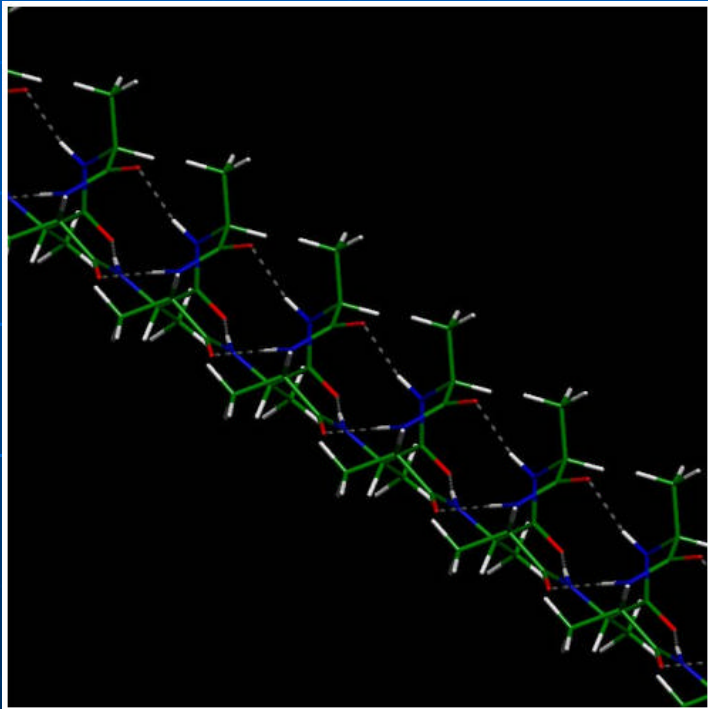


# First-principles Molecular Dynamics

Lars Ismer  
FHI Berlin

# Motivation

Example:  $3_{10}$ -helix (Polyalanine)



Vibrations at 298 K  
DFT-PBE MD run, 50 fs

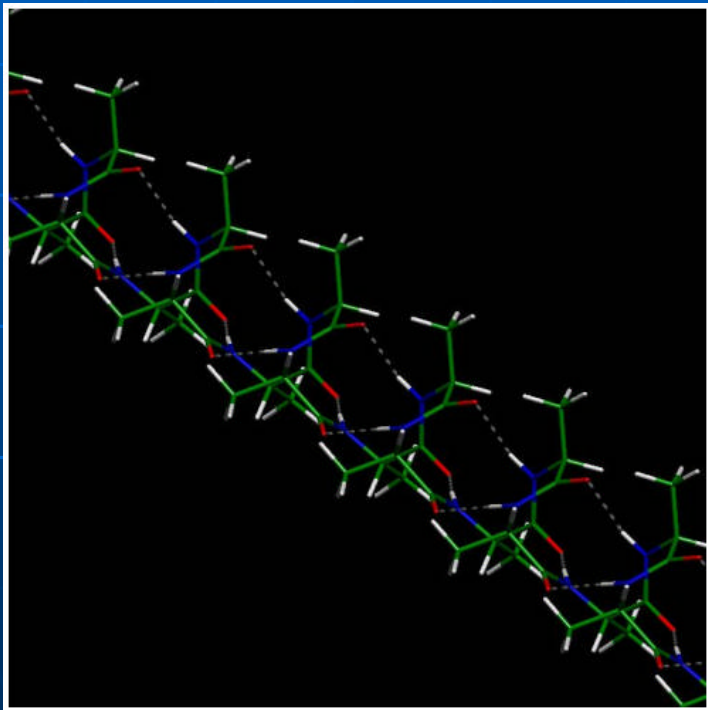
DFT allows efficient first-principles calculation of the Born-Oppenheimer surface via Kohn-Sham formalism

By analysing the electronic structure, the total energy and the bond lengths on the local minima of the BOS, many important properties of the system can be understood. A microscopical system is never totally in rest in a local minimum. It's in motion.



# Motivation

Example:  $3_{10}$ -helix (Polyalanine)



Vibrations at 298 K  
DFT-PBE MD run, 50 fs

For many processes the dynamical properties of microscopic systems play an important role:

- ⇒ chemical reactions
- ⇒ diffusion
- ⇒ stability of molecule systems

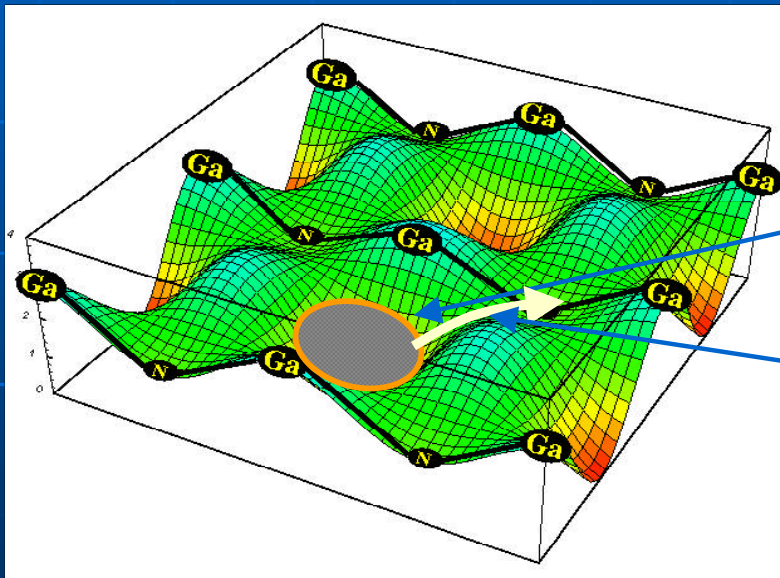
Thermal equilibrium is determined by the minimum of the free energy, not by the minimum of the energy

$$F = U - TS$$

⇒ Are there methods to describe the dynamical

# Motivation

## Example: 2-dim BO - Surface



## Harmonic Approximation:

Complete statistical description of the system based on approximated dynamics

$$H^{ion} \approx \sum_{I=1}^{N^{ions}} \frac{1}{2M_I} \frac{\partial^2}{\partial \mathbf{X}_I^2} + \frac{1}{2} \Delta \mathbf{X}^T \mathbf{H} \Delta \mathbf{X}; \quad \mathbf{X} = \{\mathbf{X}_I\}; \quad H_{ij} = \left. \frac{\partial^2 E^{BOS}}{\partial X_i \partial X_j} \right|_{\mathbf{X}_0}$$

Works well in describing the dynamics close to the local minima

Transition state theory can describe chemical reactions with high reaction barriers

$$k_b T \ll \Delta E$$

## Breakdown of harmonic approximation:

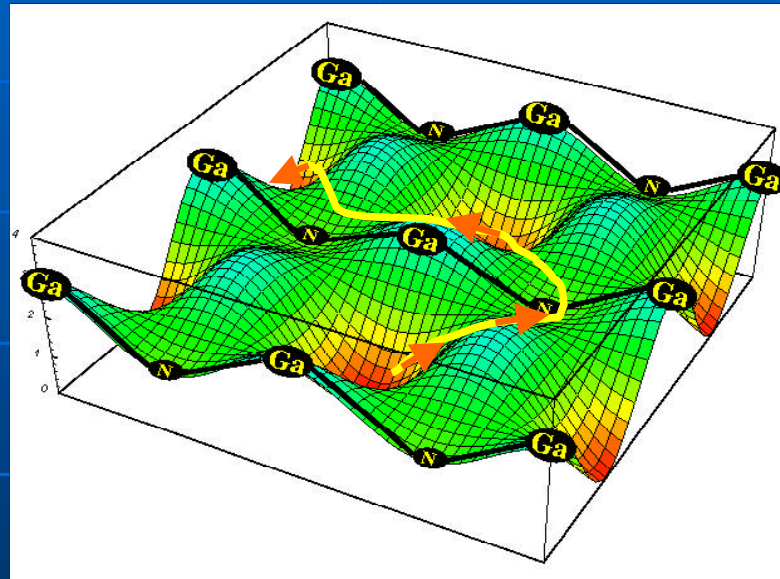
- ⇒ chemical reactions with low barriers
- ⇒ complex systems with many local minima close to each other

⇒ For these systems the harmonic approximation has to be corrected !

# Motivation

Molecular Dynamics is a method to explore the phase space

## Trajectory of a MD-run



← Analysing  
time-correlation  
functions  
e.g. calculating  
frequency spectrum

→ Watching a  
movie  
“See” what will  
happen

↓  
Calculating ensemble averages  
Deriving macroscopic observables

# Outline

## 1. History of Molecular Dynamics

## 2. How does first-principles MD work ?

- integrating Newton's equation
- CPMD, Born-Oppenheimer Dynamics

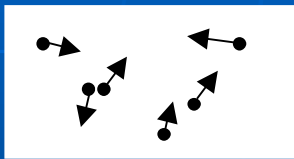
## 3. What can one do with first-principles MD ?

- MD as method to explore the phase space
- statistical ensembles, temperature
- application area of first-principles MD

## 4. Tools to explore the Born-Oppenheimer surface implemented in SFHIngX

# History of Molecular Dynamics

1957



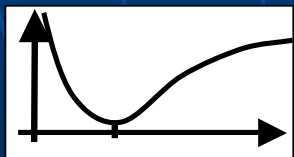
Interaction of hard spheres

⇒ insight into the behaviour of simple liquids

Alder and Wainwright, JCP 27, 1208 (1957)

---

1964



Simulation of liquid argon

⇒ first simulation using a realistic empirical interaction potential

Rahman, PRA 136, 405 (1964)

---

# History of Molecular Dynamics

1974

Simulation of liquid water

⇒ first simulation of a realistic (bio)system

Stillinger and Rahman, JCP 60, 1545 (1974)

---

1977

Simulation of Bovine Pancreatic Trypsin Inhibitor

⇒ first simulation of a proteine

McCammom et al, Nature 267, 585 (1977)

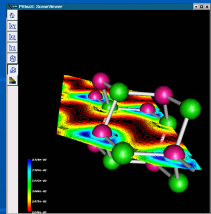
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Source: <http://www.ch.embnet.org>



# History of Molecular Dynamics

1985



Car-Parrinello Molecular Dynamics

⇒ molecular dynamics on a DFT Born-Oppenheimer surface

R. Car and M. Parrinello, PRL 55, 2471 (1985)

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1986



QUEST

⇒ QM/MM Dynamics  
ab-initio (QM) + force field (MM)

Kollmann and Singh

# What is first-principles MD ?

**Definition:** (L1) First-principles Molecular Dynamics means classically treating the dynamics of the ion cores on the DFT (ground-state) Born-Oppenheimer potential surface

**Realization:** solving Kohn-Sham equations for given ionic positions

$$\{\mathbf{X}_I\} \xrightarrow{KS} n_g(\{\mathbf{X}_I\}), E^{\text{BOS}}(\{\mathbf{X}_I\})$$

calculating the forces acting on the ions via HF-Theorem

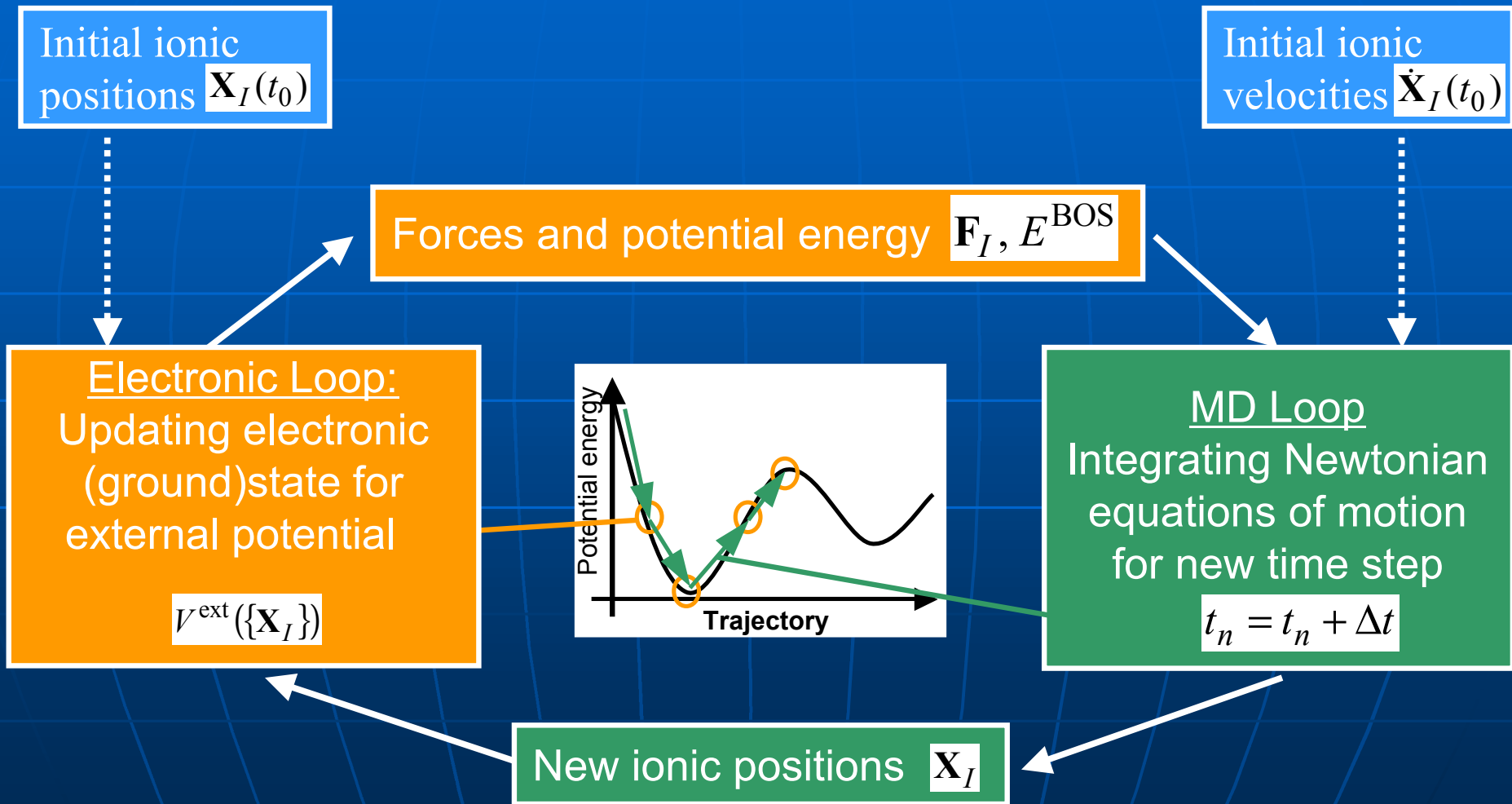
$$\{\Psi_m^{KS}\} \longrightarrow \mathbf{F}_I(\{\mathbf{X}_I\}) = -\left\langle \Psi^{KS} \left| \frac{\partial H^{el}}{\partial \mathbf{X}_I} \right| \Psi^{KS} \right\rangle$$

and solving the newtonian equations of motion

$$\ddot{\mathbf{X}}_I = \frac{\mathbf{F}_I}{M_I}$$

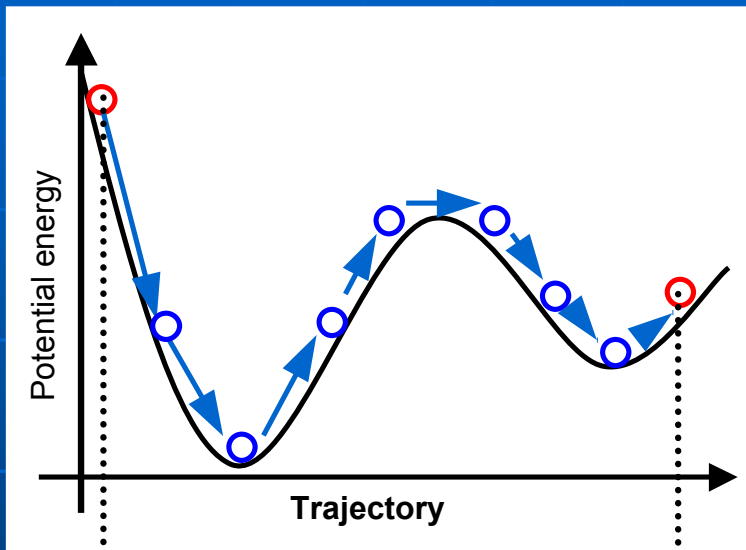
**Approximations:** Born-Oppenheimer Approximation (L2), XC-Functional (L8), classical treatment of ion cores

# MD-Loop of a DFT-Code



How are the ionic equations of motion integrated ?

# Integrating Newton's Equations



Numerical integration schemes use finite time-steps to perform the integration!

$$dt \rightarrow \Delta t$$

A “good” integration scheme:

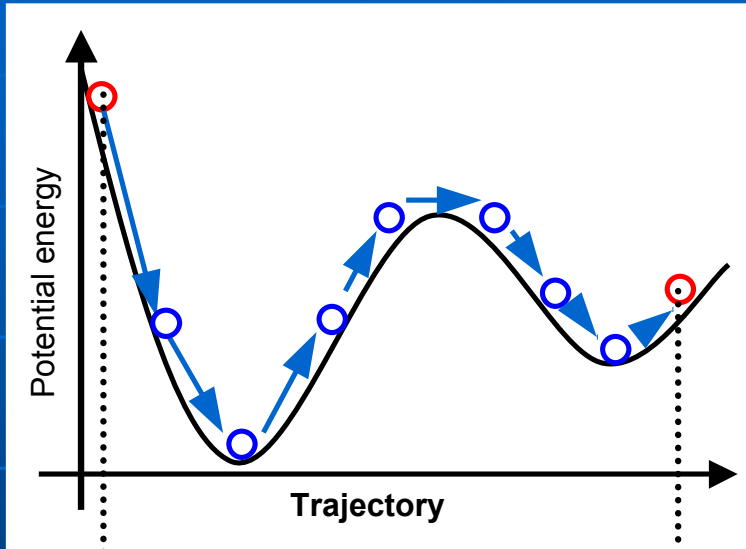
- ⇒ gives an accurate trajectory
- ⇒ conserves the total energy
- ⇒ uses as few time steps as possible

$$\{\mathbf{X}_I(t_0)\}, \{\dot{\mathbf{X}}_I(t_0)\} \xrightarrow{???\} \{\mathbf{X}_I(t_1)\}, \{\dot{\mathbf{X}}_I(t_1)\}$$

Analytical  
Integration:

$$\dot{\mathbf{X}}_I(t_1) = \dot{\mathbf{X}}_I(t_0) + \int_{t_0}^{t_1} dt \frac{\mathbf{F}_I[\mathbf{X}(t)]}{M_I}$$
$$\mathbf{X}_I(t_1) = \mathbf{X}_I(t_0) + \int_{t_0}^{t_1} dt \dot{\mathbf{X}}_I(t)$$

# Integrating Newton's Equations



## Simple example: Euler-scheme

$$\mathbf{X}_I(t_{n+1}) = \mathbf{X}_I(t_n) + \Delta t \cdot \dot{\mathbf{X}}_I(t_n)$$

$$\dot{\mathbf{X}}_I(t_{n+1}) = \dot{\mathbf{X}}_I(t_n) + \Delta t \cdot \ddot{\mathbf{X}}_I(t_n)$$

⇒ only stable for very small time steps

**1<sup>st</sup> order scheme**

**not reversible in time!**

⇒ alternative schemes ?

$$\{\mathbf{X}_I(t_0)\}, \{\dot{\mathbf{X}}_I(t_0)\} \xrightarrow{???} \{\mathbf{X}_I(t_1)\}, \{\dot{\mathbf{X}}_I(t_1)\}$$

Analytical  
Integration:

$$\dot{\mathbf{X}}_I(t_1) = \dot{\mathbf{X}}_I(t_0) + \int_{t_0}^{t_1} dt \frac{\mathbf{F}_I[\mathbf{X}(t)]}{M_I}$$

$$\mathbf{X}_I(t_1) = \mathbf{X}_I(t_0) + \int_{t_0}^{t_1} dt \dot{\mathbf{X}}_I(t)$$

# Verlet Scheme

Taylor expansion for trajectory forward ...

$$\mathbf{X}_I(t_{n+1}) = \mathbf{X}_I(t_n) + \Delta t \cdot \dot{\mathbf{X}}_I(t_n) + \frac{\Delta t^2}{2!} \cdot \ddot{\mathbf{X}}_I(t_n) + \frac{\Delta t^3}{3!} \cdot \ddot{\mathbf{X}}_I(t_n) + \dots + \cancel{O(t^4)}$$

+ ....and backward in time:

$$\mathbf{X}_I(t_{n-1}) = \mathbf{X}_I(t_n) - \Delta t \cdot \dot{\mathbf{X}}_I(t_n) + \frac{\Delta t^2}{2!} \cdot \ddot{\mathbf{X}}_I(t_n) - \frac{\Delta t^3}{3!} \cdot \ddot{\mathbf{X}}_I(t_n) + \dots + \cancel{O(t^4)}$$

time reversible 3rd order update scheme for particle positions:

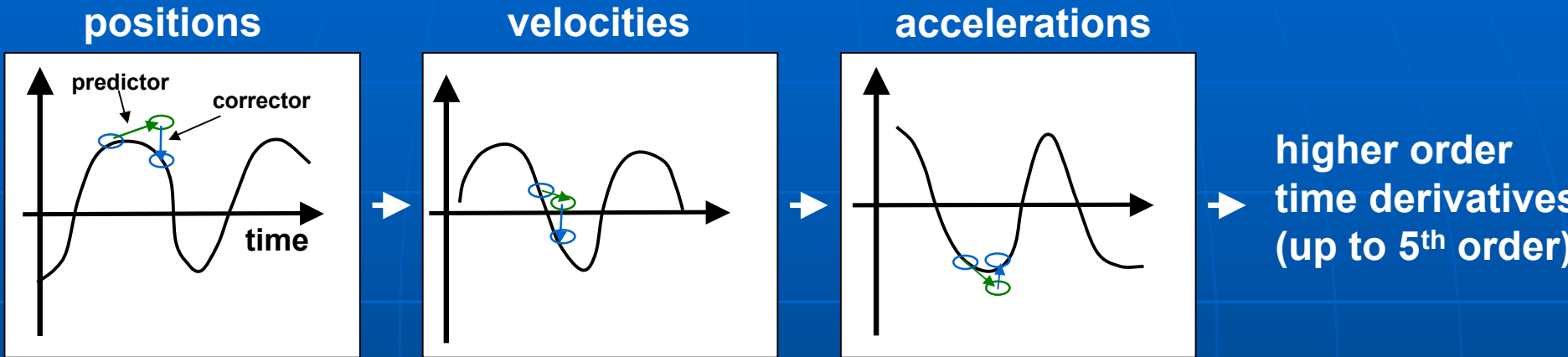
$$\mathbf{X}_I(t_{n+1}) = 2\mathbf{X}_I(t_n) - \mathbf{X}_I(t_{n-1}) + \frac{\Delta t^2}{2!} \cdot \frac{\mathbf{F}_I(t_n)}{M_I} \quad \leftarrow \quad \mathbf{F}_I = M_I \ddot{\mathbf{X}}_I$$

**Big advantage:**  
reversible in time !!

$$\dot{\mathbf{X}}_I(t_n) = \frac{\mathbf{X}_I(t_{n+1}) - \mathbf{X}_I(t_{n-1})}{2\Delta t}$$

**Disadvantage:**  
actual velocities cannot be  
calculated directly  
Connection of thermostat  
not straightforward

# Gear Predictor-Corrector



## 1. Predictor step

$$\mathbf{X}_I^p(t_{n+1}) = \mathbf{X}_I^p(t_n) + \sum_{q=1}^k \frac{\Delta t^q}{q!} \left( \frac{\partial^q \mathbf{X}_I^p}{\partial t^q} \Big|_{t_n} \right)$$

$$\mathbf{X}_I^p(t_{n+1}) = \dot{\mathbf{X}}_I^p(t_n) + \sum_{q=2}^k \frac{\Delta t^{q-1}}{(q-1)!} \left( \frac{\partial^q \mathbf{X}_I^p}{\partial t^q} \Big|_{t_n} \right)$$

$$\vdots$$

$$\frac{\partial^q \mathbf{X}_I^p}{\partial t^q} \Big|_{t_{n+1}} = \frac{\partial^q \mathbf{X}_I^p}{\partial t^q} \Big|_{t_n}$$

## 2. Force calculation evaluation of predictor step

$$\mathbf{F}_I(t_{n+1}) = \mathbf{F}_I(\{\mathbf{X}^p(t_{n+1})\})$$

$$\Delta \ddot{\mathbf{X}}_I = \frac{\mathbf{F}_I}{M_I} - \ddot{\mathbf{X}}_I^p$$

$$\Delta \tilde{\mathbf{X}}_I = \frac{1}{2} \Delta \ddot{\mathbf{X}}_I \cdot (\Delta t)^2$$

## 3. Corrector step

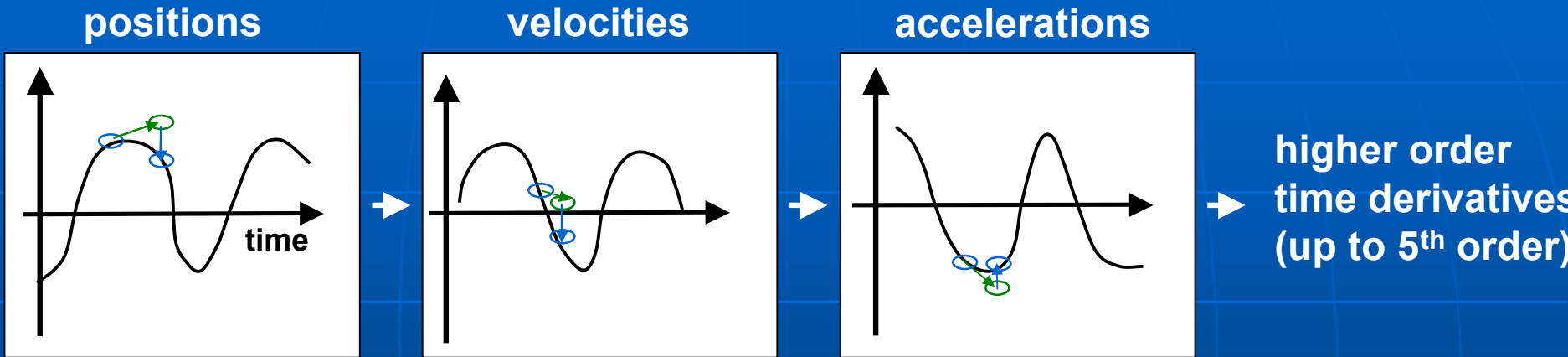
$$\mathbf{X}_I(t_{n+1}) = \mathbf{X}_I^p(t_{n+1}) + a_0 \cdot \Delta \tilde{\mathbf{X}}_I$$

$$\dot{\mathbf{X}}_I(t_{n+1}) \cdot \Delta t = \dot{\mathbf{X}}_I^p(t_{n+1}) \cdot \Delta t + a_1 \cdot \Delta \tilde{\mathbf{X}}_I$$

$$\vdots$$

$$\left( \frac{\partial^k \mathbf{X}_I}{\partial t^k} \Big|_{t_{n+1}} \right) \cdot \Delta t^k = \left( \frac{\partial^k \mathbf{X}_I^p}{\partial t^k} \Big|_{t_{n+1}} \right) \cdot \Delta t^k + a_k \cdot \Delta \tilde{\mathbf{X}}_I$$

# Gear Predictor-Corrector



Advantages:    highly accurate particle positions  $O(t^5)$   
                          accurate particle velocities     $O(t^4)$   
                          accurate particle accelerations  $O(t^3)$

⋮

Direct calculation of the velocities makes connecting a thermostat straightforward

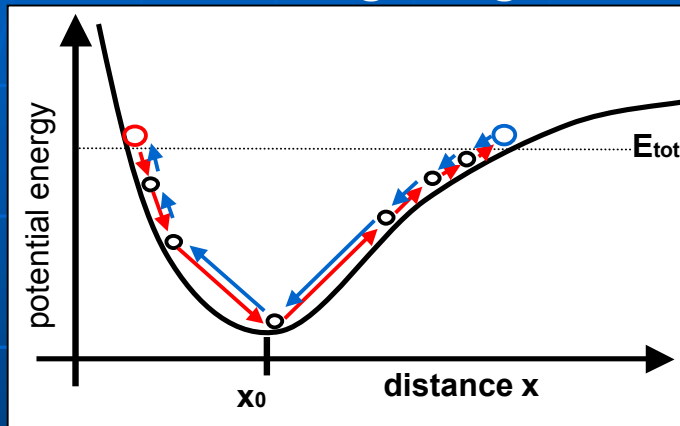
Disadvantage                      not reversible in time !



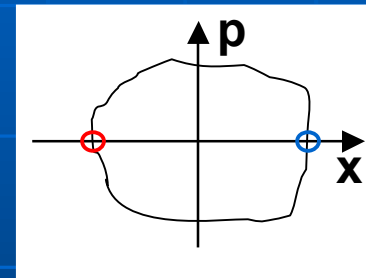
# Time Reversibility

Example : Vibrating dimer

Reversible Integrating scheme

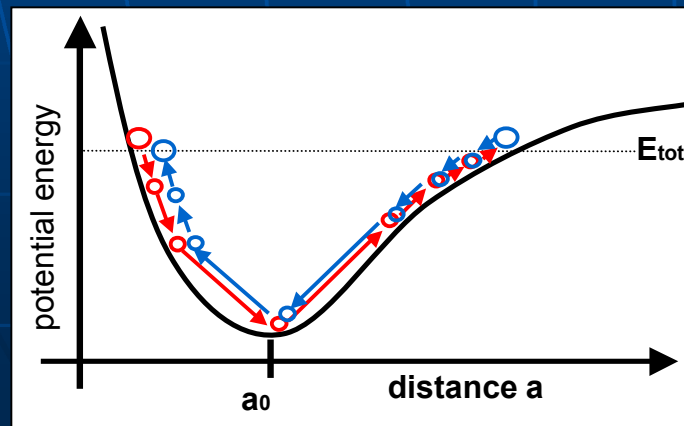


closed phase space trajectory

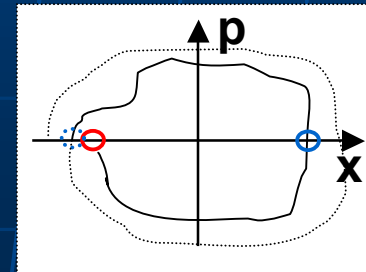


Oscillation  
keeps total  
energy

Irreversible Integrating scheme



open phase space trajectory

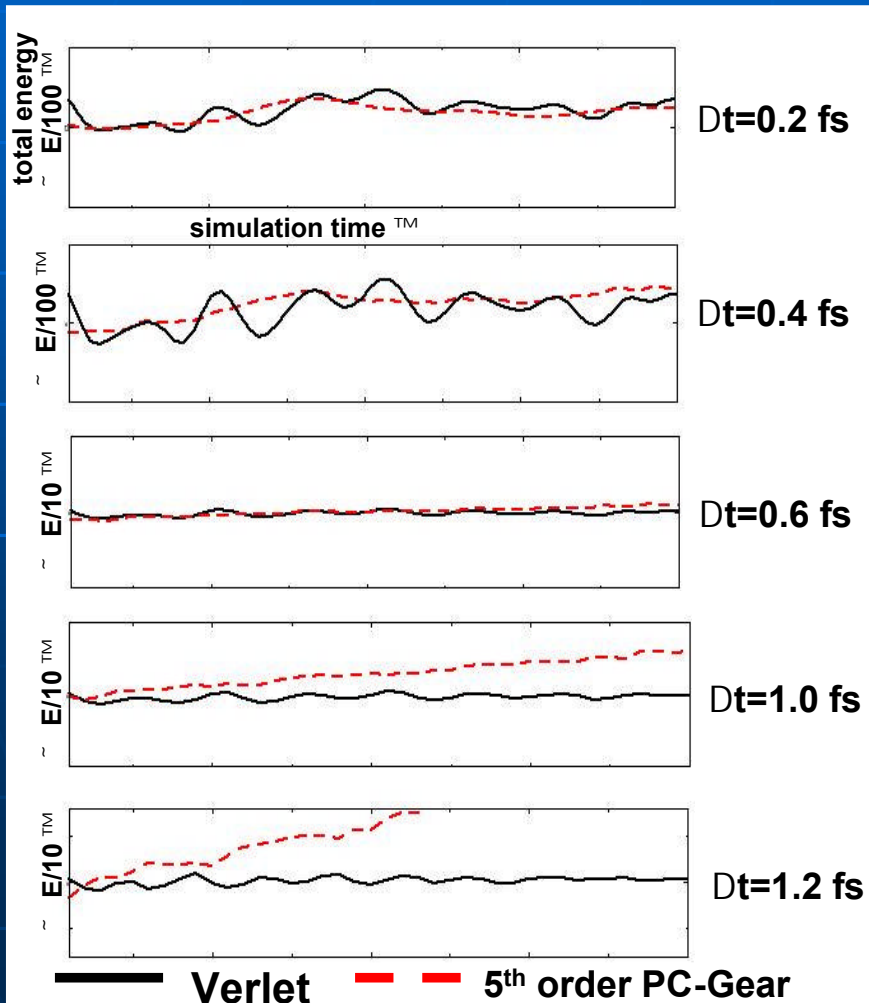


Long term  
energy  
drift

# Comparison of integration schemes

3<sub>10</sub>-helix (30 atoms)

$E_{\text{ion}}^{\text{tot}} = 0.08$  Hartree (@ 298K)



Small time steps:

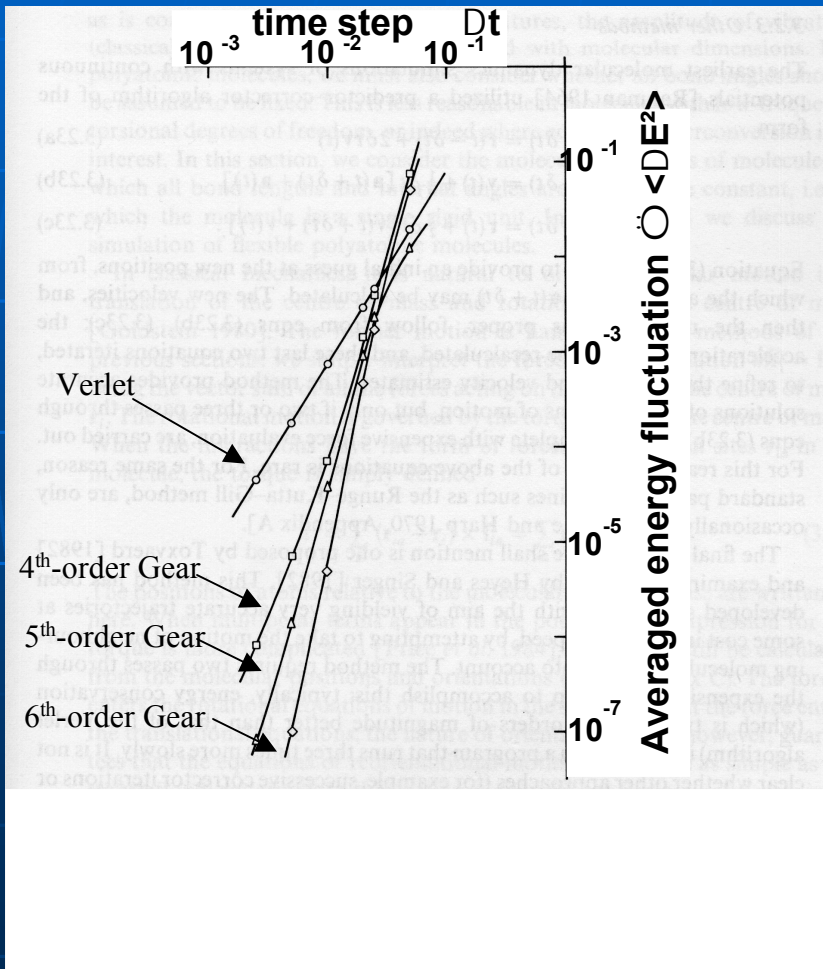
5<sup>th</sup> order Predictor-Corrector more accurate than Verlet (3<sup>rd</sup> order scheme)

Large time steps:

Non reversible PC scheme shows a strong drift in the total energy;  
Time-reversible Verlet scheme much more stable

# Comparison of integration schemes

Example: Simulation of a Liquid



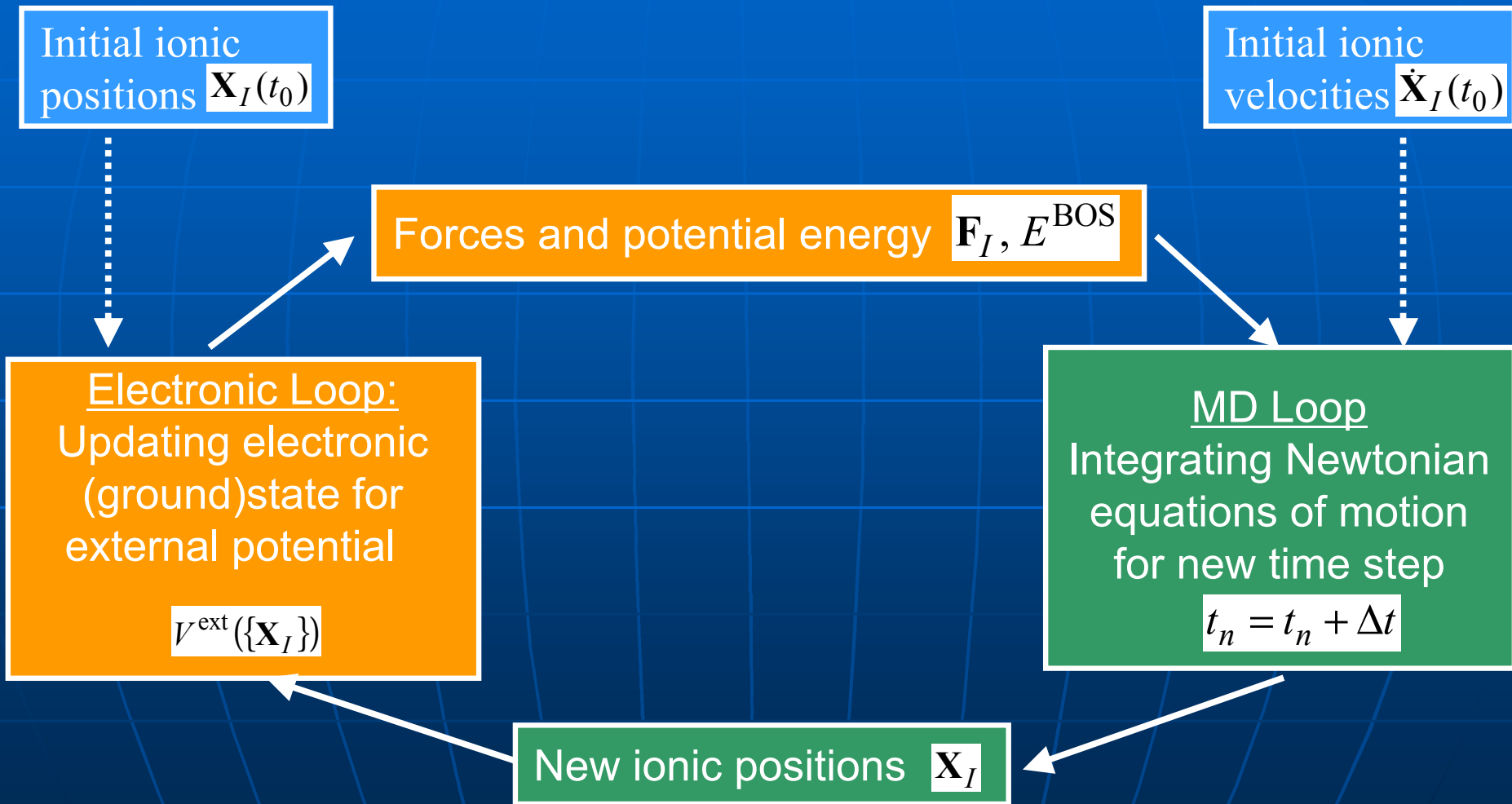
$$v^{LJ}(r) = e\left(\frac{S}{r^{12}} - \frac{S}{r^6}\right)$$

⇒ Gear Predictor Corrector more accurate for small time steps

But: Increase of error with increasing time step more drastic for PC-Gear

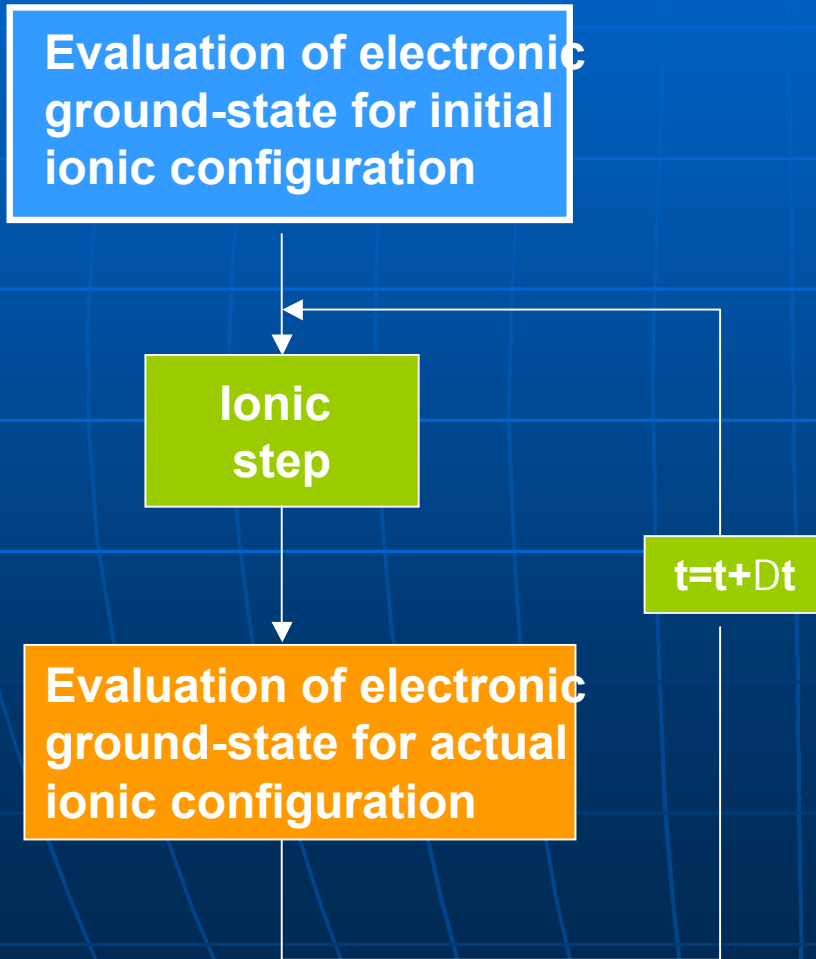
⇒ Verlet more accurate for large time steps (!!!)

# MD-Loop of a DFT-Code



How is the electronic system updated in a MD run ?

# Born-Oppenheimer Dynamics



For each ionic step the electronic system is fully relaxed to the Born-Oppenheimer surface by an iterative minimization scheme !

The ionic movement is fully decoupled from the electronic relaxation.

Time step size must sample ionic movement

in all other respects parameter free

# Car-Parrinello MD

## Car-Parrinello Lagrangian

$$L^{CP} = \sum_i m_i \langle \dot{y}_i | \dot{y}_i \rangle + \frac{1}{2} \sum_I M_I \dot{\mathbf{X}}_I^2 - \tilde{E}^{\text{BOS}}[\Psi, \mathbf{X}]$$

Small artificial electron masses  $m$

decoupled

$$M_I \ddot{\mathbf{X}}_I = - \frac{\partial \tilde{E}^{\text{BOS}}}{\partial \mathbf{X}_I} = \mathbf{F}_I^{\text{CP}}$$

$$m_i \langle \ddot{y}_i | \ddot{y}_i \rangle = - \frac{d \tilde{E}^{\text{BOS}}}{d y_i}$$

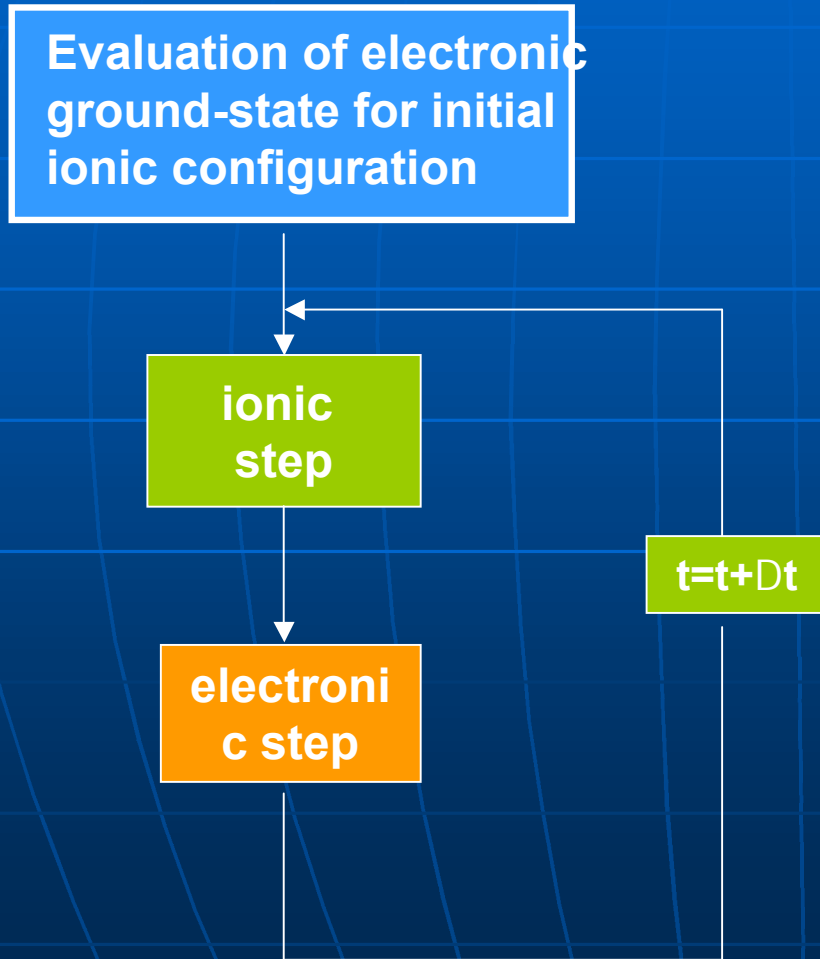
2<sup>nd</sup> order equation of motion  
for the ions

2<sup>nd</sup> order equation of motion  
for the electrons

Newtonian equations of motion  
on the BO surface

Oscillations around  
ground-state for given  
ionic positions

# Car-Parinello MD



Electronic wavefunctions and ionic positions are updated simultaneously

Electronic system performs oscillations around ground-state for given ionic positions

Electronic oscillations must be significantly faster than ionic oscillations (frequency controlled by artificial electronic masses)

Time step size must sample electronic movement

# Comparison

## Example: Simulation of water [1]

O-H vibration	» 10 fs
MD time-step on empirical potential	» 1 fs
CPMD time step	» 0.1 fs



Time step of a Born-Oppenheimer MD is » 10x larger than that of a CPMD



But: Born-Oppenheimer MD needs to fully relax the electronic groundstate



**SFHIngX:** Allstate-CCG + first order wavefunction extrapolation

⇒ 4-5 electronic steps per ionic step (for timestep of 1 fs)

⇒ 1 Allstate-CCG step needs twice the time then a 2<sup>nd</sup> order electronic minimizer

⇒ **CPMD and SFHIngX Born-Oppenheimer MD show comparable efficiency !**



# Comparison

## Example: Simulation of Metals

### Car-Parrinello MD:

lowest oscillation frequency in the electronic system is given by energy gap

$$\omega_0 = \left( \frac{2(e^{\text{LUMO}} - e^{\text{HOMO}})}{m_i} \right)^{1/2}$$

- ⇒ electronic system cannot be decoupled from ionic system in metals
- ⇒ correcting thermostat necessary, simulation not straightforward

### Born-Oppenheimer MD:

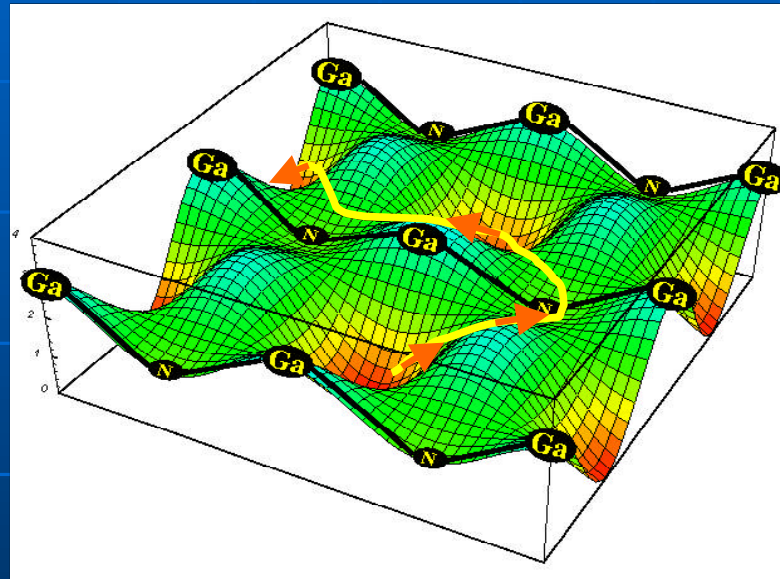
simulation as straightforward as for insulators

**(Performance comparison not yet done)**

# Exploring the phase space with MD

What can one do with a MD-run ?

## Trajectory of a MD-run



← Analysing  
time-correlation  
functions  
e.g. calculating  
frequency spectrum

→ Watching a  
movie  
“See” what will  
happen

↓  
Calculating ensemble averages  
Deriving macroscopic observables

# Statistical Ensembles

**MD-trajectory yields ensemble of possible microscopic states of the system**



**Ensemble averages can be identified with macroscopic observables**

Example:

$$p = - \left\langle \frac{\partial E^{\text{tot}}}{\partial V} \right\rangle$$

**MD connects microscopic DFT-calculation with macroscopic observables**

# Statistical Ensembles

## Example: Methane-molecule

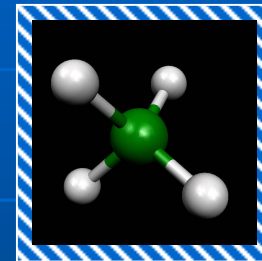
Solving Newton's equations



MD run of a closed system (isolated molecule)



microcanonical Ensemble  $N, V = \text{const}$   
 $E = \text{const}$

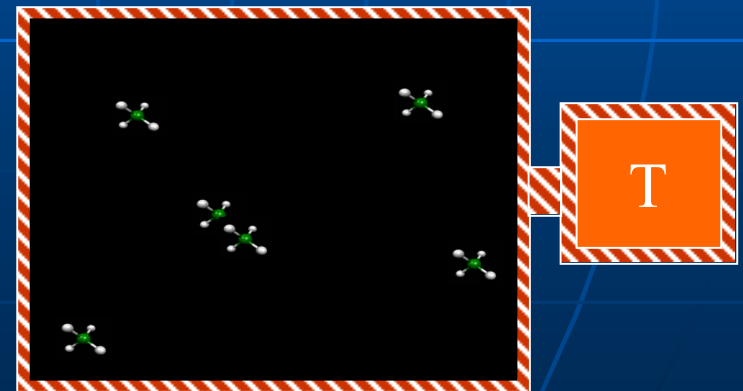


???



More realistic:  
Particle of a gas (colliding molecules)

canonical Ensemble  $N, V = \text{const}$   
 $E \neq \text{const}$   
 $\langle E \rangle @ T$



⇒ How is temperature enabled ?

# Nosé-Hoover Thermostat

Additional degree of freedom (friction  $\boxtimes$ ) simulates energy exchange with heat bath:

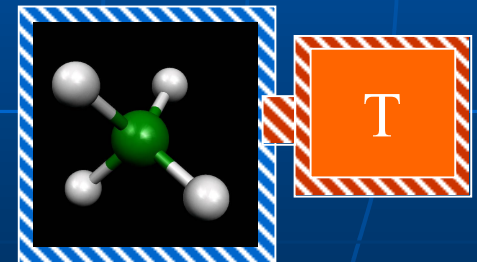
$$\ddot{\mathbf{X}}_I = \frac{\mathbf{F}_I}{M_I}$$

$\Rightarrow$

$$\ddot{\mathbf{X}}_I = \frac{\mathbf{F}_I}{M_I} - \chi \cdot \mathbf{P}_I$$
$$\dot{\chi} = \frac{1}{Q} \left( E^{\text{kin}}(\{\dot{\mathbf{X}}_I\}) - L \cdot k_B T \right)$$

L: degrees of freedom  
Q: thermostat mass  
T: temperature

- $\Rightarrow$  modified newtonian equations of motion !
- $\Rightarrow$  total energy is no longer conserved !
- $\Rightarrow$  new constant of motion for extended system !

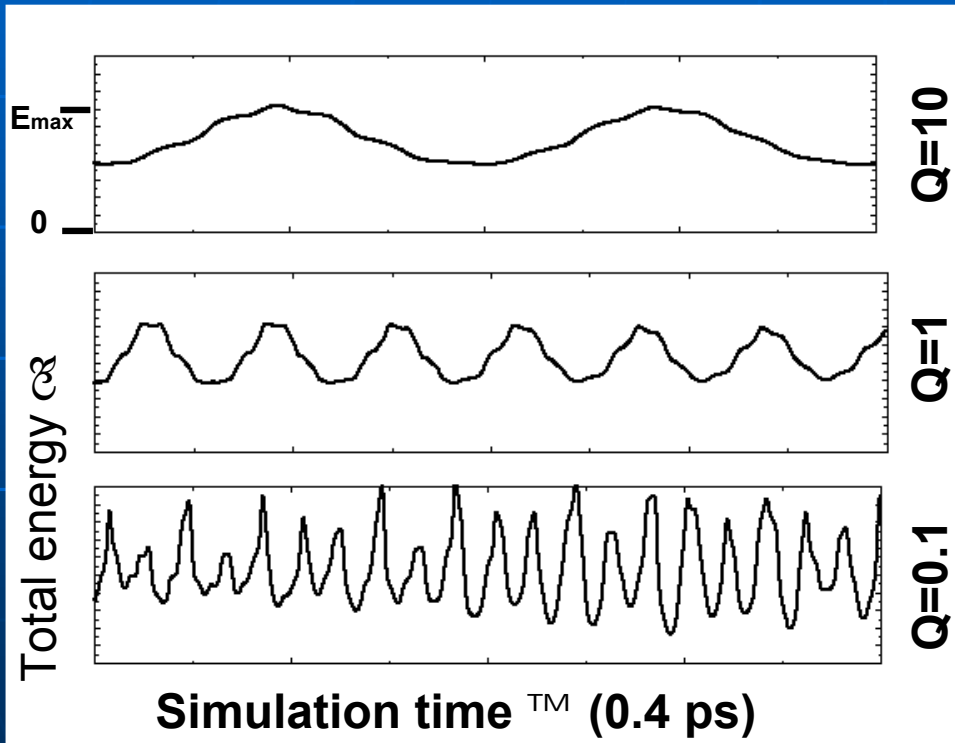


$$H^{\text{NH}} = E^{\text{tot}} + \frac{1}{2} Q \dot{\chi}^2 + \chi \frac{L}{k_B T}$$

$\Rightarrow$  Nose-Hoover thermostat exactly simulates canonical ensemble!

# The role of the thermostat mass $Q$

Example: Simulation of Methane at 298K



large  $Q$ 's

Total energy oscillates with characteristic frequency

$$W \propto 1/\sqrt{Q}$$

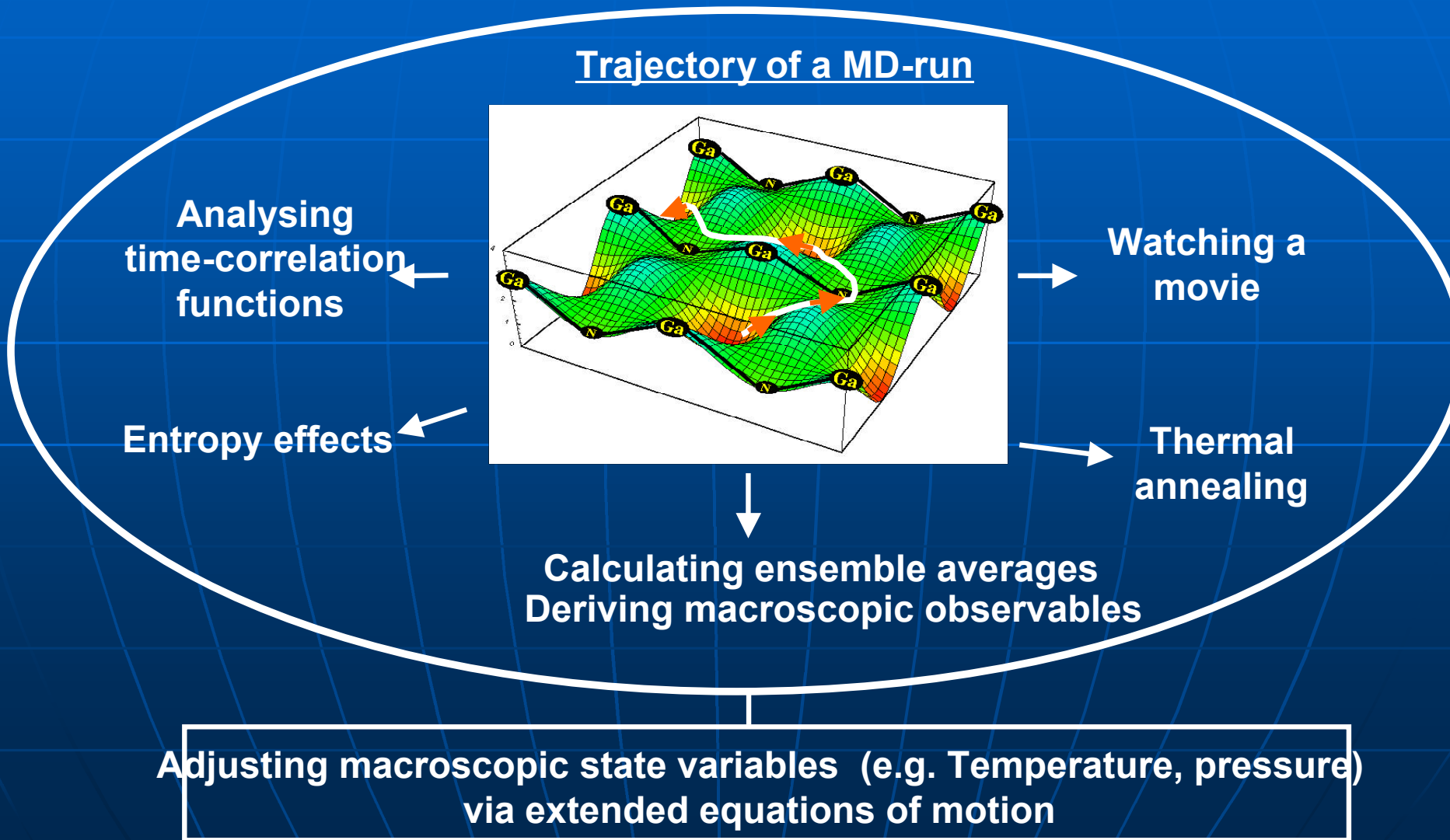
small  $Q$ 's

Characteristic frequency couples to vibrations of the system

⇒ small  $Q$  lead to faster generation of the wanted temperature  
but: too small  $Q$  lead to instabilities in the integration process

# Summary

What can one do with (first-principles) Molecular Dynamics ?



# Application-area of DFT-MD

**Maximal system size (L1)      order of 100 atoms**

**Maximal simulation time (L1)    order of 100 ps,  
10000 hydrogen-stretch vibrations**

⇒ **no simulation of “rare” events possible  
(Transition state theory, physical intuition)**

⇒ **good for analysing microscopic processes which take place on the  
time scale of 1 ps (100 hydrogen-stretch vibrations)**

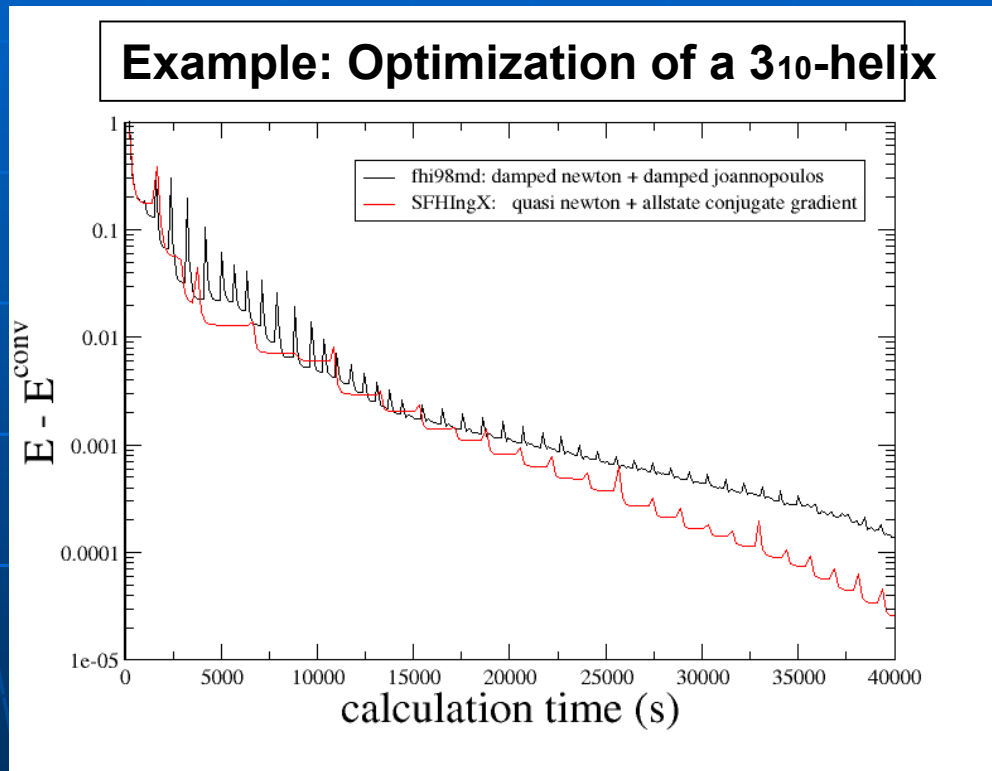
**embedding of the system in a realistic environment  
(e.g. water ) possible via QM/MM**





# Exploring the BOS with SFHIngX

## Structure optimization



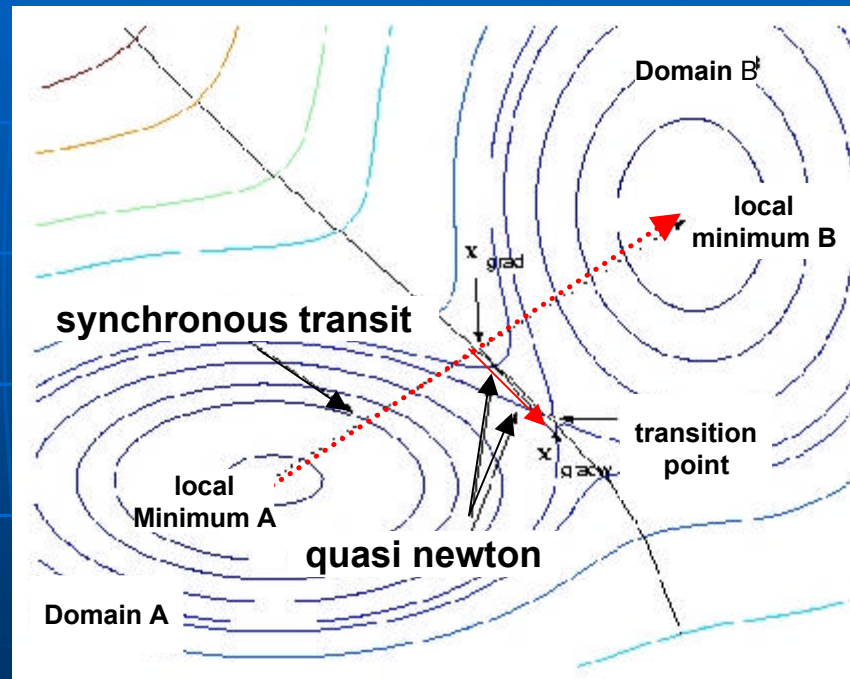
## implemented schemes

Damped Newton (Verlet)

Quasi Newton scheme

# Exploring the BOS with SFHIngX

## Transition State Search



**implemented scheme:**

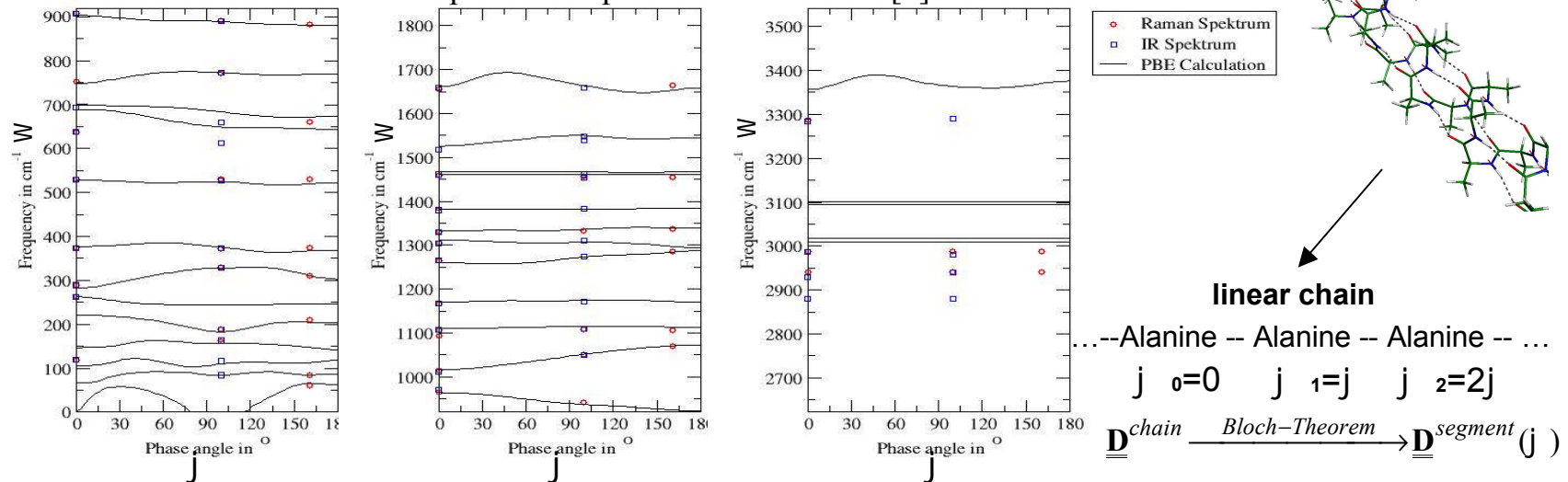
Initialization: synchronous transit

Optimization: quasi newton (gradient minimizer)

# Exploring the BOS with SFHIngX

## Vibrational analysis

Example: Phonon dispersion relation of the polyalanine  $\alpha$ -helix calculated with DFT-PBE [1] and compared to experimental values of [2]



## implemented schemes

Frozen Phonon vibrational analysis

Harmonic thermodynamic analysis (sxgetdyn)

Phonon dispersion relation (sxdispersion, not documented in manual)

[1] L. Ismer, J. Ireta, S. Boeck and J. Neugebauer, *to be published*

[2] H. Lee and S. Krimm, *Biopolymers* 46, 283 (1998)

# Exploring the BOS with SFHIngX

## Molecular Dynamics

<b>Technique</b>	<b>CCG-Born Oppenheimer Dynamics</b> <b>1<sup>st</sup> order wavefunction extrapolation</b>
<b>Integrators</b>	<b>Verlet</b> <b>Gear Predictor-Corrector</b> <b>Adams-Moulton Predictor Adams-Bashforth corrector</b>
<b>Ensembles</b>	<b>microcanonical and canonical</b>
<b>Initialisation</b>	<b>random velocities</b> <b>atom displacement in cartesian or phonon basis</b> <b>restart by file</b>