DFT total energy

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^{\star}(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] +$$
$$+E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}$$

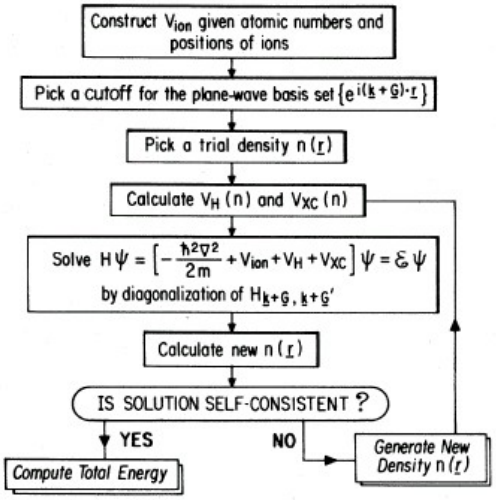


FIG. 7. Flow chart describing the computational procedure for the calculation of the total energy of a solid, using conventional matrix diagonalization.

Evaluating Hψ

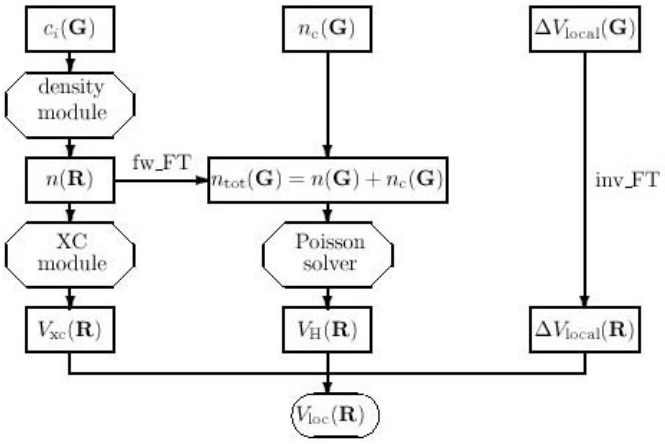


Figure 9. Flow chart for the calculation of the local potential from the Kohn–Sham orbitals. This module calculates also the charge density in real and Fourier space and the exchange and correlation energy, Hartree energy, and local pseudopotential energy.

It's really kinetic + (SCF) potential

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

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

$$\left\langle G\left|V(r)\right|G'\right\rangle = \int dr \exp(-iGr)V(r)\exp(iG'r) = V(G-G')$$

Total energy (non-SCF, sort of)

$$E = \sum\nolimits_n \varepsilon_n = \sum_n \left\langle \psi_n \left| -\frac{1}{2}\nabla^2 + V \right| \psi_n \right\rangle$$

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

$$E = \sum_n \left(\frac{1}{2}\sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{n*} c_{\vec{G}'}^n V(\vec{G}-\vec{G}') \right)$$

Dynamical evolution of c's

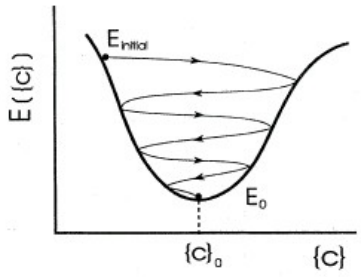


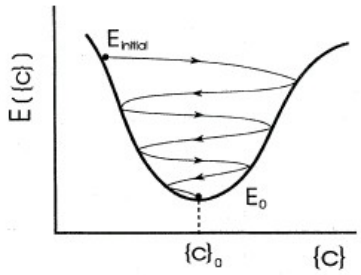
FIG. 9. Schematic representation of the damping of wave-function coefficients $\{c\}$ and the evolution of the Kohn-Sham energy functional $E[\{c\}]$ to its ground-state value E_0.

We need the "force"

$$E = E[\{\psi_i\}] \Longrightarrow F_i = -\frac{\delta E[\{\psi_i\}]}{\delta \psi_i}$$

$$= -\hat{H}\psi_i$$

Skiing down a valley



$$\mu\ddot{\psi}_i = F_i(=-H\psi)_i$$

$$\dot{\psi}_i = F_i(=-H\psi_i)$$

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

"Damped" dynamics skiing

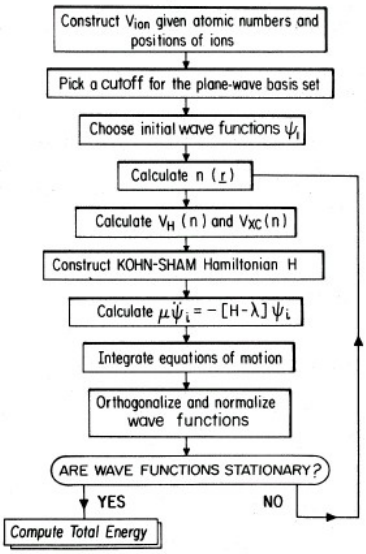


FIG. 11. Flow chart describing the computational procedure for the calculation of the total energy of a solid with molecular dynamics.

SD or CG skiing

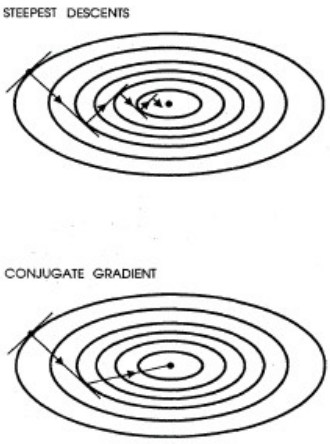


FIG. 14. Schematic illustration of two methods of convergence to the center of an anisotropic harmonic potential. Top: steepest-descents method requires many steps to converge. Bottom: Conjugate-gradients method allows convergence in two steps.

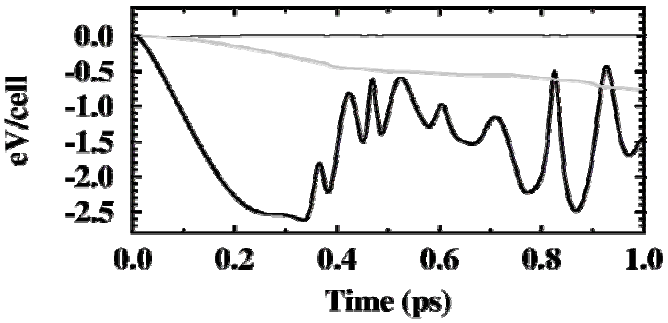
Hellmann-Feynman theorem

$$\vec{F}_i = -\frac{dE}{d\vec{R}_i} = -\frac{d\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle}{d\vec{R}_i} =$$

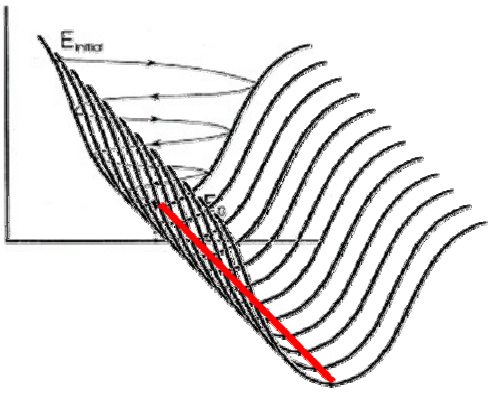
$$= \left\langle \Psi \middle| -\frac{d\hat{H}}{d\vec{R}_i} \middle| \Psi \right\rangle = \left\langle \Psi \middle| -\frac{d\hat{V}}{d\vec{R}_i} \middle| \Psi \right\rangle$$

Born-Oppenheimer Molecular Dynamics

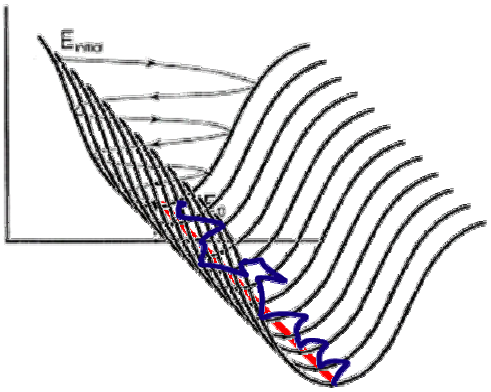
$$m_i \ddot{\vec{R}}_i = \vec{F}_i = \left\langle \Psi \left| -\frac{d\hat{V}}{d\vec{R}_i} \right| \Psi \right\rangle$$



Lots of Skiing if Atoms Move



Lots of Skiing if Atoms Move



The extended CP Lagrangian

$$\mathcal{L}_{\rm CP} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} - \underbrace{\langle \Psi_0 | \mathcal{H}_{\rm e} | \Psi_0 \rangle}_{\text{potential energy}} + \underbrace{\textit{constraints}}_{\text{orthonormality}}$$

Equations of motion

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt}\frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star}$$

Equations of motion (II)

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I}\langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle + \frac{\partial}{\partial \mathbf{R}_I}\{constraints\}$$

$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^\star}\langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^\star}\{constraints\}$$

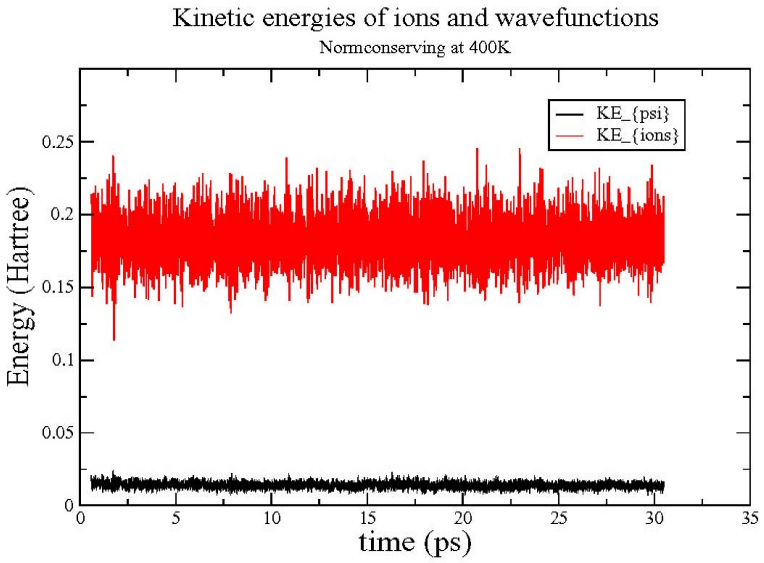
Constant(s) of motion

$$E_{cons} = \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle$$

$$E_{phys} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle = E_{cons} - T_e$$

$$V_e = \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle$$

$$T_e = \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle$$



Kolmogorov-Arnold-Moser invariant tori

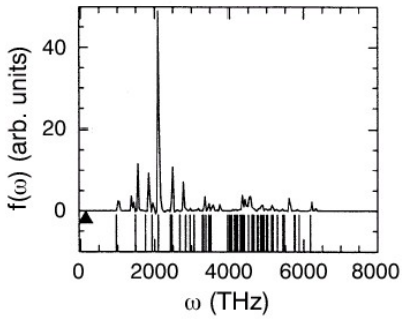
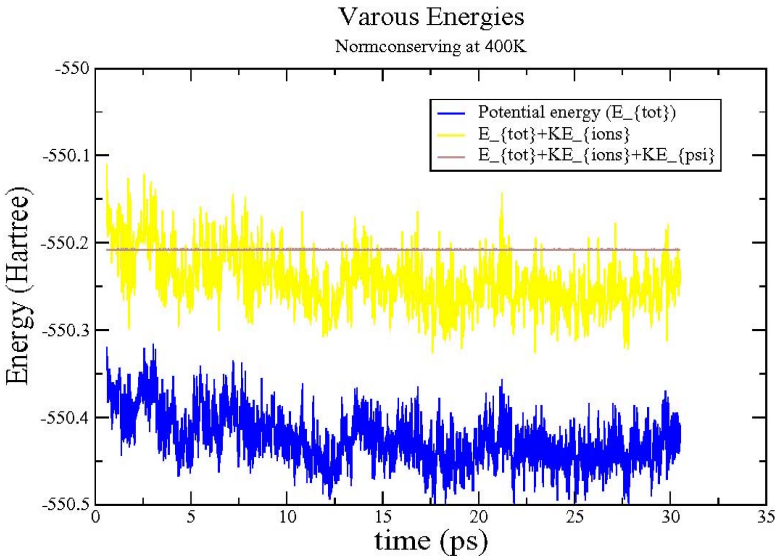
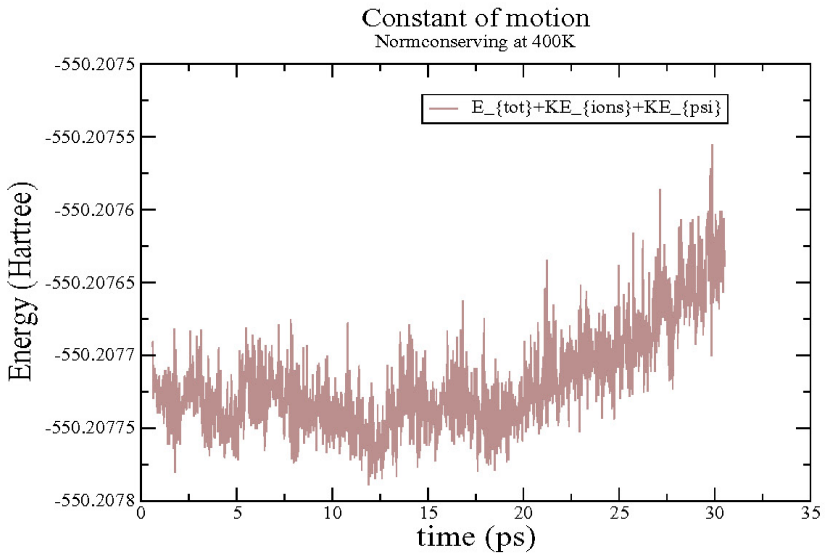


Figure 2. Vibrational density of states Eq. (47) (continuous spectrum in upper part) and harmonic approximation thereof Eq. (52) (stick spectrum in lower part) of the electronic degrees of freedom compared to the highest–frequency phonon mode ω_n^{max} (triangle) for a model system; for further details see text. Adapted from Ref. [467].





Born-Oppenheimer vs Car-Parrinello

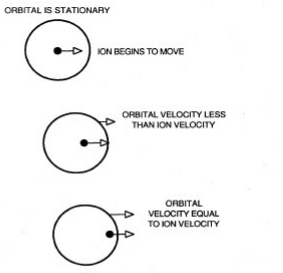


FIG. 24. Schematic illustration of how an orbital will eventually lag behind a moving ion during a simulation with $\mu\ddot{\psi} = -[H - \lambda]\psi$, as discussed in the text. Convention the same as in Fig. 23.

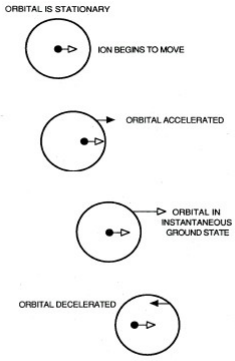


FIG. 23. Schematic illustration of how an orbital will oscillate around a moving ion during a simulation with $\mu\ddot{\psi} = -[H - \lambda]\psi$, as discussed in the text. Velocities and accelerations are designed as open and filled arrows, respectively.

HF vs CP forces

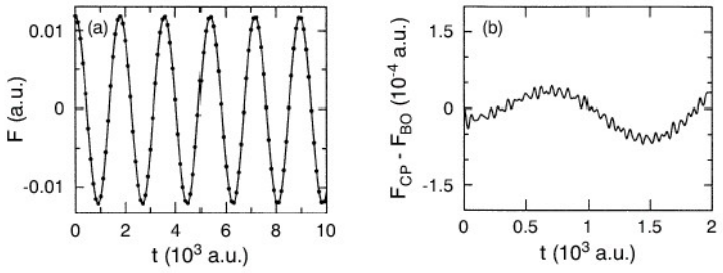


Figure 4. (a) Comparison of the x–component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well–converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. [467].

Quantum MD Bibliography

- Payne, Teter, Allan, Arias, Joannopoulos, *Rev Mod Physics* 64, 1045 (1992).
- Marx, Hutter, "Ab Initio Molecular Dynamics: Theory and Implementation", in "Modern Methods and Algorithms of Quantum Chemistry" (p. 301-449), Editor: J. Grotendorst, (NIC, FZ Jülich 2000)
- http://www.theochem.ruhr-uni-bochum.de/research/marx/cprev.en.html

Full class (videos, etc..)

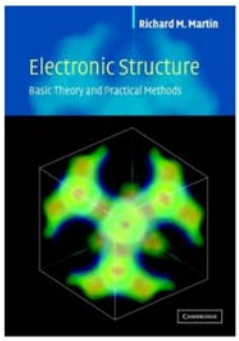
Atomistic Modeling of Materials

http://ocw.mit.edu/OcwWeb/Materials-Science-and-Engineering/3-320Spring-2005/CourseHome/index.htm

Density Functional theory Introduction

Richard M. Martin

Based upon



Cambridge University Press, 2004

ElectronicStructure.org

Resources for Electronic Structure

- Research Groups
- Research Centers
- Software
- Book Website
- Figures & images

MCC

- Schools
- Events calendar
- Career Opportunities
- Software

Thanks !

- Amy Young
- Paolo Giannozzi and the www.quantum-espresso.org gang
- Todd Martinez, Richard Martin, Duane Johnson, David Ceperley
- Axel Kohlmeyer, Stefano Baroni, Guido Fratesi