Numerical integration schemes for the equations of motion, constants of motion, control of stability, accuracy

Ari Paavo Seitsonen
École Normale Supérieure

CECAM QM/MM School, Lausanne
April 8th-12th, 2019
Molecular dynamics
Molecular dynamics

- Propagation of Newton’s equation of motion (with discrete equations of motion)
  \[ \mathbf{F}_i = M_i \mathbf{a} = M_i \ddot{\mathbf{R}}_i \]

- Alternative derivation from the Lagrange formalism:
  \[ \mathcal{L} \left( \mathbf{R}^N, \dot{\mathbf{R}}^N \right) = \sum_{i=1}^{N} \frac{1}{2} M_i \dot{\mathbf{R}}_i^2 - U \left( \mathbf{R}^N \right), \]

  \( U \) is the interaction potential between the particles. The Euler-Lagrange equation
  \[ \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_i} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_i} \]

- Most common algorithm: Verlet algorithm (in a few variations)
Verlet algorithm: Velocity Verlet

- discretisation of Newton’s equation of motion

\[ M_i \ddot{R}_i = F_i \]

i) Propagate ionic positions \( R_i(t) \) according to

\[ R_i(t + \Delta t) = R_i(t) + \Delta t \ v_i(t) + \frac{(\Delta t)^2}{2M_i} F_i(t) \]

ii) Evaluate forces \( F_i(t + \Delta t) \) at \( R_i(t + \Delta t) \)

iii) Update velocities

\[ v_i(t + \Delta t) = v_i(t) + \frac{\Delta t}{2M_i} [F_i(t) + F_i(t + \Delta t)] \]
Velocity Verlet: Advantages

Other algorithms provide can have better short time stability and allow larger time steps, but . . .

- simple and efficient; needs only forces, no higher energy derivatives
- still correct up to and including third order, $(\Delta t)^3$
- explicitly time reversible
- symplectic: conserves volume in phase space
- superior long time stability (energy conservation) of the Verlet algorithm
Velocity Verlet: Choice of time step

- The time step is in general chosen as large as possible . . .
- “Possible” = stable dynamics = energy conserved; or, drift in energy acceptable
- Rule of thumb: 6-10 times smaller than the fastest period in the system; otherwise sampling of that mode is impossible
- Time step can be changed during simulation(!)
Velocity Verlet: Choice of time step

AlCl₃ dimer
Example of a good/bad choice of time step

- Highest vibrational frequency 595 cm⁻¹ ⇒ period \( T = 56 \text{ fs} \)
- Divergence between \( \delta t = 400..500 \text{ atu} = 9.6-12.0 \text{ fs} \approx 1/5 T \)
Equations of motion: Alternative derivation

Propagation methods

- Define phase space vector $\Gamma = (x, p)$ and commutator

$$\{A, H\} = \frac{\partial A}{\partial x} \frac{\partial H}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial H}{\partial x}$$

- Hamilton’s equations of motion:

$$\frac{d\Gamma}{dt} = \{\Gamma, H\}$$

- Define $\hat{\mathcal{L}}$ so that

$$i \hat{\mathcal{L}} \Gamma = \{\Gamma, H\}$$

$$\dot{\Gamma} = i \hat{\mathcal{L}} \Gamma \Rightarrow$$

$$\Gamma(t) = e^{i\hat{\mathcal{L}}t} \Gamma(0)$$

- Such formalism has been used by Mark Tuckerman et al to derive new integrators
Tricks

- Simulated annealing
- Multiple time scales / RESPA
- Periodic boundary conditions
- Ewald summation
- Thermodynamic integration
- Cell lists *etc*
Molecular dynamics: Summary

- Molecular dynamics can be used to perform real-time dynamics in atomistic systems.
- Maximum time step $\Delta t \approx 1 \text{ fs}$ (highest ionic frequency 2000 – 3000 cm$^{-1}$).
- Temperature can be controlled via rescaling – (initial) equilibration – and thermostats (e.g. Nosé-Hoover thermostat chains) for NVT ensemble.
- Constraints can be used to pose restrictions on the atoms.
- They can be used to direct reactions, however in complicated (potential/free) energy landscapes they might not yield the correct reaction path (in reasonable simulation time, at least).
- Metadynamics looks like a promising method for finding reaction paths and (potential/free) energy surfaces.
Ab initio molecular dynamics
Realistic MD simulations

\[ M_I \ddot{R}_I = -\nabla_R E (\{R_J\}) \]

- Classical molecular dynamics: \( E (\{R_J\}) \) given e.g. by pair potentials
- How about estimating \( E (\{R_J\}) \) directly from electronic structure method?
- What is needed is \(-\nabla_R E (\{R_J\}) = -\frac{dE}{dR_I}\)
Classical vs MD simulations

- When is electronic structure needed explicitly, when is classical treatment sufficient?
  - Chemical reactions: Breaking and creation of chemical bonds
  - Changing coordination
  - Changing type of interaction
  - Difficult chemistry of elements

- Combination of both: QM/MM
Born-Oppenheimer molecular dynamics
Born-Oppenheimer Ansatz

- Separate the total wave function to quickly varying electronic and slowly varying ionic wave function:

\[ \Phi_{BO} (\{r_i\}, \{R_I\}; t) = \sum_{k=0}^{N_{BO}} \tilde{\Psi}_k (\{r_i\}, \{R_I\}) \tilde{\chi} (\{R_I\}; t) \]

- Leads to a Schrödinger-like equation for the electrons and a Newton-like equation for the ions (after some assumptions for the ionic wave function):

\[ \mathcal{H}^e \tilde{\Psi}_k (\{r_i\}, \{R_I\}) = E^e_{\{R_I\}} \tilde{\Psi}_k (\{r_i\}, \{R_I\}) \]
\[ M_i \ddot{R}_i = F_i \]

- Electrons always at the ground state when observed by the ions

- Usually valid, however there are several cases when this Ansatz fails
Born-Oppenheimer MD

- Lagrangean

\[ \mathcal{L}_{BO} \left( \mathbf{R}, \dot{\mathbf{R}} \right) = \sum_{i=1}^{N} \frac{1}{2} M_i \dot{R}^2_i - \min_{\{\psi_i\}} E_{KS} \left( \{\psi_i\}, \mathbf{R}^N \right) \]

- Equations of motion:

\[ M_i \ddot{R}_i = -\nabla_{\mathbf{R}} \left[ E_{KS} \left( \psi, \mathbf{R}^N \right) \right] = - \frac{d}{d\mathbf{R}_i} \left[ \min_{\{\psi_i\}} E_{KS} \left( \{\psi_i\}, \mathbf{R}^N \right) \right] \]

- If the right-hand side can be evaluated analytically it can be plugged directly to the Verlet algorithm
Forces in BOMD

- What is needed is

\[ - \frac{d}{dR_I} \left[ \min_{\{\psi_i\}} E_{KS} (\{\psi_i\}, R^N) \right] \]

with the constraint that the orbitals remains orthonormal; this is achieved using Lagrange multipliers in the Lagrangean

\[ E_{KS} = E_{KS} + \sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \]

- Forces

\[ \frac{dE_{KS}}{dR_I} = \frac{\partial E_{KS}}{\partial R_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle + \sum_{ij} \frac{\partial \langle \psi_i |}{\partial R_I} \left[ \frac{\partial E_{KS}}{\partial \langle \psi_i |} + \sum_j \Lambda_{ij} | \psi_j \rangle \right] \]

- When \( |\psi_i\rangle \) optimal

\[ F_{KS} (R_I) = - \frac{\partial E_{KS}}{\partial R_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_i \rangle \]
BOMD: Error in forces

- The error in the forces depends on the convergence criterion set for the electronic structure in BOMD:

![Graph showing the relationship between RMS error of ionic force and largest element of electronic gradient. The graph includes points labeled 'Energy correct to machine precision', 'Forces correct to machine precision', and 'Standard convergence'.]
BOMD: Observations

- The energy needs to be minimal in order to estimate the forces.
- The accuracy of the forces depends on the level of self-consistency.
- Thus a competition between accuracy and computational cost.
- Constant of motion:
  - **NVE:**
    \[
    \sum_{l=1}^{N} \frac{1}{2} M_l \dot{R}_l^2 + \min \{ \psi \} E_{KS} (\{ \psi \}, R^N)
    \]
  - **NVT:**
    \[
    \sum_{l=1}^{N} \frac{1}{2S^2} M_l \dot{R}_l^2 + \min \{ \psi \} E_{KS} (\{ \psi \}, R^N) + \frac{1}{2} Q_s \dot{s}^2 + gk_B T \ln(s)
    \]
Car-Parrinello method
Car-Parrinello method


- They postulated Langangean

\[
\mathcal{L}_{CP} \left( \{\psi_i\}, \{\dot{\psi}_i\}; R, \dot{R} \right) = \sum_{i=1}^{M} \frac{1}{2} \mu \left\langle \dot{\psi}_i | \dot{\psi}_i \right\rangle \\
- \min_{\{\psi_i\}} \mathcal{E}_{KS} \left( \{\psi_i\}, R^N \right) \\
+ \sum_{I=1}^{N} \frac{1}{2} M_I \dot{R}_I^2
\]

Reminder: $\mathcal{E}_{KS}$ contains the Lagrange multipliers for orthonormality of orbitals

- *Fictitious* or *fake* dynamics of electrons
- $\mu =$ *fictitious mass* or *inertia parameter*
- *Simultaneous* dynamics of ions and electrons
Car-Parrinello method: Equations of motion

- Euler-Lagrange equations

\[
\frac{d}{dt} \left( \frac{\partial L_{CP}}{\partial \dot{\psi}_i} \right) = \frac{\partial L_{CP}}{\partial \langle \psi_i \rangle}
\]
\[
\frac{d}{dt} \left( \frac{\partial L_{CP}}{\partial \dot{R}_i} \right) = \frac{\partial L_{CP}}{\partial \langle R_i \rangle}
\]

- Equations of motion

\[
\mu \ddot{\psi}_i = -\frac{\partial E_{KS}}{\partial \langle \psi_i \rangle} + \sum_j \Lambda_{ij} \langle \psi_j \rangle
\]
\[
M_i \ddot{R}_i = -\frac{\partial E_{KS}}{\partial \langle R_i \rangle} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \langle R_i \rangle} \langle \psi_i | \psi_j \rangle
\]
Car-Parrinello method: Simultaneous dynamics

- **Unified Approach for Molecular Dynamics and Density-Functional Theory**
- Electronic and ionic structure evolve *simultaneously*
- Whereas in BOMD first the electronic structure is optimised, *then* the ions are moved
Car-Parrinello method: Constant of motion

- Constant of motion

\[ E_{\text{conserved}} = \sum_{i=1}^{M} \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + E_{\text{KS}} \left( \{ \psi_i \} , R^N \right) + \sum_{l=1}^{N} \frac{1}{2} M_l \dot{R}_l^2 \]

- Note: instantaneous value of \( E_{\text{KS}} \left( \{ \psi_i \} , R^N \right) \), not minimum
- Thus no need to optimise the orbitals at each step
Does the Car-Parrinello method yield physical results even if the orbitals are not at the Born-Oppenheimer surface?

- Yes — provided that the electronic and ionic degrees of freedom remain adiabatically separated and the electrons close to the Born-Oppenheimer surface
- Why? — dynamics of the electrons is artificial, or unphysical and thus has to average out during the time scale of ionic movement

Another way of viewing: The electrons are slightly above the BO surface but remain there and average out the effects on the ions (to be considered with care)
Adiabatic separation

Pastore, Smargiassi & Buda, PRA 1991

- Vibrational spectra of electrons and ions do not overlap:

![Graph showing the vibrational spectra with a triangle indicating the highest ionic frequency.](image)

\[ \gamma(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i |\dot{\psi}_i(t)|^2 dt \]

Triangle = highest ionic frequency
Adiabatic separation

Thus there’s no efficient mechanism for exchange of energies: The two subsystems are adiabatically decoupled.

Triangle = highest ionic frequency

\[
f^e(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i \langle \dot{\psi}_i(t) | \dot{\psi}_i(0) \rangle dt
\]
Physical and conserved energy:

$$E_{\text{physical}} = E_{\text{KS}} (\{\psi_i\}, R^N) + \sum_{i=1}^{N} \frac{1}{2} M_i \dot{R}_i^2$$

$$E_{\text{conserved}} = \sum_{i=1}^{M} \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + E_{\text{KS}} (\{\psi_i\}, R^N) + \sum_{i=1}^{N} \frac{1}{2} M_i \dot{R}_i^2$$

$$= E_{\text{kin,fict}} + E_{\text{physical}}$$

The difference, $$E_{\text{kin,fict}} = \sum_{i=1}^{M} \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle$$, must thus correlate with the changes in the physical energy.
Constant of motion: Conservation of energy

Model system: Two-atom Si-fcc

Energy components

\[ E_{\text{kin},f} \]
Deviation from Born-Oppenheimer surface

- Deviation of forces in CP dynamics from the true BO forces small and/but oscillating

\[ F_x^{\text{Si}} \]

\[ F_{x,\text{CP}}^{\text{Si}} - F_{x,\text{BO}}^{\text{Si}} \]

\[ \text{Force (a.u.)} \]

\[ \text{time (10}\,^3\, \text{atu)} \]

\[ \text{F}_{\text{CP}} - F_{\text{BO}} \] (10^{-4} \text{ a.u.})

\[ \text{time (10}\,^3\, \text{atu)} \]
Control of adiabacity

- Harmonic analysis:
  \[ \omega_{ij}^e = \sqrt{\frac{2(\varepsilon_i - \varepsilon_j)}{\mu}} \]

  \( \varepsilon_i \) occupied, \( \varepsilon_j \) unoccupied (virtual) orbitals

- Lowest frequency
  \[ \omega_{\text{min}}^e \propto \sqrt{\frac{E_{\text{gap}}}{\mu}} \]

- Highest frequency
  \[ \omega_{\text{max}}^e \propto \sqrt{\frac{E_{\text{cut}}}{\mu}} \]

- Thus maximum possible time step
  \[ (\Delta t^e)_{\text{max}} \propto \sqrt{\frac{\mu}{E_{\text{cut}}}} \]
Control of adiabacity

- Lowest frequency has to be well above ionic frequencies
  \[ \omega_{\text{min}}^e \propto \sqrt{ \frac{E_{\text{gap}}}{\mu} } \]

- Highest frequency limits the maximum possible time step
  \[ \omega_{\text{max}}^e \propto \sqrt{ \frac{E_{\text{cut}}}{\mu} } \]

  \[ (\Delta t^e)_{\text{max}} \propto \sqrt{ \frac{\mu}{E_{\text{cut}}} } \]

- If $\Delta t$ fixed and $\mu$ chosen
  - too small: Electrons too light and adiabacity will be lost
  - too large: Electrons too heavy, the slowest electronic motion starts to overlap with the ionic frequencies and adiabacity will be lost
Loss of adiabacity: Difficult cases

- Vacancy in hot 64-atom Si cell

![Graph showing the change in $K_t$ over time](image)
Loss of adiabacity: Difficult cases

- \( \text{Sn}_2 \): Degeneracy of HOMO and LUMO at short distances
Analysis of adiabacity: Simplified model

Two-level, two-electron model

- Wave function

\[ \psi = \left( \cos \frac{\theta}{2} \right) \Phi_1 + \left( \sin \frac{\theta}{2} \right) \Phi_2 \]

\( \theta \) is the electronic degree of freedom

Constant gap

Opening-closing gap G
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

- Please remember: The conserved quantity changed
Thermostat on electrons

- Example: Aluminium
- Dependence of the heat transfer on the choice of $E_{\text{kin},0}$ in solid Al
Thermostat on electrons: Does it help?

- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat
Thermostat on electrons: Does it work?

- Check: Radial pair correlation function
  - Solid line: CP-MD with thermostat
  - Dashed line: Calculations by Jacucci et al
Rescaling of ionic masses

- The fictitious electronic mass exerts an extra “mass” on the ions and thereby modifies the equations of motion:

\[ M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I + \mu \sum_{i \in I} \ddot{\mathbf{R}}_i \frac{\partial \phi_i}{\partial \mathbf{r}} \frac{\partial \phi_i}{\partial \mathbf{r}} \]

- The new equations of motion:

\[ (M_I + \Delta M_I) \ddot{\mathbf{R}}_I = \mathbf{F}_I \]

where

\[ \Delta M_I = \frac{2}{3} \mu E_{\text{kin}}^I \]

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

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 \times 10^{-3} \mu</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>1.8 \times 10^{-3} \mu</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>1.7 \times 10^{-3} \mu</td>
</tr>
</tbody>
</table>
Orthonormality constraints

Equations of motion

$$\mu \ddot{\psi}_i = - \frac{\partial E_{KS}}{\partial \langle \psi_i \rangle} + \sum_j \Lambda_{ij} |\psi_j\rangle$$

- In principle differential equations, however after discretisation difference equations (Verlet algorithm)
- Therefore the algorithm for the constraints $\Lambda_{ij}$ depends on the integration method
Orthonormality constraints: RATTLE

- Define

\[ X_{ij} = \frac{\Delta t^2}{2\mu} \Lambda^p_{ij} \quad Y_{ij} = \frac{\Delta t^2}{2\mu} \Lambda^Y_{ij} \quad C \text{ wf coefficients} \]

- Equations of type

\[ XX^\dagger + XB + B^\dagger X^\dagger = I - A \quad Y = \frac{1}{2} (Q + Q^\dagger) \]

\( A, B, Q \) of type \( A_{ij} = \sum_G c^*_G c_G \)

- Solve iteratively:

\[ X^{(n+1)} = \frac{1}{2} \left[ I - A + X^{(n)} (I - B) + (I - B) X^{(n)} - X^{(n)} X^{(n)} \right] \]
CP tricks
Car-Parrinello method for structural optimisation: Simulated annealing

- In larger molecules or crystals the structural optimisation might be difficult, especially the closer to the minimum one is
- CPMD can be used to perform the optimisation by simulated annealing: Rescaling the (atomic and possibly also electronic) velocities: \[ \dot{R}'_i = \alpha \dot{R}_i \]

  Easy to incorporate into the velocity Verlet algorithm
- Optimised structure when all velocities (temperature) are \( \approx 0 \)
  - Check by calculating the ionic forces
- The ionic masses are “unphysical”: Select to “flatten” the vibrational spectrum (e.g. high mass on hydrogens)
- Faster convergence due to the “global” optimisation
Basis set dependent mass

- $\mu$ can be chosen to be dependent on the basis set:

$$\mu(G) = \begin{cases} 
\mu_0, & H(G, G) \leq \alpha \\
(\mu/\alpha) \left[ \frac{1}{2} G^2 + V(G, G) \right], & H(G, G) < \alpha 
\end{cases}$$

- Kind of “pre-conditioning” of the equation of motion
- Allows for larger time step
- However, leads to much larger corrections on the ionic frequencies and no analytical formula can be used
CP & BO
## 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,</td>
<td>$\Delta t \ll$ ionic time scales,</td>
</tr>
<tr>
<td>maximum time step possible</td>
<td>(much) shorter time step necessary</td>
</tr>
<tr>
<td>Expensive minimisation</td>
<td>Orthogonalisation only,</td>
</tr>
<tr>
<td>at each MD step</td>
<td>less expensive per MD step</td>
</tr>
<tr>
<td>Not stable against deviations</td>
<td>Stable against deviations</td>
</tr>
<tr>
<td>from BO surface</td>
<td>from BO surface</td>
</tr>
<tr>
<td>$\Rightarrow$ Energy/temperature drift,</td>
<td></td>
</tr>
<tr>
<td>thermostatting of ions necessary</td>
<td></td>
</tr>
<tr>
<td>Same machinery in zero-gap systems</td>
<td>Thermostatting of electrons to prevent energy exchange</td>
</tr>
<tr>
<td>Many applications in solids</td>
<td>Used in liquids, ...</td>
</tr>
</tbody>
</table>
STABILITY OF BO AND CP MD COMPARED

CPMD results for the 8 Si atom model system

Timings 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 vs BO: Stability

STABILITY OF BO AND CP MD COMPARED (cont’d)

$\Delta t$, convergence

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

**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., $10^{-5}$.  

**Bottom:**
- open circ.: CP, 10 a.u.;
- open diam.: BO, 100 a.u., $10^{-5}$;
- dashed line: BO, 100 a.u., $10^{-4}$.
BO: Error in forces

The error in the forces depends on the convergence criterion set for the electronic structure in BOMD:
CP vs BO: Liquid water

- Effect of $\mu$: Too large value leads to loss of adiabacity
- Thermostatting the electrons recovers the correct behaviour

Graph showing the evolution of $E_{\text{tot}}$, $E_{\text{kin,elec}}$, and temperature ($T$) over time ($t$) for different simulations:

- CPMD–800–NVE–64
- CPMD–400–NVE–12
- CPMD–800–NVT–64
CP vs BO: Liquid water: Results

- The radial distribution functions are correct and independent of the method used.
Car-Parrinello method: Summary

- 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 an electronic gap.
- The speed of the method is comparable or faster than using Born-Oppenheimer dynamics — and still more accurate (i.e. stable).