Ab initio molecular dynamics
Molecular dynamics

Why?

- allows realistic simulation of equilibrium and transport properties in Nature
- ensemble averages can be used for statistical mechanics
- time evolution of chemical reactions, phase transitions, ... can be followed
- search for reaction paths, exploration of phase space
Realistic MD simulations

\[ M_I \ddot{R}_I = -\nabla RE(\{R_J\}) \]

- 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 \( -\nabla_R E(\{R_J\}) = -\frac{dE}{dR_I} \)
Potentials

- Empirical classical potentials
  - pair potentials, three-body potentials
  - polarisable force fields
  - effective medium theory, embedded atom method

- Empirical quantum mechanical potentials
  - tight binding Hamiltonian
  - semi-empirical quantum chemistry methods

- Ab initio potentials
  - quantum chemistry, methods based on wave function
    - density functional theory
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:

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

- 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):

\[
\mathcal{H}^e \tilde{\Psi}_k (\{r_i\}, \{R_I\}) = E_{\{R_I\}}^e \tilde{\Psi}_k (\{r_i\}, \{R_I\})
\]

\[
M_I \ddot{R}_I = F_I
\]

- 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

\[ \mathcal{L}_{BO} (\mathbf{R}, \dot{\mathbf{R}}) = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{R}_I^2 - \min_{\{\psi\}} E (\{\psi\}, \mathbf{R}^N) \]

- Equations of motion:

\[ M_I \ddot{R}_I = -\nabla_{\mathbf{R}} [E (\mathbf{\psi}, \mathbf{R}^N)] = -\frac{d}{d \mathbf{R}_I} \left[ \min_{\{\psi\}} E (\{\psi\}, \mathbf{R}^N) \right] \]

- If the right-hand side can be evaluated analytically it can be plugged directly to the Verlet algorithm
Molecular dynamics

- propagation of Newton’s equation of motion (with discrete equations of motion)

\[ F_I = M_I a = M_I \ddot{R}_I \]

- alternative derivation from the Lagrange formalism:

\[ \mathcal{L} (R^N, \dot{R}^N) = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{R}_I^2 - U (R^N) , \]

\( U \) is the interaction potential between the particles. The Euler-Lagrange equation

\[ \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{R}_I} = \frac{\partial \mathcal{L}}{\partial R_I} \]

- 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
Derivation

- Taylor expansion for ionic positions $\mathbf{R}_I(t)$

$$\begin{align*}
\mathbf{R}_I(t + \Delta t) &= \mathbf{R}_I(t) + \Delta t \ddot{\mathbf{R}}_I(t) + \frac{(\Delta t)^2}{2} \dddot{\mathbf{R}}_I(t) + \ldots \\
&= \mathbf{R}_I(t) + \Delta t \mathbf{v}_I(t) + \frac{(\Delta t)^2}{2M_I} \mathbf{F}_I(t) + \ldots
\end{align*}$$

- Backward Taylor expansion for ionic positions $\mathbf{R}_I(t)$

$$\begin{align*}
\mathbf{R}_I(t + \Delta t) &= \mathbf{R}_I(t) - \Delta t \mathbf{v}_I(t + \Delta t) + \frac{(\Delta t)^2}{2M_I} \mathbf{F}_I(t + \Delta t) + \ldots
\end{align*}$$

- Add up:

$$\begin{align*}
\mathbf{R}_I(t + \Delta t) + \mathbf{R}_I(t) &= \mathbf{R}_I(t + \Delta t) + \mathbf{R}_I(t) + \Delta t [\mathbf{v}_I(t) - \mathbf{v}_I(t + \Delta t)] + \frac{(\Delta t)^2}{2M_I} [\mathbf{F}_I(t) + \mathbf{F}_I(t + \Delta t)]
\end{align*}$$

- Yields velocities

$$\begin{align*}
\mathbf{v}_I(t + \Delta t) &= \mathbf{v}_I(t) + \frac{\Delta t}{2M_I} [\mathbf{F}_I(t) + \mathbf{F}_I(t + \Delta t)]
\end{align*}$$
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
- sympletic: conserves volume in phase space
- superior long time stability (energy conservation) of the Verlet algorithm
Velocity Verlet
Choice of time step

- 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 $T = 56$ fs

- Divergence between $\delta t = 400..500$ atu $= 9.6-12.0$ 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
Ensembles

- micro-canonical ensemble NVE
- canonical ensemble NVT
- isothermal-isobaric NPT
- grand-canonical $\mu$VT
- isobaric-isoenthalpic NPH
- non-equilibrium
Ab initio Born-Oppenheimer MD

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

- equations of motion:
  \[ M_I \ddot{R}_I = -\nabla_R \left[ E_{KS} (\mathbf{R}^N) \right] = -\frac{d}{dR_I} \left[ \min_{\{\psi_i\}} E_{KS} (\{\psi_i\}, \mathbf{R}^N) \right] \]

- 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

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

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

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

- when $|\psi_i\rangle$ optimal

\[F_{KS} (R_I) = -\frac{\partial E_{KS}}{\partial R_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle\]
**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
Car-Parrinello method
Car-Parrinello method


- they postulated Lagangean

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

reminder: \( \mathcal{E}_{KS} \) contains the Lagrange multipliers for orthonormality of orbitals

- *fictitious* or *fake* dynamics of electrons

- \( \mu = \text{fictitious mass or inertia parametre} \)

- *simultaneous* dynamics of ions and electrons
Car-Parrinello method
Equations of motion

- Euler-Lagrange equations

\[
\frac{d}{dt} \frac{\partial \mathcal{L}_{CP}}{\partial \langle \dot{\psi}_i \rangle} = \frac{\partial \mathcal{L}_{CP}}{\partial \langle \dot{\psi}_i \rangle}
\]
\[
\frac{d}{dt} \frac{\partial \mathcal{L}_{CP}}{\partial \langle \dot{R}_I \rangle} = \frac{\partial \mathcal{L}_{CP}}{\partial \langle R_I \rangle}
\]

- equations of motion

\[
\mu \ddot{\psi}_i = -\frac{\partial E_{KS}}{\partial \langle \psi_i \rangle} + \sum_j \Lambda_{ij} \langle \psi_j \rangle
\]
\[
M_I \ddot{R}_I = -\frac{\partial E_{KS}}{\partial R_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle
\]
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

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

- note: instantaneous value of \( E_{\text{KS}} (\{\psi_i\}, R^N) \), not minimum

- thus no need to optimise the orbitals at each step
**Magic Car-Parrinello method**

- 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)
• Vibrational spectra of electrons and ions do not overlap:

\[
f^e(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i \langle \psi_i(t) | \psi_i(0) \rangle \, dt
\]

Triangle = highest ionic frequency
Adiabatic separation

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

\[ f^e(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i \langle \psi_i(t) | \psi_i(0) \rangle \ dt \]
Constant of motion
Conservation of energy

• 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

\[ E_{\text{kin},f} \]

Energy (hartree)

\[ -7.16 \]
\[ -7.18 \]
\[ -7.16 \]
\[ -7.18 \]

\[ 3 \times 10^{-6} \]

0

0 7 140 147 252 259

time \((10^8\ \text{atu})\)

\[ E_{\text{KS}} \]

\[ H \]

\[ H_1 \]

\[ K_t \]
Deviation from Born-Oppenheimer surface
Are the forces accurate?

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

\[
F_x(Si) - F_{x,BO}(Si)
\]

\[
F_{x,CP}(Si) - F_{x,BO}(Si)
\]
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

\[ \omega_{\text{max}}^e \propto \sqrt{\frac{E_{\text{cut}}}{\mu}} \quad (\Delta t_{\text{max}}^e) \propto \sqrt{\frac{\mu}{E_{\text{cut}}}} \]

• If \( \Delta t \) fixed and \( \mu \) chosen
  – too small: Electrons too light and adiabacity will be lost
  – too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm
Loss of adiabacity
Bad cases

- Vacancy in hot 64-atom Si cell
Loss of adiabacity

Bad cases

- 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

![Graphs showing constant gap and opening-closing gap G](image-url)
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

![Graph showing the heat transfer as a function of $E_{\text{kin},0}$ in meV.]
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

![Graph showing radial pair correlation function](image)
Rescaling of ionic masses

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

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

- The new equations of motion:

\[(M_I + dM_I) \ddot{R}_I = F_I\]

where

\[dM_I = \frac{2}{3} \mu E_{kin}^I\]

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 x 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>1.81 x 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>1.71 x 10^{-3} \mu</td>
</tr>
</tbody>
</table>
Choice of $\mu$ : Recent discussion

Liquid water
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

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

- Equations of type

\[ \begin{align*}
XX^\dagger + XB + B^\dagger X^\dagger &= I - A \\
Y &= \frac{1}{2} (Q + Q^\dagger)
\end{align*} \]

- 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:

  \[ \dot{\mathbf{R}}'_I = \alpha \dot{\mathbf{R}}_I \]

  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:

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

- 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, 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 $\Rightarrow$ Energy/temperature drift, thermostatting of ions necessary</td>
<td>Stable against deviations from BO surface</td>
</tr>
<tr>
<td>Same machinery in zero-gap systems</td>
<td>Thermostatting of electrons to prevent energy exchange</td>
</tr>
<tr>
<td>Most applications in solids</td>
<td>Superior for liquids</td>
</tr>
</tbody>
</table>
CP vs BO

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’ed)

$\Delta t$, convergence

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

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

Bottom:
open circ. : CP, 10 a.u.;
onopen 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
Stability

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

Results

- The radial distribution functions are correct and independent of the method used.
### Ehrenfest vs Car-Parrinello dynamics

<table>
<thead>
<tr>
<th>Ehrenfest dynamics</th>
<th>Car-Parrinello MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on quantum (real) adiabatic separation</td>
<td>Based on classical (fictitious) adiabatic separation</td>
</tr>
<tr>
<td>Not exactly on BO surface</td>
<td>Always slightly off BO surface</td>
</tr>
<tr>
<td>Deviations from BO surface accumulate, electrons must be quenched back onto BO surface</td>
<td>Stable against deviations from BO surface</td>
</tr>
<tr>
<td>$\Delta t \approx \text{electronic time scales, very small time step need}$</td>
<td>$\Delta t \gg \text{electronic time scales, larger time step possible}$</td>
</tr>
<tr>
<td>Orthonormality rigorously preserved at no extra cost</td>
<td>Orthonormality must be imposed using constraints</td>
</tr>
</tbody>
</table>
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: Maximum time step $\Delta t \approx 1$ fs (highest ionic frequency $2000 - 3000$ cm$^{-1}$)

- 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

- Car-Parrinello dynamics: Maximum time step $\Delta t \approx 0.1$ fs

- 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 $\mu$!