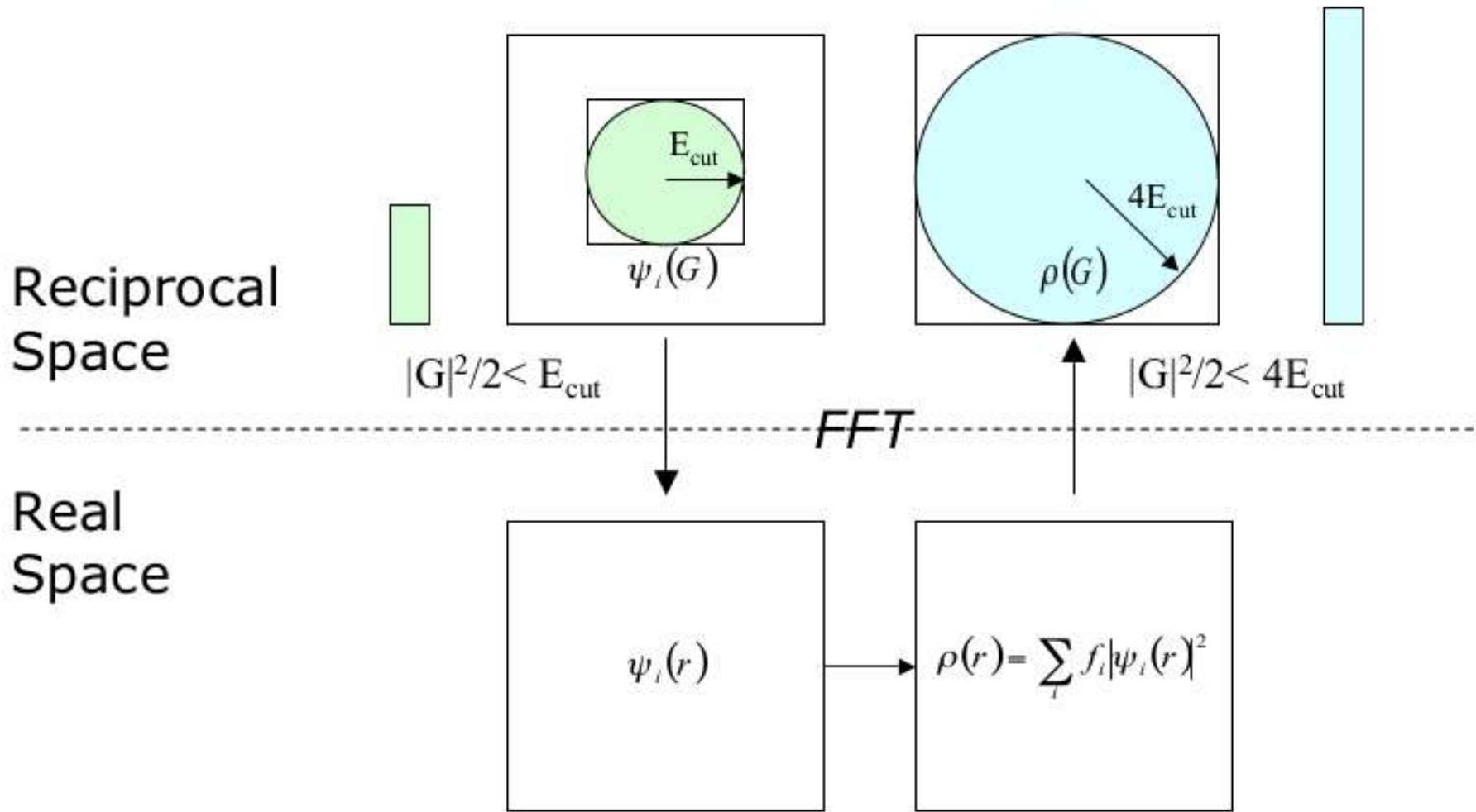$$\frac{\hbar^2}{2m}|\mathbf{G}|^2 \leq 4E_{cut}$$

and NOT up to the cutoff of the PW basis set! In general, the grid will also contain "useless" Fourier components (beyond the above-mentioned cutoff, so that $n(\mathbf{G}) = 0, V(\mathbf{G}) = 0$ etc.)

Fast Fourier Transform (FFT): allows to perform a Discrete Fourier Transform of order n with a computational cost $T_{CPU} = \mathcal{O}(n \log n)$ (instead of $\mathcal{O}(n^2)$).

Advantages of the use of FFT in PW-PP calculations: enormous, especially in conjunction with iterative techniques and of the "dual-space" technique

FFT grid

FFTs

Reciprocal Space

$|G|^2/2 < E_{cut}$

$\psi_i(G)$

$\rho(G)$

E_{cut}

$4E_{cut}$

$|G|^2/2 < 4E_{cut}$

FFT

Real Space

$\psi_i(r)$

$\rho(r) = \sum_i f_i |\psi_i(r)|^2$

(Note: $G^2/2$ is the kinetic energy in Hartree atomic units)

Dual space technique

The most important ingredient of a PW-PP calculations is

$$H\psi \equiv (T + \hat{V}_{NL} + V_{loc} + V_H + V_{xc})\psi$$

$(T\psi)$: easy in **G**-space, $T_{CPU} = \mathcal{O}(N)$

$(V_{loc} + V_H + V_{xc})\psi$: easy in **r**-space, $T_{CPU} = \mathcal{O}(N)$

$(\hat{V}_{NL}\psi)$: easy in **G**-space (also in **r**-space) if $\hat{V}$ is written in separable form
$T_{CPU} = \mathcal{O}(mN)$, $m =$number of projectors

FFT is used to jump from real to reciprocal space.
Operations are performed in the space where it is more convenient.

The same technique is used to calculate the charge density from Kohn-Sham orbitals, the exchange-correlation GGA potential from the charge density, etc.: in all cases, we move to the more convenient space to perform the required operations.