Ab initio molecular dynamics: Basic Theory and Advanced Methods

Marialore Sulpizi

Uni Mainz

October 30, 2016
Multiscale modeling enables spanning range of time and length scales

- **1 s**
- **1 ms**
- **1 μs**
- **1 ns**
- **1 ps**

**Cell Signaling Network Models**

**Continuum Mechanics Monte Carlo (MC)**

**Coarse-Grained Molecular Dynamics (CGMD)**

**Molecular Dynamics (MD)**

**Quantum Mechanics (QM)**

**1 Å**  **1 nm**  **10 nm**  **100 nm**  **1 μm**  **10 μm**
Ab-initio MD simulations are used to learn how the active site of an enzyme of hydrogen-producing bacteria could be modified so that it remains stably active in an artificial production system. Courtesy of A. Selloni, Princeton.
Unifying molecular dynamics and electronic structure
  Route 1
  Route 2

Car-Parrinello molecular dynamics
  Car-Parrinello Lagrangian and equations of motion
  Thermostat on the electrons
  Analytic and numerical error estimates
  CP vs BO
Starting point: the non-relativistic Schrödinger equation for electron and nuclei.

\[ i\hbar \frac{\partial}{\partial t} \Phi(\{r_i\}, \{R_I\}; t) = H\Phi(\{r_i\}, \{R_I\}; t) \] (1)

where \( H \) is the standard Hamiltonian:

\[ H = -\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \] (2)

\[ + \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{l,i} \frac{e^2 Z_l}{|R_l - r_i|} + \frac{1}{4\pi\epsilon_0} \sum_{l<j} \frac{e^2 Z_l Z_j}{|R_l - R_j|} \] (3)

\[ = -\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{r_i\}, \{R_I\}) \] (4)

\[ = -\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + H_e(\{r_i\}, \{R_I\}) \] (5)
Route 1:
1) The electronic problem is solved in the *time-independent* Schröedinger eq.
2) from here the *adiabatic approximation* for the nuclei is derived, and as a special case the *Born-Oppenheimer dynamics*.
3) The classical limit leads then to the *classical molecular dynamics* for the nuclei.
Goal: derive the classical molecular dynamics. As intermediate two variant of \textit{ab initio} molecular dynamics are derived.

\begin{itemize}
  \item Solve the electronic part for fixed nuclei
  \end{itemize}

\begin{equation}
H_e(\{r_i\}, \{R_I\})\psi_k = E_k(\{R_I\})\psi_k(\{r_i\}, \{R_I\}) \tag{6}
\end{equation}

where $\psi_k(\{r_i\}, \{R_I\})$ are a set of orthonormal solutions, satisfying:

\begin{equation}
\int \psi_k^* (\{r_i\}, \{R_I\}) \psi_l (\{r_i\}, \{R_I\}) d\mathbf{r} = \delta_{kl} \tag{7}
\end{equation}

Knowing the \textit{adiabatic solutions} to the electronic problem, the total wavefunction can be expanded as:

\begin{equation}
\Phi(\{r_i\}, \{R_I\}, t) = \sum_{l=0}^{\infty} \psi_l (\{r_i\}, \{R_I\}) \chi_l (\{R_I\}, t) \tag{8}
\end{equation}

Eq.8 is the \textit{ansatz} introduced by Born in 1951.
Inserting (8) into Eq.(1) (multiplying from the left by $\Psi^*_k(\{r_i\}, \{R_I\})$ and integrating over all the electronic coordinates $r$) we obtain:

$$
\left[-\sum_l \frac{\hbar^2}{2M_l} \nabla^2_l + E_k(\{R_I\})\right] \chi_k + \sum_l C_{kl} \chi_l = i\hbar \frac{\partial}{\partial t} \chi_k
$$

where:

$$
C_{kl} = \int \psi^*_k \left[-\sum_l \frac{\hbar^2}{2M_l} \nabla^2_l\right] \psi_l d\mathbf{r} + \frac{1}{M_l} \sum_l \left\{ \int \psi^*_k[-i\hbar\nabla_l] \psi_l d\mathbf{r}\right\}[-i\hbar\nabla_l]
$$

is the exact non-adiabatic coupling operator.

The adiabatic approximation to the full problem Eq.9 is obtained considering only the diagonal terms:

$$
C_{kk} = -\sum_l \frac{\hbar^2}{2M_l} \int \psi^*_k \nabla^2_l \psi_k d\mathbf{r}
$$
The motion of the nuclei proceed without changing the quantum state, \( k \), of the electronic subsystem during the evolution. The coupled wavefunction can be simplified as:

\[
\Phi(\{r_i\}, \{R_I\}, t) \approx \Psi_k(\{r_i\}, \{R_I\})\chi_k(\{R_I\}, t)
\]

the ultimate simplification consist in neglecting also the correction term \( C_{kk}(\{R_I\}) \), so that

\[
\left[ - \sum_I \frac{\hbar^2}{2M_I} \nabla^2_I + E_k(\{R_I\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k
\]

This is the Born-Oppenheimer approximation.
On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels (rotational and vibrational in the nuclear motion) as illustrated in the figure.
The next step is to derive the classical molecular dynamics for the nuclei. The route we take is the following:

\[ \chi_k(\{\mathbf{R}_I\}, t) = A_k(\{\mathbf{R}_I\}, t) \exp[iS_k(\{\mathbf{R}_I\}, t)/\hbar] \]  

(16)

the amplitude \( A_k \) and the phase \( S_k \) are both real and \( A_k > 0 \). Next we substitute the expression for \( \chi_k \) into eq. 15.

\[ \left[ -\sum \frac{\hbar^2}{2M_I} \nabla^2_I + E_k(\{\mathbf{R}_I\}) \right] A_k(\{\mathbf{R}_I\}, t) \exp[iS_k(\{\mathbf{R}_I\}, t)/\hbar] = \]  

\[ i\hbar \frac{\partial}{\partial t} (A_k(\{\mathbf{R}_I\}, t) \exp[iS_k(\{\mathbf{R}_I\}, t)/\hbar]) \]  

(17)

\[ -\sum \frac{\hbar^2}{2M_I} \nabla_I \left( \nabla_I (A_k \exp[iS_k/\hbar]) \right) + E_k A_k \exp[iS_k/\hbar] = \]  

\[ i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] + i\hbar \frac{i}{\hbar} \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \]  

(19)

\[ \left[ -\sum \frac{\hbar^2}{2M_I} \nabla^2_I \left( \nabla_I A_k \exp[iS_k/\hbar] + A_k \frac{i}{\hbar} \nabla S_k \exp[iS_k/\hbar] \right) + E_k A_k \exp[iS_k/\hbar] = \right. \]  

\[ i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] - \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \]  

(20)
\begin{align*}
- \sum_l \frac{\hbar^2}{2M_l} \nabla_i^2 A_k - \sum_l \frac{\hbar^2}{2M_l} \nabla_i A_k \frac{i}{\hbar} \nabla_i S_k - \sum_l \frac{\hbar^2}{2M_l} \nabla_i A_k \frac{i}{\hbar} \nabla_i S_k \\
- \sum_l \frac{\hbar^2}{2M_l} A_k \left( \frac{i}{\hbar} \right)^2 (\nabla S_k)^2 - \sum_l \frac{\hbar^2}{2M_l} A_k \frac{i}{\hbar} \nabla^2 S_k + E_k A_k =
\end{align*}

Separating the real and the imaginary parts, we obtain:

\begin{align*}
\frac{\partial S_k}{\partial t} + \sum_l \frac{1}{2M_l} (\nabla S_k)^2 + E_k = & - \sum_l \frac{\hbar^2}{2M_l} \nabla_i^2 A_k \\
\frac{\partial A_k}{\partial t} + \sum_l \frac{1}{M_l} \nabla_i A_k \nabla_i S_k + \sum_l \frac{1}{2M_l} A_k \nabla^2 S_k = & 0
\end{align*}
If we consider the equation for the phase:

$$\frac{\partial S_k}{\partial t} + \sum_l \frac{1}{2M_l} \left(\nabla S_k\right)^2 + E_k = -\sum_l \frac{\hbar^2}{2M_l} \frac{\nabla^2 A_k}{A_k}$$

(24)

it is possible to take the classical limit $\hbar \to 0$ which gives the equation:

$$\frac{\partial S_k}{\partial t} + \sum_l \frac{1}{2M_l} \left(\nabla S_k\right)^2 + E_k = 0$$

(25)

which is isomorphic to Hamilton-Jacobi of classical mechanics:

$$\frac{\partial S_k}{\partial t} + H_k(\{R_l\}, \{\nabla_l S_k\}) = 0$$

(26)

with the classical Hamiltonian function

$$H_k(\{R_l\}, \{P_l\}) = T(\{P_l\}) + V_k(\{R_l\})$$

(27)

With the connecting transformation: $P_l = \nabla_l S_k$.
Route 2:

1) Maintain the quantum-mechanical time evolution for the electrons introducing the separation for the electronic and nuclear \(\psi\) function in a time-dependent way.

2) Time-dependent self consistent field (TDSCF) approach is obtained.

3) Ehrenfest dynamics (and as special case Born-Oppenheimer dynamics).

4) The classical limit leads then to the classical molecular dynamics for the nuclei.
It is possible to follow an alternative route in order to maintain the
dynamics of the electron.

\[ \Phi(\{r_i\}, \{R_I\}, t) \approx \Psi(\{r_i\}, t)\chi(\{R_I\}, t)\exp\left[i\frac{\hbar}{\hbar} \int_{t_0}^{t} \tilde{E}_e(t')dt' \right] \] (28)

where:

\[ \tilde{E}_e = \int \Psi^*(\{r_i\}, t)\chi^*(\{R_I\}, t)He\Psi(\{r_i\}, t)\chi(\{R_I\}, t)drdR \] (29)

Inserting this separation ansatz (single determinant ansatz) into
\[ i\hbar \frac{\partial}{\partial t} \Phi(\{r_i\}, \{R_I\}; t) = H\Phi(\{r_i\}, \{R_I\}; t) \]
and multiplying from the left by \( \Psi^* \) and by \( \chi^* \) we obtain
This set of time-dependent Schröedinger equations define the basis of time-dependent self-consistent field (TDSCF) method. Both electrons and nuclei moves quantum-mechanically in time-dependent effective potentials.
• Classical motion induces electronic transitions
• Quantum state determines classical forces

→ Quantum – Classical Feedback: Self-Consistency
Using the same trick as before of writing
\[
\chi_k(\{R_I\}, t) = A_k(\{R_I\}, t)\exp[iS_k(\{R_I\}, t)/\hbar]
\] (34)

we obtain
\[
\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \psi^* H_e \psi \, dr = -\sum_I \frac{\hbar^2}{2M_I} \frac{\nabla^2 A_k}{A_k} \tag{35}
\]
\[
\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A_k \nabla_I S_k + \sum_I \frac{1}{2M_I} A_k \nabla^2 S_k = 0 \tag{36}
\]

And in the classical limit $\hbar \to 0$
\[
\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \psi^* H_e \psi \, dr = 0. \tag{37}
\]
The Newtonian equation of motion of the classical nuclei are:

\[
\frac{dP_I}{dt} = \nabla_I \int \Psi^* H_e \Psi \, dr
\]  \hspace{1cm} (38)

or

\[
M_I \ddot{R}_I(t) = -\nabla_I V^E_e(\{R_I(t)\})
\]  \hspace{1cm} (39)

here the nuclei move according to classical mechanics in an effective potential \( V^E_e(\{R_I(t)\}) \), often called the Ehrenfest potential.
The nuclei move according to classical mechanics in an effective potential (Ehrenfest potential) given by the quantum dynamics of the electrons obtained by solving the time-dependent Schröedinger equation for the electrons.

\[ i\hbar \frac{\partial \Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi \]

\[ + \{ \int \chi^* (\{ \mathbf{R}_I \}, t) V_{ne}(\{ \mathbf{r}_i \}, \{ \mathbf{R}_I \}) \chi (\{ \mathbf{R}_I \}, t) d\mathbf{R} \} \Psi \quad (40) \]

Note: the equation (37) still contains the full quantum-mechanics nuclear wavefunction \( \chi (\{ \mathbf{R}_I \}, t) \). The classical reduction is obtained by:

\[ \int \chi^* (\{ \mathbf{R}_I \}, t) \mathbf{R}_I \chi (\{ \mathbf{R}_I \}, t) d\mathbf{R} \rightarrow \mathbf{R}_I (t) \quad (41) \]

for \( \hbar \rightarrow 0 \).
The classical limits leads to a time-dependent wave equation for the electrons

\[
\frac{i\hbar}{\partial t} \frac{\partial \Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{ne}(\{r_i\}, \{R_I\})\Psi \quad (42)
\]

\[
\frac{i\hbar}{\partial t} \frac{\partial \Psi}{\partial t} = H_e(\{r_i\}, \{R_I\})\Psi(\{r_i\}, \{R_I\}) \quad (43)
\]

- Feedback between the classical and quantum degrees of freedom is incorporated in both direction, even though in a mean field sense.

- These equations are called Ehrenfest dynamics in honor to Paul Ehrenfest who was the first to address the problem of how Newtonian classical dynamics of point particles can be derived from Schröedinger time-dependent wave equation.
Difference between Ehrenfest dynamics and Born-Oppenheimer molecular dynamics:

- In ED the electronic subsystem evolves explicitly in time, according to a time-dependent Schröedinger equation.
- In ED transition between electronic states are possible. This can be showed expressing the electronic wavefunction in a basis of electronic states

\[
\Psi(\{r_i\}, \{R_I\}, t) = \sum_{l=0}^{\infty} c_l(t) \psi_l(\{r_i\}, \{R_I\}, t)
\]  

(44)

where

\[
\sum_{l=0}^{\infty} |c_l(t)|^2 = 1
\]  

(45)

and one possible choice for the basis functions \(\{\psi_k\}\) is obtained solving the time-independent Schröedinger equation:

\[
H_e(\{r_i\}, \{R_I\}) \psi_k(\{r_i\}, \{R_I\}) = E_k(\{R_I\}) \psi_k(\{r_i\}, \{R_I\}).
\]  

(46)
The Ehrenfest dynamics reduces to the Born-Oppenheimer molecular dynamics if only one term is considered in the sum:

\[ \Psi(\{r_i\}, \{R_I\}, t) = \sum_{l=0}^{\infty} c_l(t) \Psi_l(\{r_i\}, \{R_I\}, t) \]

namely:

\[ \Psi(\{r_i\}, \{R_I\}, t) = \Psi_0 \text{ground state adiabatic wavefunction} \quad (47) \]

This should be a good approximation if the energy difference between \(\Psi_0\) and the first excited state \(\Psi_1\) is large everywhere compared to the thermal energy scale \(K_B T\). In this approximation the nuclei move on a single adiabatic potential energy surface, \(E_0(\{R_I\})\).
Ionic Molecule (alkali halide)

Nonadiabatic Coupling: \[ d_{12} = \langle \phi_1 | \frac{\partial \phi_2}{\partial X} \rangle \]
Classical trajectory calculations on global potential energy surfaces

In BO one can think to fully decouple the task of generating classical nuclear dynamics from the task of computing the quantum potential energy surface.

- $E_0$ is computed for many different $\{R_i\}$
- data points fitted to analytical function
- Newton equation of motion solved on the computed surfaces for different initial conditions

Problem: dimensionality bottleneck. It has been used for scattering and chemical reactions of small systems in vacuum, but is not doable when nuclear degrees of freedom increase.
One possible solution to the dimensionality bottleneck is the force field based MD.

\[ V_e^E \approx V_e^{FF} = \sum_{I=1}^{N} v_1(R_I) + \sum_{I<J}^{N} v_2(R_I, R_J) + \]
\[ \sum_{I<J<K}^{N} v_3(R_I, R_J, R_K) + ... \]  

The equation of motion for the nuclei are:

\[ M_I \ddot{R}_I(t) = -\nabla_I V_e^{FF}(\{R_I(t)\}). \]

The electrons follow adiabatically the classical nuclear motion and can be integrated out. The nuclei evolve on a single BO potential energy surface, approximated by a few body interactions.
Ehrenfest molecular dynamics

To avoid the dimensionality bottleneck the coupled equations:

\[ M_i \dddot{\mathbf{R}}_i(t) = -\nabla_i \langle H_e \rangle \]  \hspace{1cm} (51)

\[ i\hbar \frac{\partial \psi}{\partial t} = \left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ne}(\{r_i\}, \{\mathbf{R}_i\}) \chi(\{\mathbf{R}_i\}, t) \right] \psi \] \hspace{1cm} (52)

can be solved simultaneously.

The time-dependent Schröedinger equation is solved \textit{on the fly} as the nuclei are propagated using classical mechanics.
Using

$$\Psi(\{r_i\}, \{R_I\}, t) = \sum_{l=0}^{\infty} c_l(t) \Psi_l(\{r_i\}, \{R_I\})$$

the Ehrenfest equations reads:

$$M_l \ddot{R}_l(t) = -\nabla_I \sum_k |c_k(t)|^2 E_k$$

$$= -\sum_k |c_k(t)|^2 \nabla_I E_k + \sum_{k,l} c_k^* c_l (E_k - E_l) d_{kl}$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_l c_k(t) D_{kl}$$

where the non-adiabatic coupling elements are given by

$$D_{kl} = \int \psi_k^* \frac{\partial}{\partial t} \psi_l dr = \sum_l \dot{R}_l \int \psi_k^* \nabla I \psi_l = \sum_l \dot{R}_l d_{kl}.$$
Combine the advantages of Ehrenfest and BO dynamics

Integrate the equation of motion on a longer time-step than in Ehrenfest, but at the same time

take advantage of the smooth time evolution of the dynamically evolving electronic subsystem
Unified Approach for Molecular Dynamics and Density-Functional Theory

R. Car
International School for Advanced Studies, Trieste, Italy

and

M. Parrinello
Dipartimento di Fisica Teorica, Università di Trieste, Trieste, Italy, and
International School for Advanced Studies, Trieste, Italy
(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.
Car-Parrinello Lagrangian and equations of motion

CP dynamics is based on the adiabatic separation between fast electronic (quantum) and slow (classical) nuclear motion. They introduced the following Lagrangian

$$\mathcal{L}_{CP} = \sum_l \frac{1}{2} M_l \dot{R}_l^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Psi_0 | H_e | \Psi_0 \rangle + \text{constraints}$$

(57)

where $\Psi_0 = 1/\sqrt{N! \det \{\phi_i\}}$

and $\mu$ is the fictitious mass of the electrons.
the associated Euler-Lagrange equations are:

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{R}_I} = \frac{\partial L}{\partial R_I} \quad (58)
\]

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{\phi}_i^*} = \frac{\partial L}{\partial \phi_i^*} \quad (59)
\]

from which the Car-Parrinello equations of motion:

\[
M_I \ddot{R}_I(t) = -\frac{\partial}{\partial R_I} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\partial}{\partial R_I} \{ constraints \} \quad (60)
\]

\[
\mu \ddot{\phi}_i(t) = -\frac{\delta}{\delta \phi_i^*} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\delta}{\delta \phi_i^*} \{ constraints \} \quad (61)
\]
For the specific case of the Kohn-Sham Theory the CP Lagrangian is:

\[
\mathcal{L}_{CP} = \sum_{I} \frac{1}{2} M_{I} \ddot{R}_{I}^{2} + \sum_{i} \mu \langle \dot{\phi}_{i} | \dot{\phi}_{i} \rangle - \langle \Psi_{0} | H_{e}^{KS} | \Psi_{0} \rangle \\
+ \sum_{i,j} \Lambda_{ij} (\langle \phi_{i} | \phi_{j} \rangle - \delta_{ij})
\] (62)

and the Car-Parrinello equations of motion:

\[
M_{I} \dddot{R}_{I}(t) = - \frac{\partial}{\partial \dot{R}_{I}} \langle \Psi_{0} | H_{e}^{KS} | \Psi_{0} \rangle
\] (63)

\[
\mu \dddot{\phi}_{i}(t) = - H_{e}^{KS} \phi_{i} + \sum_{j} \Lambda_{ij} \phi_{j}
\] (64)

The nuclei evolve in time with temperature \( \propto \sum_{I} M_{I} \dot{R}_{I}^{2} \);
the electrons have a fictitious temperature \( \propto \sum_{i} \mu \langle \dot{\phi}_{i} | \dot{\phi}_{i} \rangle \).
Why does the CP method work?

- Separate in practice nuclear and ionic motion so that electrons keep cold, remaining close to $\min\{\phi_i\} < \Psi_0|H_e|\Psi_0 >$, namely close to the Born-Oppenheimer surface.

$$f(\omega) = \int_0^\infty \cos(\omega t) \sum_i < \dot{\phi}_i; t | \dot{\phi}_i; 0 > dt$$ (65)
Energy Conservation

\[ E_{\text{cons}} = \sum_l \frac{1}{2} M_l \dot{R}_l^2 + \sum_i \mu < \dot{\phi}_i | \dot{\phi}_i > + < \Psi_0 | H_{eKS} | \Psi_0 > \] (66)

\[ E_{\text{phys}} = \sum_l \frac{1}{2} M_l \dot{R}_l^2 + < \Psi_0 | H_{eKS} | \Psi_0 > = E_{\text{cons}} - T_e \] (67)

\[ V_e = < \Psi_0 | H_{eKS} | \Psi_0 > \] (68)

\[ T_e = \sum \mu < \dot{\phi}_i | \dot{\phi}_i > \] (69)
Energy Conservation

- Electrons do not heat-up, but fluctuate with same frequency as $V_e$
- Nuclei drag the electrons
- $E_{phys}$ is essentially constant
Deviation from Born-Oppenheimer surface

Deviation of forces in CP dynamics from the true BO forces small and/or oscillating.
How to control of adiabaticity?

In a simple harmonic analysis of the frequency spectrum yields

\[ \omega_{ij} = \sqrt{\frac{2(\epsilon_i - \epsilon_j)}{\mu}} \]  \hspace{1cm} (70)

where \( \epsilon_i \) and \( \epsilon_j \) are the eigenvalues of the occupied/unoccupied orbitals of the Kohn-Sham Hamiltonian. The lowest possible electronic frequency is:

\[ \omega_{e}^{\text{min}} \propto \sqrt{\frac{E_{\text{gap}}}{\mu}}. \]  \hspace{1cm} (71)

The highest frequency

\[ \omega_{e}^{\text{max}} \propto \sqrt{\frac{E_{\text{cut}}}{\mu}}. \]  \hspace{1cm} (72)

Thus maximum possible time step

\[ \Delta t_{\text{max}} \propto \sqrt{\frac{\mu}{E_{\text{cut}}}}. \]  \hspace{1cm} (73)
In order to guarantee adiabatic separation between electrons and nuclei we should have

\[ \text{large } \omega_e^{\text{min}} - \omega_n^{\text{max}}. \]

\( \omega_n^{\text{max}} \) and \( E_{\text{gap}} \) depend on the physical system, so the parameter to control adiabaticity is the mass \( \mu \).

However the mass cannot be reduced arbitrarily otherwise the timestep becomes too small.

Alternatively if \( \Delta t \) is fixed and \( \mu \) is chosen

\[ \text{▷ } \mu \text{ too small: Electrons too light and adiabacity will be lost} \]
\[ \text{▷ } \mu \text{ too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm} \]
Loss of adiabaticity: the bad cases

- Vacancy in hot 64-atom Si cell

Due to the presence of the vacancy there is a small gap in the system.
Loss of adiabaticity: the bad cases

- $\text{Sn}_2$: Degeneracy of HOMO and LUMO at short distances

In this system the gap is periodically opened (up to 0.3 eV) and nearly closed at short distances. The electrons gain kinetic energy in phase with the ionic oscillations.
Zero or small electronic gaps: thermostatted electrons

- One way to (try to) overcome the problem in coupling of electronic and ionic dynamics is to thermostat also the electrons (Blöchl & Parrinello, PRB 1992)
- Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- Target fictitious kinetic energy $E_{\text{kin},0}$ instead of temperature
- Mass of thermostat to be selected appropriately:
  - Too light: Adiabacity violated (electrons may heat up)
  - Too heavy: Ions dragged excessively
- Note: Introducing the thermostat the conserved quantity changes
\[ M_I \ddot{R}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} < \psi_0 | H_{e}^{KS} | \psi_0 > - M_I \dot{R}_I \dot{x}_R \]  

(74)

\[ \mu \ddot{\phi}_i(t) = -H_{e}^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j - \mu \dot{\phi}_i \dot{x}_e \]  

(75)

in blue are the frictious terms governed by the following equations:

\[ Q_e \ddot{x}_e = 2 \left[ \sum_i \mu \dot{\phi}_i^2 - E_{kin,0} \right] \]  

(76)

\[ Q_R \ddot{x}_R = 2 \left[ \sum_I \frac{1}{2} M_I \dot{R}_I^2 - \frac{1}{2} gK_B T \right] \]  

(77)

The masses \( Q_e \) and \( Q_R \) determines the time scale for the thermal fluctuations. The conserved quantity is now:

\[ E_{tot} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_i \mu < \dot{\phi}_i | \dot{\phi}_i > + < \psi_0 | H_{e}^{KS} | \psi_0 > \]

\[ + \frac{1}{2} Q_e \dot{x}_e^2 + 2E_{kin,0} \dot{x}_e + \frac{1}{2} Q_R \dot{x}_R^2 + gK_B T \dot{x}_R \]  

(78)
Thermostat on the electrons: examples

- Example: Aluminium

- Dependence of the heat transfer on the choice of $E_{\text{kin},0}$ in solid Al

![Graph showing the dependence of heat transfer on $E_{\text{kin},0}$](image-url)
Thermostat on the electrons: examples

- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat

![Graph showing the comparison between with and without thermostat](image.png)
Thermostat on the electrons: examples

- Check: Radial pair correlation function
  - Solid line: CP-MD with thermostat
  - Dashed line: Calculations by Jacucci et al
The CP forces necessarily deviate from the BO

The primary effect of \(\mu\) makes the ions "heavier"

No effect on the thermodynamical and structural properties, but affect the dynamical quantities in a systematic way (vibrational spectra)

\[
\phi_i(t) = \phi_i^0(t) + \delta \phi_i(t)
\]  (79)

Inserting this expression into the CP equations of motions:

\[
\mathbf{F}_{l,\alpha}^{CP}(t) = \mathbf{F}_{l,\alpha}^{BO}(t) + \sum_i \mu \{ < \ddot{\phi}_i | \frac{\partial |\phi_i^0\rangle}{\partial \mathbf{R}_{l,\alpha}} > \frac{\partial < \phi_i^0 |}{\partial \mathbf{R}_{l,\alpha}} |\ddot{\phi}_i \rangle \} + O(\delta \phi_i^2)  \]  (80)

the additional force is linear in the mass \(\mu\) so that it vanishes properly as \(\mu \to 0\).
The new equations of motion:

\[(M_I + \Delta \mu M_I)\ddot{R}_I = F_I\]  \hspace{1cm} (81)

where, in the isolated atom approximation,

\[
\Delta \mu M_I = \frac{2}{3} \mu E_{kin} = \frac{2}{3} \frac{m_e}{\hbar^2} \sum_j <\phi_j^-| - \frac{\hbar^2}{2m_e} \nabla_j^2 |\phi_j^+> > 0 \hspace{1cm} (82)
\]

is an unphysical mass, or drag, due to the fictitious kinetics of the electrons

▶ for a system where electrons are strongly localized close to the nuclei there more pronounced renormalization effect
Example: Vibrations in water molecule

<table>
<thead>
<tr>
<th>mode</th>
<th>harmonic</th>
<th>BOMD</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>dM/M [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bend</td>
<td>1548</td>
<td>1543</td>
<td>1539</td>
<td>1535</td>
<td>1529</td>
<td>1514</td>
<td>0.95×10^{-3}μ</td>
</tr>
<tr>
<td>sym.</td>
<td>3515</td>
<td>3508</td>
<td>3494</td>
<td>3478</td>
<td>3449</td>
<td>3388</td>
<td>1.81×10^{-3}μ</td>
</tr>
<tr>
<td>asym.</td>
<td>3621</td>
<td>3616</td>
<td>3600</td>
<td>3585</td>
<td>3556</td>
<td>3498</td>
<td>1.71×10^{-3}μ</td>
</tr>
</tbody>
</table>

To correct for finite-μ effects:

- Perform simulation for different μ-values and extrapolate for μ → 0.
- use mass renormalization according to:

\[
ω_{BO} = \omega_{CP} \sqrt{1 + \frac{Δ\mu M}{M}}
\]  

(83)
## Car-Parrinello vs Born-Oppenheimer dynamics

<table>
<thead>
<tr>
<th>Born-Oppenheimer MD</th>
<th>Car-Parrinello MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exactly on BO surface</td>
<td>Always slightly off BO surface</td>
</tr>
<tr>
<td>$\Delta t \approx$ ionic time scales, maximum time step possible</td>
<td>$\Delta t \ll$ ionic time scales, (much) shorter time step necessary</td>
</tr>
<tr>
<td>Expensive minimisation at each MD step</td>
<td>Orthogonalisation only, less expensive per MD step</td>
</tr>
<tr>
<td>Not stable against deviations from BO surface</td>
<td>Stable against deviations from BO surface</td>
</tr>
<tr>
<td>$\Rightarrow$ Energy/temperature drift, thermostatting of ions necessary</td>
<td>Thermostatting of electrons to prevent energy exchange</td>
</tr>
<tr>
<td>Same machinery in zero-gap systems</td>
<td>Superior for liquids</td>
</tr>
</tbody>
</table>

**Marialore Sulpizi**

*Ab initio molecular dynamics: Basic Theory and Advanced Methods*
CP vs BO: energy conservation

\[ \Delta t, \text{ convergence} \]

\textbf{Top:}
- solid line : CP, 5 a.u.;
- open circ. : CP, 10 a.u.;
- filled squar. : BO, 10 a.u., $10^{-6}$.  

\textbf{Middle:}
- open circl. : CP, 10 a.u.;
- filled squar. : BO, 10 a.u., $10^{-6}$;
- filled trian. : BO, 100 a.u., $10^{-6}$;
- open diam. : BO, 100 a.u., $10^{-5}$.  

\textbf{Bottom:}
- open circ. : CP, 10 a.u.;
- open diam. : BO, 100 a.u., $10^{-5}$;
- dashed line : BO, 100 a.u., $10^{-4}$.  

\( t \) (ps)}
### Timing in CPU seconds and energy conservation in a.u./ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

<table>
<thead>
<tr>
<th>Method</th>
<th>Time step</th>
<th>Convergence</th>
<th>Conservation (au/ps)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>5</td>
<td>—</td>
<td>$6 \times 10^{-8}$</td>
<td>3230</td>
</tr>
<tr>
<td>CP</td>
<td>7</td>
<td>—</td>
<td>$1 \times 10^{-7}$</td>
<td>2310</td>
</tr>
<tr>
<td>CP</td>
<td>10</td>
<td>—</td>
<td>$3 \times 10^{-7}$</td>
<td>1610</td>
</tr>
<tr>
<td>BO</td>
<td>10</td>
<td>$10^{-6}$</td>
<td>$1 \times 10^{-6}$</td>
<td>16590</td>
</tr>
<tr>
<td>BO</td>
<td>50</td>
<td>$10^{-6}$</td>
<td>$1 \times 10^{-6}$</td>
<td>4130</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>$10^{-6}$</td>
<td>$6 \times 10^{-6}$</td>
<td>2250</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>$10^{-5}$</td>
<td>$1 \times 10^{-5}$</td>
<td>1660</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>$10^{-4}$</td>
<td>$1 \times 10^{-3}$</td>
<td>1060</td>
</tr>
</tbody>
</table>
CP of liquid water: Energy conservation

![Graph showing energy conservation over time for different simulations.](image)

- CPMD-800-NVE-64
- CPMD-400-NVE-128
- CPMD-800-NVT-64


Marialore Sulpizi

Ab initio molecular dynamics: Basic Theory and Advanced Methods
CP of liquid water: structure

The radial distribution functions are correct and independent of the method used.

Car-Parrinello method: Summary

- Molecular dynamics can be used to perform real-time dynamics in atomistic systems.
- Verlet algorithm yields stable dynamics (in CPMD implemented algorithm velocity Verlet).
- Born-Oppenheimer dynamics: Max time step 1 fs (highest ionic frequency $2000-3000 \text{ cm}^{-1}$)
  
  Car-Parrinello dynamics: Max time step 0.1 fs
- Car-Parrinello method can yield very stable dynamical trajectories, provided the electrons and ions are adiabatically decoupled.
- The method is best suited for e.g. liquids and large molecules with a wide electronic gap.
- The speed of the method is comparable or faster than using Born-Oppenheimer dynamics and still more accurate (i.e. stable).
- One has to be careful with the choice of $\mu$!
Forces calculation

Efficient calculation of the forces

One possibility is the numerical evaluation of:

\[
\mathbf{F}_I = -\nabla \langle \psi_0 | H_e | \psi_0 \rangle
\]  \hspace{1cm} (84)

which can be costly and not so accurate. So analytical derivative is desirable:

\[
\nabla I \langle \psi_0 | H_e | \psi_0 \rangle = \langle \psi_0 | \nabla I H_e | \psi_0 \rangle + \langle \nabla I \psi_0 | H_e | \psi_0 \rangle + \langle \psi_0 | H_e | \nabla I \psi_0 \rangle \]  \hspace{1cm} (85)

For the Hellmann Feymann Theorem:

\[
\mathbf{F}_I^{HFT} = \langle \psi_0 | \nabla I H_e | \psi_0 \rangle \]  \hspace{1cm} (87)

if \( \psi_0 \) is an exact eigenfunction of \( H_e \).

In numerical calculation that is not the case and contribution to the forces also arise from variation of the \( \psi \) with respect to atomic positions.
We need to calculate the additional forces coming from the \( \psi \) contribution.

Let’s start with

\[
\psi_0 = 1/N! \det \phi_i
\]  

(88)

where the orbitals \( \phi_i \) can be expanded as:

\[
\phi_i = \sum_{\nu} c_{i\nu} f_{\nu}(r, \{R_I\})
\]  

(89)

Two contributions to the forces emerge from the variation of the \( \psi \):

\[
\nabla_I \phi_i = \sum_{\nu} (\nabla_I c_{i\nu}) f_{\nu}(r, \{R_I\}) + \sum_{\nu} c_{i\nu} (\nabla_I f_{\nu}(r, \{R_I\})
\]  

(90)
We calculate now the contribution due to the incomplete-basis-set correction. Using:

\[ \nabla_I \phi_i = \sum_{\nu} (\nabla_I c_{i\nu}) f_\nu(r, \{R_I\}) + \sum_{\nu} c_{i\nu} (\nabla_I f_\nu(r, \{R_I\})) \quad (91) \]

into

\[ \langle \nabla_I \Psi_0 | H_e | \Psi_0 \rangle + \langle \Psi_0 | H_e | \nabla_I \Psi_0 \rangle \quad (92) \]

we obtain:

\[ \sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} \left( \langle \nabla_I f_\mu | H_e | f_\nu \rangle + \langle f_\mu | H_e | \nabla_I f_\nu \rangle \right) + \quad (93) \]

\[ \sum_{i\mu\nu} (\nabla_I c_{i\mu}^* H_{\mu\nu} c_{i\nu} + c_{i\mu}^* H_{\mu\nu} \nabla_I c_{i\nu}) \quad (94) \]

Making use of

\[ \sum_{\nu} H_{\mu\nu} c_{i\nu} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{i\nu} \quad (95) \]
We obtain:

$$\sum_{i \mu \nu} c_{i \mu}^* c_{i \nu} (\langle \nabla f_{\mu} | H_e | f_{\nu} \rangle + \langle f_{\mu} | H_e | \nabla f_{\nu} \rangle) + \sum_{i \mu \nu} \epsilon_i (\nabla f_{\mu} c_{i \mu}^* S_{\mu \nu} c_{i \nu} + c_{i \mu}^* S_{\mu \nu} \nabla f_{\nu} c_{i \nu})$$

(96)

which can be rewritten as:

$$\sum_{i \mu \nu} c_{i \mu}^* c_{i \nu} (\langle \nabla f_{\mu} | H_e | f_{\nu} \rangle + \langle f_{\mu} | H_e | \nabla f_{\nu} \rangle) + \sum_{i \mu \nu} \epsilon_i S_{\mu \nu} \nabla f_{\nu} (c_{i \mu}^* c_{i \nu})$$

(97)

and

$$\sum_{i \mu \nu} c_{i \mu}^* c_{i \nu} (\langle \nabla f_{\mu} | H_e | f_{\nu} \rangle + \langle f_{\mu} | H_e | \nabla f_{\nu} \rangle) +$$

$$\sum_{i \mu \nu} \epsilon_i \left[ \nabla f_{\nu} \sum_{\mu \nu} S_{\mu \nu} c_{i \mu}^* c_{i \nu} - \sum_{i \mu \nu} \nabla f_{\nu} S_{\mu \nu} c_{i \mu}^* c_{i \nu} \right]$$

(98)

(99)

And finally:

$$\sum_{i \mu \nu} c_{i \mu}^* c_{i \nu} (\langle \nabla f_{\mu} | H_e - \epsilon_i | f_{\nu} \rangle + \langle f_{\mu} | H_e - \epsilon_i | \nabla f_{\nu} \rangle)$$

(100)
In the case of plane waves Pulay forces vanish
- this is due to the fact that plane wave do not depend on the atomic coordinates
- it is only true if number of plane waves is kept fixed.
An additional contribution to the forces comes from the non-self-consistency

\[ F_{NSC} = - \int dr (\nabla_I n)(V^{SCF} - V^{NSC}) \] (101)

Such a force vanishes when the self consistency is reached, meaning \( \Psi_0 \) is the exact wavefunction within the subspace spanned by the finite basis set.
In Car-Parrinello, as well as in Ehrenfest MD there is no minimization full self-consistency is not required, so this force is irrelevant.