DFT total energy

\[
E[\{\psi_i\}] = \sum_{i=1}^{N} \left( \frac{1}{2} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \, d\mathbf{r} + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r} \right)
\]
**Evaluating Hψ**

![Diagram](image1)

**Figure 9.** Flow chart for the calculation of the local potential from the Kohn-Sham orbitals. This module calculates also the charge density in real and Fourier space and the exchange and correlation energy, Hartree energy, and local pseudopotential energy.
It’s really kinetic + (SCF) potential

\[ \hat{H} = -\frac{1}{2} \nabla^2 + V(r) \]

\[ \langle G \mid -\frac{1}{2} \nabla^2 \mid G' \rangle = \int dr \exp(-iGr) \left[ -\frac{1}{2} \nabla^2 \right] \exp(iG'r) = \frac{1}{2} G^2 \delta_{G,G'} \]

\[ \langle G \mid V(r) \mid G' \rangle = \int dr \exp(-iGr)V(r) \exp(iG'r) = V(G - G') \]

Total energy (non-SCF, sort of)

\[ E = \sum_n \varepsilon_n = \sum_n \langle \psi_n \mid \frac{1}{2} \nabla^2 + V \mid \psi_n \rangle \]

\[ \psi_n (\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^n \exp(i \vec{G} \cdot \vec{r}) \]

\[ E = \sum_n \left( \frac{1}{2} \sum_{\vec{G}} \left| c_{\vec{G}}^n \right|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{n*} c_{\vec{G}'}^n V(\vec{G} - \vec{G}') \right) \]
Dynamical evolution of c’s

We need the “force”

\[
E = E[\{\psi_i\}] \quad \Rightarrow \quad F_i = -\frac{\delta E[\{\psi_i\}]}{\delta \psi_i} = -\hat{H}\psi_i
\]
Skiing down a valley

\[ \mu \dot{\psi}_i = F_i \left( = -H \psi \right)_i \]

\[ \dot{\psi}_i = F_i \left( = -H \psi_i \right) \]

FIG. 9. Schematic representation of the damping of wave-function coefficients \(| c \rangle \) and the evolution of the Kohn-Sham energy functional \( E [ | c \rangle ] \) to its ground-state value \( E_0 \).

“Damped” dynamics skiing

FIG. 11. Flow chart describing the computational procedure for the calculation of the total energy of a solid with molecular dynamics.
SD or CG skiing

**FIG. 14.** Schematic illustration of two methods of convergence to the center of an anisotropic harmonic potential. Top: steepest-descents method requires many steps to converge. Bottom: Conjugate-gradients method allows convergence in two steps.

Hellmann-Feynman theorem

\[ \vec{F}_i = -\frac{dE}{d\vec{R}_i} = -\frac{d\langle\Psi|\hat{H}|\Psi\rangle}{d\vec{R}_i} = \]

\[ = \langle\Psi| - \frac{d\hat{H}}{d\vec{R}_i}|\Psi\rangle = \langle\Psi| - \frac{d\hat{V}}{d\vec{R}_i}|\Psi\rangle \]
Born-Oppenheimer Molecular Dynamics

\[ m_i \ddot{R}_i = \vec{F}_i = \langle \Psi | - \frac{d\hat{V}}{d\vec{R}_i} | \Psi \rangle \]

Lots of Skiing if Atoms Move
Lots of Skiing if Atoms Move

The extended CP Lagrangian

\[ \mathcal{L}_{\text{CP}} = \sum_i \frac{1}{2} M_i \dot{R}_i^2 + \sum_i \frac{1}{2} \mu_i \langle \dot{\psi}_i, \dot{\psi}_i \rangle - \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle + \text{constraints} + \text{orthonormality} \]
Equations of motion

\[ \frac{d}{dt} \frac{\partial L}{\partial \dot{R}_I} = \frac{\partial L}{\partial R_I} \]
\[ \frac{d}{dt} \frac{\delta L}{\delta \dot{\psi}_i^*} = \frac{\delta L}{\delta \psi_i^*} \]

Equations of motion (II)

\[ M_I \ddot{R}_I(t) = -\frac{\partial}{\partial \dot{R}_I} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \frac{\partial}{\partial R_I} \{ \text{constraints} \} \]
\[ \mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^*} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^*} \{ \text{constraints} \} \]
Constant(s) of motion

\[ E_{\text{cons}} = \sum_i \frac{1}{2} \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle \]

\[ E_{\text{phys}} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle = E_{\text{cons}} - T_e \]

\[ V_e = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle \]

\[ T_e = \sum_i \frac{1}{2} \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle \]
Kolmogorov-Arnold-Moser invariant tori

Figure 2. Vibrational density of states Eq. (17) (continuous spectrum in upper part) and harmonic approximation thereof Eq. (12) (discrete spectrum in lower part) of the electronic degrees of freedom compared to the highest-frequency phonon mode \( w_0 \) (triangle) for a model system; for further details see text. Adapted from Ref. 167.

Various Energies
Nonconserving at 400K

Energy (Hartree)


Potential energy \( E_{\text{tot}} \)
\( E_{\text{tot}}+K_{\text{elec}}(\text{ions}) \)
\( E_{\text{tot}}+K_{\text{elec}}(\text{ions})+K_{\text{ph}}(\text{ps}) \)

time (ps)
FIG. 23. Schematic illustration of how an orbital will oscillate around a moving ion during a simulation with $\mu E = -(H - \lambda)\hbar$, as discussed in the text. Velocities and accelerations are depicted as open and filled arrows, respectively.

FIG. 24. Schematic illustration of how an orbital will eventually lag behind a moving ion during a simulation with $\mu E = -(H - \lambda)\hbar$, as discussed in the text. Convention the same as in Fig. 23.
HF vs CP forces

Figure 4. (a) Comparison of the x-component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well-converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. 407.

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Full class (videos, etc..)

Atomistic Modeling of Materials


Density Functional theory
Introduction

Richard M. Martin

Based upon

Cambridge University Press, 2004
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