

# *Ab initio* molecular dynamics

# Realistic MD simulations

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

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

## 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

# Ehrenfest dynamics

## Real time wave function evolution

- Electron dynamics follows slow motion of ionic position in nuclear potential  $v_{\text{ext}}$
- Time step is determined by real time electronic dynamics, in plane wave basis set it is in practise the kinetic energy of the narrowest plane wave

$$\omega_e^{\text{max}} \sim E_{\text{cut}} \text{ a.u.} \longrightarrow \Delta t = 0.01 \text{ a.u.} = 0.2 \times 10^{-3} \text{ fs}$$

- However, the instantaneous density ja Hartree and XC potentials introduce non-linearity

# Ehrenfest dynamics

- Use product *Ansatz* for the many body wave function:

$$\Phi_E(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \approx \Psi(\{\mathbf{r}_i\}; t) \chi(\{\mathbf{R}_I\}; t) \exp \left[ \frac{i}{\hbar} \int_{t=t_0}^t \bar{E}_e(t') dt' \right]$$

with the phase

$$\bar{E}_e = \int_{\mathbf{r}} \int_{\mathbf{R}} \Psi^*(\{\mathbf{r}_i\}; t) \chi^*(\{\mathbf{R}_I\}; t) \mathcal{H}_e \Psi(\{\mathbf{r}_i\}; t) \chi(\{\mathbf{R}_I\}; t) d\mathbf{R} d\mathbf{r}$$

- These equations lead to Schrödinger-like equations for the electrons and ions

$$i\hbar \frac{\partial \Psi(\{\mathbf{r}_i\}; t)}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi(\{\mathbf{r}_i\}; t) + \left\{ \int_{\mathbf{R}} \chi^*(\{\mathbf{R}_I\}; t) \mathcal{V}_{e-I}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \chi(\{\mathbf{R}_I\}; t) d\mathbf{R} \right\} \Psi(\{\mathbf{r}_i\}; t)$$

$$i\hbar \frac{\partial \chi(\{\mathbf{R}_I\}; t)}{\partial t} = - \sum_i \frac{\hbar^2}{2M_I} \nabla_I^2 \chi(\{\mathbf{R}_I\}; t) + \left\{ \int_{\mathbf{r}} \Psi^*(\{\mathbf{r}_i\}; t) \mathcal{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \Psi(\{\mathbf{r}_i\}; t) d\mathbf{r} \right\} \chi(\{\mathbf{R}_I\}; t)$$

# Ehrenfest dynamics

- The equations are solved by propagating the equations of motion
- However, usually classical limit is taken for ions first
- Several wave functions can be propagated simultaneously (no variational principle assumed)
- Real dynamics of electrons obtained
- Thus the time step must be (very) small

Born-Oppenheimer  
molecular dynamics

# Born-Oppenheimer *Ansatz*

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

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

- 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):

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

- 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

- Lagrangian

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

- equations of motion:

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

- 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

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

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

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

- forces

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

- when  $|\psi_i\rangle$  optimal

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

# 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 Lagrangean

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

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

- *fictitious* or *fake* dynamics of electrons
- $\mu =$  *fictitious mass* or *inertia parametre*
- *simultaneous* dynamics of ions and electrons

# Car-Parrinello method

## Equations of motion

- Euler-Lagrange equations

$$\frac{d}{dt} \frac{\partial \mathcal{L}_{CP}}{\partial \langle \dot{\psi}_i |} = \frac{\partial \mathcal{L}_{CP}}{\partial \langle \psi_i |}$$
$$\frac{d}{dt} \frac{\partial \mathcal{L}_{CP}}{\partial \langle \dot{\mathbf{R}}_I |} = \frac{\partial \mathcal{L}_{CP}}{\partial \langle \mathbf{R}_I |}$$

- equations of motion

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

# 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

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

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



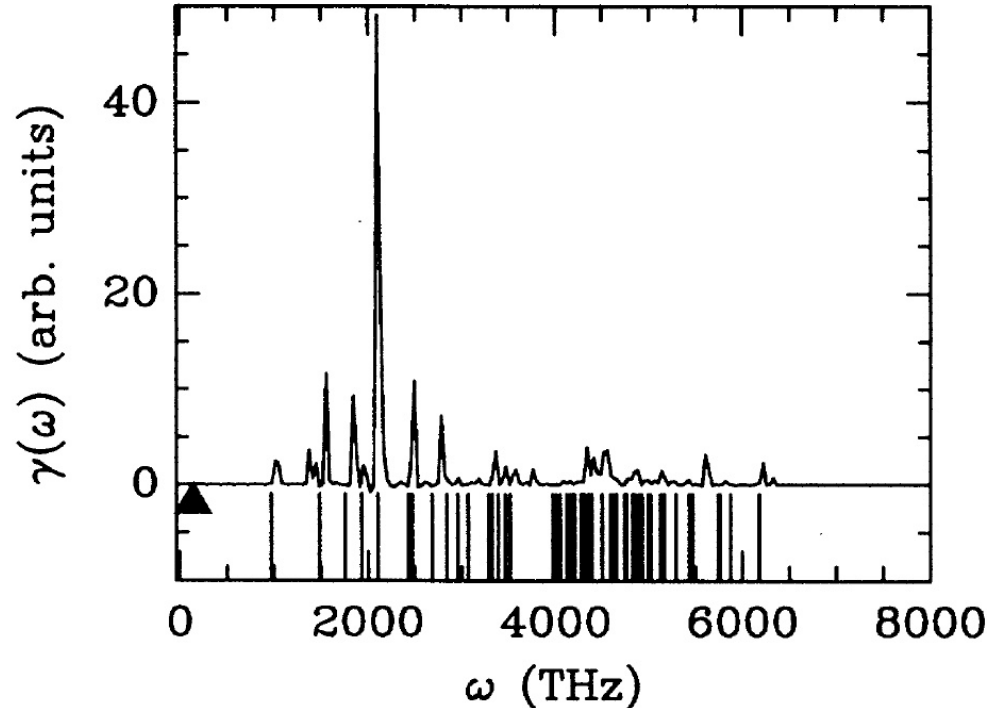
## *Magic* Car-Parrinello method

- 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)

# Adiabatic separation

Pastore, Smargiassi & Buda, PRA 1991

- Vibrational spectra of electrons and ions do not overlap:

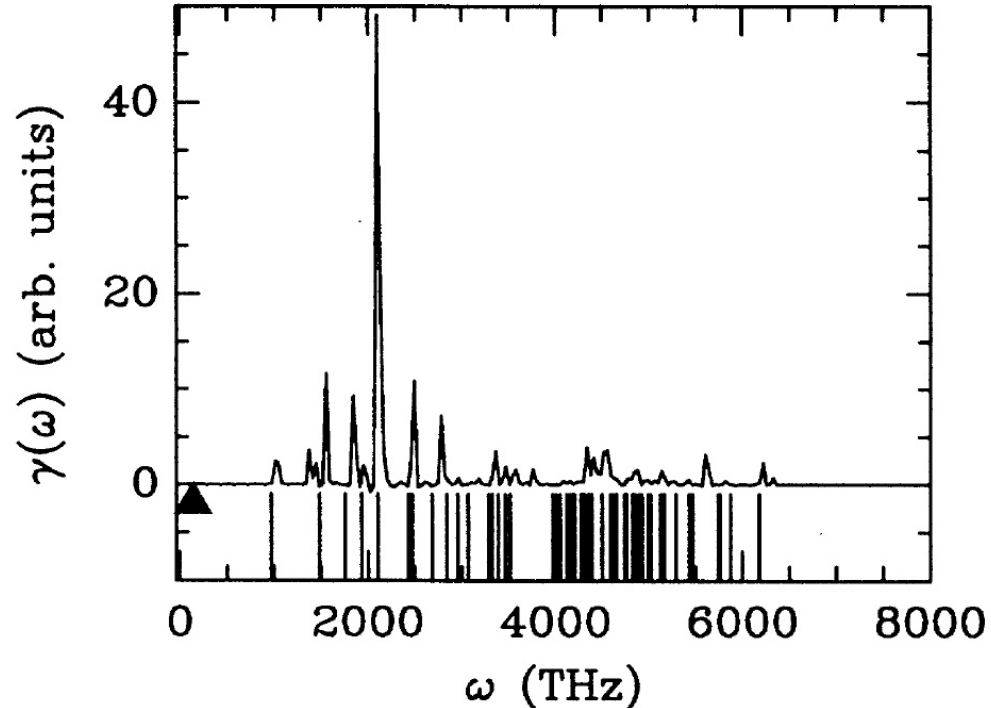


Triangle = highest ionic frequency

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

# Adiabatic separation

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



Triangle = highest ionic frequency

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

# Constant of motion

## Conservation of energy

- Physical and conserved energy:

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

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

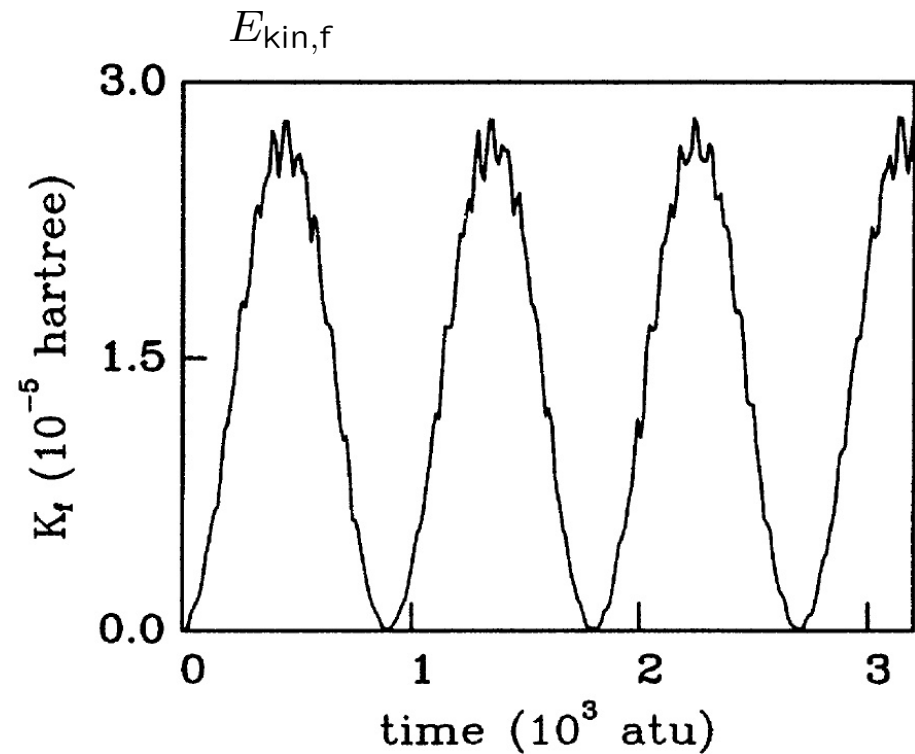
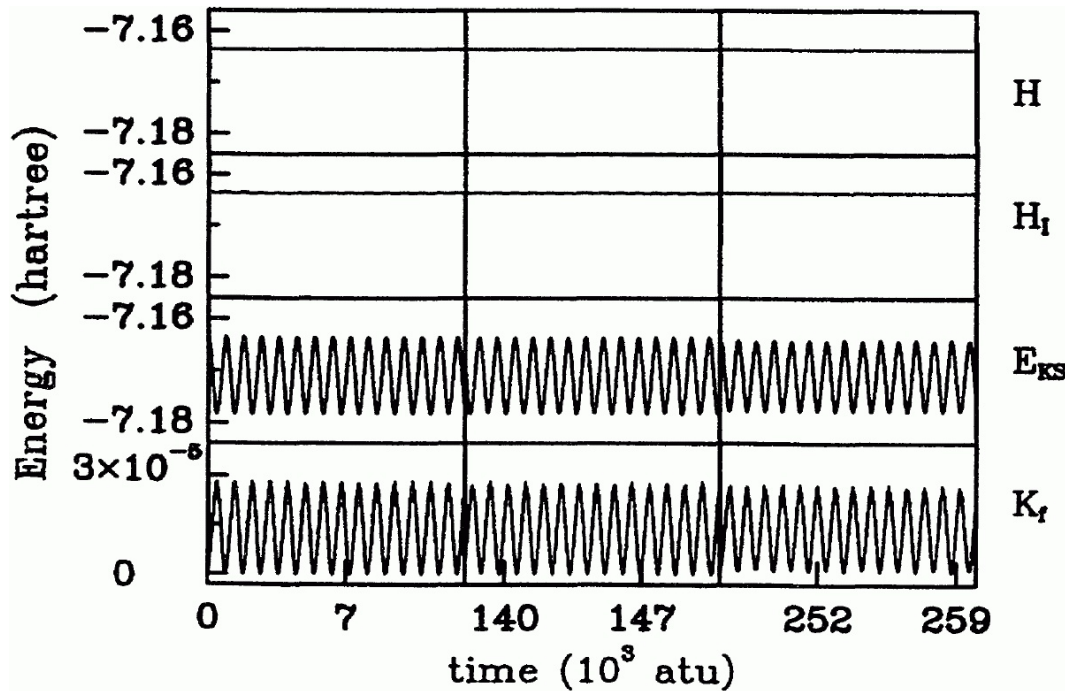
- The difference,  $E_{\text{kin,fict}} = \sum_{i=1}^M \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle$ , must thus correlate with the changes in the physical energy

# Constant of motion

Conservation of energy

Model system: Two-atom Si-fcc

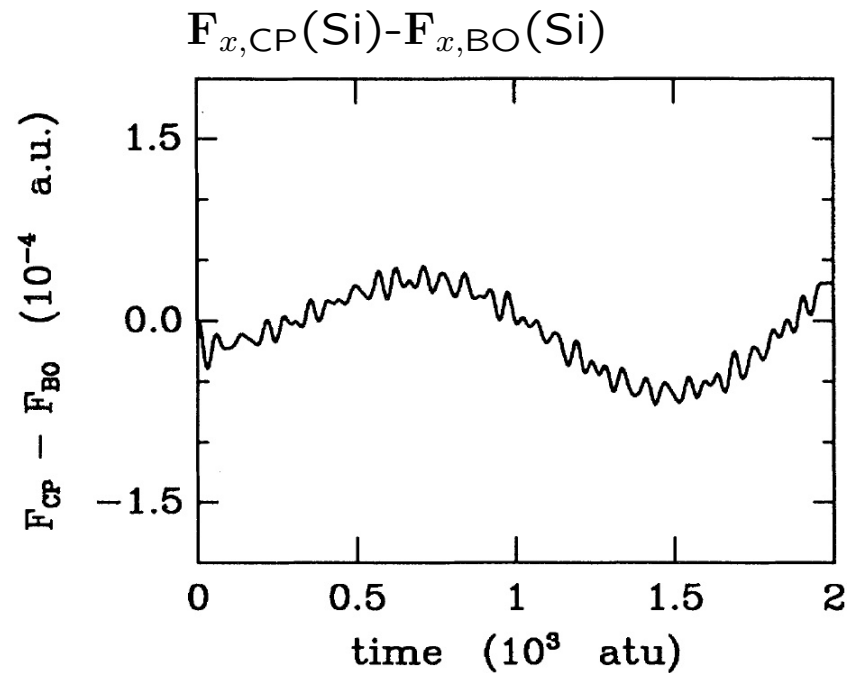
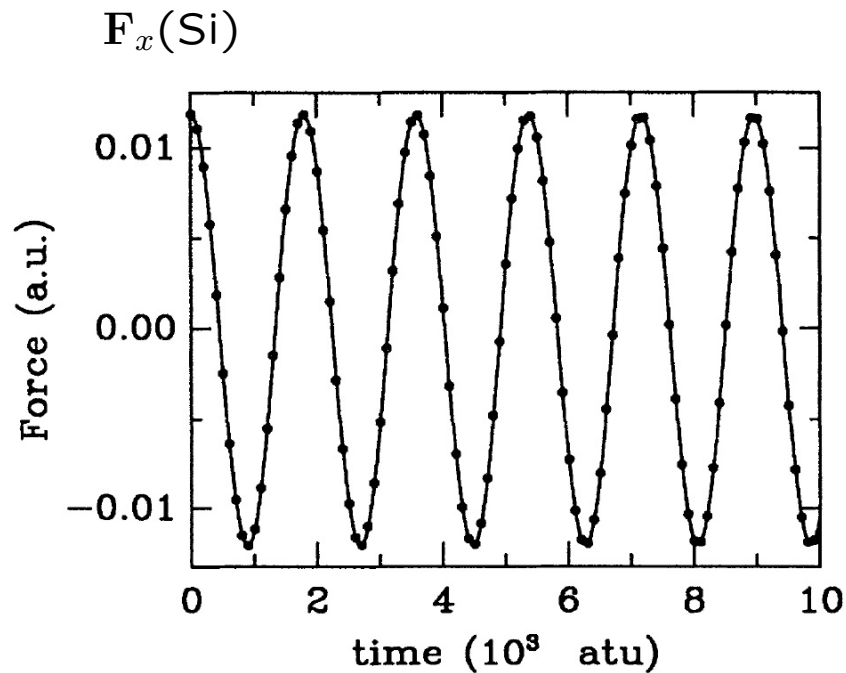
Energy components



# Deviation from Born-Oppenheimer surface

Are the forces accurate?

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



# 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

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

- Highest frequency

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

- Thus maximum possible time step

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

# Control of adiabacity

- Lowest frequency has to be well above ionic frequencies

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

- Highest frequency limits the maximum possible time step

$$\omega_{\max}^e \propto \sqrt{\frac{E_{\text{cut}}}{\mu}} \quad (\Delta t^e)_{\max} \propto \sqrt{\frac{\mu}{E_{\text{cut}}}}$$

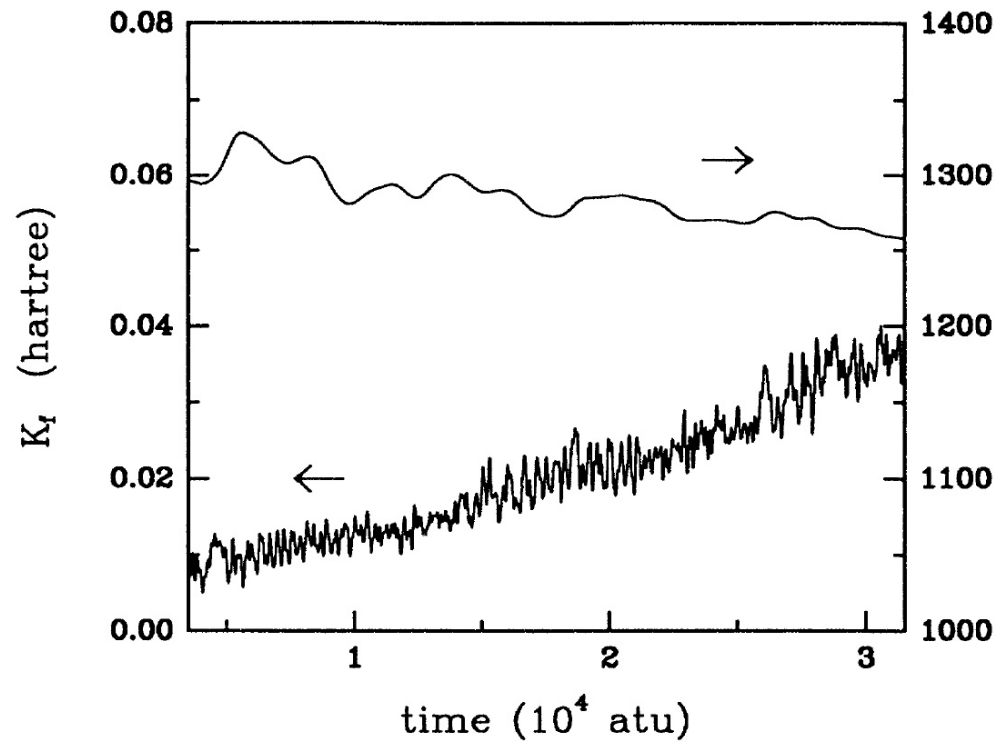
- If  $\Delta t$  fixed and  $\mu$  chosen
  - too small: Electrons too light and adiabacity will be lost
  - too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm



# Loss of adiabaticity

Bad cases

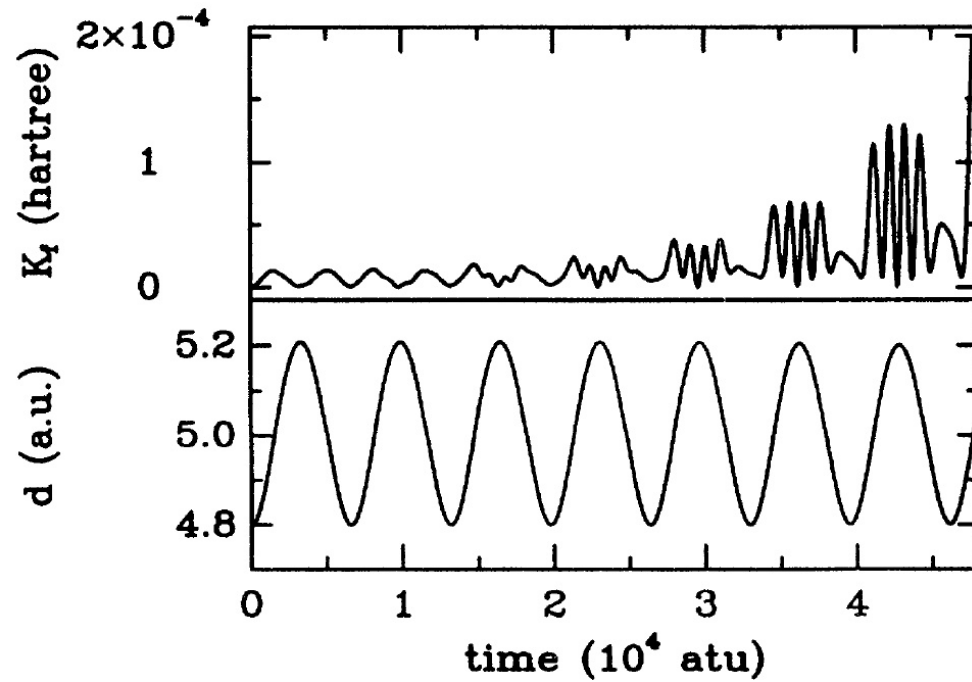
- Vacancy in hot 64-atom Si cell



# Loss of adiabaticity

Bad cases

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



# Analysis of adiabaticity

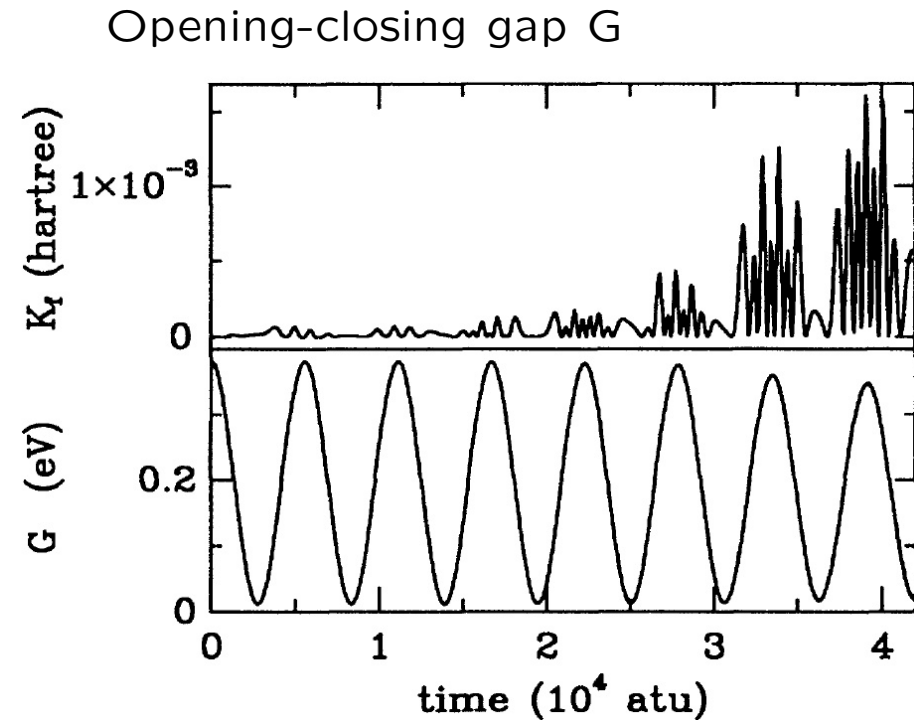
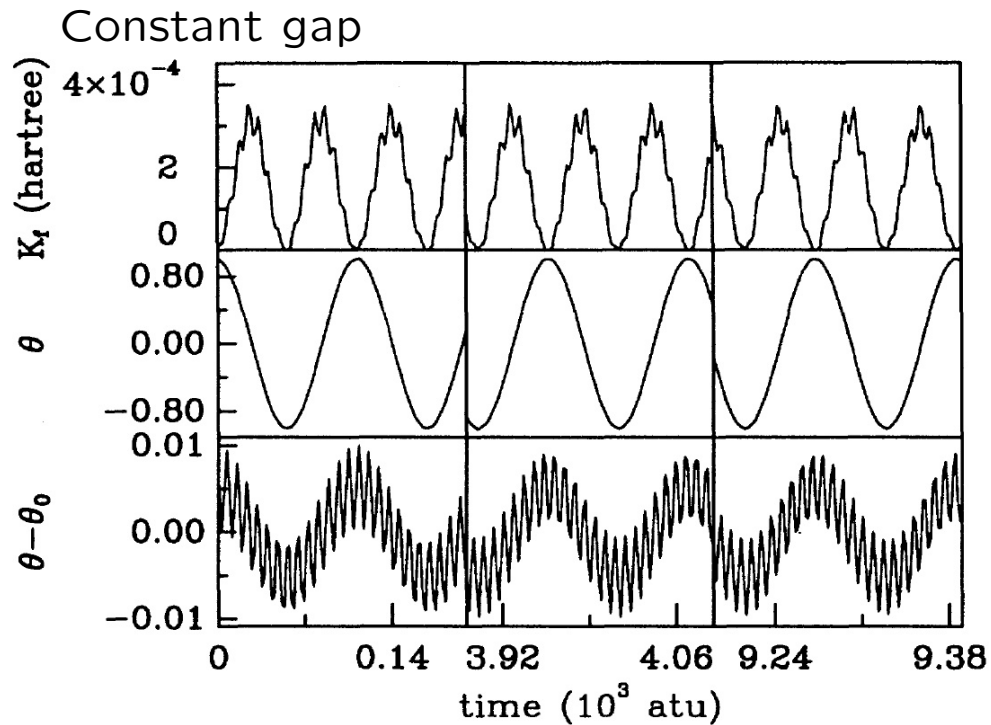
## Simplified model

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



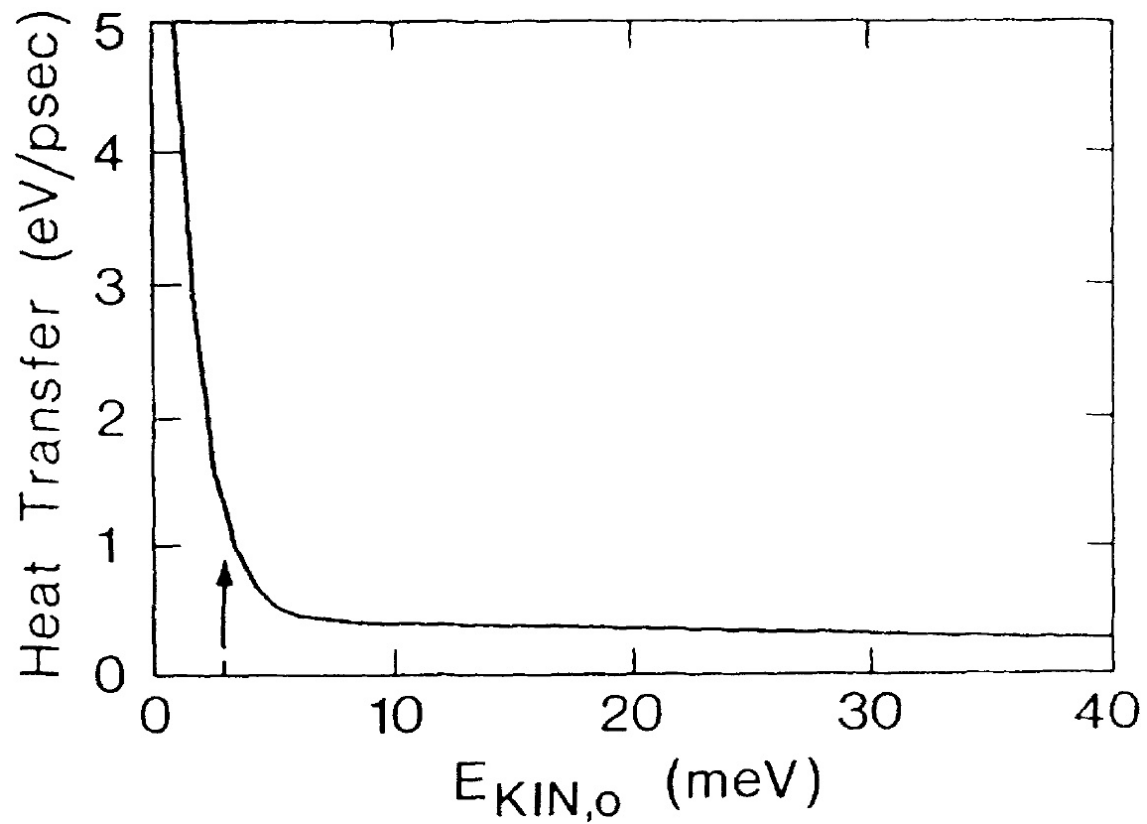
# Zero or small electronic gaps

## 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

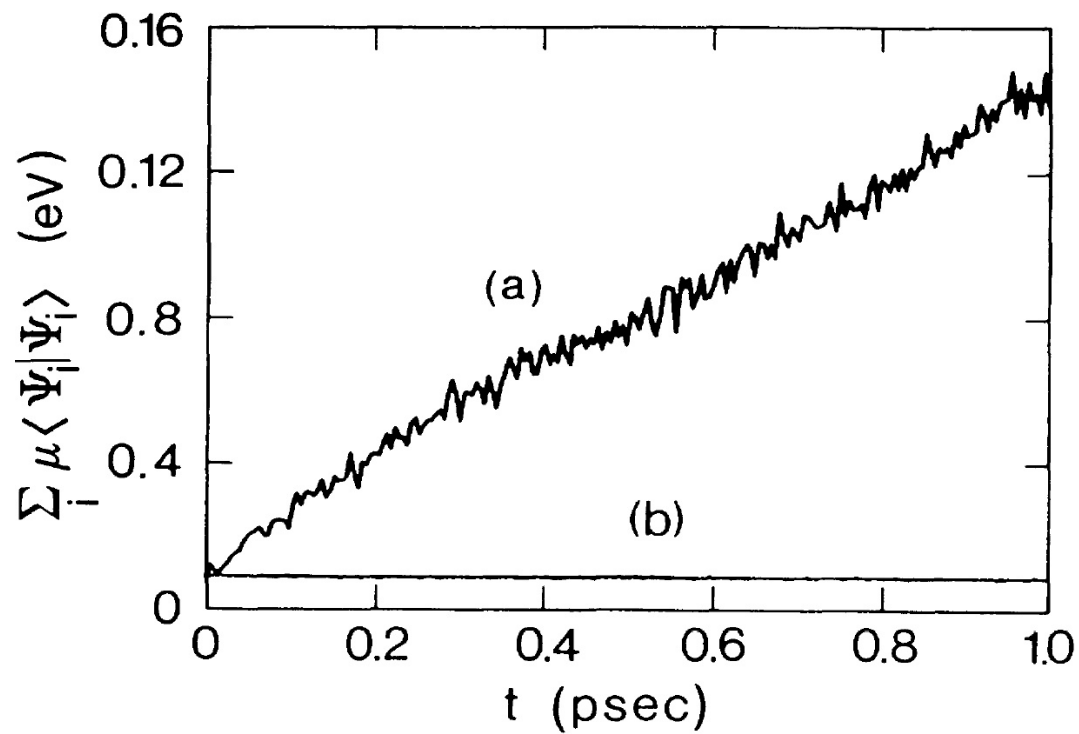
- Example: Aluminium
- Dependence of the heat transfer on the choice of  $E_{\text{kin},0}$  in solid Al



# Thermostat on electrons

Does it help?

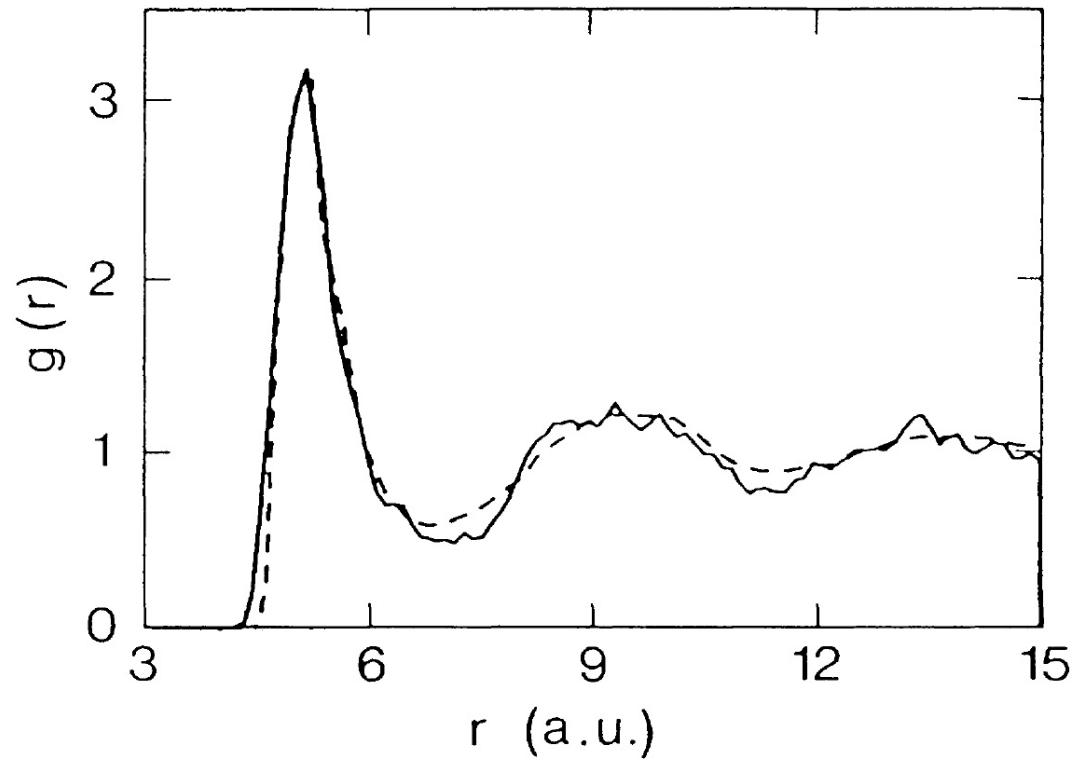
- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat



# 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:

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

- The new equations of motion:

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

where

$$dM_I = \frac{2}{3} \mu E_{\text{kin}}^I$$

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

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

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

# Orthonormality constraints

## RATTLE

- Define

$$\mathbf{X}_{ij} = \frac{\Delta t^2}{2\mu} \Lambda_{ij}^p \quad \mathbf{Y}_{ij} = \frac{\Delta t^2}{2\mu} \Lambda_{ij}^v \quad \text{C wf coefficients}$$

- Equations of type

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

A, B, Q of type  $A_{ij} = \sum_G c_{Gi}^* c_{Gj}$

- Solve iteratively:

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

# 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  $\approx 0$ 
  - 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:

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

- 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

Born-Oppenheimer MD

Exactly on BO surface

$\Delta t \approx$  ionic time scales,  
maximum time step possible

Expensive minimisation  
at each MD step

Not stable against deviations  
from BO surface  
 $\Rightarrow$  Energy/temperature drift,  
thermostatting of ions necessary

Same machinery in zero-gap systems

Most applications in solids

Car-Parrinello MD

Always slightly off BO surface

$\Delta t \ll$  ionic time scales,  
(much) shorter time step necessary

Orthogonalisation only,  
less expensive per MD step

Stable against deviations  
from BO surface

Thermostatting of electrons  
to prevent energy exchange

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

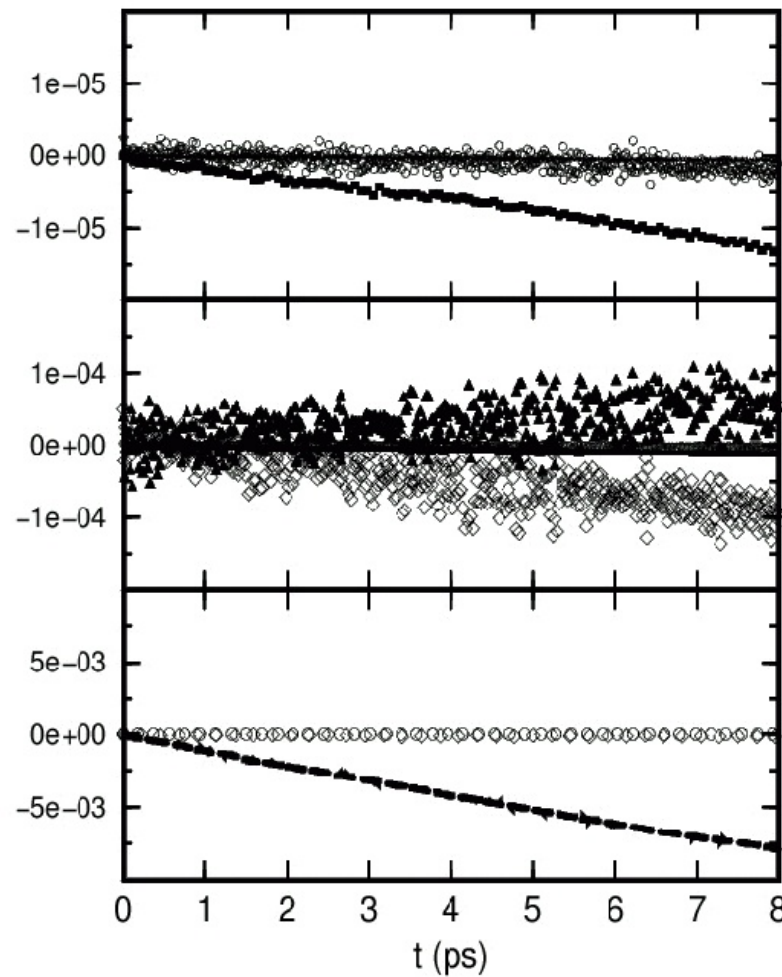
Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	$6 \times 10^{-8}$	3230
CP	7	—	$1 \times 10^{-7}$	2310
CP	10	—	$3 \times 10^{-7}$	1610
BO	10	$10^{-6}$	$1 \times 10^{-6}$	16590
BO	50	$10^{-6}$	$1 \times 10^{-6}$	4130
BO	100	$10^{-6}$	$6 \times 10^{-6}$	2250
BO	100	$10^{-5}$	$1 \times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



# 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:*

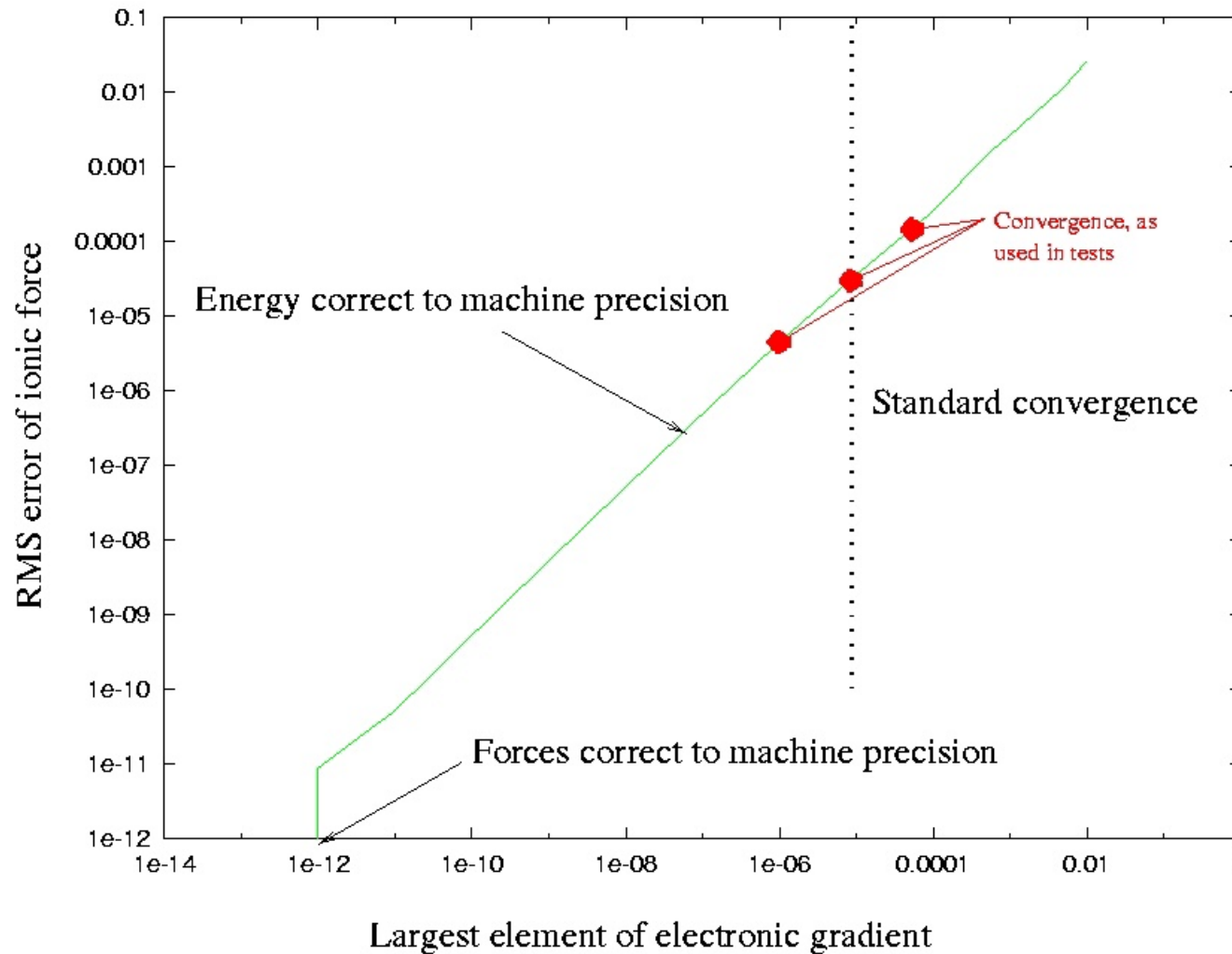
open circl. : CP, 10 a.u.;  
filled squar. : BO, 10 a.u.,  $10^{-6}$ ;  
filled trian. : BO, 100 a.u.,  $10^{-6}$ ;  
open diam. : BO, 100 a.u.,  $10^{-5}$ .

*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

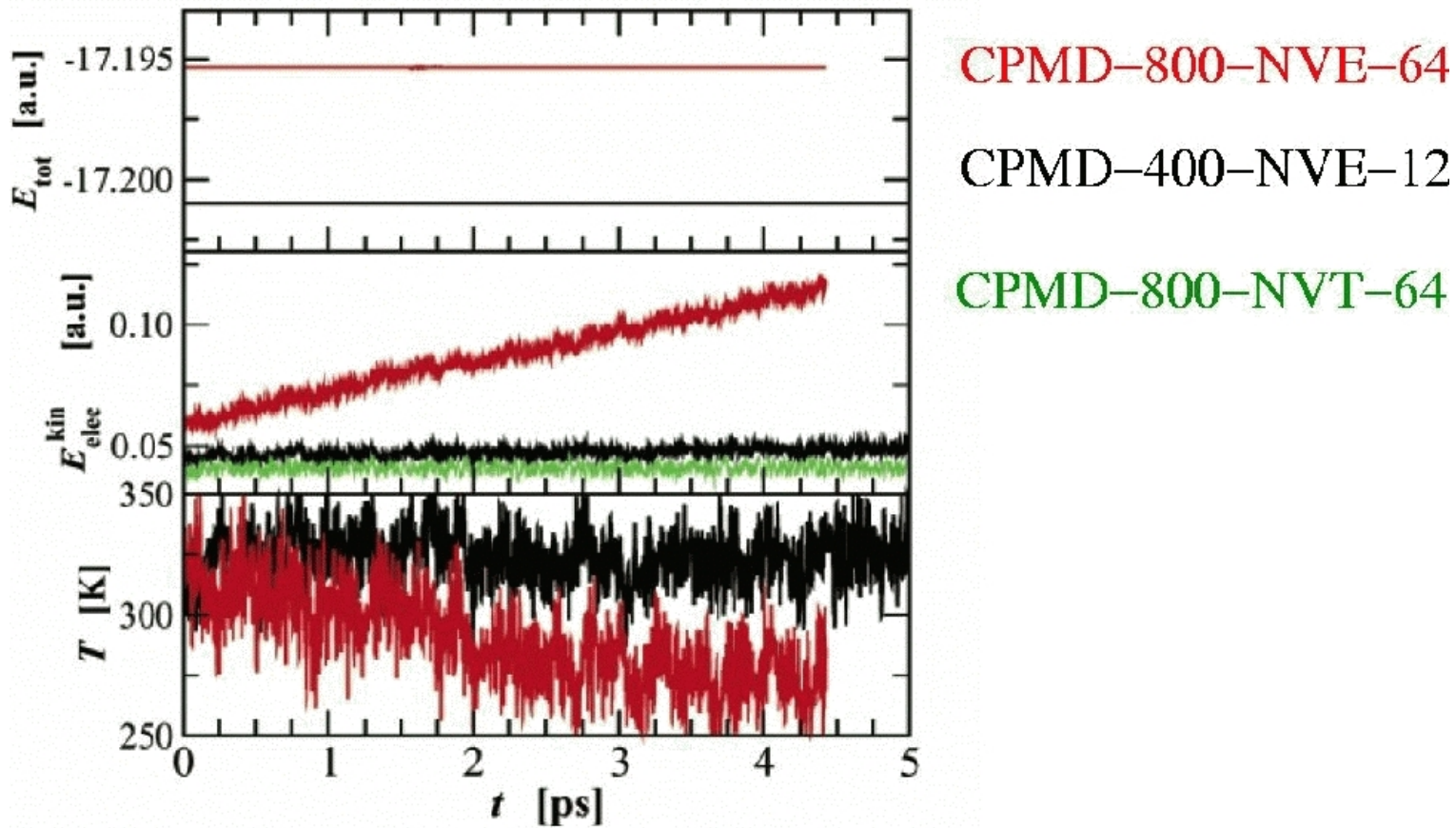
- The error in the forces depends on the convergence criterion set for the electronic structure in BOMD:



# CP vs BO: Liquid water

## Stability

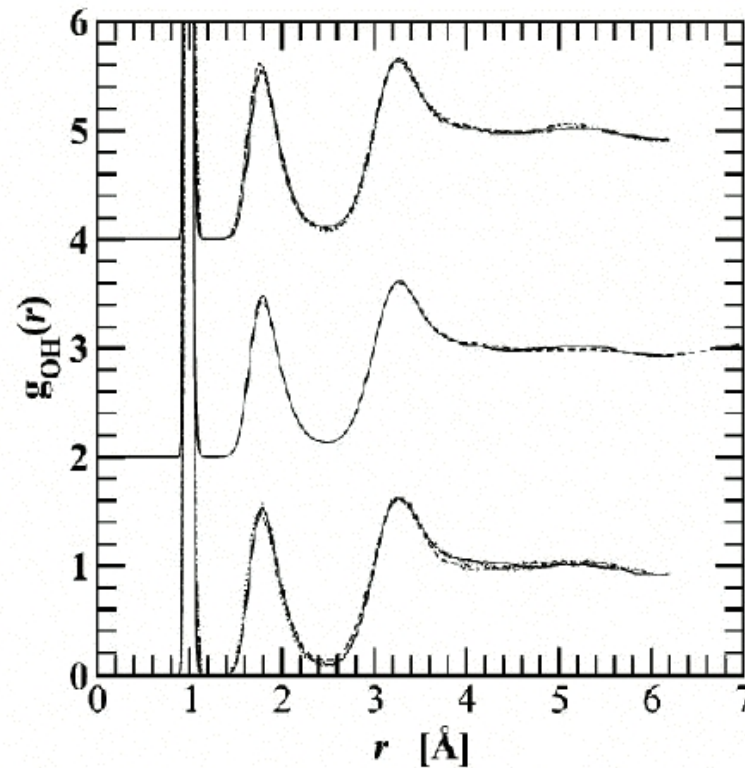
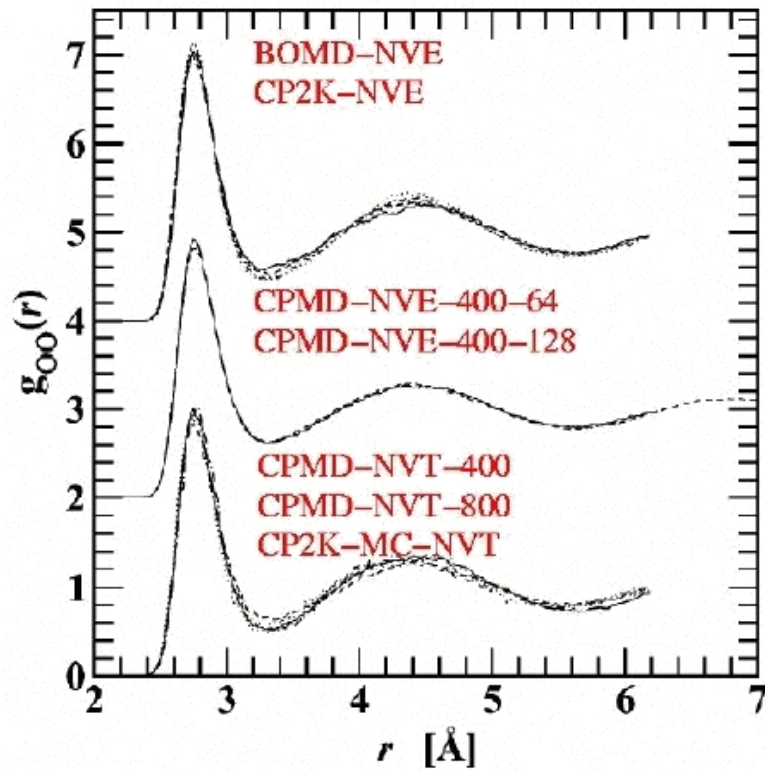
- Effect of  $\mu$ : Too large value leads to loss of adiabacity
- Thermostatting the electrons recovers the correct behaviour



# CP vs BO: Liquid water

## Results

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



# Ehrenfest vs Car-Parrinello dynamics

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

- 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)