

Introduction to Car-Parrinello *Ab Initio* MD

Basic Concepts

It is more important than ever to study molecular scale physics:

- Understanding molecular scale devices will lead to faster, cheaper FETs.
- Understanding enzyme catalysis will allow the design of cheap, artificial catalysts (biomimetics) of high efficiency
- Understanding properties of novel materials such as ceramics will yield new materials with higher resistance to breakdown, fatigue and temperature.

Basic Concepts

How can one model molecular scale properties:

- Continuum models yield mesoscale physics.
- Finite elements models treat nanoscale physics.
- Atomistic models with empirical force laws cannot treat bond-forming or breaking, extreme conditions or give insight into electronic properties.
- *Ab Initio* (treating the electrons explicitly) Calculations?

Basic Concepts

How can *Ab Initio* methods address our needs:

- Standard *ab initio* calculations are done at zero T.
- Reactions treated by finding a minimum energy path.
- Helpful sometimes not others.

Basic Concepts

Car-Parrinello *Ab Initio* MD:

- Combine *ab initio* methods with Molecular Dynamics.
- Study bond forming and breaking on free energy surfaces.
- Study materials under high stress, high temperatures ...

Electronic Structure : Kohn-Sham DFT

The electron density is expanded in a set of orbitals $\{\psi_i(\mathbf{r})\}$

$$n(\mathbf{r}) = \sum_{i=1}^n o_i |\psi_i(\mathbf{r})|^2$$

and the energy functional is given by

$$E[n] = T_s[\{\psi_i\}] + E_H[n] + E_{xc}[n] + E_{\text{ext}}[n]$$

where T_s is the kinetic energy of a system of noninteracting electrons, E_H is the Hartree energy, E_{xc} is the exchange and correlation energy and the o_i are the occupation numbers of the orbitals. Here, $E_{\text{ext}}[n]$ is the electron-nuclear interaction.

Combining with Molecular Dynamics

Treat the nuclei classically

$$\begin{aligned} H(\mathbf{P}, \mathbf{R}) &= \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_0(\mathbf{R}) \\ &= T_{class}(\mathbf{P}) + V_{BO}(\mathbf{R}) \end{aligned}$$

where $E_0(\mathbf{R})$ is the energy obtained when $E[n]$ is functionally minimized and $V_{BO}(\mathbf{R})$ is the ground state Born-Oppenheimer surface.

Integrate numerically Hamilton's Equations of motion

$$\begin{aligned} \dot{\mathbf{R}}_i &= \frac{\mathbf{P}_i}{M_i} \\ \dot{\mathbf{P}}_i &= \mathbf{F}_{BO}(\mathbf{R}) = -\nabla_I V_{BO}(\mathbf{R}) \end{aligned}$$

We will see later how to perform a combined MD for both the electronic structure and particles.

Electronic Structure : Kohn-Sham DFT

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$$E[n] = T_s[\{\psi_i\}] + E_H[n] + E_{xc}[n] + E_{\text{ext}}[n]$$

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Kohn-Sham DFT

The orbitals and the electron density can be expanded in a plane wave basis set

$$\begin{aligned}
 \psi_j(\mathbf{r}) &= \frac{1}{\sqrt{V}} \sum_{\hat{\mathbf{g}}} \bar{\psi}_j(\mathbf{g}) \exp(i\mathbf{g} \cdot \mathbf{r}) \\
 n(\mathbf{r}) &= \frac{1}{V} \sum_{\hat{\mathbf{g}}} \bar{n}(\mathbf{g}) \exp(i\mathbf{g} \cdot \mathbf{r}) \\
 \bar{n}(\mathbf{g}) &= \int_{D(\hat{\mathbf{h}})} d\mathbf{r} \exp[-i\mathbf{g} \cdot \mathbf{r}] n(\mathbf{r}) \\
 &= V \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} ds_a ds_b ds_c \exp(i2\pi\hat{\mathbf{g}} \cdot \mathbf{s}) n(\mathbf{h}\mathbf{s})
 \end{aligned}$$

Here

- \mathbf{h} is the parallelepiped surrounding the system, $V = \det \mathbf{h}$ is the volume of the cell and \mathbf{s} are the fractional coordinates.
- $\mathbf{g} = \mathbf{h}_s^{\leftrightarrow -1} \hat{\mathbf{g}}$, and the integers $\hat{\mathbf{g}} = \{g_a, g_b, g_c\}$, index the reciprocal space.
- The plane-wave cutoff is $E_{cut} \geq \hbar^2 |\mathbf{g}|^2 / 2m$ with $E_{cut}^{(density)} = 4E_{cut}$.

Kohn-Sham DFT

Two terms act at long range, Hartree, $E_{\text{Hartree}}[n]$

$$E_{\text{H}}[n] = \frac{e^2}{2} \sum_{\hat{\mathbf{S}}} \int_{D(\vec{\mathbf{h}})} d\mathbf{r} \int_{D(\vec{\mathbf{h}})} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}' + \mathbf{h}\hat{\mathbf{S}}|}$$

and the local pseudopotential energy, $E_{\text{loc}}[n]$,

$$E_{\text{loc}}[n] = \sum_{\hat{\mathbf{S}}} \sum_{I=1}^N \int_{D(\vec{\mathbf{h}})} d\mathbf{r} \phi_{\text{loc},I}(\mathbf{r} - \mathbf{R}_I + \mathbf{h}\hat{\mathbf{S}})n(\mathbf{r})$$

Here,

- \mathbf{R}_I is the Cartesian position of the I th ion,
- \mathbf{h} is the cell matrix whose columns contain the d cell vectors, $\det \mathbf{h} = V$ is the volume.
- $\hat{\mathbf{S}} = \{\hat{s}_a, \hat{s}_b, \hat{s}_c\}$ is a vector of integers indexing the periodic replicas
- In clusters, only $\hat{\mathbf{S}} = \{0, 0, 0\}$ is allowed while in solids/liquids the three integers span the full range.

Plane Wave Basis : Standard

When employing a plane wave basis set, these terms are evaluated in reciprocal space.

$$\begin{aligned}
 E_{\text{H}} &= \frac{e^2}{2V} \sum'_{\hat{\mathbf{g}}} |\bar{n}(\mathbf{g})|^2 \left[\frac{4\pi}{g^2} + \hat{\phi}^{(\text{screen,Coul})}(\mathbf{g}) \right] \\
 &\quad + \left(\frac{e^2}{2V} \right) \hat{\phi}^{(\text{screen,Coul})}(0) |\bar{n}(0)|^2 \\
 E_{\text{loc}} &= \frac{1}{V} \sum'_{\hat{\mathbf{g}}} \sum_{I=1}^N \bar{n}^*(\mathbf{g}) \exp(-i\mathbf{g} \cdot \mathbf{R}_I) \left[\tilde{\phi}_{\text{loc},I}(\mathbf{g}) - eq_I \hat{\phi}^{(\text{screen,Coul})}(\mathbf{g}) \right] \\
 &\quad + \frac{1}{V} \sum_{I=1}^N \bar{n}(0) \left[\tilde{\phi}_{\text{loc},I}^{(0)} - eq_I \hat{\phi}^{(\text{screen,Coul})}(0) \right].
 \end{aligned}$$

Here,

- $\tilde{\phi}_{\text{loc},I}$ is the Fourier Transform of the local pseudopotential
- $\tilde{\phi}_{\text{loc},I}^{(0)}$ is the non-singular part of the local pseudopotential at $\mathbf{g} = 0$.
- The screening function, $\hat{\phi}^{(\text{screen,Coul})}(\mathbf{g})$, allows the formalism to treat cluster, wires, surfaces and solids/liquids.

Plane Wave Basis : Standard

The kinetic energy is also evaluated in reciprocal space:

$$T_s[n] = \frac{\hbar^2}{2m} \sum_j o_j \sum_{\mathbf{g}} |\bar{\psi}_j(\mathbf{g})|^2 |\mathbf{g}|^2$$

The exchange correlation energy is evaluated in real space:

$$E_{xc}[n] = V \sum_{\hat{s}_a} \sum_{\hat{s}_b} \sum_{\hat{s}_c} n(\mathbf{h}\mathbf{s}) \epsilon_{xc}(n(\mathbf{h}\mathbf{s}))$$

Basic Kernels

Consider a function, $\psi(\mathbf{r})$, expressed in finite plane basis set,

$$\psi(\mathbf{r}) \equiv \frac{1}{V} \sum_{\hat{g}_a=-P_a/2+1}^{P_a/2} \sum_{\hat{g}_b=-P_b/2+1}^{P_b/2} \sum_{\hat{g}_c=-P_c/2+1}^{P_c/2} \exp(i\mathbf{g} \cdot \mathbf{r}) \bar{\psi}(\mathbf{g}),$$

where

$$\bar{\psi}(\mathbf{g}) = \int_{D(\vec{\mathbf{h}})} d\mathbf{r} \exp[-i\mathbf{g} \cdot \mathbf{r}] \psi(\mathbf{r})$$

The Fourier coefficients can also be determined (exactly) from a discrete sum over a real space grid

$$\bar{\psi}(\mathbf{g}) \equiv \frac{V}{P_a P_b P_c} \sum_{\hat{s}_a=0}^{P_a-1} \sum_{\hat{s}_b}^{P_b-1} \sum_{\hat{s}_c=0}^{P_c-1} e^{-2\pi i \hat{g}_a \hat{s}_a / P_a} e^{-2\pi i \hat{g}_b \hat{s}_b / P_b} e^{-2\pi i \hat{g}_c \hat{s}_c / P_c} \psi(\mathbf{h}\mathbf{s})$$

Here, P_a , P_b , and P_c are both the number of reciprocal lattice points along each direction and the number of points discretizing the \mathbf{a} , \mathbf{b} , \mathbf{c} axes of the cell, while $s_\alpha = \hat{s}_\alpha / P_\alpha$. Importantly, these discrete equations can be evaluated using a three dimensional Fast Fourier Transforms (3D-FFT)

Basic Kernels

The Energy is evaluated as follows:

1. For each state, 3D-FFT $\bar{\psi}_k(\mathbf{g})$ to produce $\psi_k(\mathbf{r})$. Square $|\psi_k(\mathbf{r})|^2$ and add to produce the density $n(\mathbf{r})$
2. Inverse 3D-FFT $n(\mathbf{r})$ to produce $\bar{n}(\mathbf{g})$.
3. Evaluate External potential and Hartree using $\bar{n}(\mathbf{g})$ and accumulate $v_{ks}(\mathbf{g})$
4. 3D-FFT $v_{ks}(\mathbf{g})$ to produce $v_{ks}(\mathbf{r})$.
5. Evaluate Exchange correlation using $n(\mathbf{r})$ and accumulate $v_{ks}(\mathbf{r})$

Forces on the coefficients need to be evaluate in order to minumimize E. For each state,

1. 3D-FFT $\bar{\psi}_k(\mathbf{g})$ to produce $\psi_k(\mathbf{r})$.
2. Multiply $\psi_k(\mathbf{r})v_{ks}(\mathbf{r})$
3. Inverse 3D-FFT to produce $F_{\psi_k}(\mathbf{g})$.

Basic Kernels

The states $\bar{\psi}_k(\mathbf{r})$ must be kept orthonormal.

$$\begin{aligned} O_{ij} &= \int_{D(\vec{\mathbf{h}})} d\mathbf{r} \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij} \\ &= \sum_{\mathbf{g}} \bar{\psi}_j^*(\mathbf{g}) \bar{\psi}_i(\mathbf{g}) = \delta_{ij} \end{aligned}$$

Evaluating the overlap matrix involves a matrix square
(Nstate x ncoef)*(ncoef x Nstate)= Nstate x Nstate.

Combining BO-MD with Coefficient MD

It is natural to consider running MD to evolve both the coefficients, \mathbf{c} of a general basis set describing all the orbitals and the particles simulataneously.

We can write

$$H(\mathbf{P}, \mathbf{P}_c, \mathbf{R}, \mathbf{c}) = \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_0(\mathbf{R}, \mathbf{c}) + \frac{\mathbf{P}_c^2}{2m_c}$$

Here, $E_0(\mathbf{R}, \mathbf{c})$ is the current energy obtained from $E[n]$. The evolution must be performed subject to the set of holonomic constraints such that the KS-orbitals are orthonormal. More formally we should have introduced the Lagrangian but for simplicity of the analysis this is omitted.

Integrate numerically the equations of motion

$$\begin{aligned} \dot{\mathbf{R}}_i &= \frac{\mathbf{P}_i}{M_i} \\ \dot{\mathbf{P}}_i &= \mathbf{F}(\mathbf{R}, \mathbf{c}) \\ \dot{\mathbf{c}} &= \frac{\mathbf{P}_c}{m_c} \\ \dot{\mathbf{P}}_c &= \mathbf{F}_c(\mathbf{R}, \mathbf{c}) - \lambda \sigma \end{aligned}$$

where σ represents the $N^*(N+1)/2$ constraints and λ the $N^*(N+1)/2$ associated Lagrange multipliers. The Shake/Rattle method allows

velocity Verlet to be used to evolve systems with holonomic constraints. Thus it is straightforward to perform the evolution numerically.

Car-Parrinello MD : Why does it work?

Clearly, the evolution must generate an approximate BO surface. Thus, we can imagine keeping the coefficients cold and moving rapidly compared to the nuclear motion so that the functional is approximately minimized. One way to accomplish this is to introduce a set of Nose'-Hoover chain thermostats to keep the coefficients cold, a small mass, m_c to keep the coefficients moving rapidly and a set of thermostats to keep the particles warm.

Can the intuitive scheme be analyzed?

Car-Parrinello MD : Why does it work? : A simple model

Two sets of thermostats are invoked. One is coupled to fast (\mathbf{x}) degrees of freedom and assigned inverse temperature β_x and the second is coupled to the slow (\mathbf{y}) degrees of freedom and assigned inverse temperature β_y . The system is subject to a potential $V(\mathbf{x}, \mathbf{y})$.

The dynamics of the resulting system of equations can be analyzed using a decomposition of the evolution operator

$$\exp(iLt) = \left[\exp\left([iL - iL_{ref}] \frac{\Delta t}{2}\right) \exp(iL_{ref}\Delta t) \exp\left([iL - iL_{ref}] \frac{\Delta t}{2}\right) \right]^P + \mathcal{O}\left(\frac{t^3}{P^2}\right)$$

where

$$\begin{aligned} iL &= \mathbf{v}_x \cdot \nabla_x + \frac{\mathbf{F}_x(\mathbf{x}, \mathbf{y})}{m_x} \cdot \nabla_{\mathbf{v}_x} - v_{\eta(1,x)} \mathbf{v} \cdot \nabla_{\mathbf{v}_x} + iL_{NHC}^x \\ &+ \frac{\mathbf{F}_y(\mathbf{x}, \mathbf{y})}{m_y} \cdot \nabla_{\mathbf{v}_x} + iL_{ref} \\ iL_{ref} &= \mathbf{v}_y \cdot \nabla_y - v_{\eta(1,y)} \mathbf{v} \cdot \nabla_{\mathbf{v}_y} + iL_{NHC}^y \end{aligned}$$

Car-Parrinello MD : Why does it work?

The approximate solution to the equations of motion for the \mathbf{y} subsystem determined from the action of the short-time evolution operator

$$\exp\left([iL - iL_{ref}] \frac{\Delta t}{2}\right) \exp(iL_{ref}\Delta t) \exp\left([iL - iL_{ref}] \frac{\Delta t}{2}\right)$$

is

$$\begin{aligned} \mathbf{y}(\Delta t) &= \mathbf{y}_{ref} [\mathbf{y}(0), \mathbf{v}_y(\Delta t/2), \mathbf{v}_{\eta_y}(0); \Delta t] \\ \mathbf{v}_y(\Delta t) &= \mathbf{v}_{y_{ref}} [\mathbf{y}(0), \mathbf{v}_y(\Delta t/2), \mathbf{v}_{\eta_y}(0); \Delta t] \\ &\quad + \frac{1}{m_y} \int_0^{\Delta t/2} dt' \mathbf{F}_y \{ \mathbf{x}_{adb}[\mathbf{x}(\Delta t/2), \mathbf{v}_x(\Delta t/2), \mathbf{v}_{\eta_x}(\Delta t/2); \mathbf{y}(\Delta t); t'], \mathbf{y}(\Delta t) \} \end{aligned}$$

where

$$\mathbf{v}_y(\Delta t/2) = \mathbf{v}_y(0) + \frac{1}{m_y} \int_0^{\Delta t/2} dt' \mathbf{F}_y \{ \mathbf{x}_{adb}[\mathbf{x}(0), \mathbf{v}_x(0), \mathbf{v}_{\eta_x}(0); \mathbf{y}(0); t'], \mathbf{y}(0) \}$$

The functions $\mathbf{x}_{adb}[\mathbf{x}', \mathbf{v}'_x, \mathbf{v}'_{\eta_x}; \mathbf{y}; t]$ and $\mathbf{v}_{x_{adb}}[\mathbf{x}', \mathbf{v}'_x, \mathbf{v}'_{\eta_x}; \mathbf{y}; t]$ denote the positions and velocities at time, t , determined from the Nosé-Hoover chain dynamics of the \mathbf{x} subsystem with potential energy $V(\mathbf{x}, \mathbf{y})$ at fixed \mathbf{y} and initial condition $\{\mathbf{x}', \mathbf{v}'_x, \mathbf{v}'_{\eta_x}\}$. Similarly, the functions $\mathbf{y}_{ref}[\mathbf{y}', \mathbf{v}'_y, \mathbf{v}'_{\eta_y}; t]$ and $\mathbf{v}_{y_{ref}}[\mathbf{y}', \mathbf{v}'_y, \mathbf{v}'_{\eta_y}; t]$ denote the positions and velocities at time, t , determined from the action of the reference evolution operator, $\exp(iL_{ref})$, on the \mathbf{y} subsystem with initial condition, $\{\mathbf{y}', \mathbf{v}'_y, \mathbf{v}'_{\eta_y}\}$.

Car-Parrinello MD : Why does it work?

If the time average is taken equal to the phase space average then the equations of motion of the \mathbf{y} subsystem become

$$\begin{aligned} \mathbf{y}(\Delta t) &= \mathbf{y}_{ref} \left[\mathbf{y}(0), \mathbf{v}_y(0) - \frac{\Delta t}{2\beta_x m_y} \nabla_y \log[Q_x(\beta_x, \mathbf{y}(0))], \mathbf{v}_{\eta_y}(0); \Delta t \right] \\ \mathbf{v}_y(\Delta t) &= \mathbf{v}_{y_{ref}} \left[\mathbf{y}(0), \mathbf{v}_y(0) - \frac{\Delta t}{2\beta_x m_y} \nabla_y \log[Q_x(\beta_x, \mathbf{y}(0))], \mathbf{v}_{\eta_y}(0); \Delta t \right] \\ &\quad - \frac{\Delta t}{2\beta_x m_y} \nabla_y \log[Q_x(\beta_x, \mathbf{y}(\Delta t))] \end{aligned}$$

where $Q_x(\beta_x, \mathbf{y})$ is the canonical partition function for the \mathbf{x} subsystem at temperature β_x and potential $V(\mathbf{x}, \mathbf{y})$ with \mathbf{y} fixed.

Car-Parrinello MD : Why does it work?

The form of the $\mathbf{x}(\Delta t)$ and $\mathbf{y}(\Delta t)$ under canonical dynamics allows straightforward formal simplification.

$$\exp(i\bar{L}\Delta t) \sim \exp\left(\frac{\Delta t \bar{\mathbf{F}}}{2m_y} \cdot \nabla_{\mathbf{v}_y}\right) \exp\left(\left[i\bar{L} - \frac{\bar{\mathbf{F}}}{m_y} \cdot \nabla_{\mathbf{v}_y}\right] \Delta t\right) \exp\left(\frac{\Delta t \bar{\mathbf{F}}}{2m_y} \cdot \nabla_{\mathbf{v}_y}\right)$$

where

$$\begin{aligned} i\bar{L} &= \mathbf{v}_y \cdot \nabla_y - v_{\eta(1,y)} \mathbf{v} \cdot \nabla_{\mathbf{v}_y} + \frac{\bar{\mathbf{F}}(\mathbf{y})}{m_y} \cdot \nabla_{\mathbf{v}_y} + iL_{NHC}^y \\ \bar{\mathbf{F}}(\mathbf{y}) &= -\nabla_y \bar{V}(\mathbf{y}) \\ \bar{V}(\mathbf{y}) &= \frac{1}{\beta_x} \log[Q_x(\beta_x, \mathbf{y})]. \end{aligned}$$

In the limit $\Delta t \rightarrow 0$ and the masses $\{m_x, Q_x\}$ are chosen to vanish such that the time averages over the \mathbf{x} dynamics can be taken equal to their corresponding phase space average as Δt goes to zero, the approximate evolution operator, Eq.(6), can be resummed to give

$$\exp\left(\frac{\Delta t \bar{\mathbf{F}}}{2m_y} \nabla_{\mathbf{v}_y}\right) \exp\left(\left[i\bar{L} - \frac{\bar{\mathbf{F}}}{m_y} \nabla_{\mathbf{v}_y}\right] \Delta t\right) \exp\left(\frac{\Delta t \bar{\mathbf{F}}}{2m_y} \nabla_{\mathbf{v}_y}\right) = \exp(i\bar{L}\Delta t).$$

Car-Parrinello MD : Why does it work?

The dynamics of the \mathbf{y} degrees of freedom is Nosé-Hoover chain dynamics at inverse temperature, $1/\beta_y$, with potential, $\bar{V}(\mathbf{y})$ for all time, t . The limiting distribution of this dynamics is the canonical distribution (cf. Eq. 2.11) at inverse temperature, β_y .

The CP adiabatic dynamics scheme can be recovered from the preceding analysis. If β_x is taken to be large (low temperature) and $\beta_y = \beta$. then $\bar{V}(\mathbf{y}) = \min_x[V(\mathbf{x}, \mathbf{y})]$ and the thermal, slow \mathbf{y} degrees of freedom evolve on a potential energy surface that is instantaneously minimal with respect to the cold, fast \mathbf{x} .

However, if β_x is taken equal to β and β_y is taken to be large (cold), the free energy of the \mathbf{x} will be parametrically minimized with respect to the \mathbf{y} . This defines an inverse scheme. Note, that if $\beta_x = \beta_y = \beta$ then the time average of the \mathbf{y} dynamics will be distributed canonically regardless of time scale and the \mathbf{y} will move on the equilibrium free energy surface formed by the \mathbf{x} subsystem. However, if $\beta_x \neq \beta_y$, we have only been able to identify a traditional ensemble in the adiabatic limit.