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

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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

$$M_I\ddot{\mathbf{R}}_I = \mathbf{F}_I$$

i) Propagate ionic positions $\mathbf{R}_I(t)$ according to

$$\mathbf{R}_I(t+\Delta t) = \mathbf{R}_I(t) + \Delta t\, \mathbf{v}_I(t) + \frac{(\Delta t)^2}{2M_I}\mathbf{F}_I(t)$$

ii) Evaluate forces $\mathbf{F}_I(t+\Delta t)$ at $\mathbf{R}_I(t+\Delta t)$

iii) Update velocities

$$\mathbf{v}_I(t+\Delta t) = \mathbf{v}_I(t) + \frac{\Delta t}{2M_I}\left[\mathbf{F}_I(t) + \mathbf{F}_I(t+\Delta t)\right]$$

Velocity Verlet: Advantages

Other algorithms provides 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*

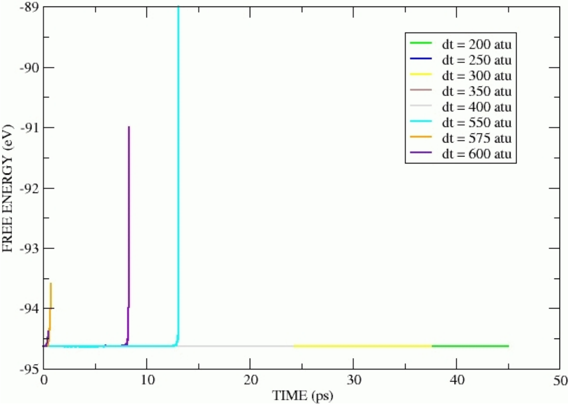
Velocity Verlet: Choice of time step

- 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

$AlCl_3$ dimer
Example of a good/bad choice of time step

- Highest vibrational frequency 595 cm^{-1} $\Rightarrow$ 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

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 $\Delta t \approx 1\ \mathrm{fs}$ (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

$$M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}} E\left(\{\mathbf{R}_J\}\right)$$

- Classical molecular dynamics: $E\left(\{\mathbf{R}_J\}\right)$ given *e. g.* by pair potentials
- How about estimating $E\left(\{\mathbf{R}_J\}\right)$ directly from electronic structure method?
- What is needed is $-\nabla_{\mathbf{R}} E\left(\{\mathbf{R}_J\}\right) = -\frac{dE}{d\mathbf{R}_I}$

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:

$$\Phi_{\mathrm{BO}}\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t\right)=\sum_{k=0}^{N_{\mathrm{BO}}}\tilde{\Psi}_k\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)\tilde{\chi}\left(\{\mathbf{R}_I\};t\right)$$

- 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):

$$\begin{aligned}\mathcal{H}^e\tilde{\Psi}_k\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right) &= E^e_{\{\mathbf{R}_I\}}\tilde{\Psi}_k\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)\\ M_I\ddot{\mathbf{R}}_I &= \mathbf{F}_I\end{aligned}$$

- 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

$$\mathcal{L}_{\mathrm{BO}}\left(\mathbf{R},\dot{\mathbf{R}}\right)=\sum_{I=1}^{N}\frac{1}{2}M_I\dot{\mathbf{R}}_I^2-\min_{\{\psi_i\}}E_{\mathrm{KS}}\left(\{\psi_i\},\mathbf{R}^N\right)$$

- equations of motion:

$$M_I\ddot{\mathbf{R}}_I=-\nabla_{\mathbf{R}}\left[E_{\mathrm{KS}}\left(\Psi,\mathbf{R}^N\right)\right]=-\frac{d}{d\mathbf{R}_I}\left[\min_{\{\psi_i\}}E_{\mathrm{KS}}\left(\{\psi_i\},\mathbf{R}^N\right)\right]$$

- 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

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

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

$$\mathcal{E}_{\mathrm{KS}} = E_{\mathrm{KS}} + \sum_{ij} \Lambda_{ij} \left(\langle\psi_i|\ \psi_j\rangle - \delta_{ij}\right)$$

- Forces

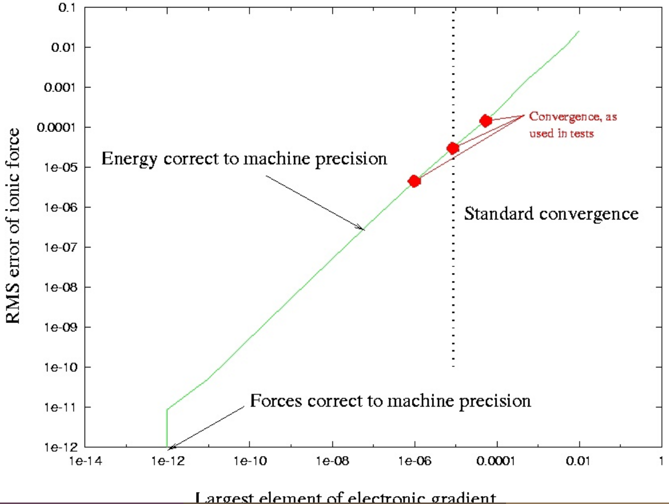
$$\frac{d\mathcal{E}_{\mathrm{KS}}}{d\mathbf{R}_I} = \frac{\partial E_{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle\psi_i|\ \psi_j\rangle + \sum_{ij} \frac{\partial \langle\psi_i|}{\partial \mathbf{R}_I} \left[\frac{\partial E_{\mathrm{KS}}}{\partial \langle\psi_i|} + \sum_j \Lambda_{ij} |\psi_j\rangle\right]$$

- When $|\psi_i\rangle$ optimal

$$F_{\mathrm{KS}}(\mathbf{R}_I) = -\frac{\partial E_{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle\psi_i|\ \psi_j\rangle$$

BOMD: Error in forces

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



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:

$$\sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \min_{\{\psi_i\}} E_{\mathrm{KS}} \left(\{\psi_i\}, \mathbf{R}^N \right)$$

  - NVT:

$$\sum_{I=1}^{N} \frac{1}{2s^2} M_I \dot{\mathbf{R}}_I^2 + \min_{\{\psi_i\}} E_{\mathrm{KS}} \left(\{\psi_i\}, \mathbf{R}^N \right) + \frac{1}{2} Q_s \dot{s}^2 + g k_{\mathrm{B}} T \ln(s)$$

Car-Parrinello method

Car-Parrinello method

Roberto Car & Michele Parrinello, *Physical Review Letters* **55**, 2471 (1985)

- They postulated Langangean

$$\begin{aligned}\mathcal{L}_{\mathrm{CP}}\left(\{\psi_i\},\left\{\dot{\psi}_i\right\};\mathbf{R},\dot{\mathbf{R}}\right) &= \sum_{i=1}^{M}\frac{1}{2}\mu\left\langle\dot{\psi}_i\mid\dot{\psi}_i\right\rangle \\ &\quad -min_{\{\psi_i\}}\mathcal{E}_{\mathrm{KS}}\left(\{\psi_i\},\mathbf{R}^N\right) \\ &\quad +\sum_{I=1}^{N}\frac{1}{2}M_I\dot{\mathbf{R}}_I^2\end{aligned}$$

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

- *Fictitious* or *fake* dynamics of electrons
- μ = *fictitious mass* or *inertia parametre*
- *Simultaneous* dynamics of ions and electrons

Car-Parrinello method: Equations of motion

- Euler-Lagrange equations

$$
\begin{aligned}
\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \left\langle \dot{\psi}_i \right|} &= \frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \left\langle \psi_i \right|} \\
\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \left\langle \dot{\mathbf{R}}_I \right|} &= \frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \left\langle \mathbf{R}_I \right|}
\end{aligned}
$$

- Equations of motion

$$
\begin{aligned}
\mu \ddot{\psi}_i &= -\frac{\partial E_{\mathrm{KS}}}{\partial \left\langle \psi_i \right|} + \sum_j \Lambda_{ij} \left| \psi_j \right\rangle \\
M_I \ddot{\mathbf{R}}_I &= -\frac{\partial E_{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \left\langle \psi_i \middle| \psi_j \right\rangle
\end{aligned}
$$

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

$$E_{\text{conserved}} = \sum_{i=1}^{M} \frac{1}{2}\mu \left\langle \dot{\psi}_i \mid \dot{\psi}_i \right\rangle + E_{\text{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right) + \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2$$

- Note: instantaneous value of $E_{\text{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right)$, not minimum
- Thus no need to optimise the orbitals at each step

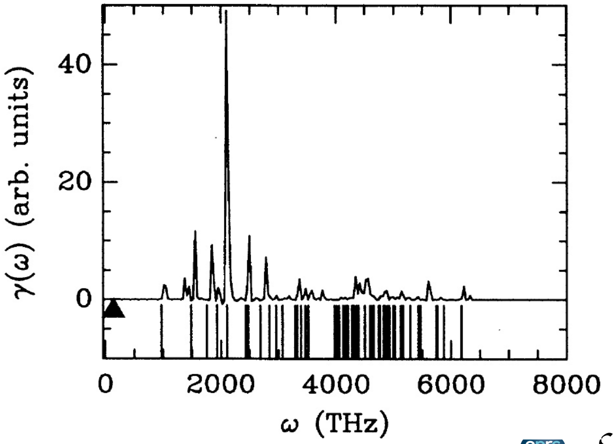
Magic Car-Parrinello method

- 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)

Adiabatic separation

Pastore, Smargiassi & Buda, PRA 1991

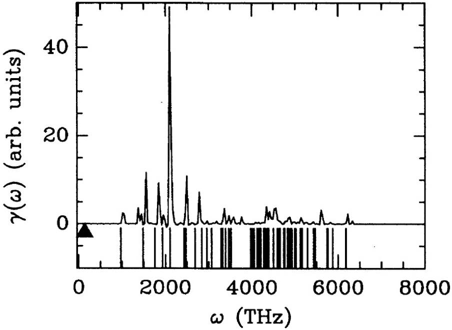
- Vibrational spectra of electrons and ions do not overlap:



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

$$f^e(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i \left\langle \dot{\psi}_i(t) \middle| \dot{\psi}_i(0) \right\rangle dt$$

Constant of motion

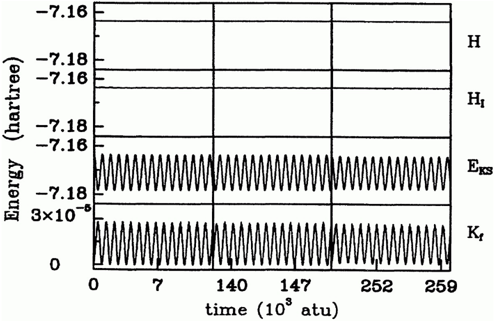
- Physical and conserved energy:

$$
\begin{aligned}
E_{\mathrm{physical}} &= E_{\mathrm{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right) + \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \\
E_{\mathrm{conserved}} &= \sum_{i=1}^{M} \frac{1}{2} \mu \left\langle \dot{\psi}_i \mid \dot{\psi}_i \right\rangle + E_{\mathrm{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right) + \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \\
&= E_{\mathrm{kin,fict}} + E_{\mathrm{physical}}
\end{aligned}
$$

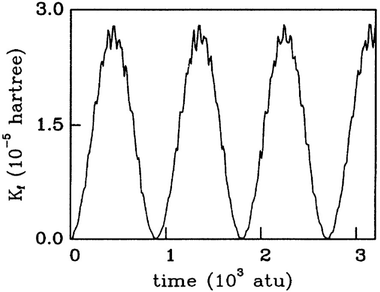
- The difference, $E_{\mathrm{kin,fict}} = \sum_{i=1}^{M} \frac{1}{2} \mu \left\langle \dot{\psi}_i \mid \dot{\psi}_i \right\rangle$, must thus correlate with the changes in the physical energy

Constant of motion: Conservation of energy

Model system: Two-atom Si-fcc
Energy components



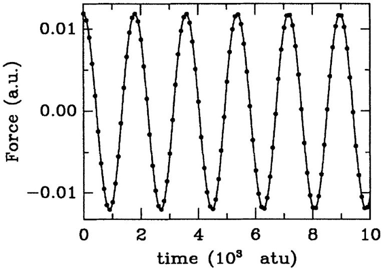
$E_{\mathrm{kin,f}}$



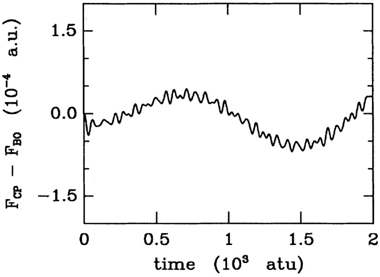
Deviation from Born-Oppenheimer surface

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

$\mathbf{F}_x$(Si)



$\mathbf{F}_{x,\mathrm{CP}}$(Si)-$\mathbf{F}_{x,\mathrm{BO}}$(Si)



Control of adiabacity

- Harmonic analysis:

$$\omega_{ij}^{e} = \sqrt{\frac{2\left(\varepsilon_i - \varepsilon_j\right)}{\mu}}$$

ε_i occupied, ε_j unoccupied (virtual) orbitals

- Lowest frequency

$$\omega_{\mathrm{min}}^{e} \propto \sqrt{\frac{E_{\mathrm{gap}}}{\mu}}$$

- Highest frequency

$$\omega_{\mathrm{max}}^{e} \propto \sqrt{\frac{E_{\mathrm{cut}}}{\mu}}$$

- Thus maximum possible time step

$$\left(\Delta t^{e}\right)_{\mathrm{max}} \propto \sqrt{\frac{\mu}{E_{\mathrm{cut}}}}$$

Control of adiabacity

- Lowest frequency has to be well above ionic frequencies

$$\omega^e_{\mathrm{min}} \propto \sqrt{\frac{E_{\mathrm{gap}}}{\mu}}$$

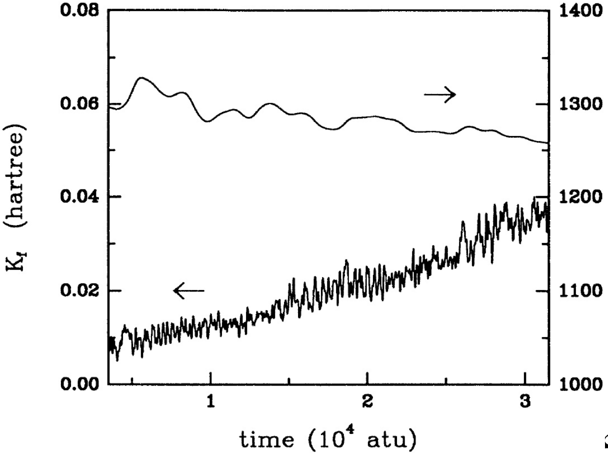
- Highest frequency limits the maximum possible time step

$$\omega^e_{\mathrm{max}} \propto \sqrt{\frac{E_{\mathrm{cut}}}{\mu}} \qquad (\Delta t^e)_{\mathrm{max}} \propto \sqrt{\frac{\mu}{E_{\mathrm{cut}}}}$$

- If Δt fixed and μ 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

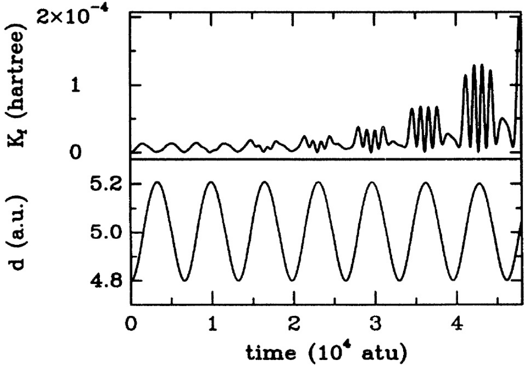
Loss of adiabacity: Difficult cases

- Vacancy in hot 64-atom Si cell



Loss of adiabacity: Difficult cases

- Sn_2: Degeneracy of HOMO and LUMO at short distances



Analysis of adiabacity: Simplified model

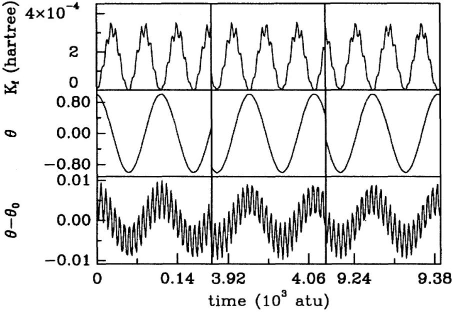
Two-level, two-electron model

- Wave function

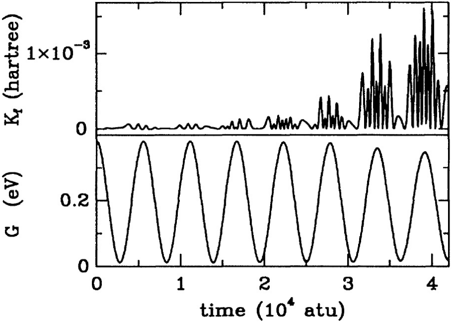
$$\psi = \left(\cos\frac{\theta}{2}\right)\Phi_1 + \left(\sin\frac{\theta}{2}\right)\Phi_2$$

θ is the electronic degree of freedom

Constant gap



Opening-closing gap G

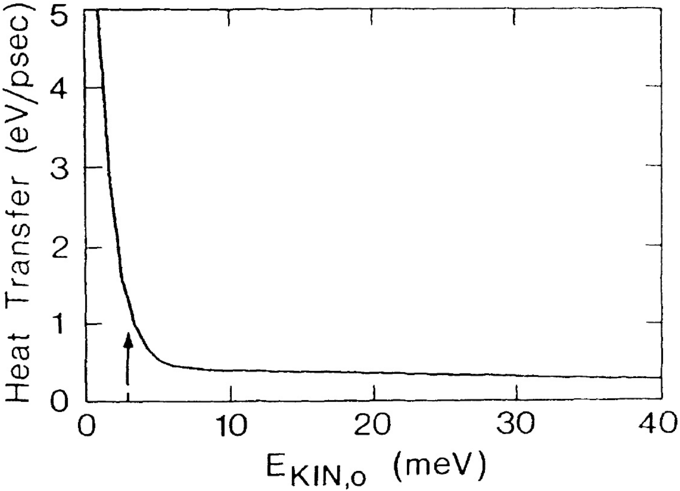


Zero or small electronic gaps: Thermostatted electrons

- 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 $E_{\mathrm{kin},0}$ 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

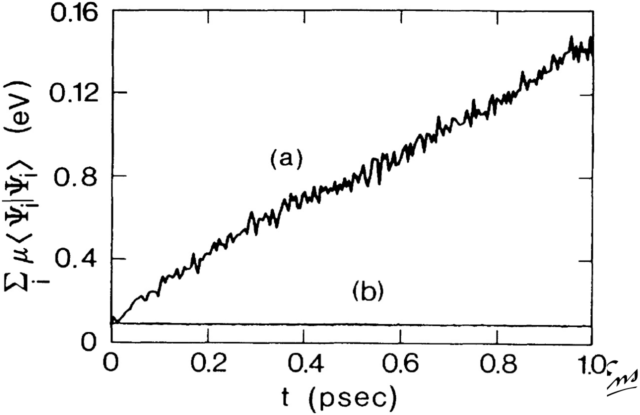
Thermostat on electrons

- Example: Aluminium
- Dependence of the heat transfer on the choice of $E_{\mathrm{kin},0}$ in solid Al



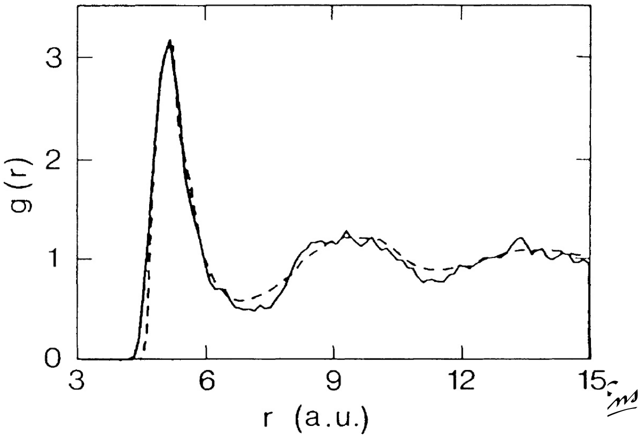
Thermostat on electrons: Does it help?

- 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:

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

- The new equations of motion:

$$(M_I + dM_I)\, \ddot{\mathbf{R}}_I = \mathbf{F}_I$$

where

$$dM_I = \frac{2}{3} \mu E^I_{\mathrm{kin}}$$

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

Example: Vibrations in water molecule

mode	harmonic	BOMD	50	100	200	400	dM/M [%]
bend	1548	1543	1539	1535	1529	1514	$0.95 \times 10^{-3} \mu$
sym.	3515	3508	3494	3478	3449	3388	$1.81 \times 10^{-3} \mu$
asym.	3621	3616	3600	3585	3556	3498	$1.71 \times 10^{-3} \mu$

Orthonormality constraints

Equations of motion

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

- In principle differential equations, however after discretisation difference equations (Verlet algorithm)
- Therefore the algorithm for the constraints Λ_{ij} depends on the integration method

Orthonormality constraints: RATTLE

- Define

$$\mathbf{X}_{ij} = \frac{\Delta t^2}{2\mu}\Lambda^p_{ij} \qquad \mathbf{Y}_{ij} = \frac{\Delta t^2}{2\mu}\Lambda^v_{ij} \qquad \mathbf{C} \text{ wf coefficients}$$

- Equations of type

$$\mathbf{X}\mathbf{X}^\dagger + \mathbf{X}\mathbf{B} + \mathbf{B}^\dagger\mathbf{X}^\dagger = \mathbf{I} - \mathbf{A} \qquad \mathbf{Y} = \frac{\mathbf{1}}{\mathbf{2}}\left(\mathbf{Q} + \mathbf{Q}^\dagger\right)$$

  A, **B**, **Q** of type $\mathbf{A}_{ij} = \sum_{\mathbf{G}} c^*_{\mathbf{G}i} c_{\mathbf{G}j}$

- Solve iteratively:

$$\mathbf{X}^{(\mathrm{n}+1)} = \frac{\mathbf{1}}{\mathbf{2}}\left[\mathbf{I} - \mathbf{A} + \mathbf{X}^{(\mathrm{n})}\left(\mathbf{I} - \mathbf{B}\right) + \left(\mathbf{I} - \mathbf{B}\right)\mathbf{X}^{(\mathrm{n})} - \mathbf{X}^{(\mathrm{n})}\mathbf{X}^{(\mathrm{n})}\right]$$

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 ≈ 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

- μ can be chosen to be dependent on the basis set:

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

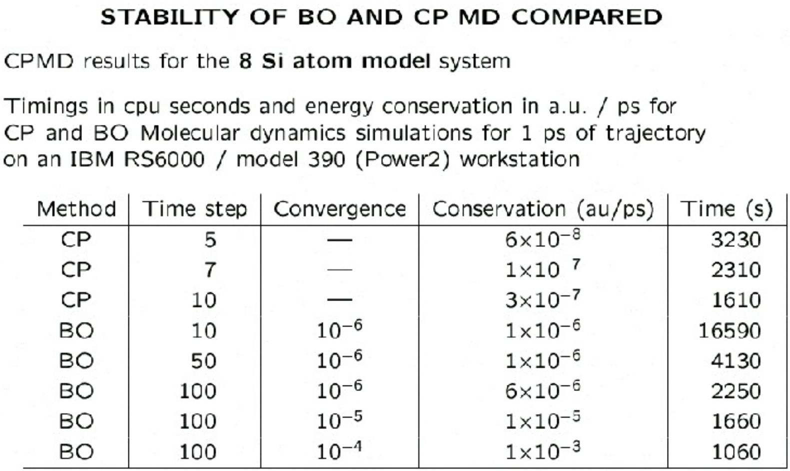
- Kind of “pre-conditioning” of the equation of motion
- Allows for larger time step
- However, leads to much larger corrections on the ionic frequencies and no analytical formula can be used

CP & BO

Car-Parrinello *vs* Born-Oppenheimer dynamics

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

CP *vs* BO



STABILITY OF BO AND CP MD COMPARED

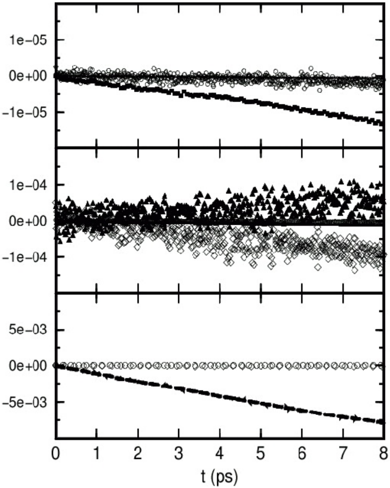
CPMD results for the **8 Si atom model** system

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

Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	1×10^{-7}	2310
CP	10	—	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

CP *vs* BO: Stability

STABILITY OF BO AND CP MD COMPARED (cont'ed)



Δt, convergence

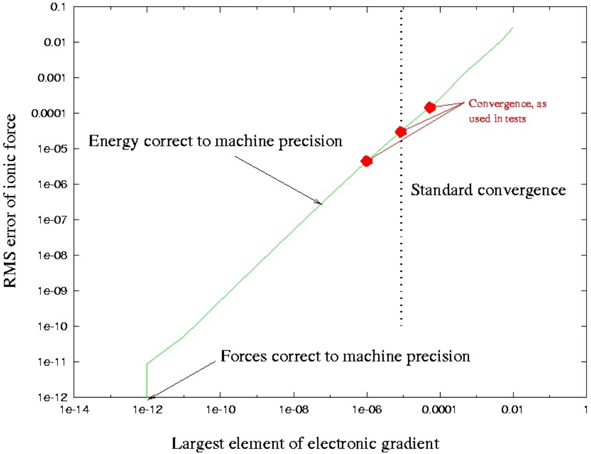
Top:
solid line : CP, 5 a.u.;
open circ. : CP, 10 a.u.;
filled squar. : BO, 10 a.u., 10^{-6}.

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}

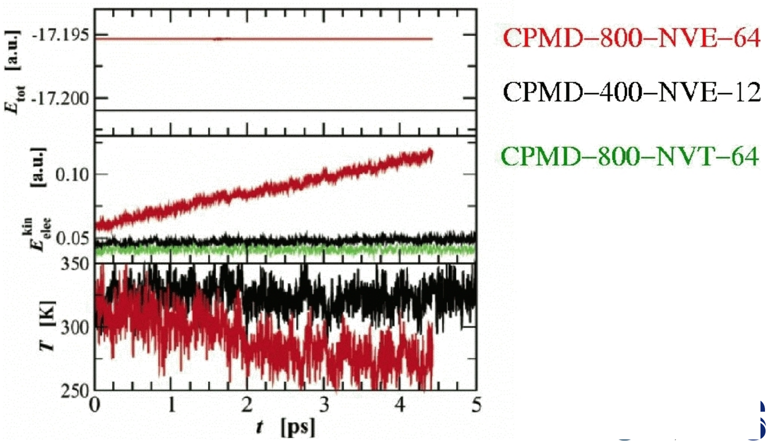
BO: Error in forces

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



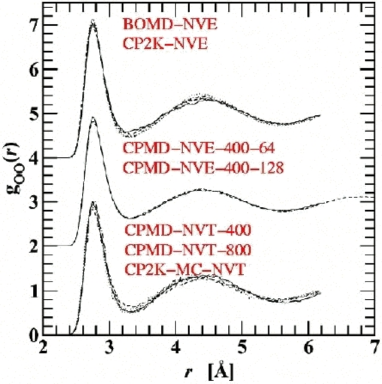
CP *vs* BO: Liquid water

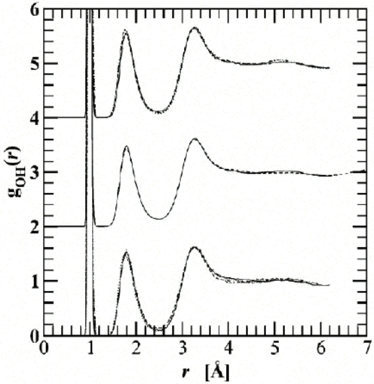
- Effect of μ: Too large value leads to loss of adiabacity
- Thermostatting the electrons recovers the correct behaviour



CP *vs* BO: Liquid water: Results

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





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)