

Energy and Forces in DFT

Total Energy as a function of nuclear positions $\{\mathbf{R}\}$

$$E_{tot}(\{\mathbf{R}\}) = E_{DFT}(\{\mathbf{R}\}) + E_{II}(\{\mathbf{R}\}) \quad (1)$$

where $E_{DFT}(\{\mathbf{R}\}) =$ DFT energy calculated for the ground-state density charge-density $n(\mathbf{r})$

Hellmann-Feynman forces:

$$\mathbf{F}_i = -\frac{dE}{d\mathbf{R}_i} = -\int n(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \mathbf{R}_i} d\mathbf{r} - \frac{\partial E_{II}}{\partial \mathbf{R}_i} \quad (2)$$

where $V\{\mathbf{R}\} =$ external potential acting on electrons

DFT and Molecular Dynamics

Let us assume i) classical nuclei, ii) electrons in the ground state. We can introduce a classical Lagrangian:

$$L = \frac{1}{2} \sum_i M_i \dot{\mathbf{R}}_i^2 - E_{tot}(\{\mathbf{R}\}) \quad (3)$$

describing the motion of nuclei. Equations of motion:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{R}}_i} - \frac{\partial L}{\partial \mathbf{R}_i} = 0, \quad \mathbf{P}_i = \frac{\partial L}{\partial \dot{\mathbf{R}}_i} \quad (4)$$

are nothing but usual Newton's equations:

$$\mathbf{P}_i \equiv M_i \mathbf{V}_i, \quad M_i \dot{\mathbf{V}}_i = \mathbf{F}_i \quad (5)$$

Discretization of the equation of motion

Verlet algorithm:

$$\mathbf{R}_i(t + \delta t) = 2\mathbf{R}_i(t) - \mathbf{R}_i(t - \delta t) + \frac{\delta t^2}{M_i} \mathbf{F}_i(t) + \mathcal{O}(\delta t^4) \quad (6)$$

$$\mathbf{V}_i(t) = \frac{1}{2\delta t} [\mathbf{R}_i(t + \delta t) - \mathbf{R}_i(t - \delta t)] + \mathcal{O}(\delta t^3). \quad (7)$$

Velocity Verlet:

$$\mathbf{V}_i(t + \delta t) = \mathbf{V}_i(t) + \frac{\delta t}{2M_i} [\mathbf{F}_i(t) + \mathbf{F}_i(t + \delta t)] \quad (8)$$

$$\mathbf{R}_i(t + \delta t) = \mathbf{R}_i(t) + \delta t \mathbf{V}_i(t) + \frac{\delta t^2}{2M_i} \mathbf{F}_i(t). \quad (9)$$

Both sample the *microcanonical ensemble*, or NVE: the energy is conserved.

Thermodynamical averages

Averages ($\rho =$ probability of a microscopic state):

$$\langle A \rangle = \int \rho(\mathbf{R}, \mathbf{P}) A(\mathbf{R}, \mathbf{P}) d\mathbf{R} d\mathbf{P} \quad (10)$$

are usually well approximated by averages over time:

$$\lim_{T \rightarrow \infty} A_T \rightarrow \langle A \rangle \quad (11)$$

and the latter by discrete average over a trajectory:

$$A_T = \frac{1}{T} \int_0^T A(\mathbf{R}(t), \mathbf{P}(t)) dt \simeq \frac{1}{M} \sum_{n=1}^M A(t_n), \quad t_n = n\delta t, \quad t_M = M\delta t = T. \quad (12)$$

Constant-Temperature and constant-pressure dynamics

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

$$\left\langle \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} \right\rangle_{NVT} = \frac{3}{2} N k_B T \quad (13)$$

is fixed

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

In both cases, additional (fictitious) degrees of freedom are considered

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 mode.
- calculations of forces must be very accurate at each time step (good self-consistency needed) or else a systematic energy drift will appear

Note that:

- error for DFT energy is *quadratic* in the SCF error of the charge density
- error for DFT forces is *linear* in the SCF error of the charge density

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

Very simple and effective! All classical MD technology can be used
Requires a judicious choice of simulation parameters

Car-Parrinello Lagrangian

$$L = \frac{\mu}{2} \sum_k \int d\mathbf{r} |\dot{\psi}_k(\mathbf{r})|^2 + \frac{1}{2} \sum_i M_i \dot{\mathbf{R}}_i^2 - E_{tot}(\{\mathbf{R}\}, \{\psi\}) + \sum_{k,l} \Lambda_{kl} \left(\int \psi_k^*(\mathbf{r}) \psi_l(\mathbf{r}) d\mathbf{r} - \delta_{kl} \right) \quad (14)$$

generates equations of motion:

$$\mu \ddot{\psi}_k = H \psi_k - \sum_l \Lambda_{kl} \psi_l, \quad M_i \ddot{\mathbf{R}}_i = -\frac{\partial E_{tot}}{\partial \mathbf{R}_i} \quad (15)$$

μ = fictitious electronic mass

Λ_{kl} = Lagrange multipliers enforce orthonormality constraints.

Car-Parrinello Lagrangian (2)

- electronic degrees of freedom ψ_k are the expansion coefficients of KS orbitals into PW
- "forces" on electrons are determined by the KS Hamiltonian calculated from current values of ψ_k and of \mathbf{R}_i
- "forces" acting on nuclei have the Hellmann-Feynman form:

$$\frac{\partial E_{tot}}{\partial \mathbf{R}_i} = \sum_k \langle \psi_k | \frac{\partial V}{\partial \mathbf{R}_i} | \psi_k \rangle \quad (16)$$

but they slightly differ from "true" forces

Car-Parrinello technicalities

- Starting point: bring the electrons to the ground state at fixed ions
- The simulation is performed using classical MD technology (Verlet) on both nuclear positions and electronic degrees of freedom
- Orthonormality constraints are exactly imposed at each time step, using an iterative procedure
- The choice of parameters (fictitious electronic mass μ and time step δt) must ensure that there is no energy transfer from nuclei to electrons, i.e. the “kinetic energy” of the electronic degrees of freedom does not systematically increase

Choice of the parameters

The fictitious electronic mass μ and time step δt must be chosen in such a way that:

- μ is be big enough to enable the use of a reasonable time step, small enough to guarantee
 - *adiabaticity*, i.e. no energy transfer from nuclei to electrons, which always remain close to the ground state
 - *correctness* of the nuclear trajectory

Typical values: $\sim 100 \div 400$ electron masses

- δt should be the largest value that yields a stable dynamics (no drifts, no loss of orthonormality)

Why Car-Parrinello works

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

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

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

If $\omega_{max}^{ph} \ll \omega_{min}^{el}$ 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.

(Pastore, Smargiassi, Buda, PRA 44, 6334, 1991).