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

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

- 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 $-\nabla_{\mathbf{R}} E\left(\{\mathbf{R}_J\}\right) = -\frac{dE}{d\mathbf{R}_I}$

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:

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

- 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

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

- equations of motion:

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

- if the right-hand side can be evaluated analytically it can be plugged directly to the Verlet algorithm

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

Derivation

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

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

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

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

- Add up:

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

- Yields velocities

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

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

- 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

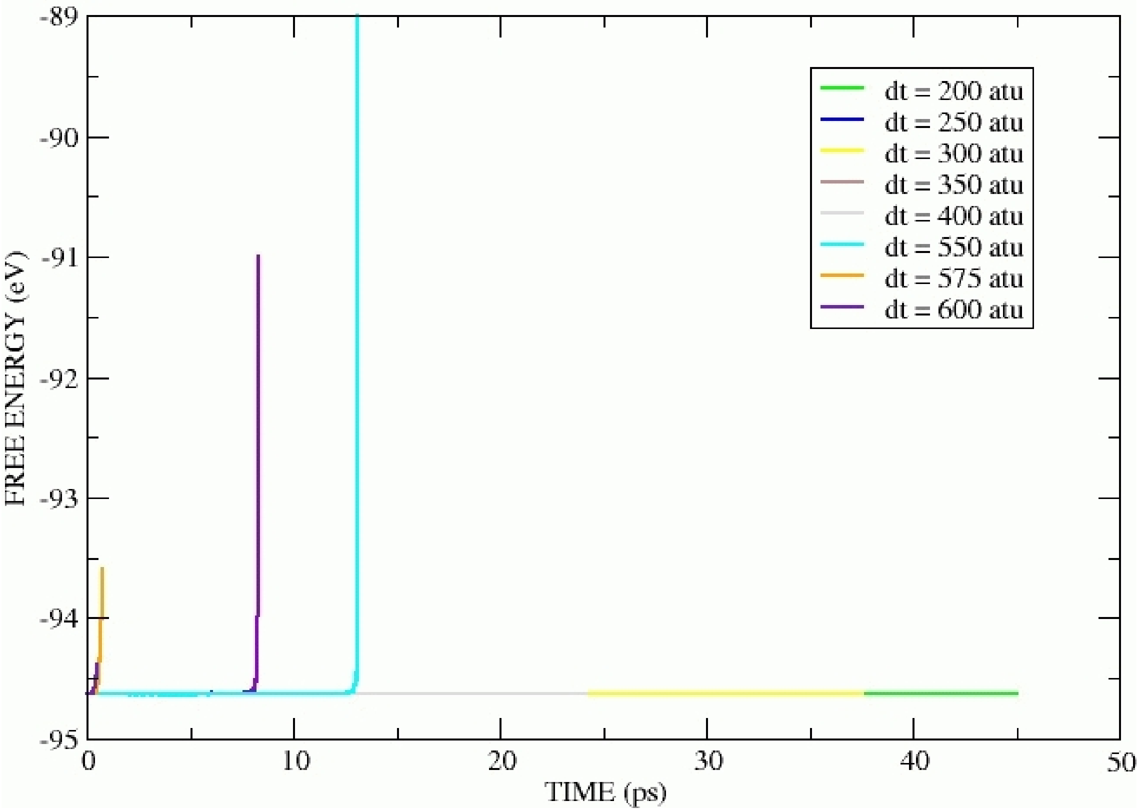
- time step can be changed during simulation(!)

Velocity Verlet: Choice of time step

$AlCl_3$ dimer

Example of a good/bad choice of time step

- Highest vibrational frequency 595 $\text{cm}^{-1} \Rightarrow$ period $T = 56$ fs
- Divergence between $\delta t = 400..500$ atu $= 9.6\text{-}12.0$ 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 μVT
- isobaric-isoenthalpic NPH
- non-equilibrium

Ab initio 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

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

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

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

- forces

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

- when $|\psi_i\rangle$ optimal

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

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

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

- they postulated Langangean

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

  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

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

- equations of motion

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

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

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

- 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

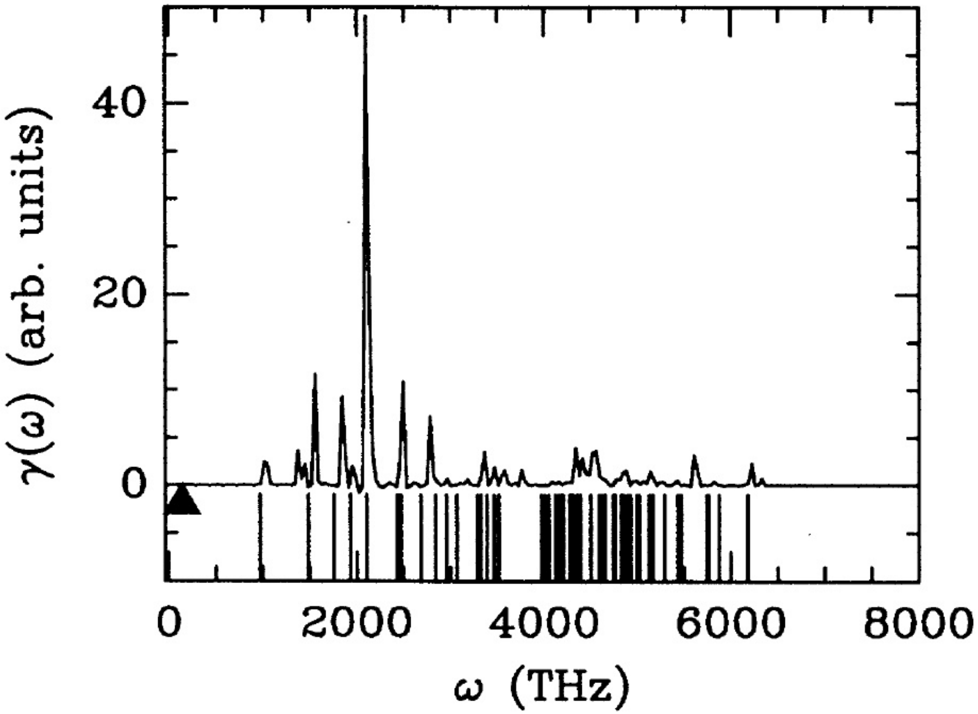
Magic Car-Parrinello method

- 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:

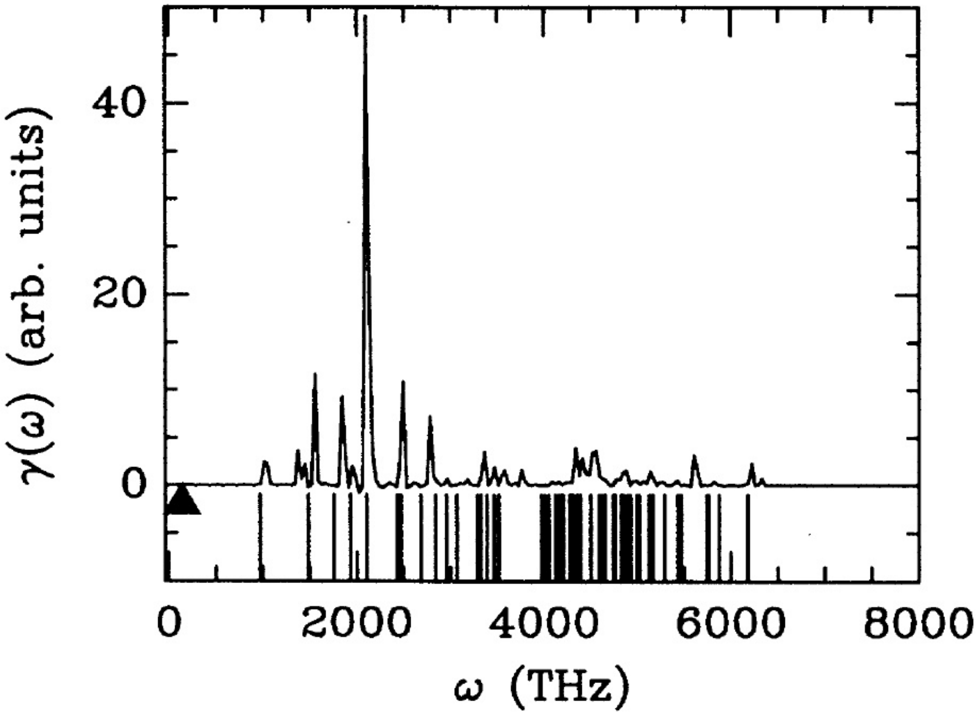


Triangle = highest ionic frequency

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

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

Conservation of energy

- Physical and conserved energy:

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

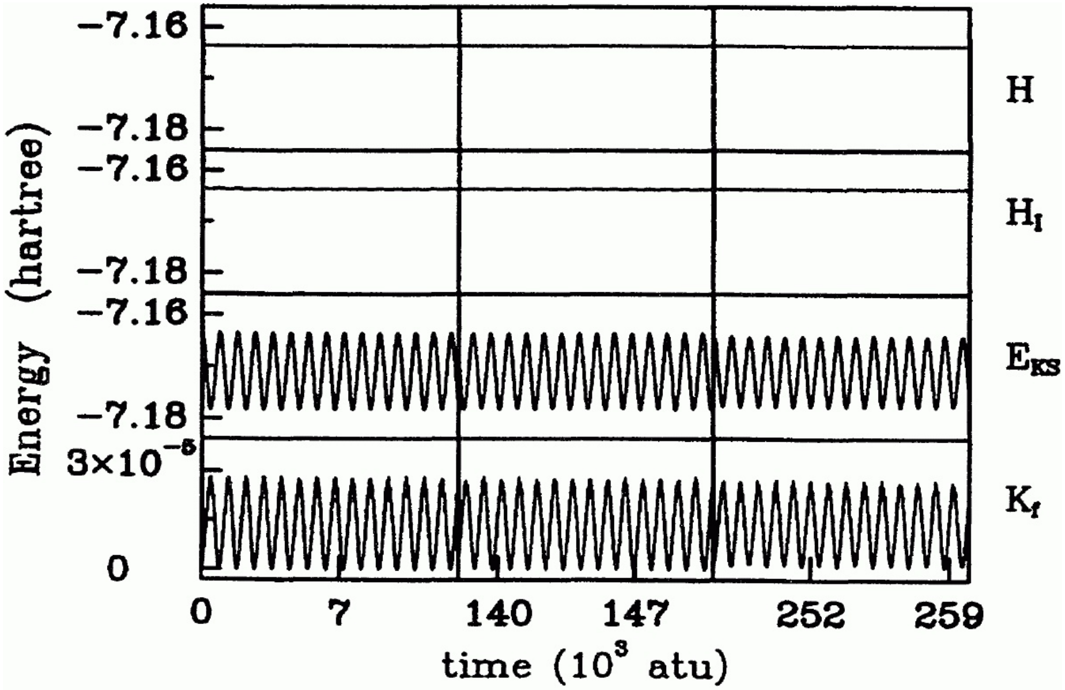
- The difference, $E_{\text{kin,fict}}=\sum_{i=1}^{M}\frac{1}{2}\mu\left\langle\dot{\psi}_i\left|\dot{\psi}_i\right.\right\rangle$, must thus correlate with the changes in the physical energy

Constant of motion

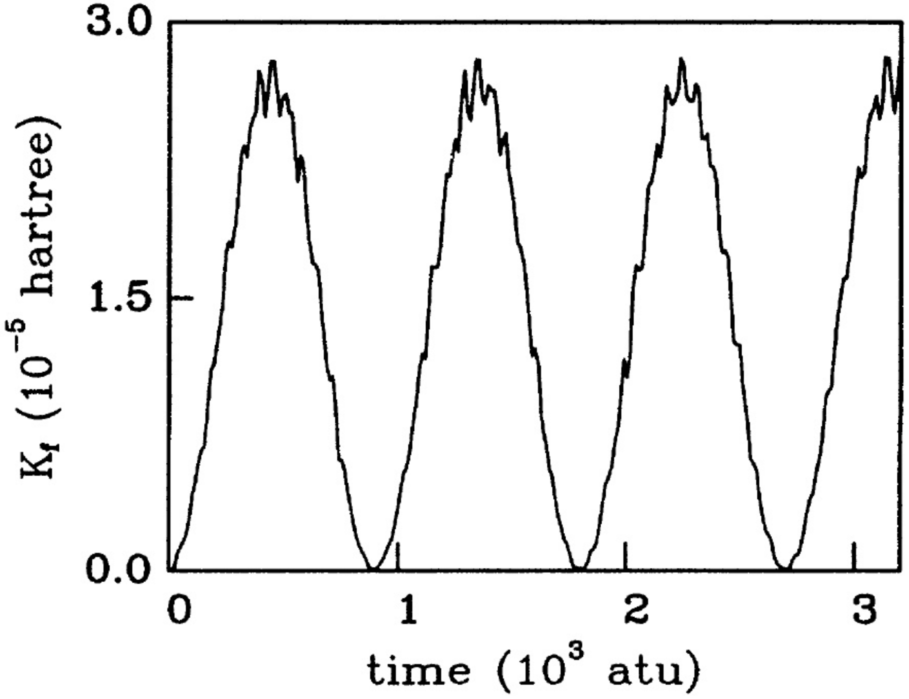
Conservation of energy

Model system: Two-atom Si-fcc

Energy components



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

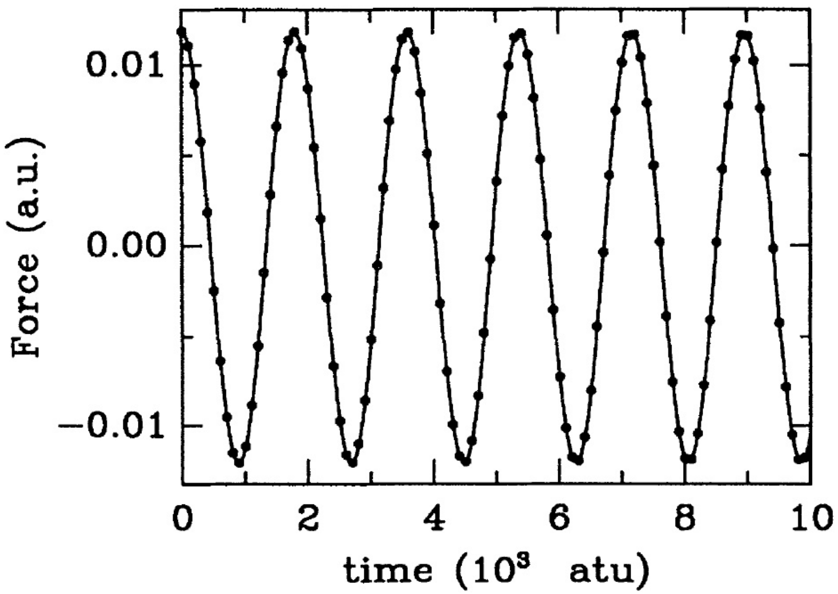


Deviation from Born-Oppenheimer surface

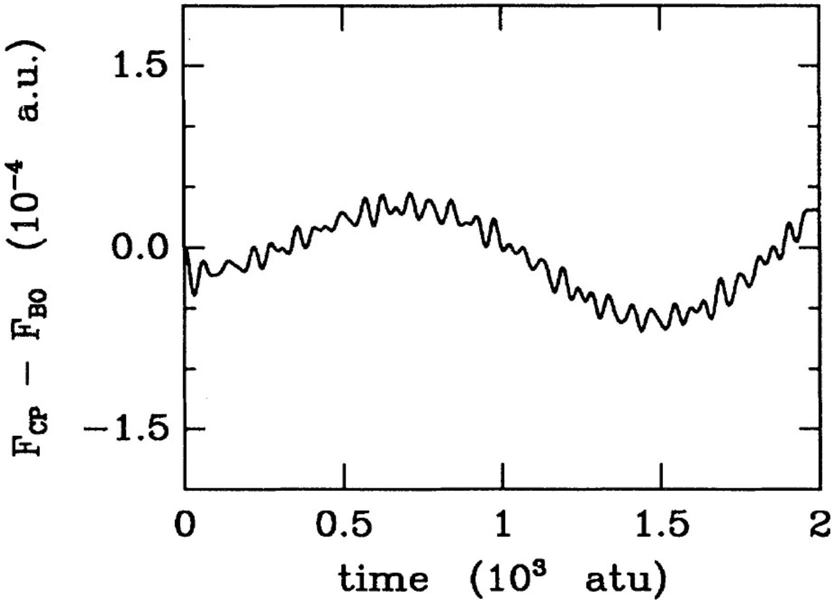
Are the forces accurate?

- 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

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

- 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

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

- Highest frequency limits the maximum possible time step

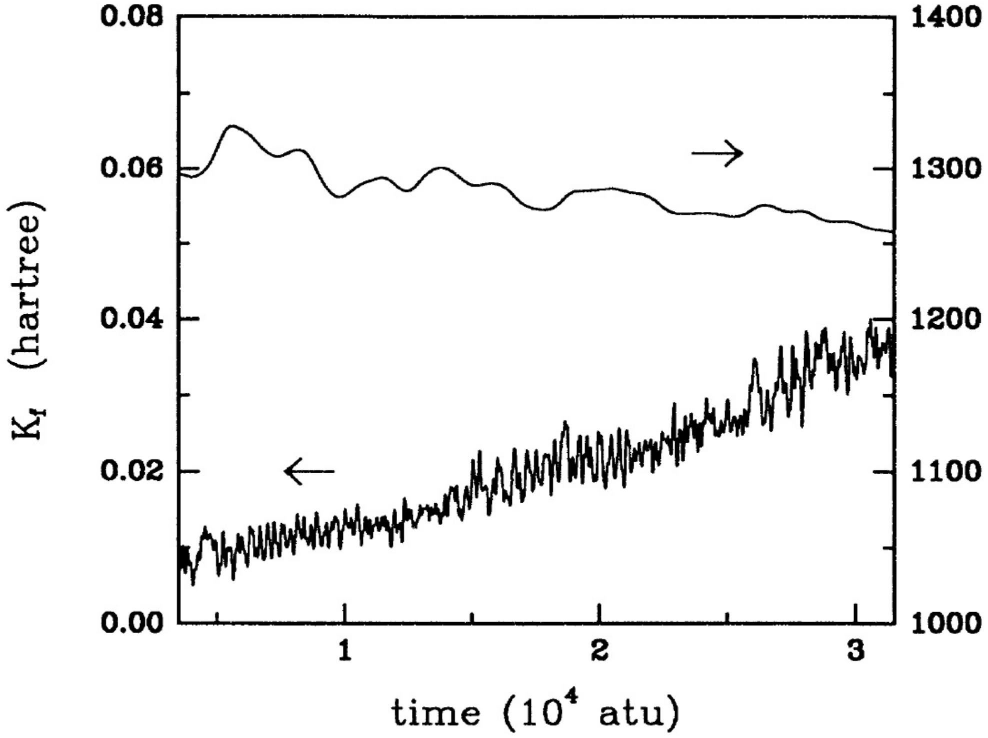
$$\omega^e_{\text{max}} \propto \sqrt{\frac{E_{\text{cut}}}{\mu}} \qquad (\Delta t^e)_{\text{max}} \propto \sqrt{\frac{\mu}{E_{\text{cut}}}}$$

- If Δt fixed and μ 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

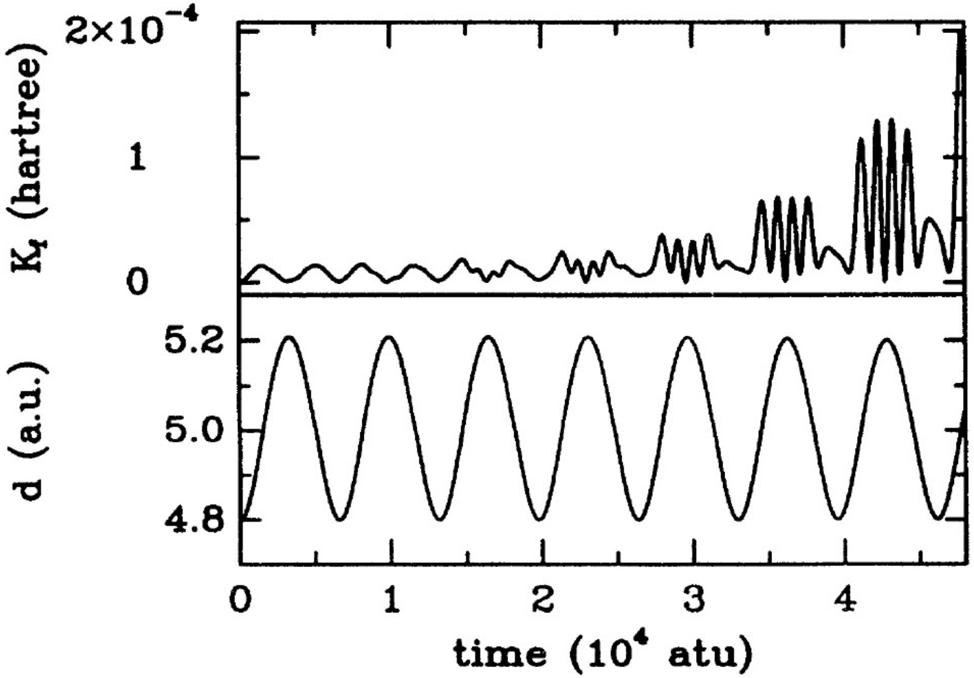
- Vacancy in hot 64-atom Si cell



Loss of adiabacity

Bad cases

- Sn_2: Degeneracy of HOMO and LUMO at short distances



Analysis of adiabacity

Simplified model

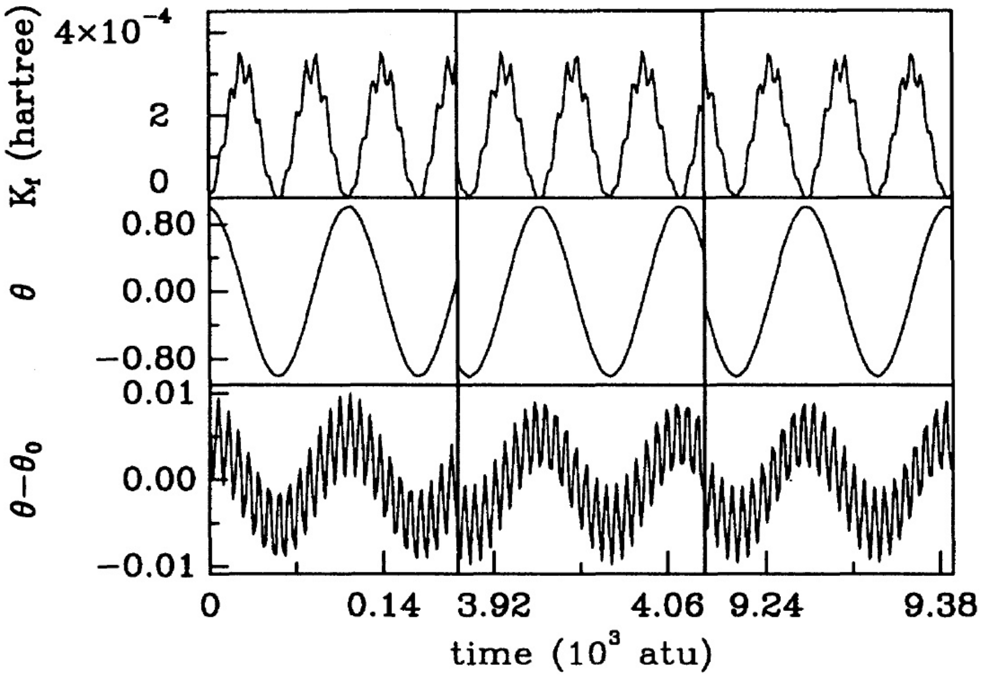
Two-level, two-electron model

- Wave function

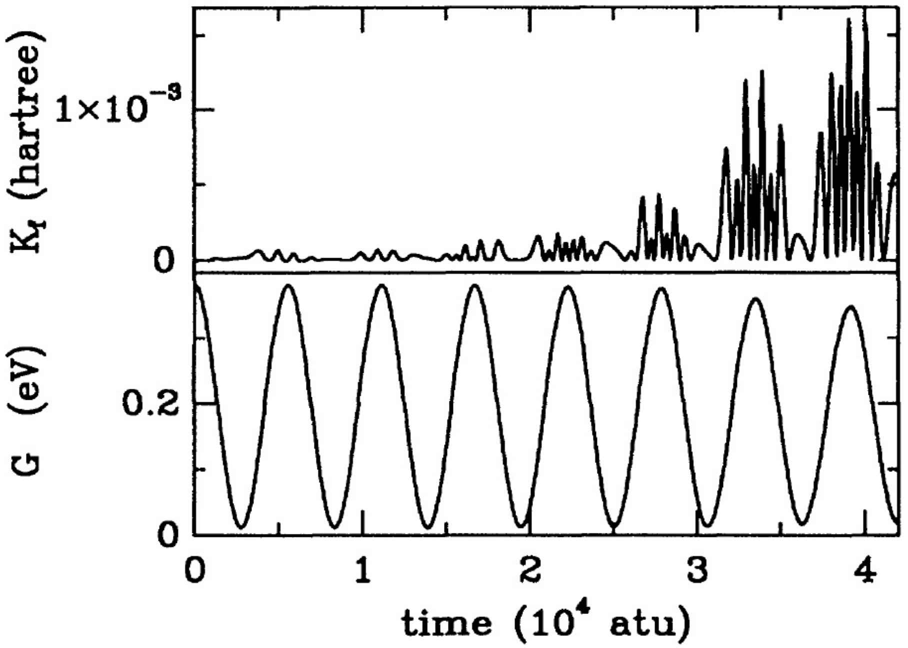
$$\psi = \left(\cos \frac{\theta}{2} \right) \Phi_1 + \left(\sin \frac{\theta}{2} \right) \Phi_2$$

θ is the electronic degree of freedom

Constant gap



Opening-closing gap G



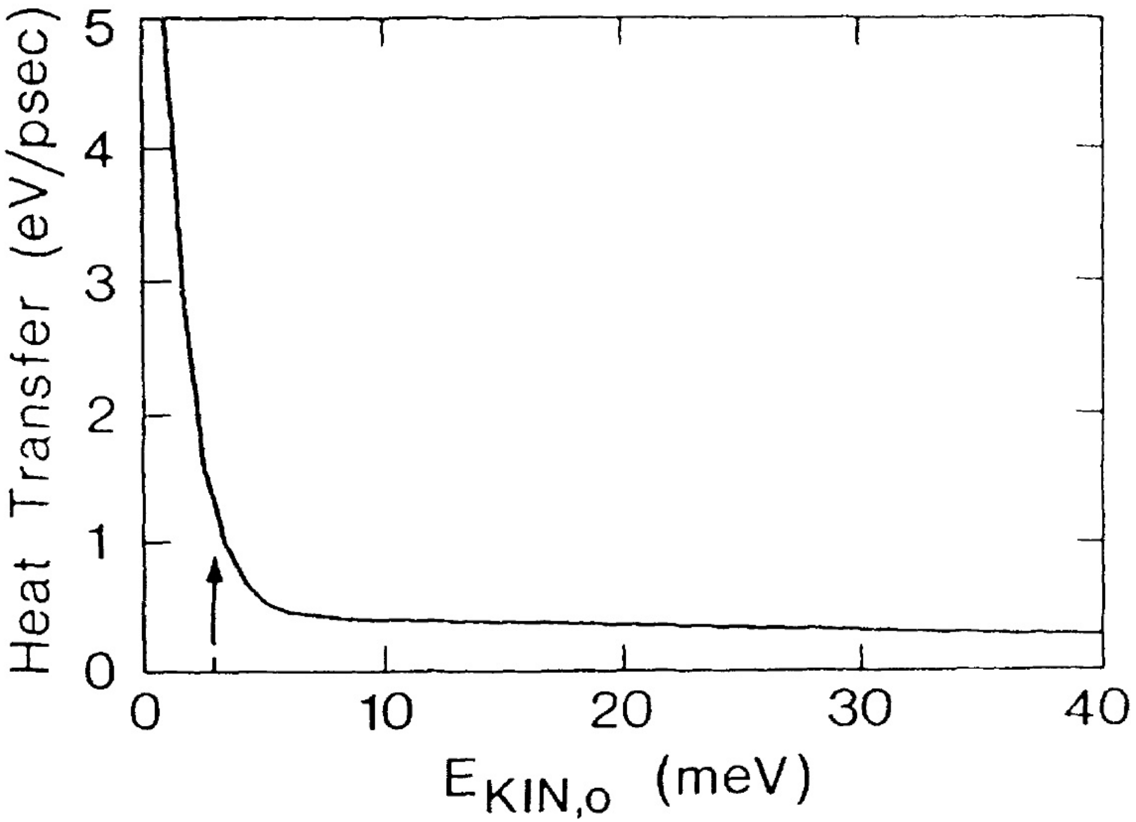
Zero or small electronic gaps

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

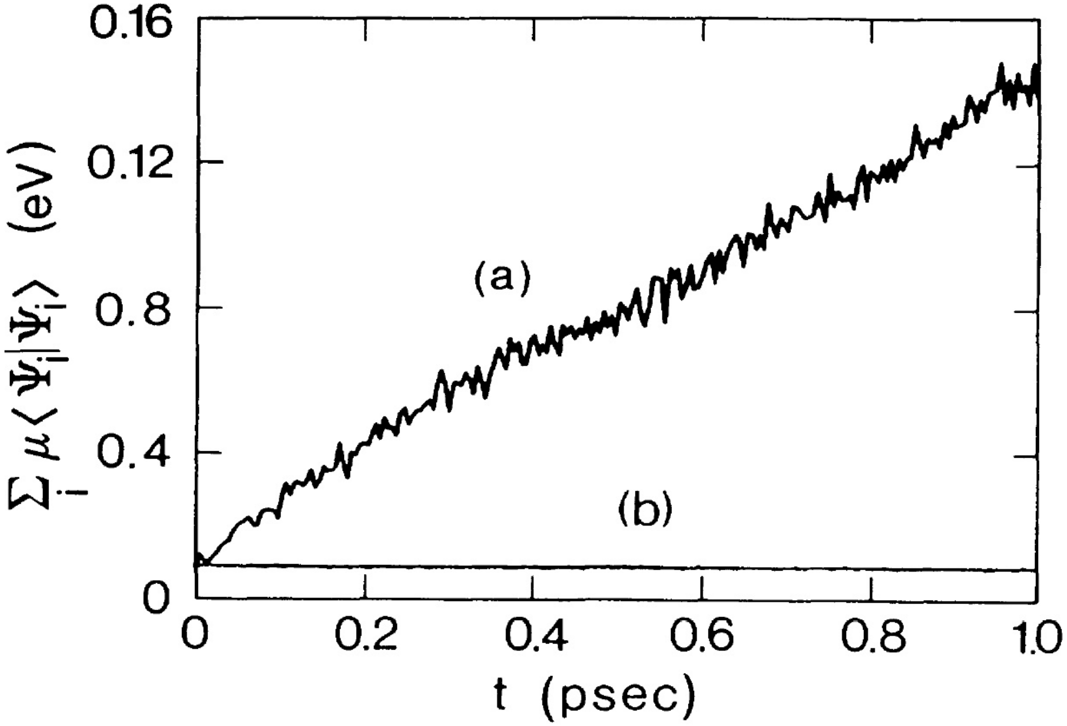
- Example: Aluminium
- Dependence of the heat transfer on the choice of $E_{\text{kin},0}$ in solid Al



Thermostat on electrons

Does it help?

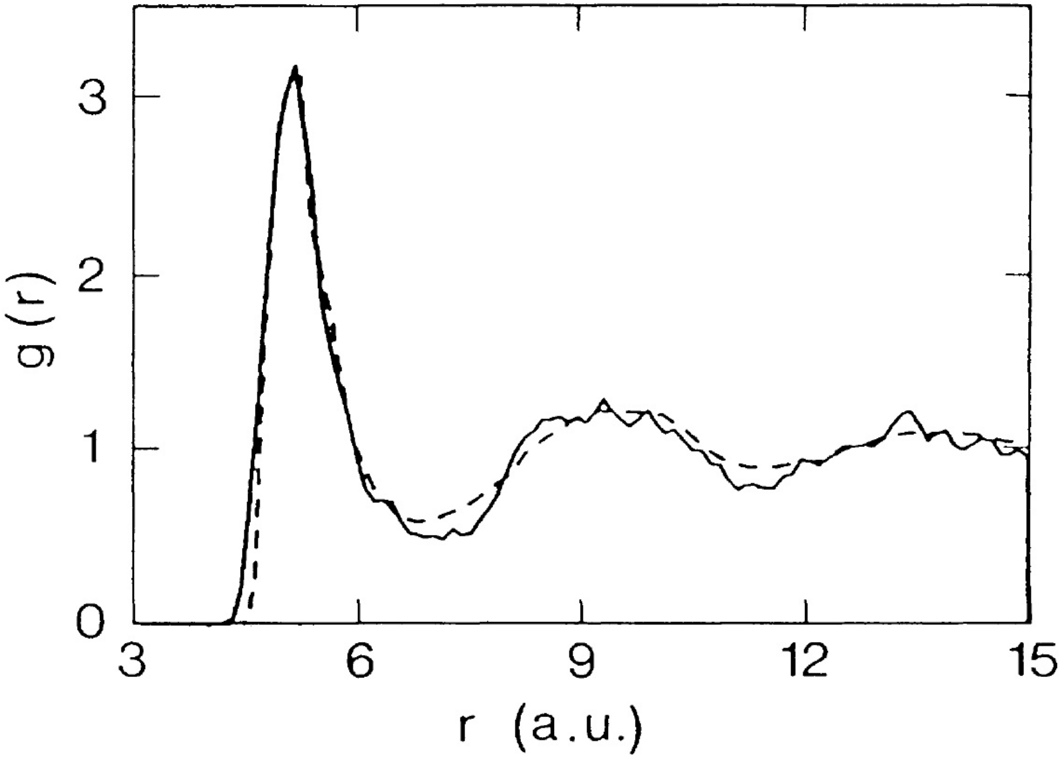
- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat



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:

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

- The new equations of motion:

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

  where

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

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

Example: Vibrations in water molecule

			μ				
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	$1.71 \times 10^{-3} \mu$

Choice of μ : Recent discussion

Liquid water

Orthonormality constraints

Equations of motion

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

- 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

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

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

- Solve iteratively:

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

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 ≈ 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
Most applications in solids	Superior for liquids

CP *vs* BO

STABILITY OF BO AND CP MD COMPARED

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

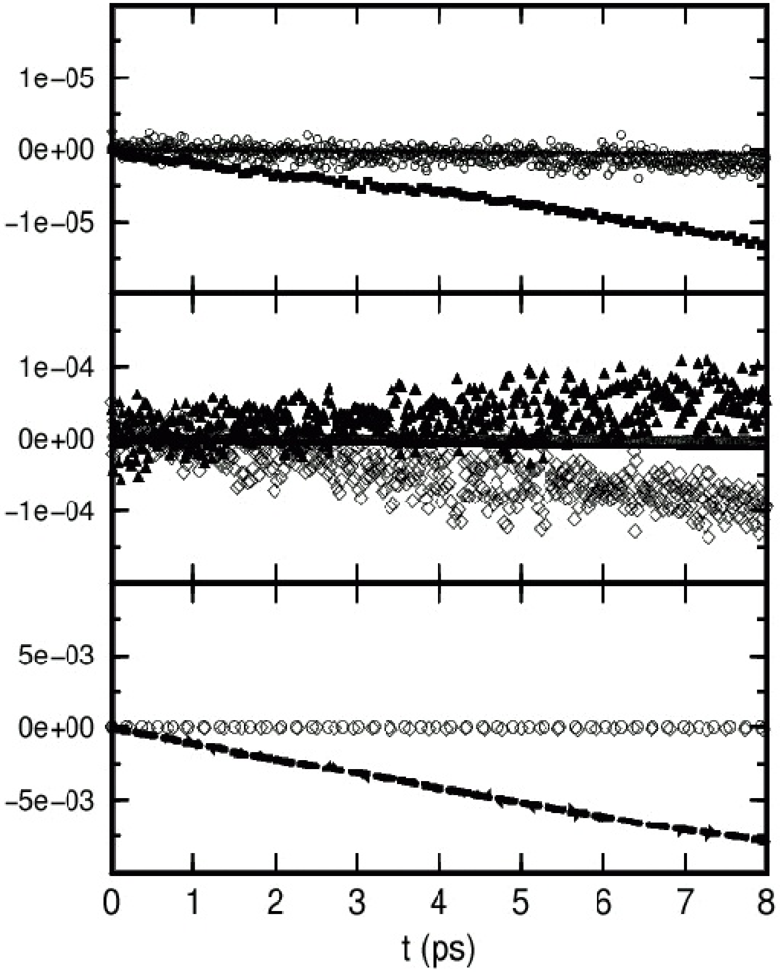
Timings in cpu seconds and energy conservation in a.u. / ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	$1\times10^{\ 7}$	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:

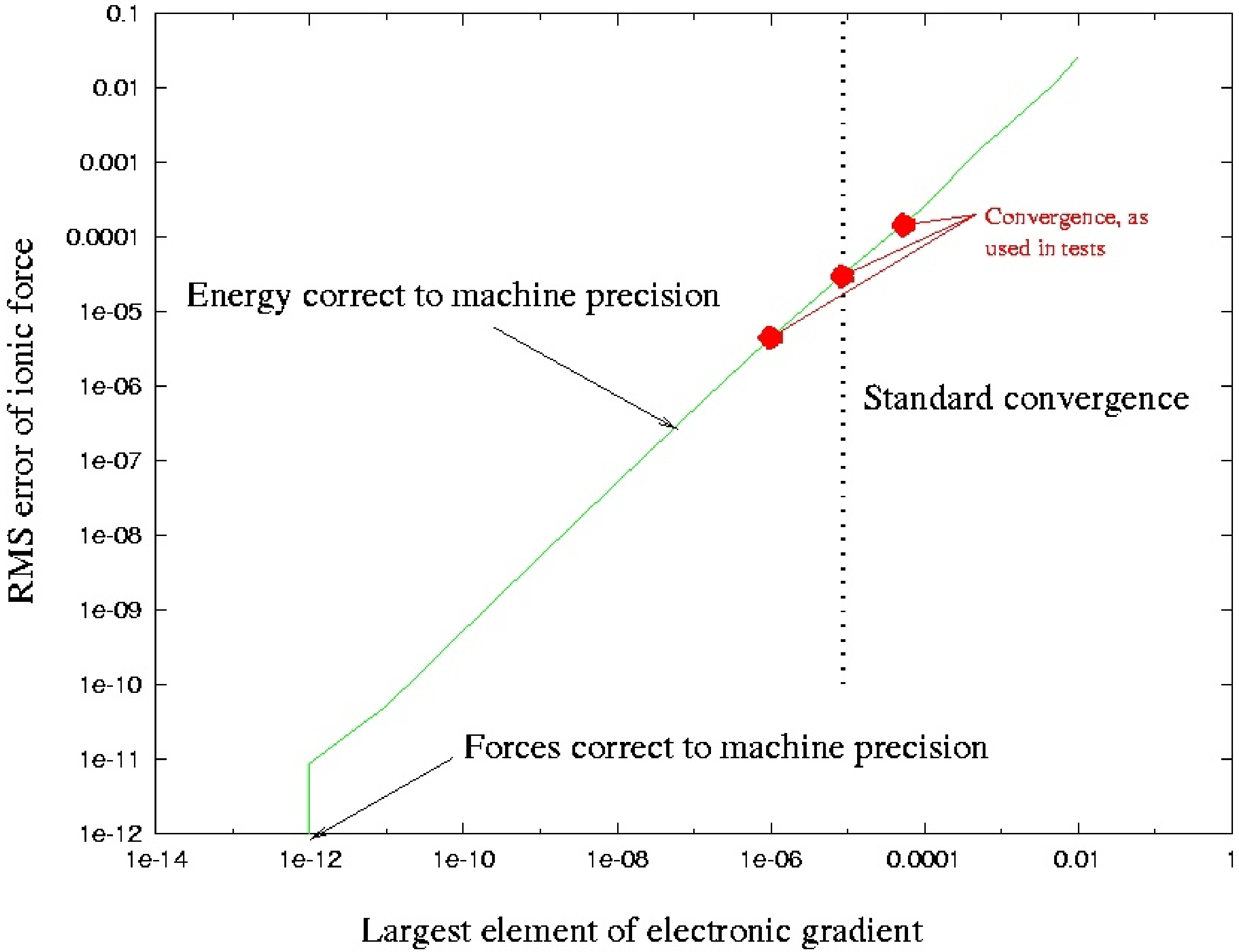
open circl. : CP, 10 a.u.;
filled squar. : BO, 10 a.u., 10^{-6};
filled trian. : BO, 100 a.u., 10^{-6};
open diam. : BO, 100 a.u., 10^{-5}.

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

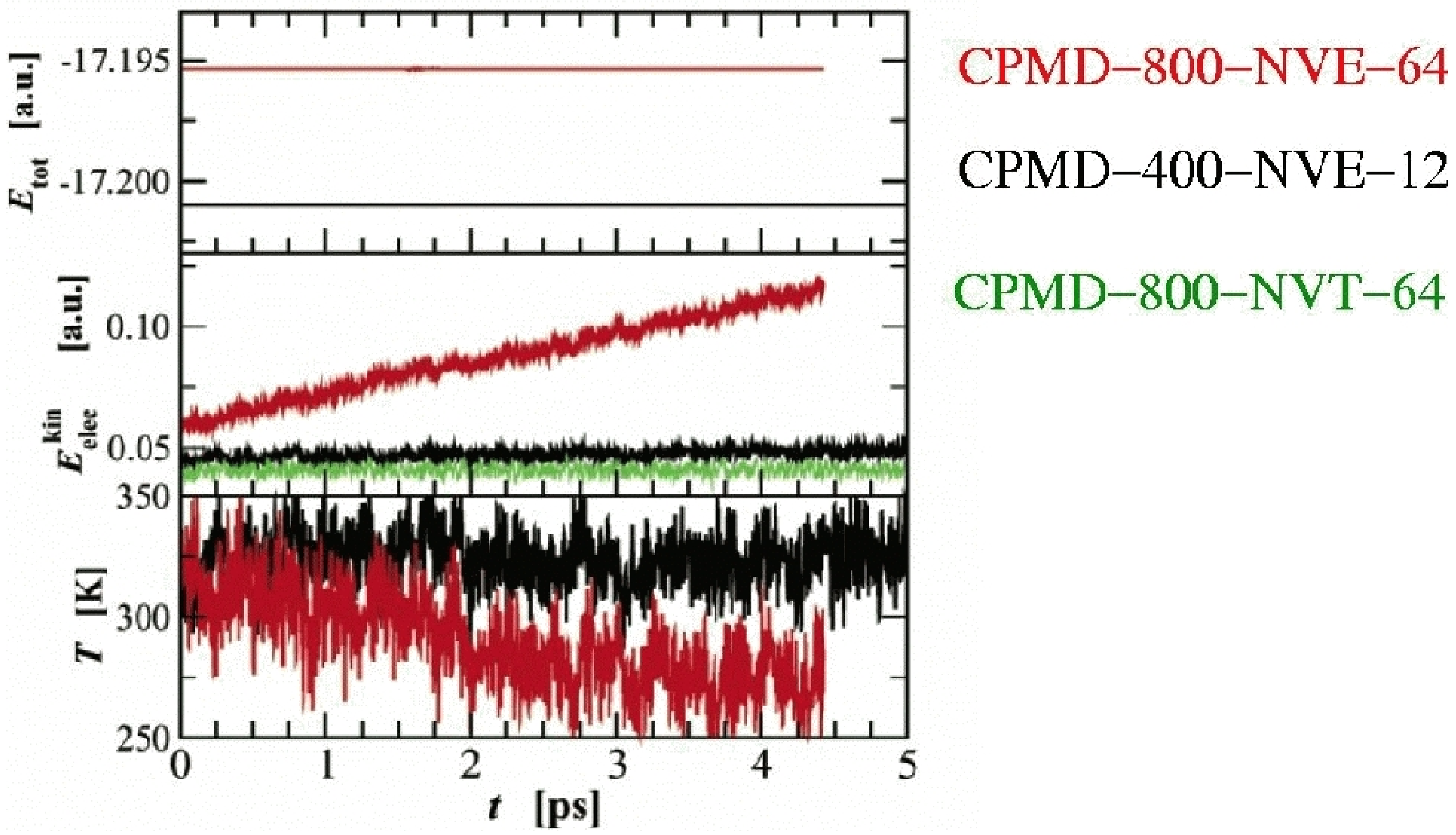
- The error in the forces depends on the convergence criterion set for the electronic structure in BOMD:



CP *vs* BO: Liquid water

Stability

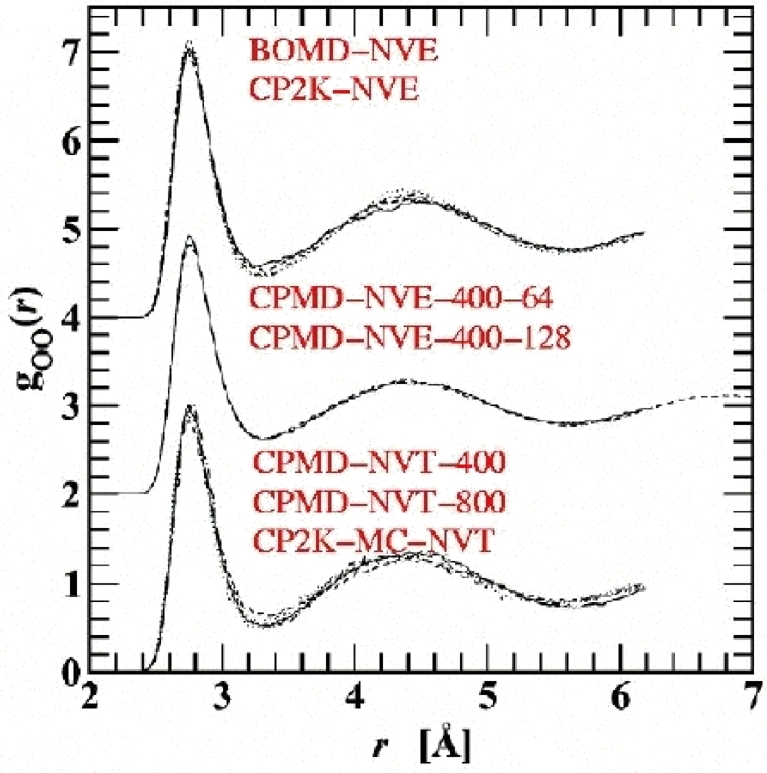
- Effect of μ: Too large value leads to loss of adiabacity
- Thermostatting the electrons recovers the correct behaviour

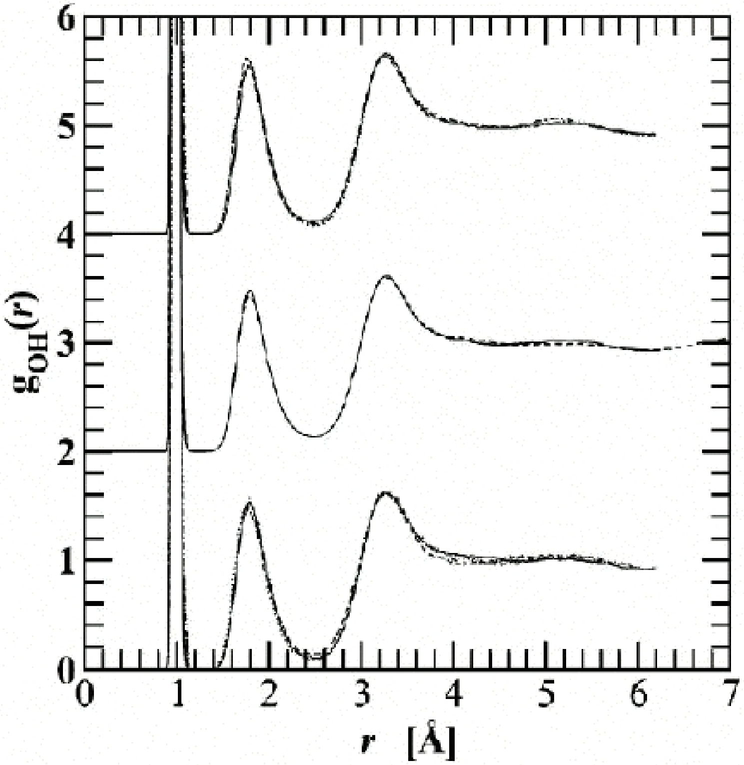


CP *vs* BO: Liquid water

Results

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





Ehrenfest *vs* Car-Parrinello dynamics

Ehrenfest dynamics	Car-Parrinello MD
Based on quantum (real) adiabatic separation	Based on classical (fictitious) adiabatic separation
Not exactly on BO surface	Always slightly off BO surface
Deviations from BO surface accumulate, electrons must be quenched back onto BO surface	Stable against deviations from BO surface
$\Delta t \approx$ electronic time scales, very small time step need	$\Delta t \gg$ electronic time scales, larger time step possible
Orthonormality rigorously preserved at no extra cost	Orthonormality must be imposed using constraints

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 μ!