Forces, stresses and structural optimization

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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:

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

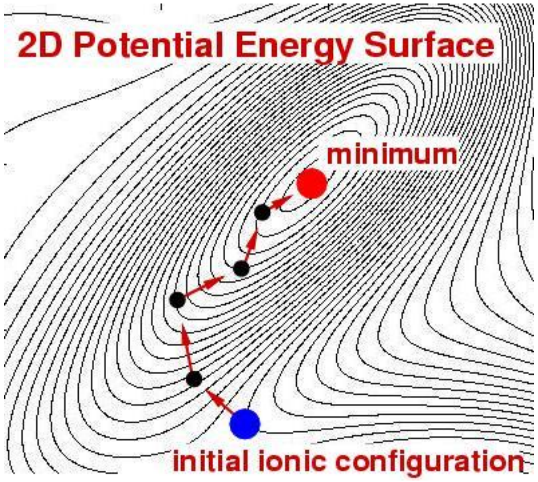
The red term cancels due to the *variational character* of DFT: $\delta E / \delta n(\mathbf{r}) = \mu$, constant.

The calculation of the Hellmann-Feynman forces is straightforward (in principle, not necessarily in practice!) once the self-consistent electronic structure is calculated.

Structural Optimization and Molecular Dynamics

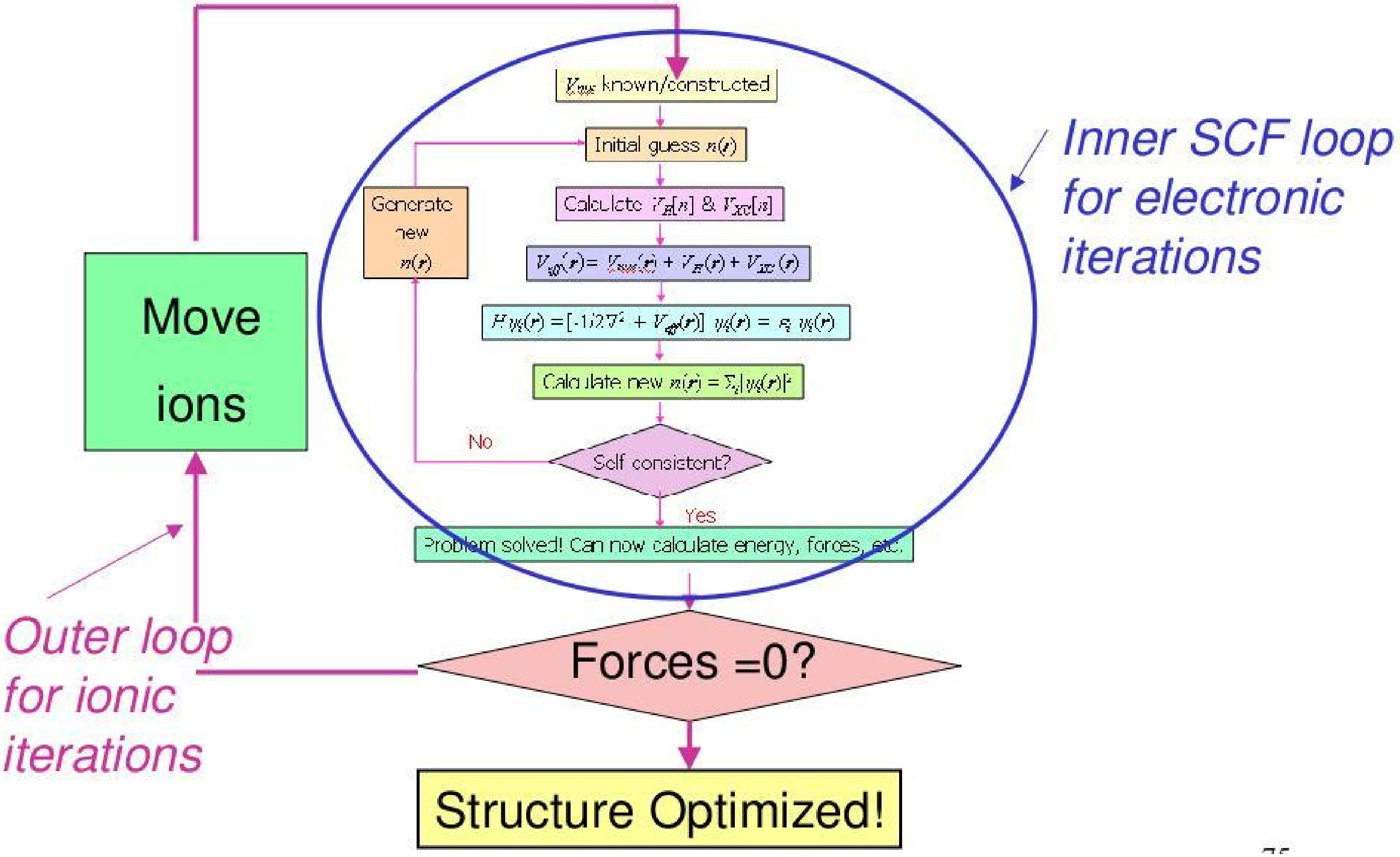
Within the *Born-Oppenheimer*, or *adiabatic* approximation, the total energy as a function of atomic positions, or *Potential Energy Surface* (PES), determines the behaviour of nuclei.

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 (also known as "relaxation"), 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*.

Structural optimization



Inner SCF loop for electronic iterations

Outer loop for ionic iterations

Structural optimization in periodic systems

Beware: in a periodic system, there are two *distinct* kinds of displacements:

- atomic displacements *inside* the unit cell, determined by the *forces*. Forces are the derivatives of the total energy *with respect to atomic positions in the cell* and are computed as

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

- elastic displacements changing the *shape* of the unit cell, determined by the *stresses*. If a strain $\epsilon_{\alpha\beta}$ is applied to all coordinates: $r_\alpha \longrightarrow (1 + \sum_\gamma \epsilon_{\alpha\gamma} r_\gamma)$, the stress $\sigma_{\alpha\beta}$ is the derivatives of the total energy *with respect to the strain*:

$$\sigma_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial E}{\partial \epsilon_{\alpha\beta}}$$

  and can be computed from the ground-state Kohn-Sham orbitals. [1]

  Note that the pressure is related to the stress via $P = -\frac{1}{3}\mathrm{Tr}\sigma$.

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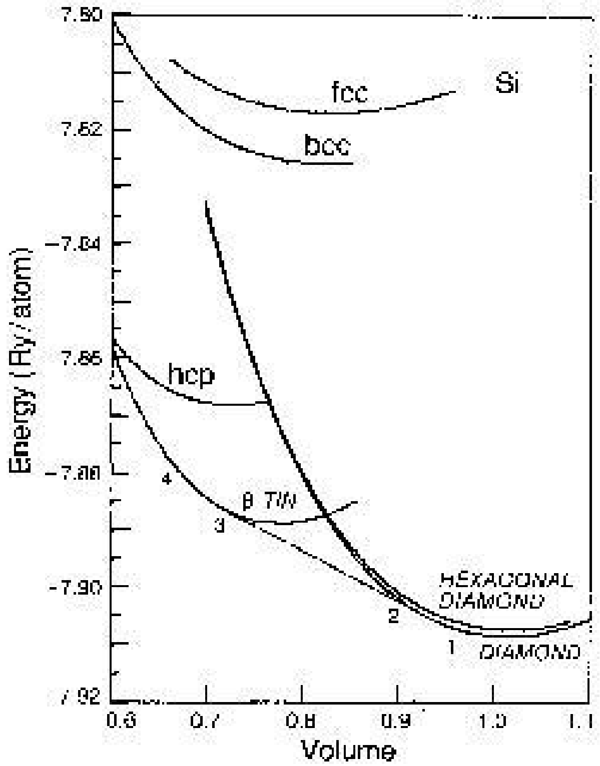
[1] Nielsen and Martin, PRB 3780 and 3792, 1985

Simple case: finding the equilibrium volume

For simple crystals, the global ground state can be found by calculating for a few values of the lattice parameter the $E(V)$ curve, fitting it to a phenomenological *equation of state* (EOS) like Murnaghan's:



$$P(V) = \frac{B}{B'}\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right]$$

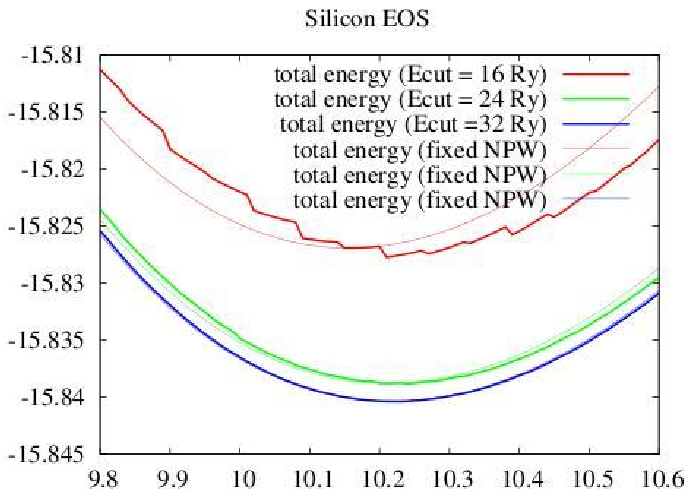
(the $E(V)$ formula can be obtained by observing that the pressure $P = -\partial E/\partial V$). Equilibrium volume V_0, bulk modulus B and its pressure derivative B' are the fit parameters.

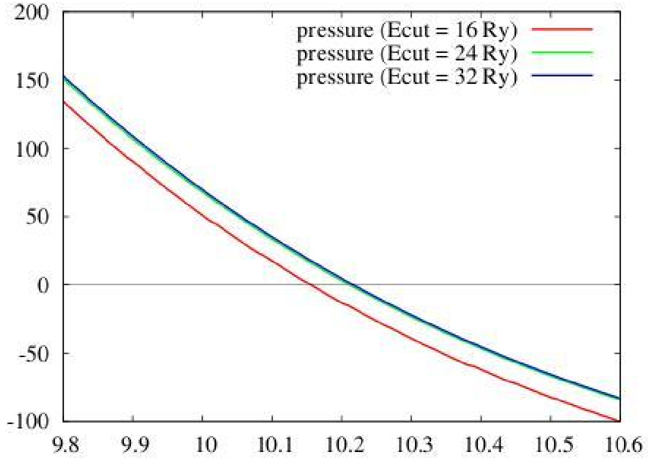
In the picture from a famous Yin-Cohen 1980 paper, the energies of different candidate structures for Si can be compared, phase transitions under pressure found.

Note that in simple crystalline structures *the force on atoms can be zero* by symmetry, even if the system is *not at equilibrium*!

Note on incompleteness of the PW basis set

Practical calculations are invariable performed with a cutoff "as low as possible", sometimes quite far from convergence. The consequence are especially visible when comparing the $E(V)$ curve at fixed cutoff and the same at fixed number of plane waves: the curve at low cutoff is "rigged", the pressures calculated from the stress and from the equation of state do not match. This is a manifestation of the *Pulay* incomplete-basis-set error on the stress: plane waves *depend upon the strain* via the unit cell.





The strategy "fixed cutoff + fit to an EOS" converges faster than fixing the number of PWs. The latter is equivalent to locating the zero of the computed pressure (via the stress).

The incompleteness of basis set is not as serious as it may look: energy *differences* between different structures, structural parameters such as lattice parameters and bond lengths, converge much quicker than absolute energies.

Quasi-Newton algorithms for structural optimization

The BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm is the workhorse for structural minimization, either at fixed cell or with variable cell.

Close to an equilibrium point $\vec{X}^{(eq)}$, for which $\nabla E(\vec{X}^{(eq)}) = 0$ holds, a quadratic form is assumed for the function $E(\vec{X})$ (H is the Hessian matrix):

$$E(\vec{X}) \simeq E(\vec{X}^{(eq)}) + \frac{1}{2}(\vec{X} - \vec{X}^{(eq)})^T H (\vec{X} - \vec{X}^{(eq)})$$

Given two points $\vec{X}_1$ and $\vec{X}_0$ and corresponding gradients $\vec{g} = \nabla E(\vec{X})$, this means $\vec{g}_1 - \vec{g}_0 = H(\vec{X}_1 - \vec{X}_0)$, that is, $\vec{g}_1 = 0$ if $\vec{X}_1 = \vec{X}_0 - H^{-1}\vec{g}_0$ (*Newton-Raphson step*).

Practical algorithm: a sequence of calculations at positions $\vec{X}_i$

$$\vec{X}_{i+1} = \vec{X}_i + T_k^L \frac{\vec{s}_k^{NR}}{|s_k^{NR}|}, \qquad \vec{s}_k^{NR} = -H_k^{-1}\vec{g}_k$$

where T_k^L is called "trust radius".

The inverse Hessian matrix is updated at each step using the BFGS scheme:

$$H_{k+1}^{-1} = H_k^{-1} + \left(1 + \frac{\gamma_k^T H_k^{-1} \gamma_k}{s_k^T \gamma_k}\right) \frac{s_k s_k^T}{s_k^T \gamma_k} - \left(\frac{s_k \gamma_k^T H_k^{-1} + H_k^{-1} \gamma_k s_k^T}{s_k^T \gamma_k}\right)$$

$$\gamma_k = g_{k+1} - g_k$$

- At fixed cell:
  - $\vec{X} = (\vec{d}_1, \ldots, \vec{d}_N)$, atomic positions
  - $\vec{g} = -(\vec{f}_1, \ldots, \vec{f}_N)$, Hellmann-Feynman forces on atoms

- With variable cell:
  - $\vec{X} = (\vec{d}_1, \ldots, \vec{d}_N, \epsilon_{\alpha\beta})$, atomic positions and cell strains
  - $\vec{g} = -(\vec{f}_1, \ldots, \vec{f}_N, \sigma_{\alpha\beta})$, Hellmann-Feynman forces on atoms and stresses

Some important aspects of structural optimization

- Structural optimization may find only the closest minimum: it cannot overcome potential barriers, so it may be trapped into a local minimum.

- Structural optimization *does not break crystal symmetry*, at least in principle (numerical noise may occasionally break the symetry).

- In variable-cell optimization, the PW basis set is kept fixed during optimization. This means that the final result is not exactly equal to what one gets by starting the calculation from scratch with the same cutoff, because the two basis sets are not exactly the same.

- Structural optimization uses both energies and forces to locate the minima along search directions. Discrepancies between those values, due to insufficient scf convergence, will lead to bad convergence of the BFGS algorithm or even to errors. Remember that the error on forces is *linear* in the self-consistency error, while the error on energies is *quadratic* due to its variational character.

Born-Oppenheimer Molecular Dynamics

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

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

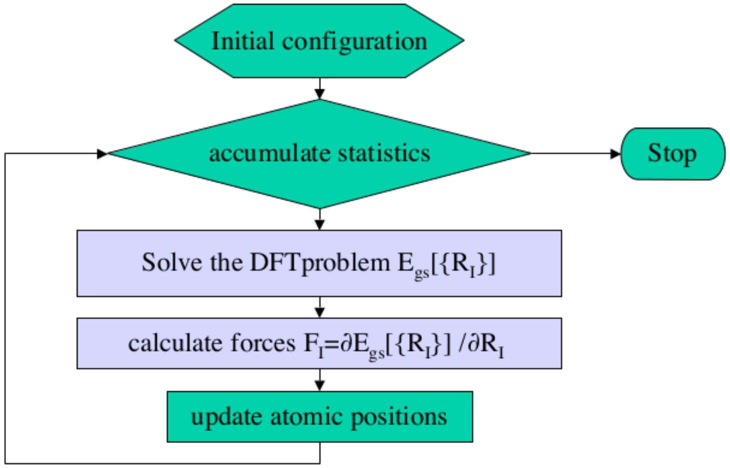
describing the motion of nuclei. The equations of motion:

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

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 DFTproblem $E_{gs}[\{R_I\}]$

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*:

$$\begin{aligned} \mathbf{R}_\mu(t+\delta t) &= 2\mathbf{R}_\mu(t) - \mathbf{R}_\mu(t-\delta t) + \frac{\delta t^2}{M_\mu}\mathbf{F}_\mu(t) + \mathcal{O}(\delta t^4) \\ \mathbf{V}_\mu(t) &= \frac{1}{2\delta t}\left[\mathbf{R}_\mu(t+\delta t) - \mathbf{R}_\mu(t-\delta t)\right] + \mathcal{O}(\delta t^3). \end{aligned}$$

or the *Velocity Verlet*:

$$\begin{aligned} \mathbf{V}_\mu(t+\delta t) &= \mathbf{V}_\mu(t) + \frac{\delta t}{2M_\mu}\left[\mathbf{F}_\mu(t) + \mathbf{F}_\mu(t+\delta t)\right] \\ \mathbf{R}_\mu(t+\delta t) &= \mathbf{R}_\mu(t) + \delta t\mathbf{V}_\mu(t) + \frac{\delta t^2}{2M_\mu}\mathbf{F}_\mu(t). \end{aligned}$$

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

More kinds of molecular dynamics

- By adding a damping term, *damped dynamics* may be used as an alternative to BFGS for energy minimization. Usually BFGS is faster, but damped dynamics allows to easily implement constraints via the SHAKE technique

- With appropriate thermostats, molecular dynamics samples the *canonical ensemble* (NVT): the average temperature

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

  is fixed (while the instantaneous value may oscillate around the desired value)

- *Variable-cell* molecular dynamics samples the NPT ensemble, i.e., at fixed average pressure (and temperature).

A variety of molecular dynamics algorithms and of thermostats are available in Quantum ESPRESSO.

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

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:

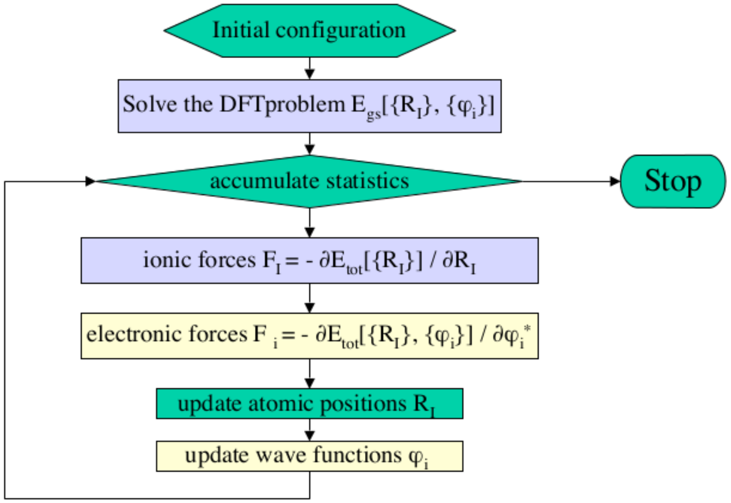
$$L = \frac{m^*}{2} \sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2} \sum_\mu M_\mu \dot{\mathbf{R}}_\mu^2 - E[\mathbf{R}, \psi] + \sum_{i,j} \Lambda_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} - \delta_{ij} \right)$$

generates equations of motion:

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

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

CPMD Car-Parrinello Molecular Dynamics



Initial configuration
Solve the DFTproblem $E_{gs}[\{R_I\}, \{\varphi_i\}]$
accumulate statistics
Stop
ionic forces $F_I = - \partial E_{tot}[\{R_I\}] / \partial R_I$
electronic forces $F_i = - \partial E_{tot}[\{R_I\}, \{\varphi_i\}] / \partial \varphi_i^*$
update atomic positions R_I
update wave functions φ_i

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