Ab Initio Molecular Dynamics

Winter school for Theoretical Chemistry and Spectroscopy
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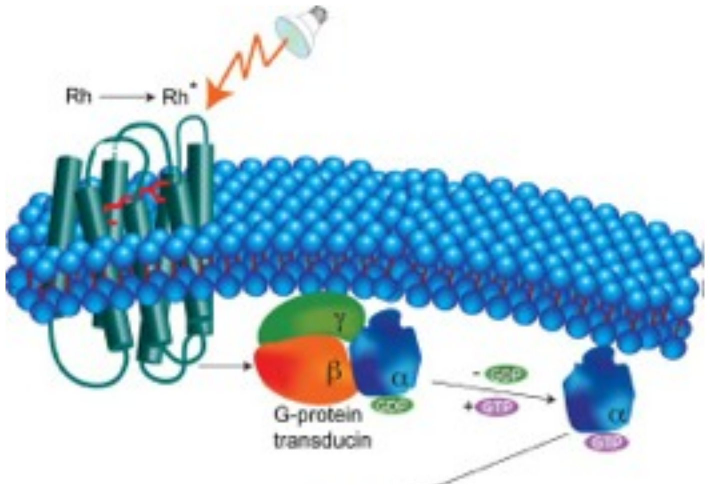
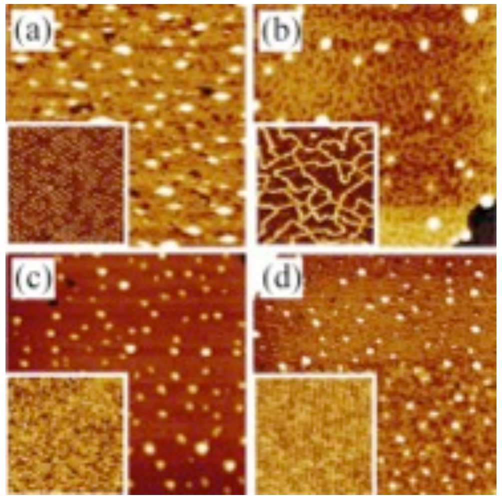
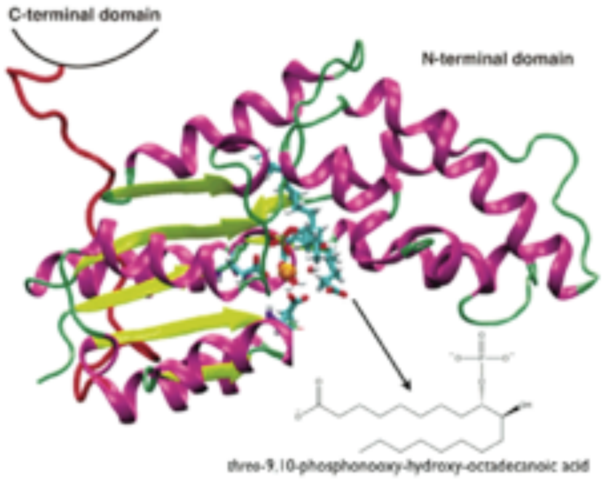
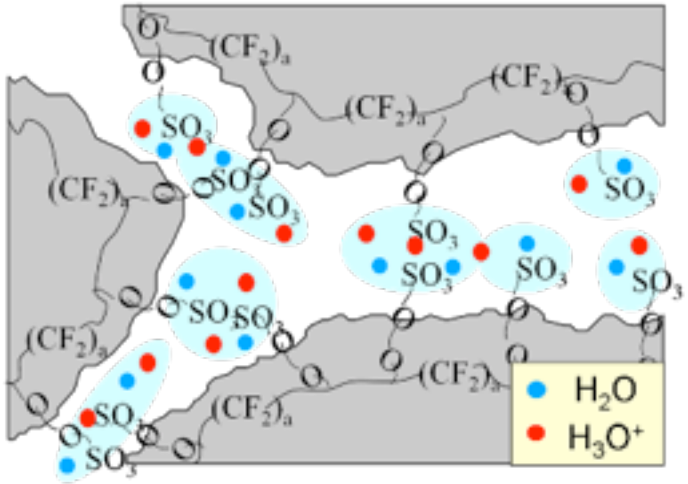
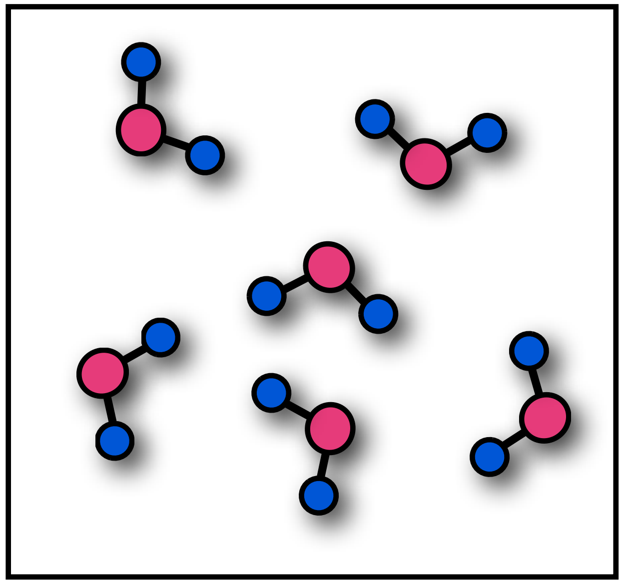
Molecular Simulation











Molecular Dynamics

Behavior of many atoms and molecules

$$\Delta t \approx 1\,\mathrm{fs} = 0.000000000000001\,\mathrm{sec}$$

atom positions and velocities

$$r(t+\Delta t) = r(t) + v(t+\Delta t/2)\Delta t$$
$$v(t+\Delta t/2) = v(t-\Delta t/2) + \Delta t\frac{f(t)}{m}$$

forcefield

$$V(\mathbf{r}) = \sum_{bonds} k_r(r-r_{eq})^2 + \sum_{angles} k_\theta(\theta-\theta_{eq})^2 + \sum_{dihedrals} \frac{1}{2}\nu_n(1+cos(n\phi-\phi_0)) + \sum_{i<j}\left(\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^{6}} + \frac{q_iq_j}{\epsilon r_{ij}}\right)$$

bonds bends torsions non-bonded

Schrödinger equation

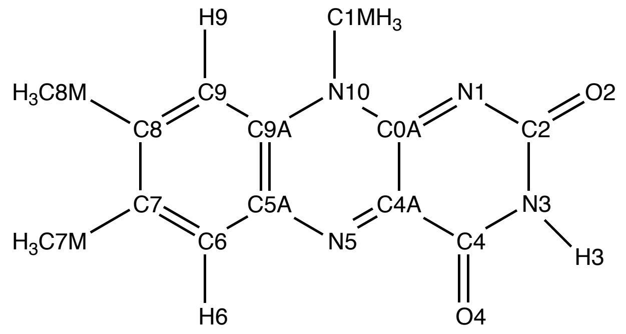
$$\hat{H}\Psi = E\Psi$$

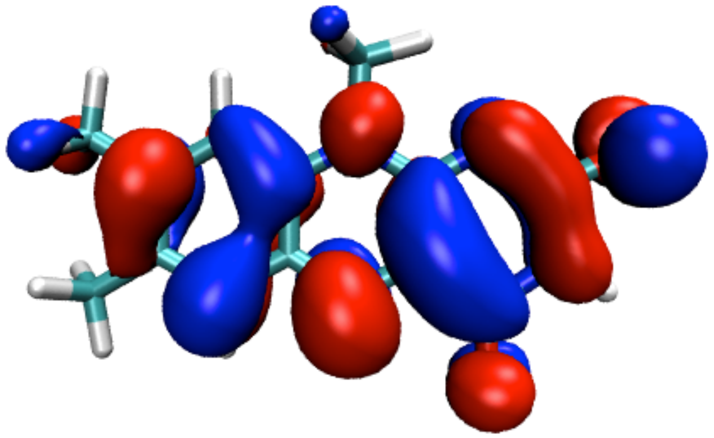
Density Functional Theory

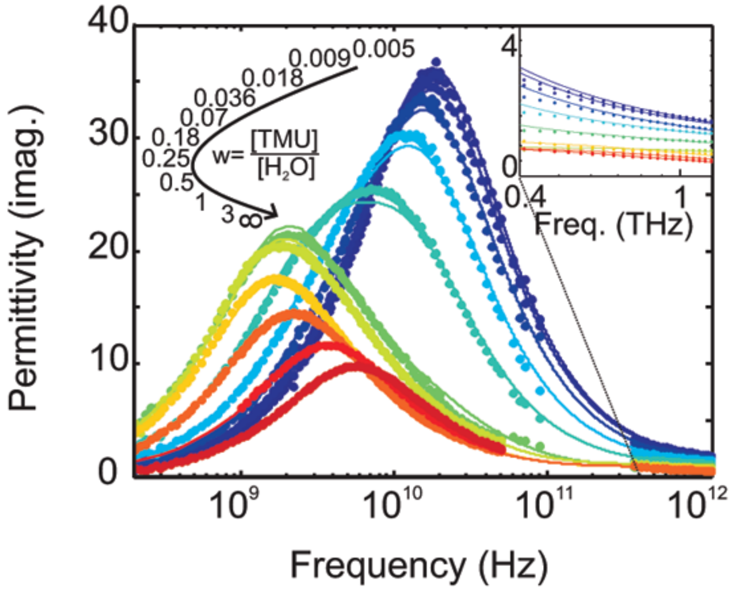
$$E = E[\rho(\mathbf{r})]$$

$$\rho(\mathbf{r}) = 2\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

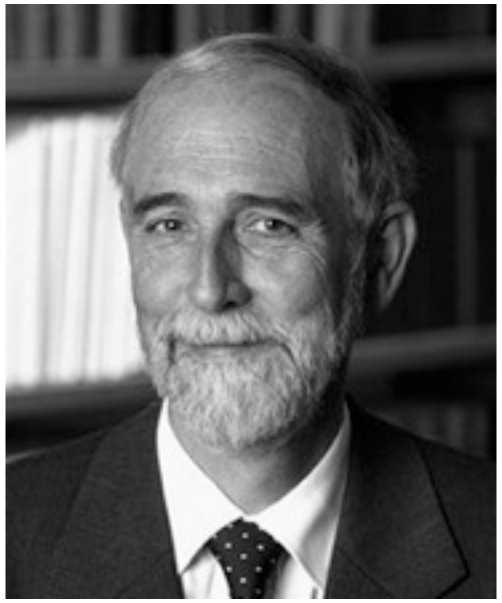
Electronic Structure







Electronic structure theory and Molecular dynamics



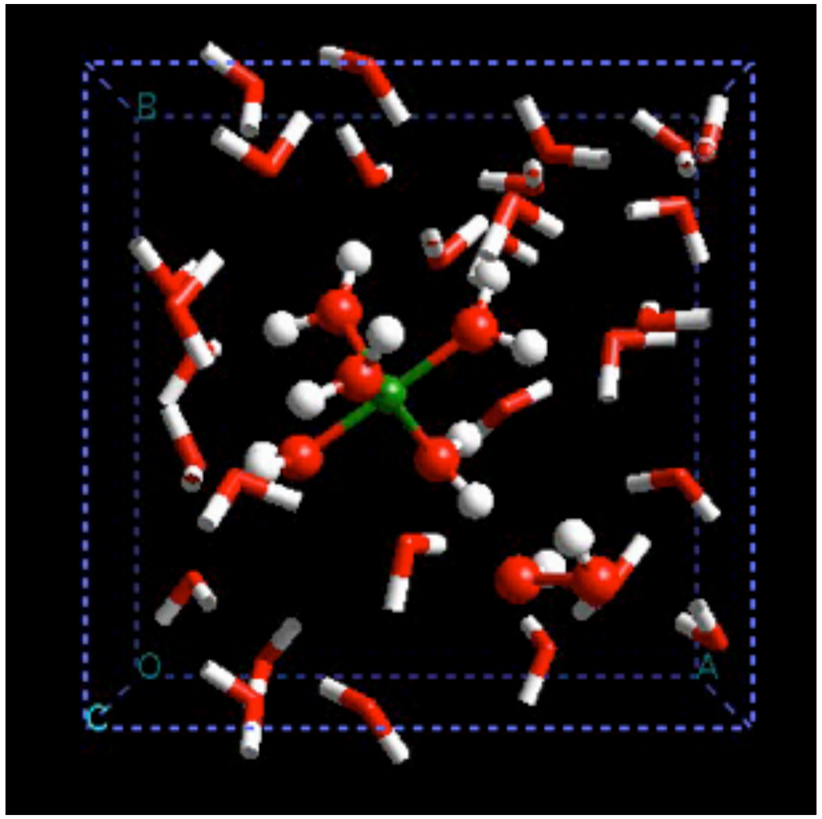
A happy marriage

Quantumchemistry and Statistical Mechanics

Ab initio Molecular Dynamics

Car-Parrinello MD
Born-Oppenheimer MD

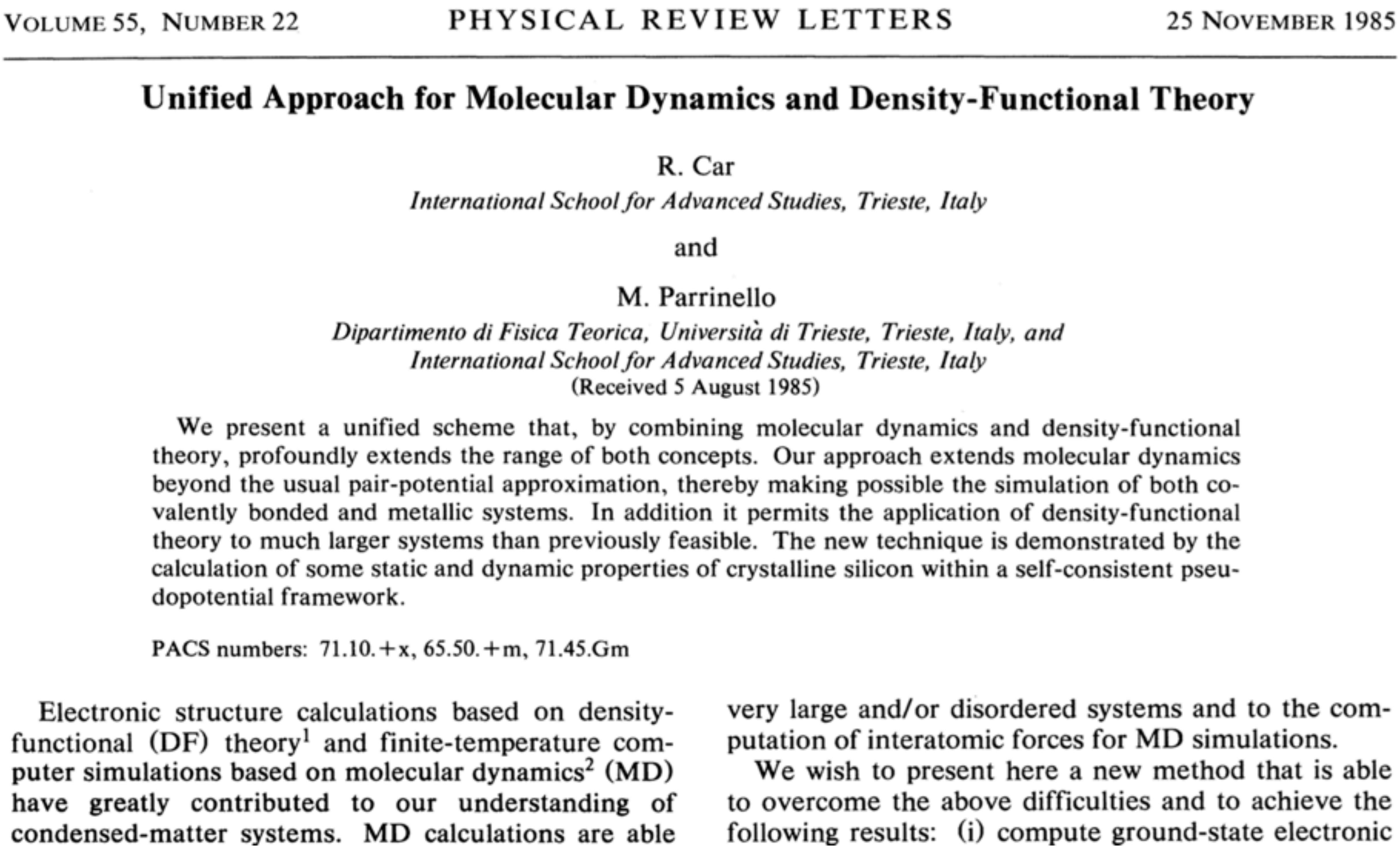
chemistry in explicit water



Content

- Introduction
- Classical Molecular dynamics
- Density Functional Theory
- Car-Parrinello Molecular Dynamics
- Born-Oppenheimer Molecular Dynamics
- Extensions
- Applications

Car-Parrinello MD



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Unified Approach for Molecular Dynamics and Density-Functional Theory

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(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

PACS numbers: 71.10.+x, 65.50.+m, 71.45.Gm

Electronic structure calculations based on density-functional (DF) theory[1] and finite-temperature computer simulations based on molecular dynamics[2] (MD) have greatly contributed to our understanding of condensed-matter systems. MD calculations are able

very large and/or disordered systems and to the computation of interatomic forces for MD simulations.

We wish to present here a new method that is able to overcome the above difficulties and to achieve the following results: (i) compute ground-state electronic

Car-Parrinello MD

Roberto Car (1947)
Princeton, USA

Michele Parrinello (1945)
ETH Zurich (Lugano),
Switzerland

- CPMD (or AIMD or FPMD or DFT-MD) was invented in Trieste (Sissa)
- The 1985 CPMD paper is the 5th most cited paper in Phys. Rev. Lett.
- In 2009, Car and Parrinello were awarded the Dirac Medal

Starting point

Time-dependent non-relativistic Schrödinger equation

$$i\hbar\frac{\partial}{t}\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = H\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)$$

Hamiltonian

$$H = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2$$

$$+\frac{1}{4\pi\epsilon_0}\sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0}\sum_{I,i}\frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0}\sum_{I<J}\frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electrons and nuclei

Separation of the wave function:

$$\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \approx \psi(\{\mathbf{r}_i\};t)\,\chi(\{\mathbf{R}_I\};t)$$

(omitting a phase factor)

Coupled time-dependent Schrödinger equations:

$$i\hbar\frac{\partial\psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\psi + \left\{\int \chi^* V_{\mathrm{n-e}}\,\chi\,d\mathbf{R}\right\}\psi$$

electrons move in mean-field of nuclei

$$i\hbar\frac{\partial\chi}{\partial t} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\chi + \left\{\int \psi^* V_{\mathrm{n-e}}\,\psi\,d\mathbf{r}\right\}\chi$$

nuclei move in mean-field of electrons

time-dependent SCF method, introduced by Dirac in 1930

Ehrenfest dynamics

Nuclei are heavy.

Replace the nuclear density $|\chi(\{\mathbf{R}_I\};t)|^2$ in the limit of $\hbar \to 0$ by delta functions centered at the positions of classical particles.

$$M_I \frac{d^2\mathbf{R}_I}{dt^2} = -\nabla_I V_e^E(\{\mathbf{R}_I(t)\})$$

V^E: Ehrenfest potential

$$i\hbar\frac{\partial\psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\psi + V_{\mathrm{n-e}}\Big(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\}\Big)\psi$$

$$\psi = \psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)$$

The Hamiltonian and the electronic wave function depend now parametrically on the nuclear positions.

Ehrenfest approach to AIMD includes non-adiabatic transitions between electronic states using classical nuclear motion and the mean field (TDSCF) approximation.

Born-Oppenheimer dynamics

Nuclei are heavy.
Adiabatic separation between nuclei and electrons.
Electrons remain in the ground-state.

Time-independent Schrödinger equation for the electrons

$$\sum_i \frac{-\hbar^2}{2m_e}\nabla_i^2\psi + V_{\mathrm{n-e}}\Big(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\}\Big)\psi_0 = E_0\psi_0$$

$$M_I\frac{d^2\mathbf{R}}{dt^2} = -\nabla_I \min_{\psi_0}\{\langle\psi_0|H_e|\psi_0\rangle\}$$

newtonian nuclear motion

The wave function needs to be minimized every time step of the nuclear dynamics (contrary to Ehrenfest dynamics).

In principle Born-Oppenheimer dynamics also be applied to some specific electronically excited state, however without including interference with other states...

Content

Classical Molecular Dynamics

Why MD simulations?

1. observe the dynamics of atoms and molecules
2. compute ensemble averages of model systems

Limitations:

- many particle systems exhibit chaotic dynamics
  - trajectories starting from similar initial conditions diverge exponentially fast:

$|\delta \mathbf{Z}(\mathbf{t})| \approx \mathbf{e}^{\lambda \mathbf{t}} |\delta \mathbf{Z_0}|$ with λ a (positive) Lyapunov exponent

- choice of initial conditions is inaccurate
- models are inaccurate
- integration of equations of motions contains discretization errors
- computers have rounding errors

Therefore:

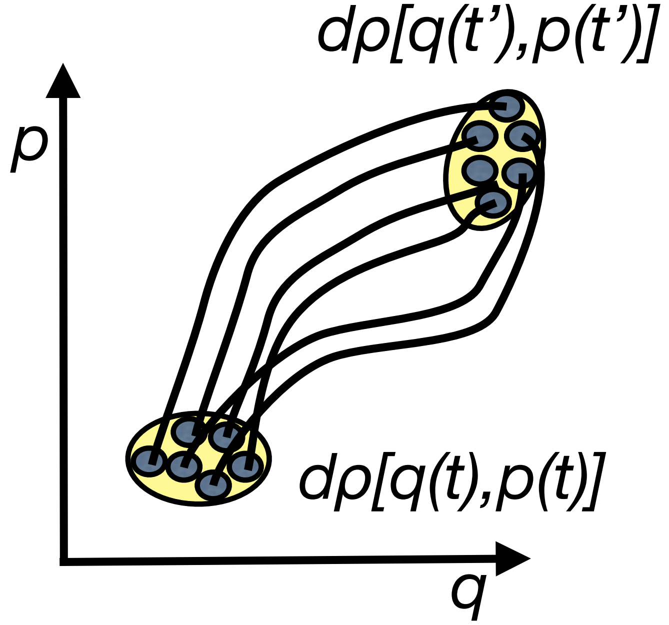
- A single trajectory is not likely do represent any “true” molecular trajectory.
- But statistical averages over trajectories are useful to estimate ensemble averages

Classical Molecular Dynamics [1,2]

How can we trust the statistics from MD trajectories?
(Considering the limitations of MD simulations)

A trustworthy integrator (MD algorithm) has the following features:

- time-reversible
- phase-space conserving



The phase space density is constant along the trajectory (Liouville's theorem)

The Hamiltonian is the sum of kinetic energy and potential energy

$$H(p,q) = T(p) + V(q)$$

q: position
p: momentum

$$\dot{p} = -\frac{\partial H}{\partial q}$$

$$\dot{q} = \frac{\partial H}{\partial p}$$

Integrators

Algorithms to numerically solve ordinary differential equations (ODE)
ODE is an equation that relates the function value to the value(s) of its derivatives

Examples of applications:

- Calculation of an integral
- Solving Schrödingers' equation:
- Geometry optimization
- Molecular dynamics:

$$E\psi(r) = -\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r)$$

$$H = \frac{1}{2}\sum_i m_i\dot{r}_i^2 + V(r)$$

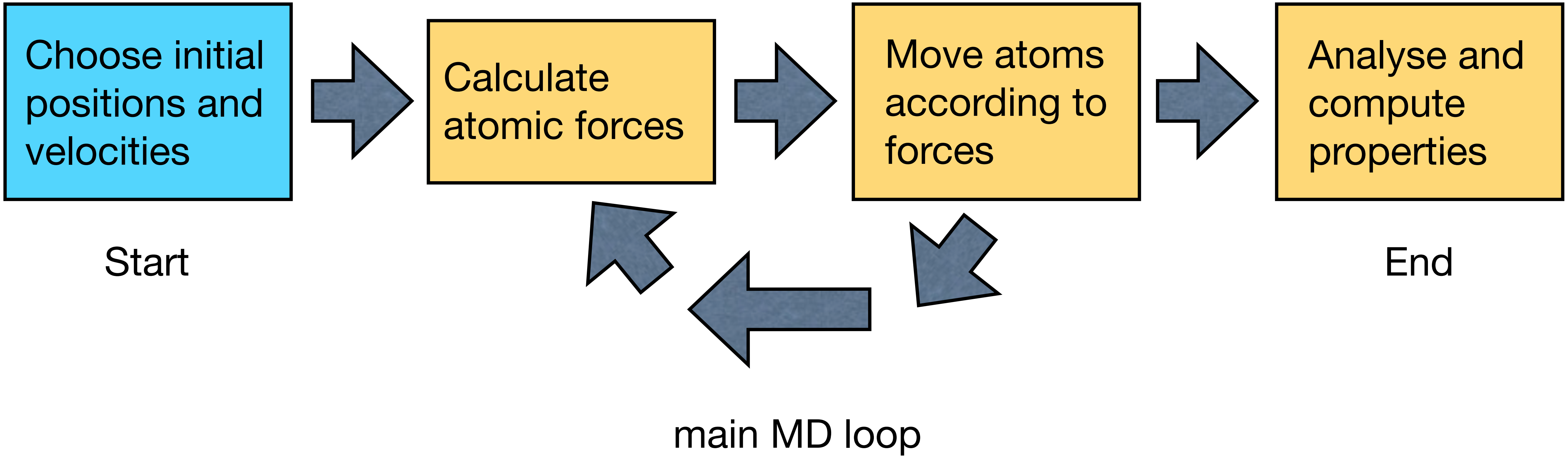
Examples of integrators:

- Euler method
- Runga-Kutta
- Verlet
- Velocity Verlet
- Leap-frog
- Beeman's algorithm
- ...

Molecular dynamics

Integration of Newton's equations

$$\begin{aligned} F &= m \cdot a \\ F &= -\nabla V \end{aligned} \quad \Rightarrow \quad -\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$


Choose initial positions and velocities

Calculate atomic forces

Move atoms according to forces

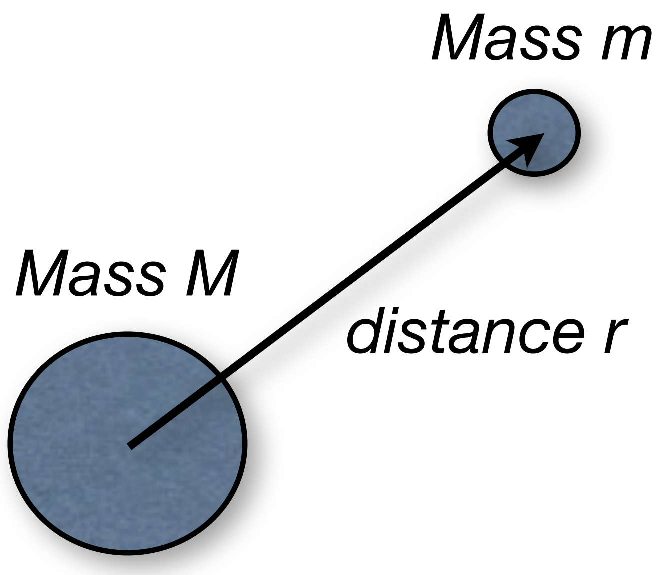
Analyse and compute properties

Start

End

main MD loop

Example

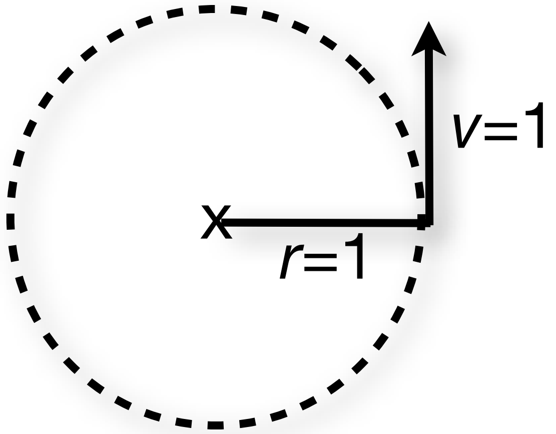


- Newton’s Law of Gravitation
  - – force is an inverse square law
  - – same equations of motion as MD

$$H = \frac{1}{2}\sum_i m_i \mathbf{v}_i^2 + \frac{GMm}{|\mathbf{r}|}$$

- Simple Numerical Model in Reduced Units:
  - – Assume Sun is stationary (M >> m)
  - – For convenience we use Earth Units
    - GM=1
    - circular orbit for r=v=1
    - each revolution takes 2 time!units

$$F = -\frac{GMm}{r^2} \qquad \frac{d^2\mathbf{r}}{dt^2} = -\frac{1}{r^3}\mathbf{r}$$



Integrator (1): Euler method

- Truncate Taylor expansion after the acceleration term
  - Local Error: O(Δt^3) in position and O(Δt^2) in velocity

$$x(t+\Delta t) = x(t) + v(t)\Delta t + a(t)\frac{(\Delta t)^2}{2}$$

$$v(t+\Delta t) = v(t) + a(t)\Delta t$$

- Euler method is OK for projectiles, but for MD ...

Integrator (1): Euler method

Matlab/Octave script

```
h=0.1;          % timestep
pos=[1 0];      % initial position
vel=[0 1.0];    % initial velocity
plot(1,0,'g-',pos(1),pos(2),'ko',0,0,'ro')

for i=1:100
  x(i)=pos(1);
  y(i)=pos(2);

  plot(x,y,'g-',pos(1),pos(2),'k*',0,0,'r+')
  title(num2str(i*h))
  axis equal;
  axis([-2.0 2.0 -2.0 2.0]);
  pause(0.05);

  r=norm(pos);
  accel=-1/r^2 * pos/r;

  pos=pos + h*vel + 0.5*h*h*accel;
  vel=vel + h*accel;
end
```

Consider:

- h=0.1 ; steps=100
- h=0.05 ; steps=200

Plotting instructions

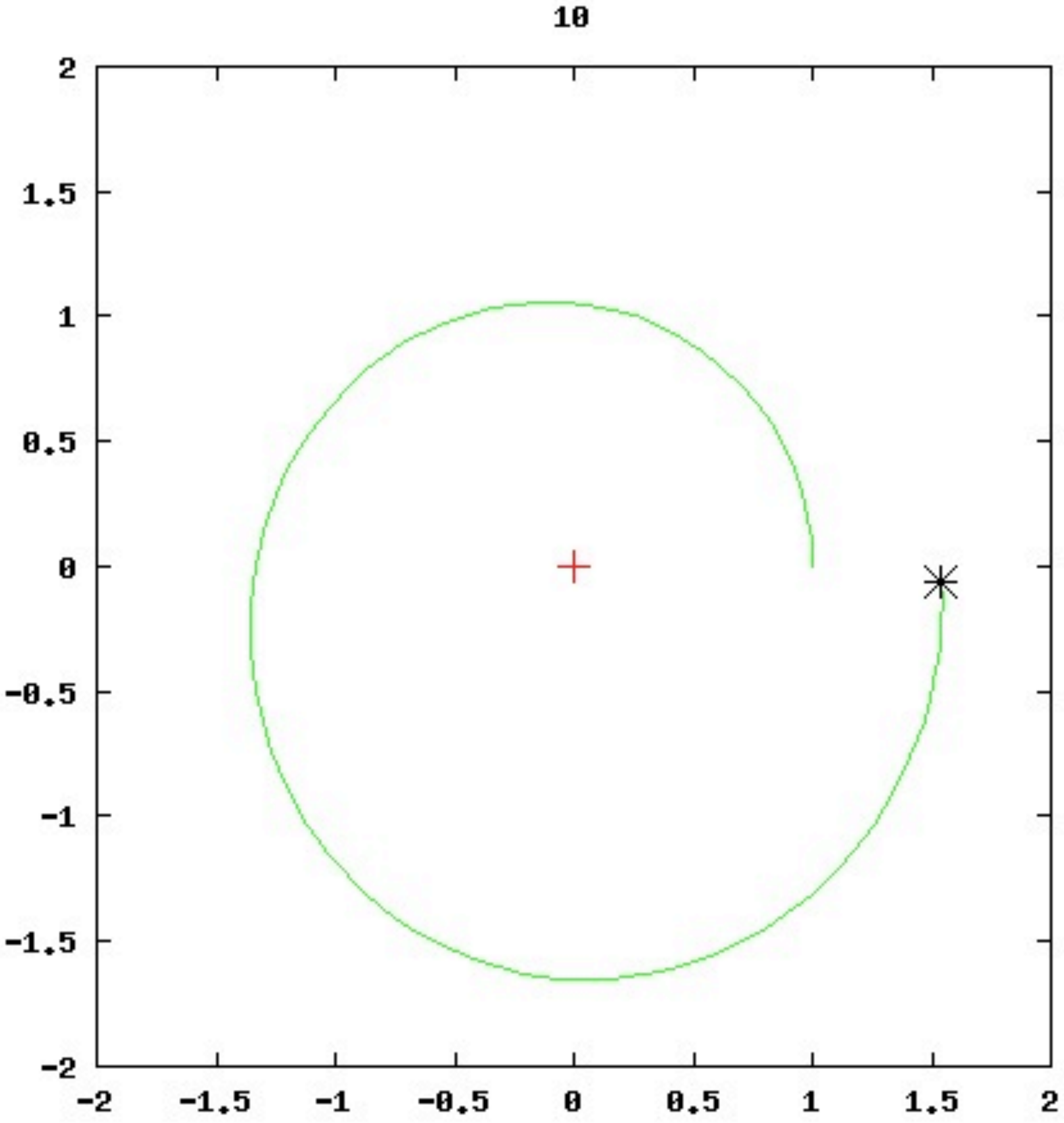
Compute force

Integrate

Integrator (1): Euler method

Euler method is OK for projectiles, but for MD ...

– trajectory spirals outward
– local error accumulates with time (i.e. large global error)
– reducing timestep h just delays the inevitable



Improved integrators

- Symplectic integrators correctly reproduce long-time dynamics

- Common ODE methods such as Runge-Kutta are not suitable
  - error always accumulates in a manner analogous to the Euler example – unreliable long-term behaviour

- A good MD integrator should:
  - be time reversible (thus honouring Newtonian mechanics)
  - conserve phase-space volume (pendulum is illustrative)

Integrator (2): Verlet method

- Combine forward and backward Taylor expansions
  - Local Error: O(Δt^4) in position and O(Δt^2) in velocity

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + a(t)(\Delta t)^2$$

$$v(t) = \frac{1}{2\Delta t}[x(t+\Delta t) - x(t-\Delta t)$$

- Velocities not required: [x(t–Δt),x(t)] ⟶ [x(t+Δt)]
- Not self-starting – apply a single Euler step to begin
  - stable even with large time!steps
  - local error does not accumulate (i.e. small global error)

Integrator (2): Verlet method

Matlab/Octave script

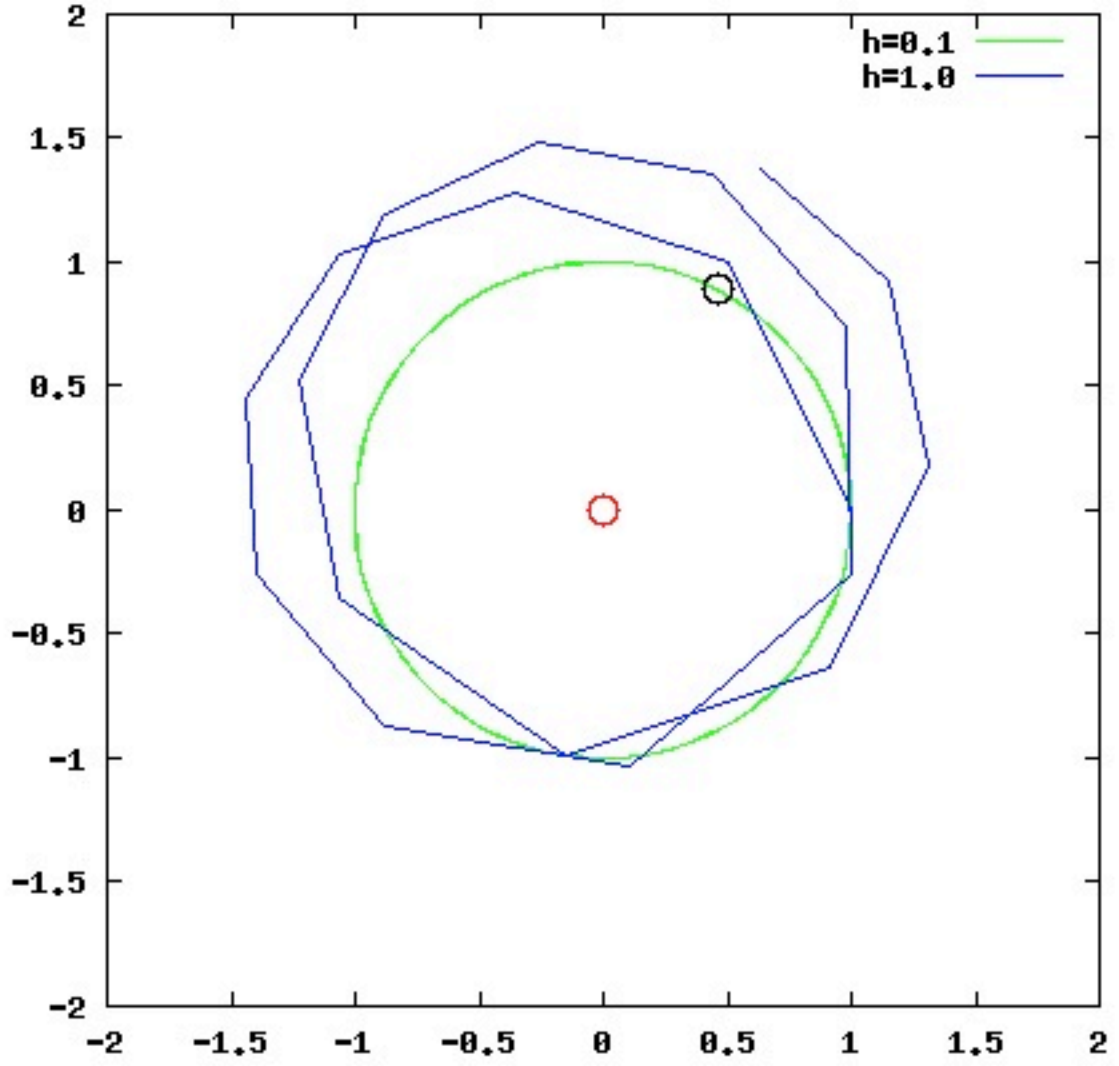
```
h=0.2;         % timestep
pos=[1 0];     % initial position
vel=[0 1.0];   % initial velocity

for i=1:50
  x(i)=pos(1);
  y(i)=pos(2);

  ...         % plotting instructions

  r=norm(pos);
  accel=-1/r^2 * pos/r;

  if i==1
    next=pos + h*vel + 0.5*h*h*accel;
  else
    next=2*pos - prev + h*h*accel;
    vel=(next-prev)/(2*h);
  end

  Etot(i)=0.5*norm(vel)^2 + 1/norm(pos);

  prev=pos;
  pos=next;
end
```

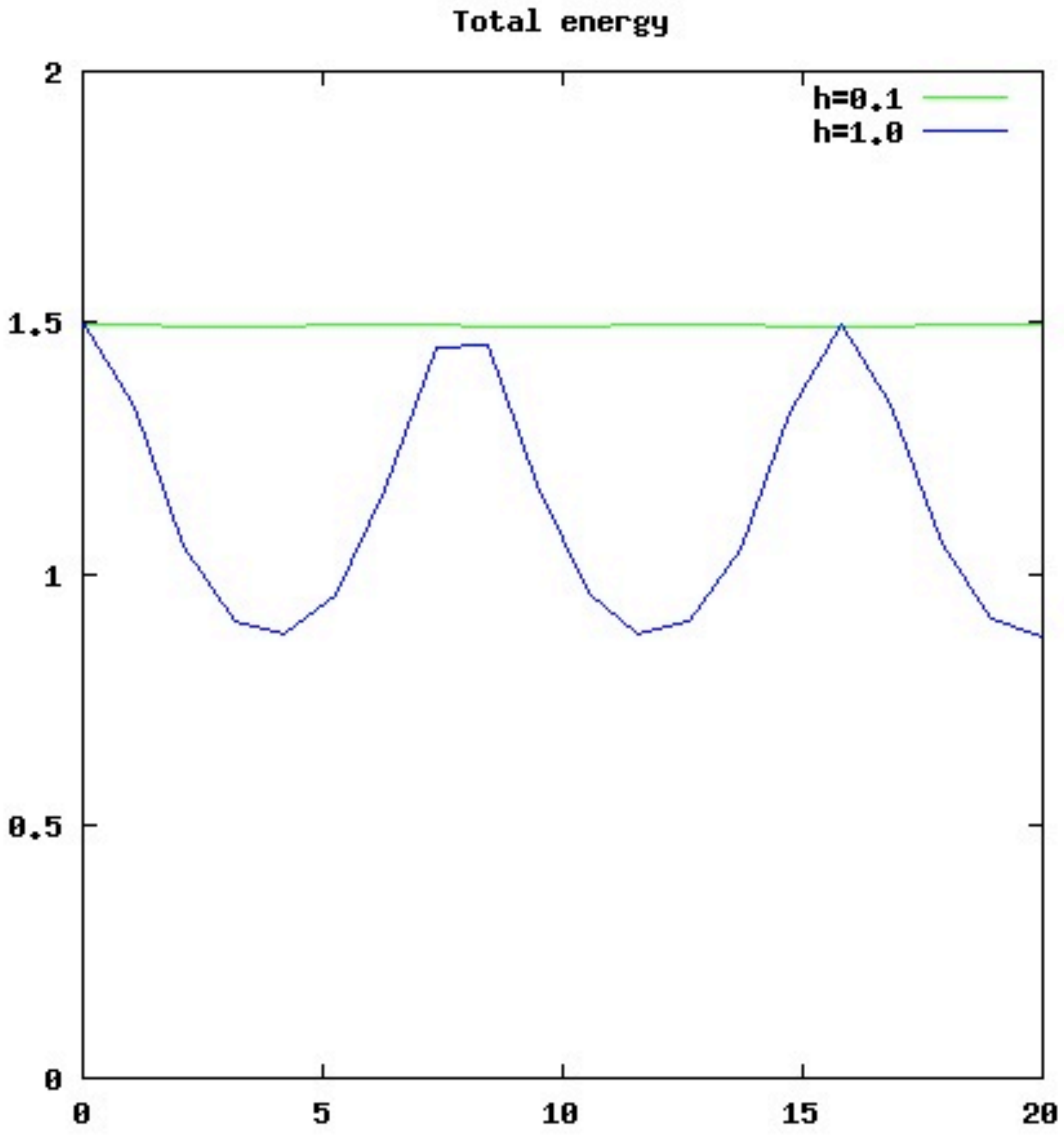
Consider:

- h=0.1 ; steps=100
- h=0.5 ; steps=100
- h=1.5 ; steps=50

Conserved quantity

Integrator (2): Verlet method





Conserved quantities

- We can't *exactly* numerically integrate, yet "good" integrators oscillate around the true solution
  - Numerical trajectory 'shadows' the exact orbit, with the proximity to the exact orbit varying with Δt
  - Despite lacking the exact solution, we can gauge the Global Error numerically via conserved quantities
  - Momentum (linear & angular) can be conserved too
  - Linear drift in the conserved quantity is a sign that the equations of motion are not being integrated correctly
- Even with high precision integration, trajectories are extremely sensitive to initial conditions (i.e. chaotic)

Integrator (3): Velocity Verlet

- Resembles Euler method (but with two-step update)
  - Local Error: O(Δt^4) in position and O(Δt^3) in velocity

$$x(t+\Delta t) = x(t) + v(t)\Delta t + a(t)\frac{(\Delta t)^2}{2}$$

$$v(t+\Delta t) = v(t) + \frac{[a(t) + a(t+\Delta t)]}{2}\Delta t$$

Reduces to Euler method
if $a(t+\Delta t) = a(t)$

- Identical Trajectory to Verlet Method
- Uses present state only: $[x(t),v(t)] \longrightarrow [x(t+\Delta t),v(t+\Delta t)]$
  - Self-starting
  - Easy to change the time-step

half-step velocities

- Velocity Verlet is often represented in half-steps:

$$v(t+\frac{1}{2}\Delta t) = v(t) + a(t)\frac{\Delta t}{2}$$

apply thermostat

$$x(t+\Delta t) = x(t) + v(t+\frac{1}{2}\Delta t)\Delta t$$

compute forces

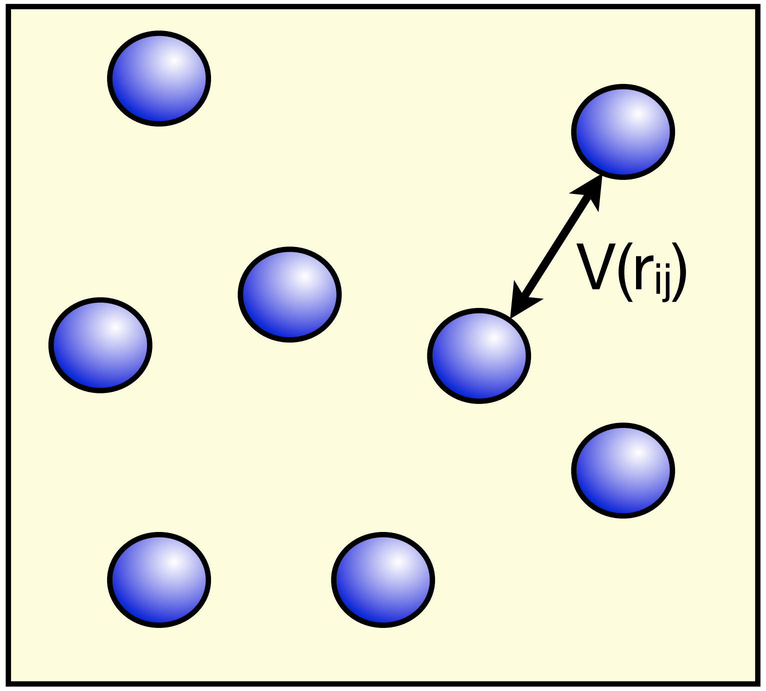
$$v(t+\Delta t) = v(t+\frac{1}{2}\Delta t) + a(t+\Delta t)\frac{\Delta t}{2}$$

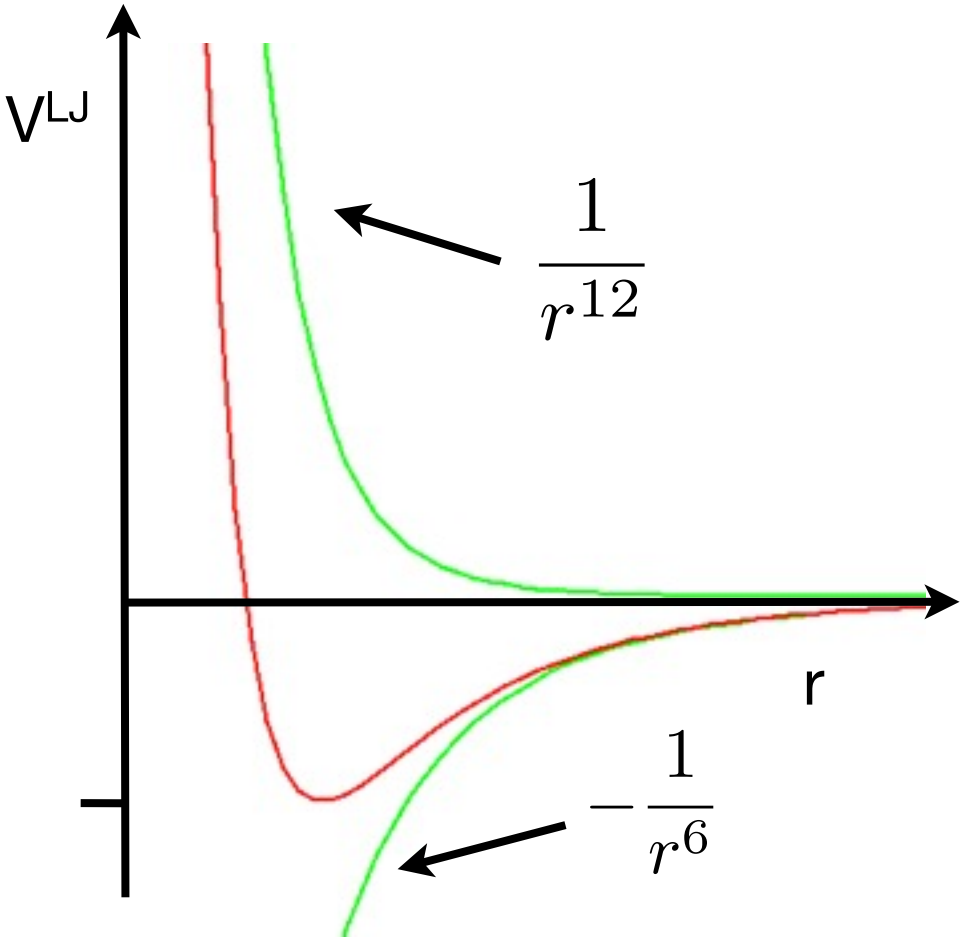
- In Leap-Frog Verlet the coordinates are defined at full timesteps (t, t+Δt, t+2Δt...), while the velocities are defined at half-steps (t-Δt/2, t+Δt/2, t+3Δt/2...).

What is your Hamiltonian?

The model: how are the interactions approximated?

- Empirical forcefields



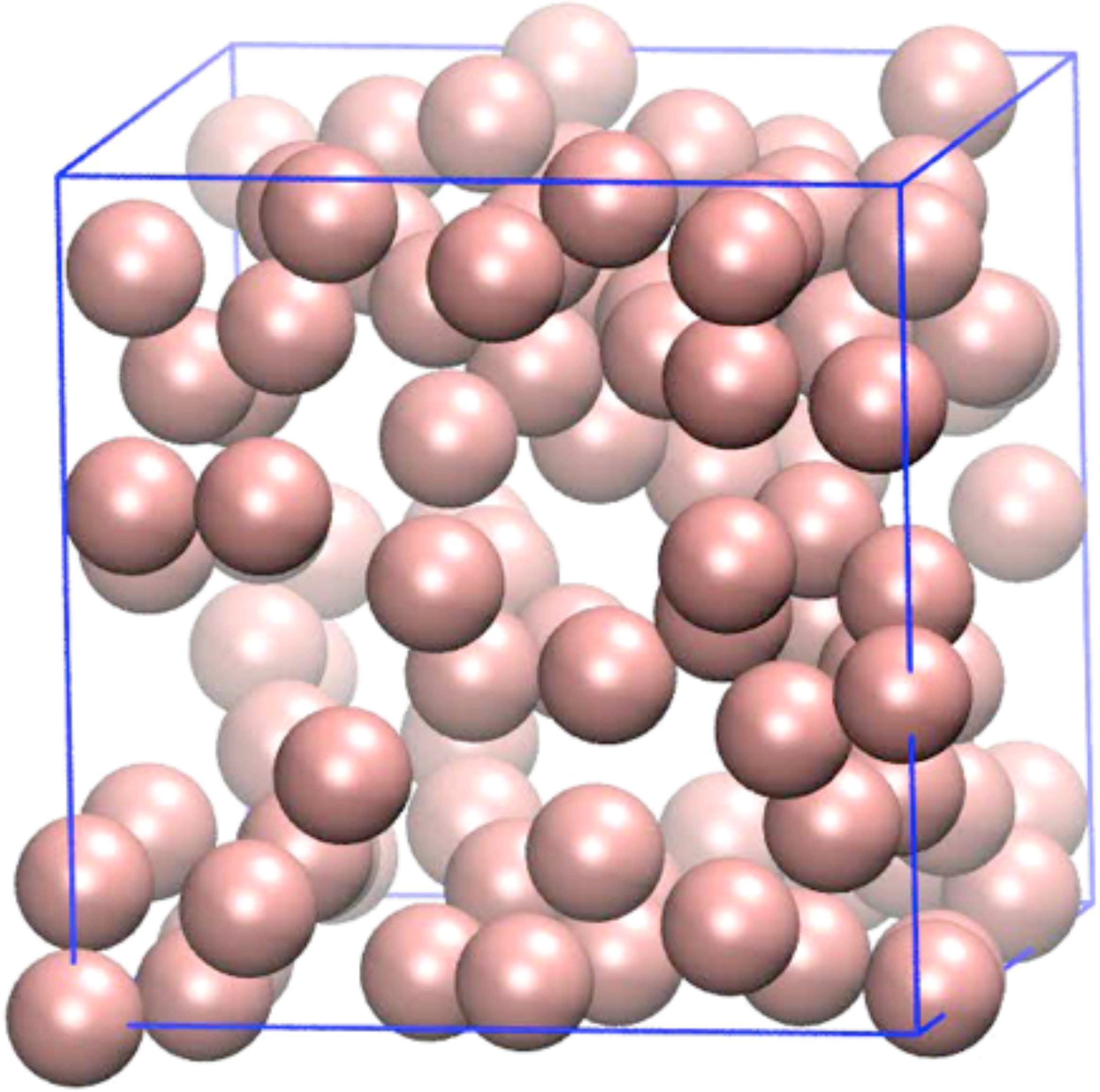


Lennard-Jones pair-potential

$$V^{\mathrm{LJ}}(r) = -4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

Lennard-Jonesium

$$V^{\mathrm{LJ}}(r) = -4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$



Phase transitions of the Lennard-Jones system,
Jean-Pierre Hansen and Loup Verlet,
Phys. Rev. 184 (1969), 151

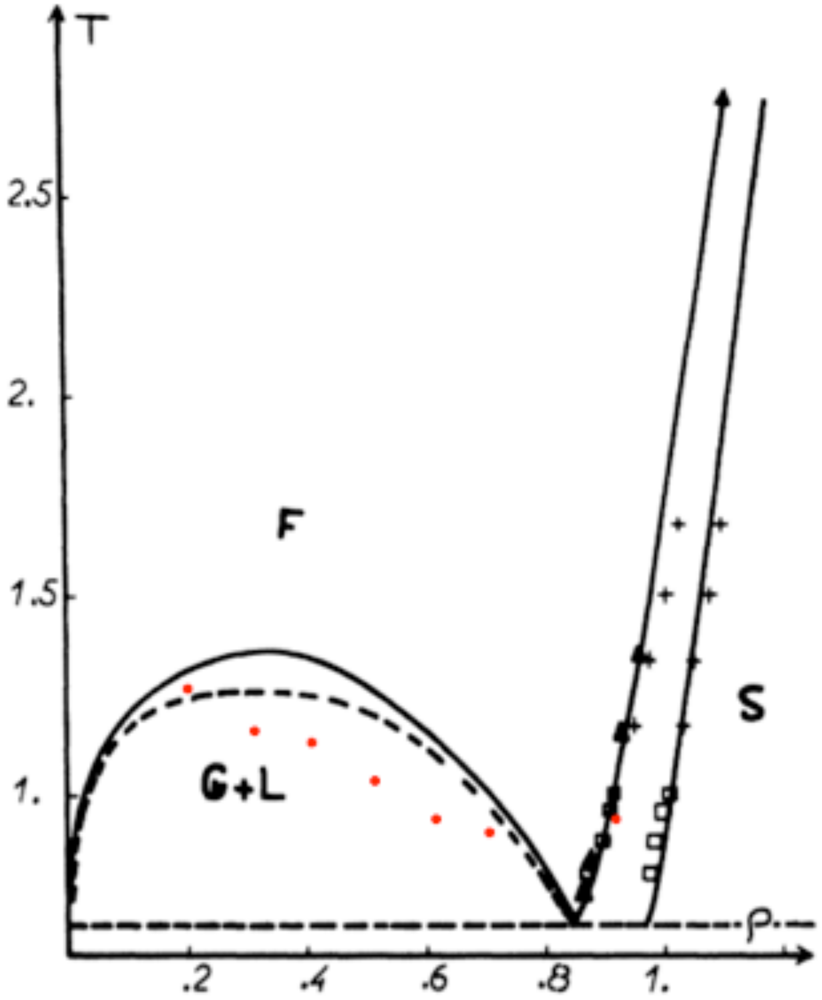


FIG. 3. Coexistence curve for the Lennard-Jones system (temperatures and densities in reduced units). The solid line gives our theoretical results. The broken line gives the experimental argon liquid-gas coexistence line taken from Michels *et al.*[17,22] The circles are experimental argon melting data taken from van Witzenburg and Stryland,[20] the crosses are experimental melting data taken from Crawford and Daniels.[21] The triangles indicate the crystallization densities according to the "law" stating that crystallisation occurs whenever $S(k_0)$ reaches the value 2.85.

Empirical forcefields

Non-bonded interactions

- Van der Waals
  (Lennard-Jones, Buckingham, ...)

$$V^{\mathrm{LJ}}(r) = -4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

$$V^{\mathrm{Buck}}(r) = A\exp(-Br) - \frac{C}{r^6}$$

- Electrostatic interaction

$$V^{\mathrm{Coulomb}}(r) = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}$$

- H-bonds, 3-body interaction, polarization, ...

Bonded interactions

- bond $V^{\mathrm{harm}}(r) = \frac{1}{2}k_b(r - r_0)^2$ $\qquad V^{\mathrm{morse}}(r) = D_e(1 - e^{-\alpha(r - r_e)})^2$
- angle $V^{\mathrm{harm}}(\theta) = \frac{1}{2}k_\alpha(\theta - \theta_0)^2$
- dihedral $V^{\mathrm{Fourier}}(\omega) = \sum_n \frac{1}{2}V_n[1 + \cos(n\omega - \gamma)]$
- improper
- ....

Empirical forcefields

Total potential

$$E^{\mathrm{pot}} = E^{\mathrm{bonded}} + E^{\mathrm{non-bonded}}$$

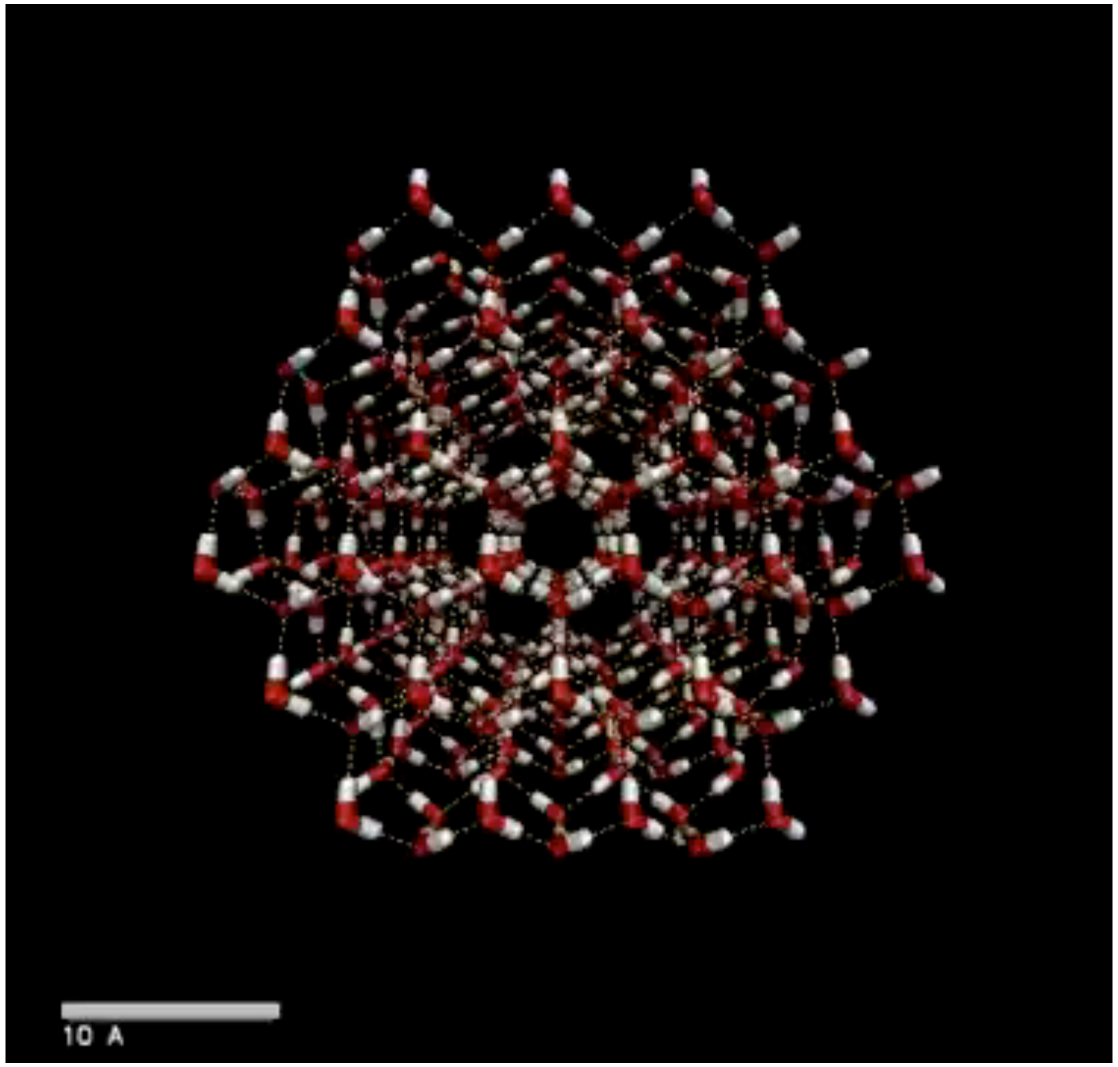
$$E^{\mathrm{pot}} = \sum_{\mathrm{bonds}} V^{\mathrm{bond}} + \sum_{\mathrm{angles}} V^{\mathrm{angle}} \sum_{\mathrm{dihedrals}} V^{\mathrm{torsion}} + \sum_{\mathrm{i}} \sum_{\mathrm{j \neq i}} V^{\mathrm{LJ}} + \sum_{\mathrm{i}} \sum_{\mathrm{j \neq i}} V^{\mathrm{Coulomb}}$$

Common forcefields

MMS
CFF
AMBER
CHARMM
GROMOS
OPLS
UFF

MARTINI (CG)

Simulated heating of water molecules



Empirical forcefields

Total potential

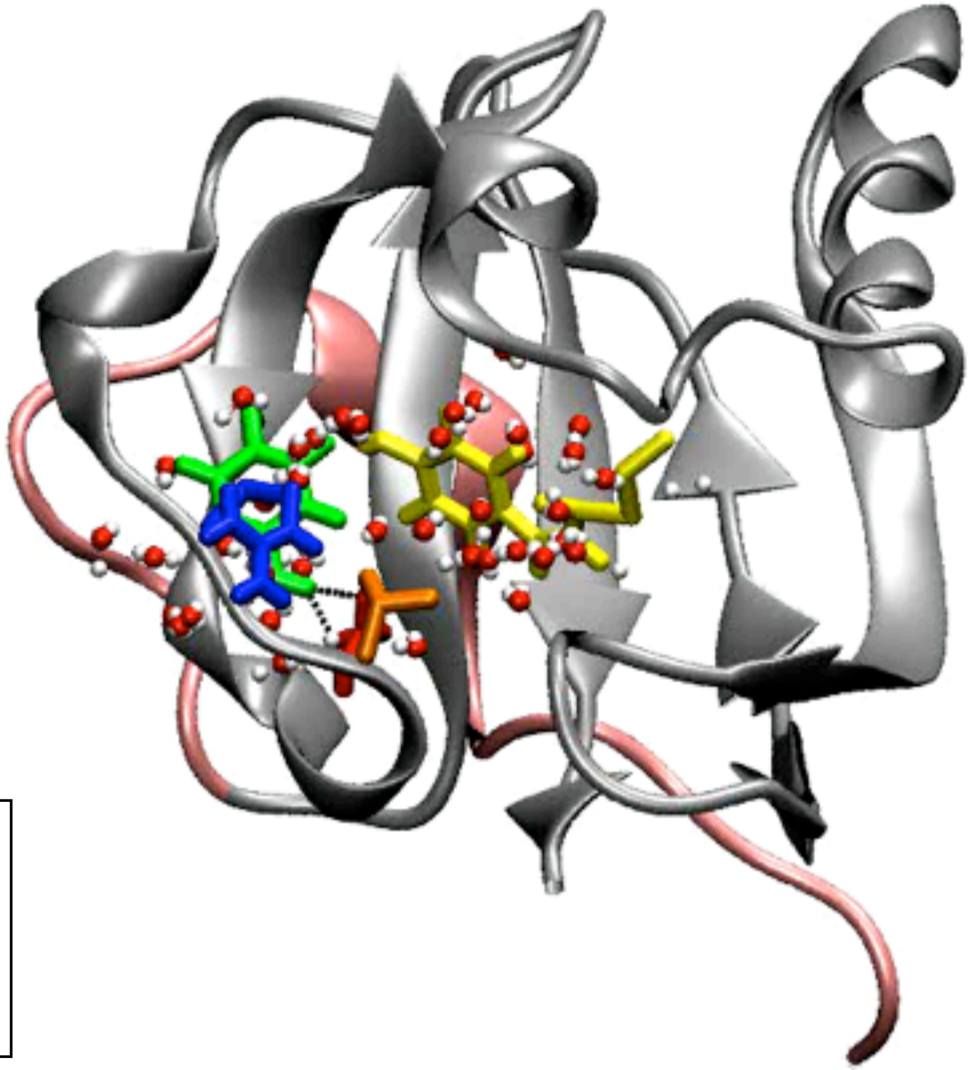
$$E^{\mathrm{pot}} = E^{\mathrm{bonded}} + E^{\mathrm{non-bonded}}$$

$$E^{\mathrm{pot}} = \sum_{\mathrm{bonds}} V^{\mathrm{bond}} + \sum_{\mathrm{angles}} V^{\mathrm{angle}} \sum_{\mathrm{dihedrals}} V^{\mathrm{torsion}} + \sum_{\mathrm{i}} \sum_{\mathrm{j} \neq \mathrm{i}} V^{\mathrm{LJ}} + \sum_{\mathrm{i}} \sum_{\mathrm{j} \neq \mathrm{i}} V^{\mathrm{Coulomb}}$$

Common forcefields

- MMS
- CFF
- AMBER
- CHARMM
- GROMOS
- OPLS
- UFF

- MARTINI (CG)



partial unfolding of photoactive yellow protein

Empirical forcefields

Classical (Forcefield) Molecular Dynamics

- parameterizations available
- implemented in efficient parallel programs
- system sizes of 10^6 particles
- simulation times of ~ microseconds

Limitations

- transferability (molecular environment, thermodynamic state)
- often: no polarization, many-body interactions
- no bond-breaking (chemistry)
- no information on the electronic structure (spectroscopy)

Ab initio molecular dynamics

Empirical forcefields are often fitted to ab initio calculations.
Why not obtain the ab initio potential on the fly?

Which level of ab initio theory?
- (semi-emprical), HF, DFT, MP2, CASSCF, CC,... would all be possible.

Density Functional Theory is a good compromise between accuracy and computational cost.
- GGA functionals may have limited accuracy
- Van der Waals interactions are problematic
- better non-local functionals, hybrid functionals, etc, are costly

Content

- Introduction
- Classical Molecular dynamics
- Density Functional Theory
- Car-Parrinello Molecular Dynamics
- Born-Oppenheimer Molecular Dynamics
- Extensions
- Applications

Density Functional Theory

The energy is a functional of the electron density

$$E = E[\rho(\mathbf{r})]$$

Hohenberg & Kohn (1964)

Variation principle:

$$\langle\Psi[\rho]\ |\hat{H}|\Psi[\rho]\rangle = \int d\mathbf{r}\, v(\mathbf{r})\,\rho(\mathbf{r}) + T[\rho] + V_{\mathrm{ee}}[\rho] = E_v[\rho] \geq E_0[\rho]$$

external potential (nuclei)

kinetic energy

electron-electron interaction

second HK theorem

Non-interaction potential yields the same density:

$$E[\rho] = T_s[\rho] + V_{\mathrm{N}}[\rho] + J_{\mathrm{ee}}[\rho] + E_{\mathrm{xc}}[\rho]$$

Kohn-Sham (1965)

$$\rho(\mathbf{r}) = 2\sum_i^{occ} |\psi_i(\mathbf{r})|^2$$

Walter Kohn (1923)
Nobelprize 1998

Density Functional Theory

$$E[\rho] = T_s[\rho] + V_{\mathrm{N}}[\rho] + J_{\mathrm{ee}}[\rho] + E_{\mathrm{xc}}[\rho]$$

non-interaction kinetic energy	nuclear potential	Coulomb interaction	Exchange + correlation

$$T_s(\rho) = -\frac{\hbar^2}{2m}\sum_i^N \int d\mathbf{r}\, \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})$$

$$V_{\mathrm{N}}[\rho] = \int d\mathbf{r}\, v^{\mathrm{ext}}(\mathbf{r})\,\rho(\mathbf{r})$$

$$J_{\mathrm{ee}}[\rho] = \frac{e^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{\mathrm{xc}}[\rho] = V_{\mathrm{ee}} - J_{\mathrm{ee}}[\rho] + T[\rho] - T_s[\rho]$$

the rest

Density Functional Theory

Minimization of the Kohn-Sham equations (variational principle)

$$\hat{H}^{\mathrm{KS}}\psi_i = [-\frac{\hbar^2}{2m}\nabla^2 + v^{\mathrm{ext}} + \frac{e^2}{2}\int d\mathbf{r}\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}]\psi_i = \epsilon_i\psi_i$$

Local Density Approximation:

$$E_{\mathrm{xc}}^{\mathrm{LD}} = \int d\mathbf{r}\,\rho(\mathbf{r})\,\epsilon_{\mathrm{xc}}$$

Generalized Gradient Approximation

Becke Exchange functional (1988)

$$\epsilon_{\mathrm{xc}}^{\mathrm{B}} = -\beta\rho^{1/3}\frac{x^2}{(1+6\beta x\sinh^{-1}x)}$$

$$x = \frac{|\nabla\rho|}{\rho^{4/3}}$$

$$\beta = 0.0042$$

Born-Oppenheimer dynamics

Nuclei are heavy.
Adiabatic separation between nuclei and electrons.
Electrons remain in the ground-state.

Time-independent Schrödinger equation for the electrons

$$\sum_i \frac{-\hbar^2}{2m_e}\nabla_i^2\psi + V_{\mathrm{n-e}}\Big(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\}\Big)\psi_0 = E_0\psi_0$$

$$M_I\frac{d^2\mathbf{R}}{dt^2} = -\nabla_I \min_{\psi_0}\{\langle\psi_0|H_e|\psi_0\rangle\}$$

Newtonian nuclear motion

Rigorous wave function minimization every MD step
(matrix diagonalization).

Basis sets

To optimize the Kohn–Sham orbitals

$$\hat{H}\psi_i = \epsilon\psi_i$$

these one electron wave functions are expanded in an orthogonal basis

$$\psi_i = \sum_k c_k^i \chi_k$$

for example: Gaussians, Slater functions, or plane waves.

Plane waves describe well free electrons (valence electrons in metals)

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{k}} c_k^i \exp(i\mathbf{kr})$$

$$|\mathbf{k}|^2 \leq E_{\text{cut}}$$

- frozen core approximation
- pseudo-potential replaces nucleus + core electrons
- valence electrons are represented by pseudo-wave functions
- projector augmented wave (PAW): local functions + (pseudo-) plane waves

Summary of yesterday

- Method by Car and Parrinello (1985)
- BOMD: Combine classical MD of nuclei with QM time-independent Schrödinger equation of the electrons
- Classical MD
  - Integrators: Euler versus Verlet
  - time-reversibility, phase-space conserving (can be checked)
  - force fields (harmonic bonds, Lennard-Jones, ...)
  - parameters: Amber, Gromos, OPLS, CHARMM, UFF, ReaxFF
  - programs: Amber, NAMD, DLPoly, LAMMPS, Gromacs
- Density Functional Theory (see Prof. Baerends lecture)
  - simulated annealing versus matrix diagonalization
  - equation of motion for coefficient dynamics
  - fictitious “electron” mass, constraint orthogonality
- CP extended Lagrangian

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Car-Parrinello MD

Optimizing the coefficients to minimize the Kohn-Sham energy has some analogy with a geometry optimization.

- the coefficients move in a coefficient space
- with the constraint of orthonormality

$$\sum_k c_k^{i*} c_k^j = \delta_{ij} \quad \text{with} \quad \delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases}$$

We can even define equations of motions:

$$\mu_k \frac{d^2 c_k^i}{dt^2} = -\frac{\partial E}{\partial c_k^{i*}} - \sum_j \lambda_{ij} c_k^j$$

(m a = F)

fictitious mass acceleration gradient force constraint force

Wave functions optimization through Simulated Annealing

- start from random coefficients
- integrate EOMs
- damp dynamics to converge
- Alternative for matrix diagonalization
- Useful for large systems

Car-Parrinello MD

Simultaneous dynamics of the nuclei and the wave function coefficients

Lagrangian formalism of CPMD

$$\mathcal{L} = \sum_I \frac{1}{2} M_I \left| \frac{d\mathbf{R}_I}{dt} \right|^2 + \sum_{i,k} \frac{1}{2} \mu_k \left| \frac{dc_k^i}{dt} \right|^2 - E[\{c_k^i\}, \{\mathbf{R}_I\}] + \sum_{i,j} \lambda_{ij} (\sum_{k,l} c_l^i c_k^j S_{kl} - \delta_{ij})$$

kinetic energy of nuclei

"kinetic energy" coefficients

Kohn-Sham potential

holonomic constraints

Hellman-Feynman forces

$$-\frac{\partial E[\{c_k^i\}, \{\mathbf{R}_I\}]}{\partial \mathbf{R}_I} = \frac{\partial \langle \Psi_0 | H | \Psi_0 \rangle}{\partial \mathbf{R}_I} = \langle \Psi_0 | \frac{\partial H}{\partial \mathbf{R}_I} | \Psi_0 \rangle$$

In the electronic ground state, the wave function derivatives are zero

How can this work?

Simultaneous dynamics of the nuclei and the wave function coefficients

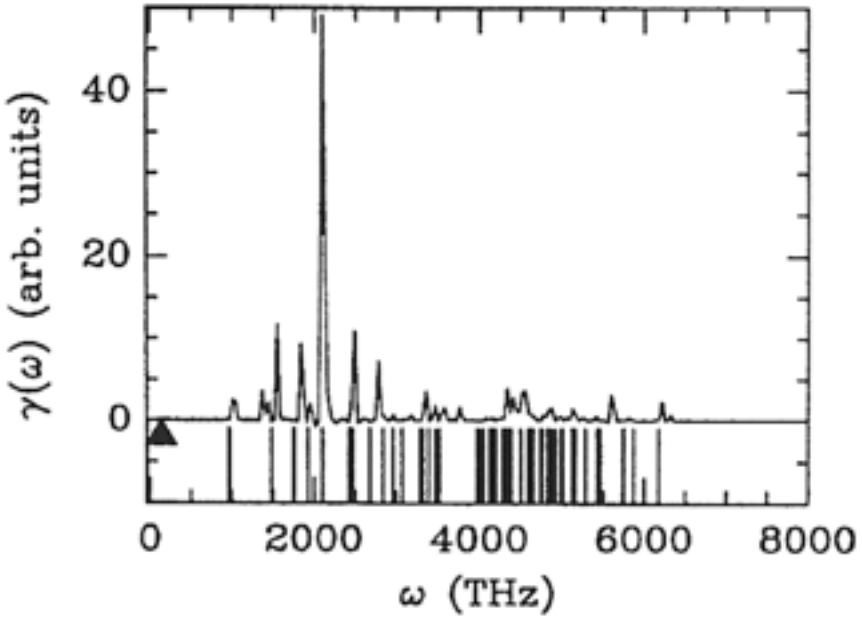
The wave function dynamics should be cold
- sufficiently close to the ground state
- but fast enough to follow the nuclei

Adiabatic separation of nuclei and wave function dynamics

$$\mu_e << M_I \quad \Rightarrow \quad \omega_e >> \omega_I$$

$$T_e << T_I \quad \Rightarrow \quad E^{\mathrm{tot}} \approx T_I + V^{\mathrm{KS}}$$

conserved quantity



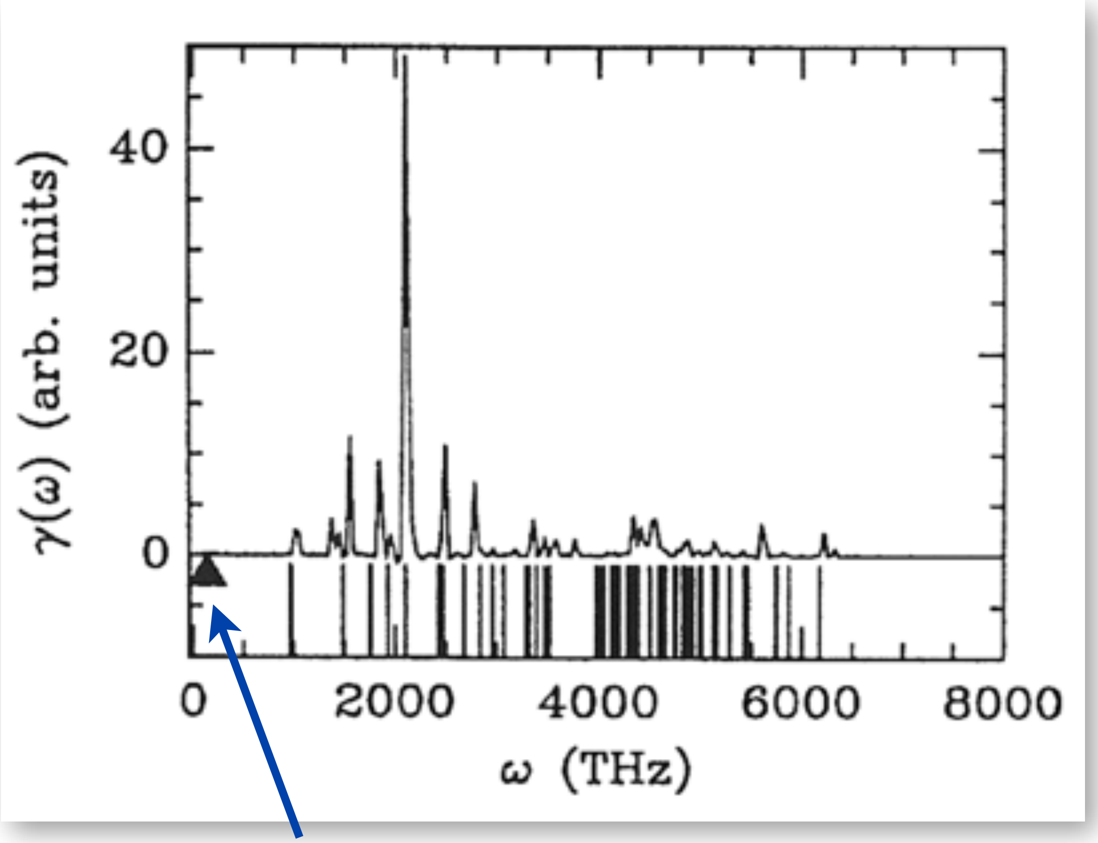
periodic super cell
containing 8 Si atoms in
the diamond structure

G. Pastore, E. Smargiassi,
F Buda, *Phys. Rev. A* **44**
(1991), 6334

How can this work?

Simultaneous dynamics of the nuclei and the wave function coefficients

spectrum of electronic modes



fastest ionic mode

periodic super cell containing 8 Si atoms in the diamond structure

G. Pastore, E. Smargiassi, F Buda, *Phys. Rev. A* **44** (1991), 6334

$$\omega_{ij} = \sqrt{\frac{f_j(\epsilon_i - \epsilon_j)}{\mu}}$$

small gap leads to coupling (metals require thermostats)

Clear separation between characteristic electronic and ionic frequencies

- small fictious mass (μ=300 au = 0.165 Dalton)
- small time step (dt = 5 atu = 0.12 fs)

CPMD versus BOMD

BOMD

- matrix diagonization
- at Ψ_0 every MD step
- time step: ~1 fs
- converged (HF) forces
- risk of growing global error

VASP program

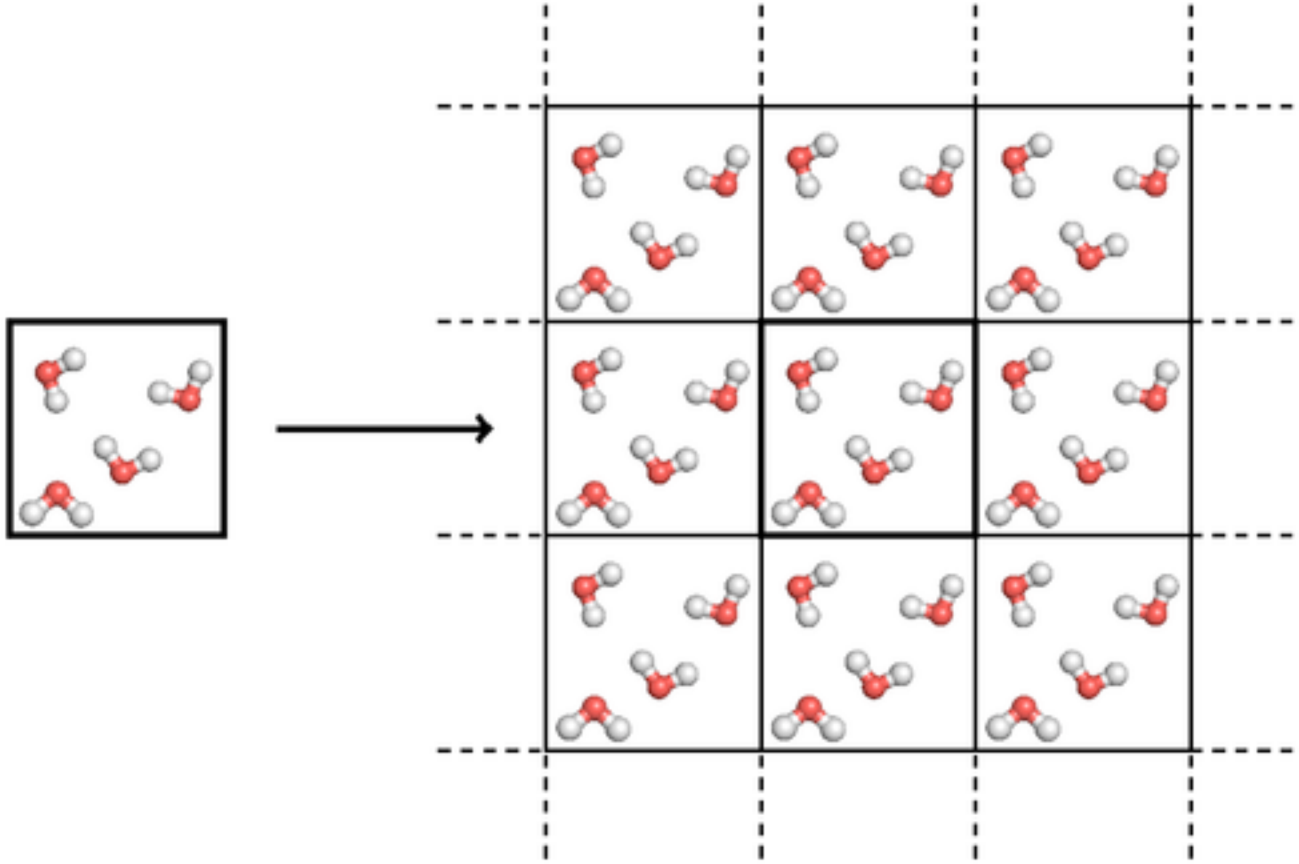
cp2k program

CPMD

- wave function dynamics
- close to Ψ_0 every MD step
- time step: ~0.1 fs
- noisy forces
- small global error (E^{tot} conserved, when adiabatic)

cpmd program

Periodic boundary conditions



Copies of the system in all directions
- effects due to walls are avoided
- finite size effects are less
- plane waves are already periodic

Con's
- isolated systems are difficult
- fictitious periodicity

Ensembles

The equation of motion derived from Lagrangian (or Hamiltonian) dynamics conserve the total energy of the system.
- The micro-canonical ensemble is sampled (NVE)

Other ensembles:

NVT ensemble, by coupling the system to a thermostat (“heat bath”)
- Nose-Hoover chain (deterministic)
- Canonical Sampling through Velocity Rescaling (“bussi thermostat”)
- Langevin dynamics

NPT ensemble, coupling to a thermostat and a barostat
- Parrinello-Rahman
- Berendsen

Grand canonical (μPT), coupling to bath of particles (i.e. electrons)

....

Computing properties

Ergodicity hypothesis

$$\langle A \rangle = \frac{\iint d\mathbf{r}^N d\mathbf{p}^N A(\mathbf{r}^N, \mathbf{p}^N) \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)]}{\iint d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)]}$$

ensemble average

$$\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' A(\mathbf{r}^N, \mathbf{p}^N)$$

time average

Time correlation functions can be related to transport properties

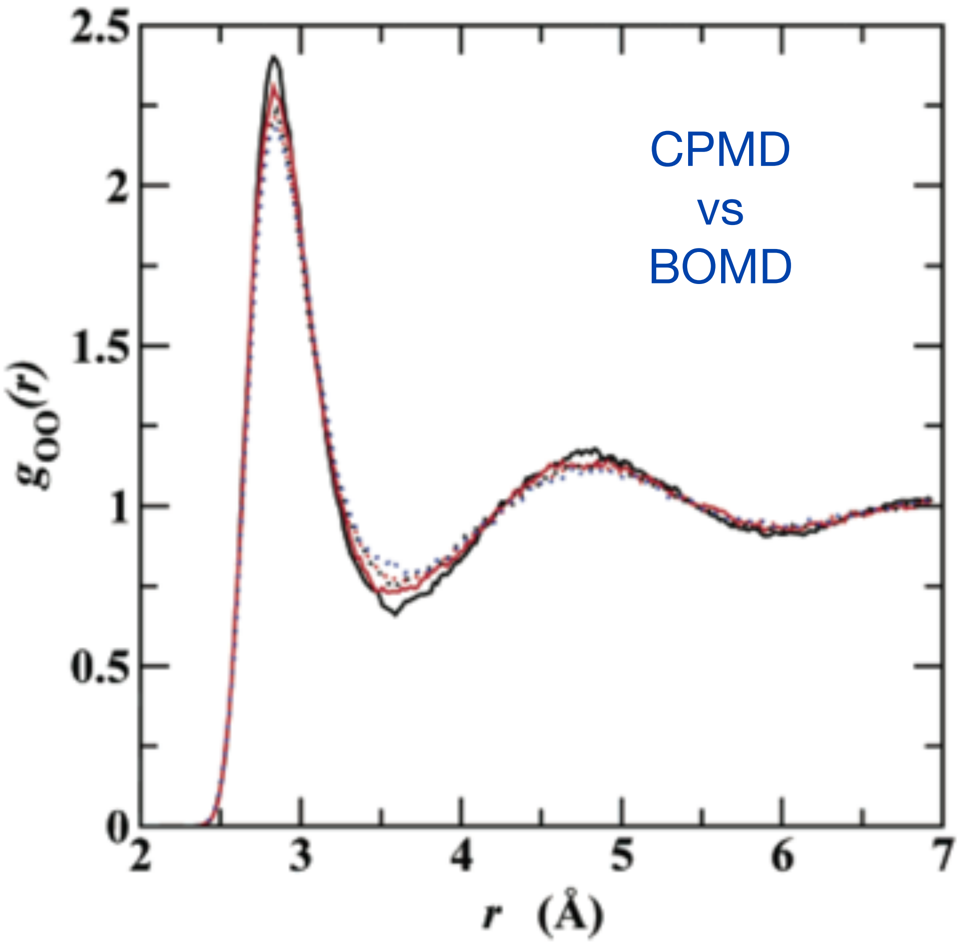
$$D_i = \int_0^\infty d\tau \langle v_i(\tau) v_i(0) \rangle$$

diffusion coeffient

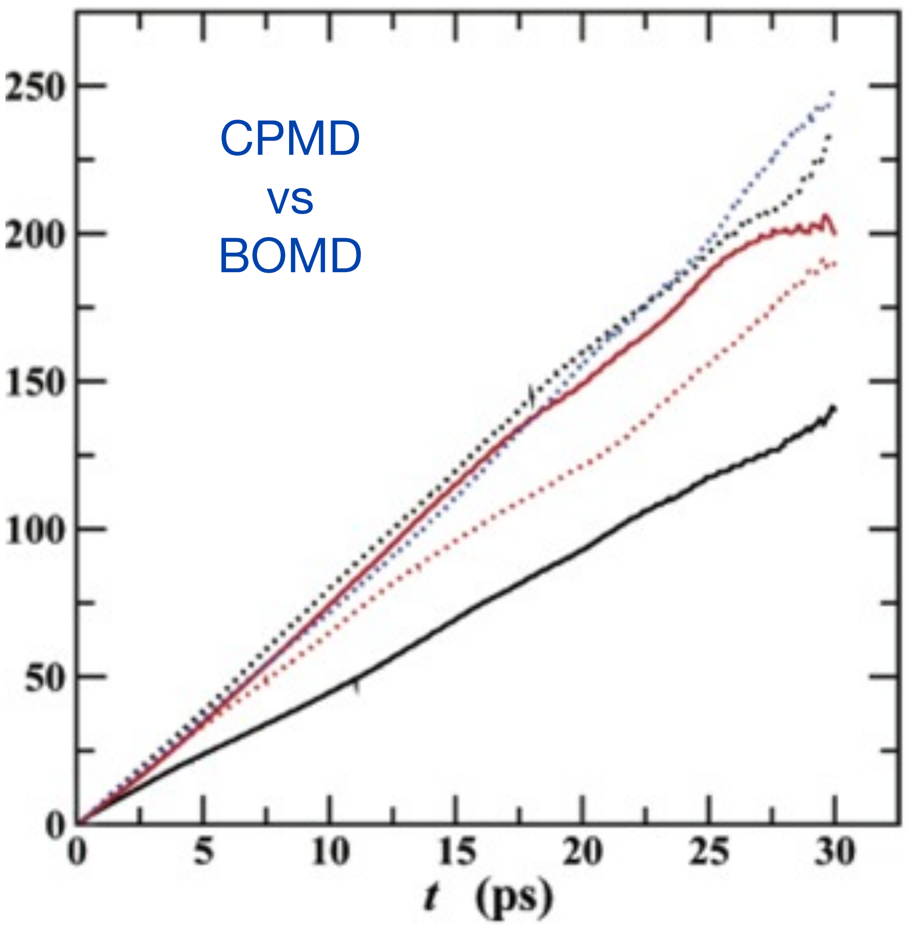
Fourier transform of time-correlation functions allow for experimental spectra

Water

O-O Radial distribution function



mean square displacement

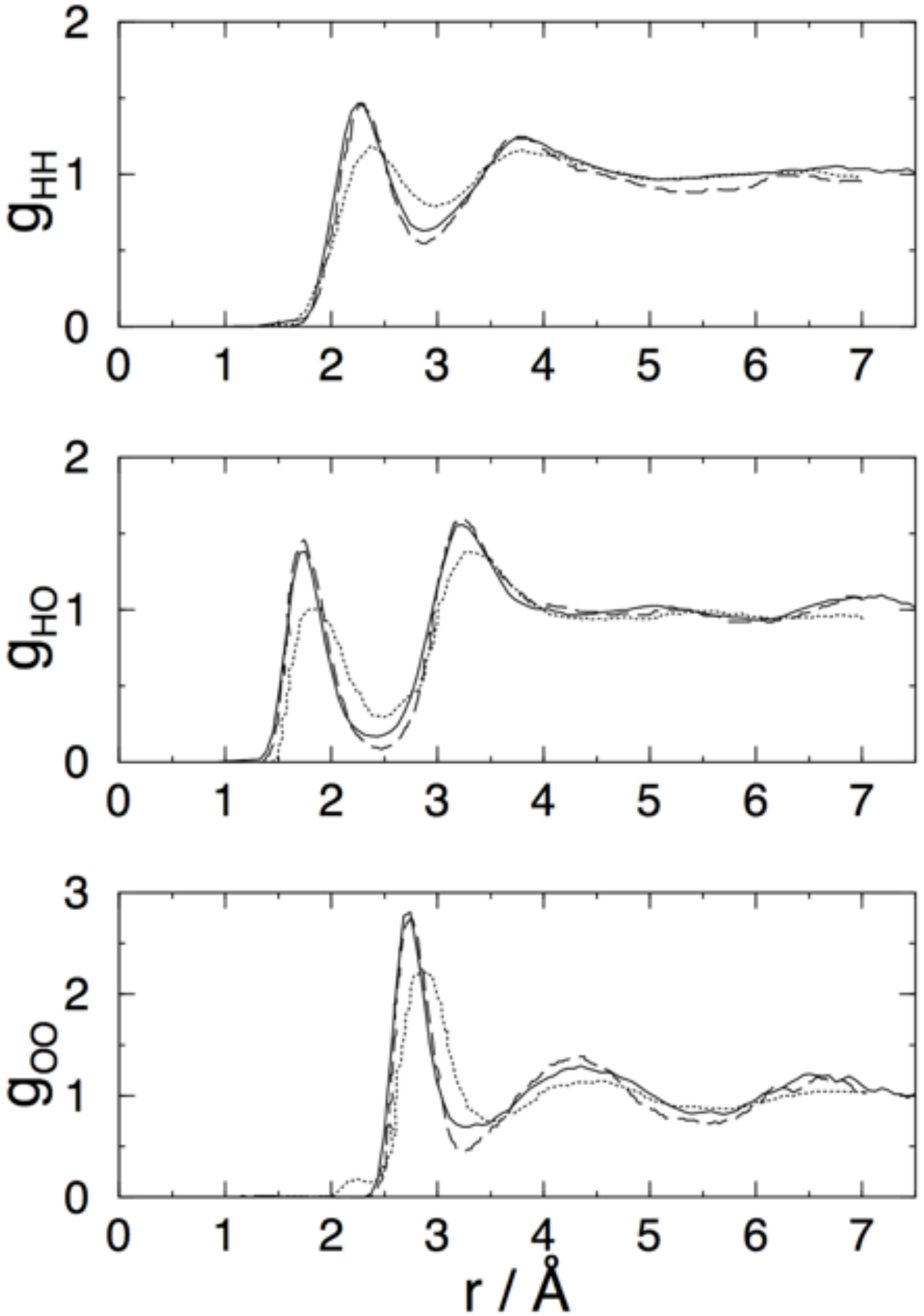


64 water molecules
BLYP functional
30 ps simulation
NVE (T~423 K)

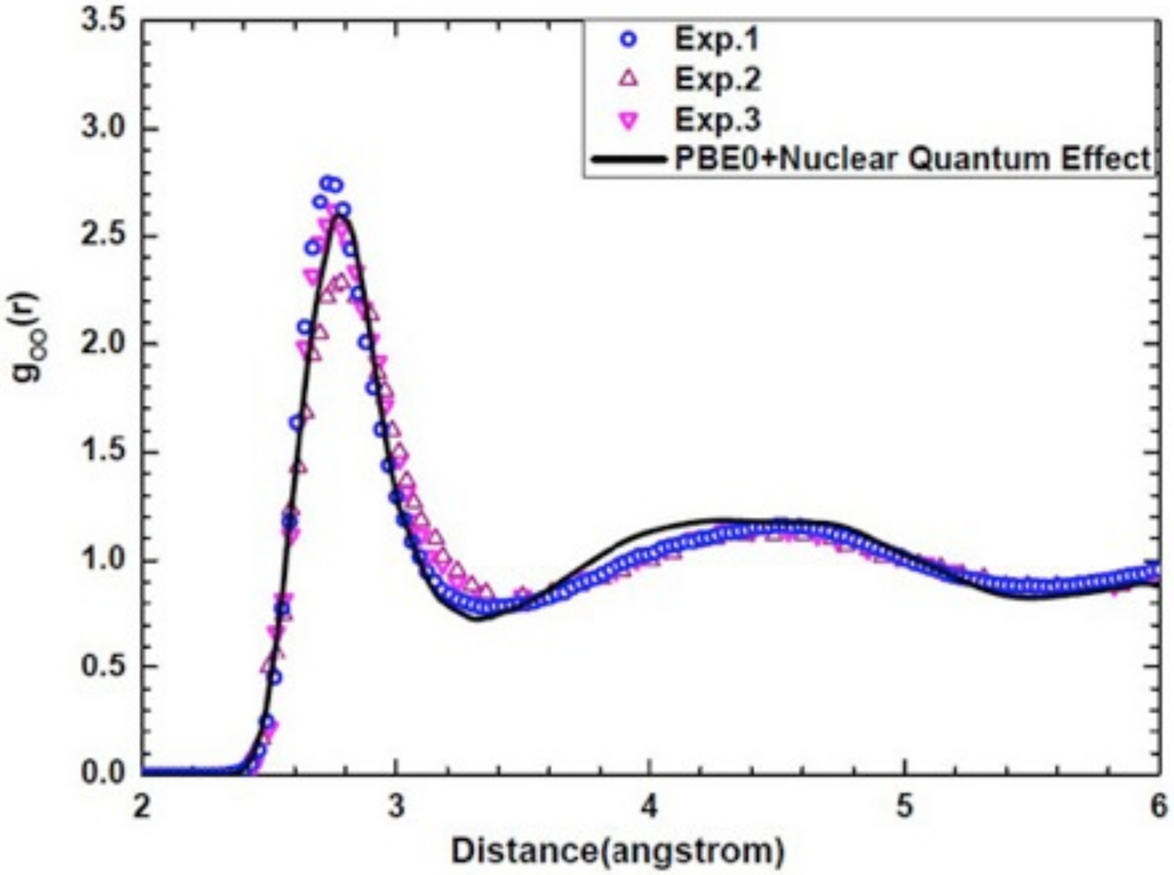
Time-Dependent Properties of Liquid Water: A Comparison of Car-Parrinello and Born-Oppenheimer Molecular Dynamics Simulations
I-F.W. Kuo, C.J. Mundy, M.J. McGrath and J.I. Siepmann
J. Chem. Theory Comput. 2006

Water

2 CPMD results BLYP, BP
versus Neutron diffraction (dotted)



Nuclear quantum effects
Path-integral CPMD
Robert Car et al. (website)



- DFT GGA water is too structured
- Diffusion coefficient is too low

(BP: 0.35 10^{-5} vs EXP: 2.35 10^{-5} cm^2/s)

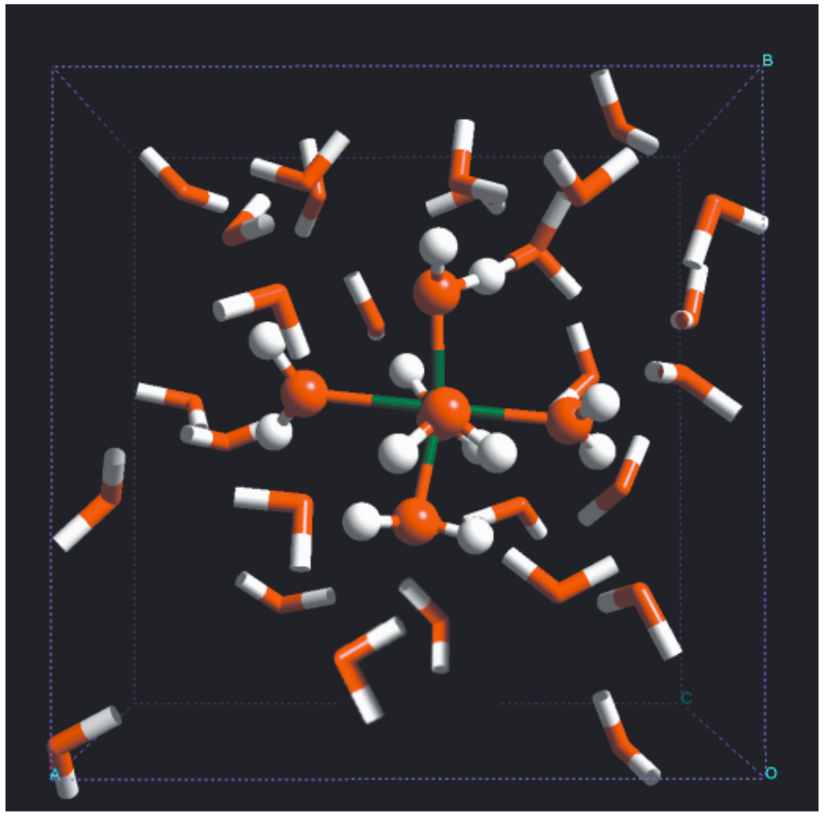
- correcting for VdW is important
- ZPE correction can be included

CPMD contributed significantly to understanding water and solvation

Acidity of Fe(III)

$$\mathrm{Fe^{III}(H_2O)_6^{3+} + H_2O <\!\!\longrightarrow\!\!> Fe^{III}(H_2O)_5(OH)^{2+} + H_3O^+}$$

$$pKa = -\log\left(\frac{[\mathrm{B}^-][\mathrm{H_3O^+}]}{[\mathrm{HB}]}\right) = -\log\left(\frac{(x(\mathrm{H_3O^+}))^2[\mathrm{HB}]_0}{1 - x(\mathrm{H_3O^+})}\right)$$



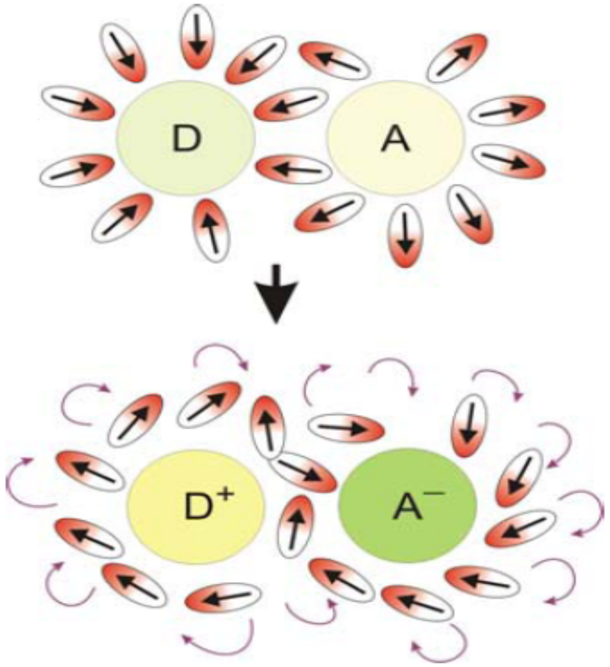
Method	$x(H_3O)^+$	kA	pkA
CPMD	0.130	0.034	1.47
static DFT		10,000	-4.00
expt		0.006	2.2

Redox potentials

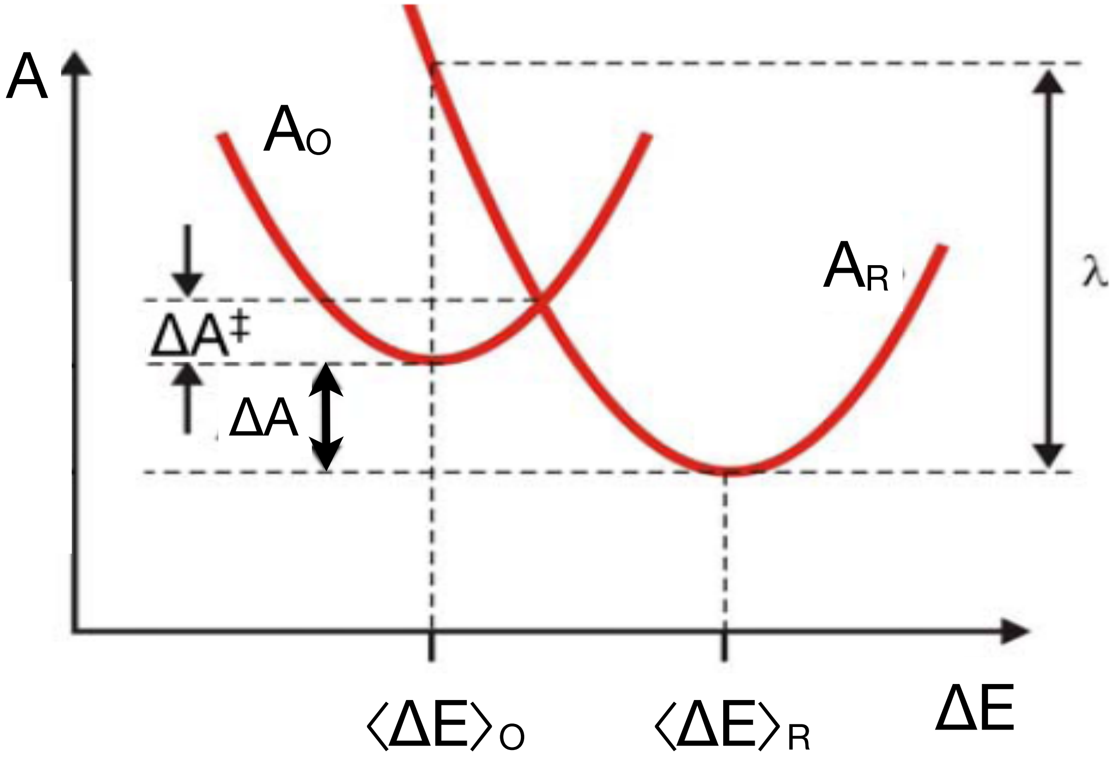
Warshel, Sprik,
Blumberger, Sulpizi,
Cheng, and others

Rudolph A. Marcus
1992 Nobel prize in Chemistry

$$\Delta\varepsilon = IP_D + EA_A$$



HOMO-LUMO gap is not a good estimate of the redox potential



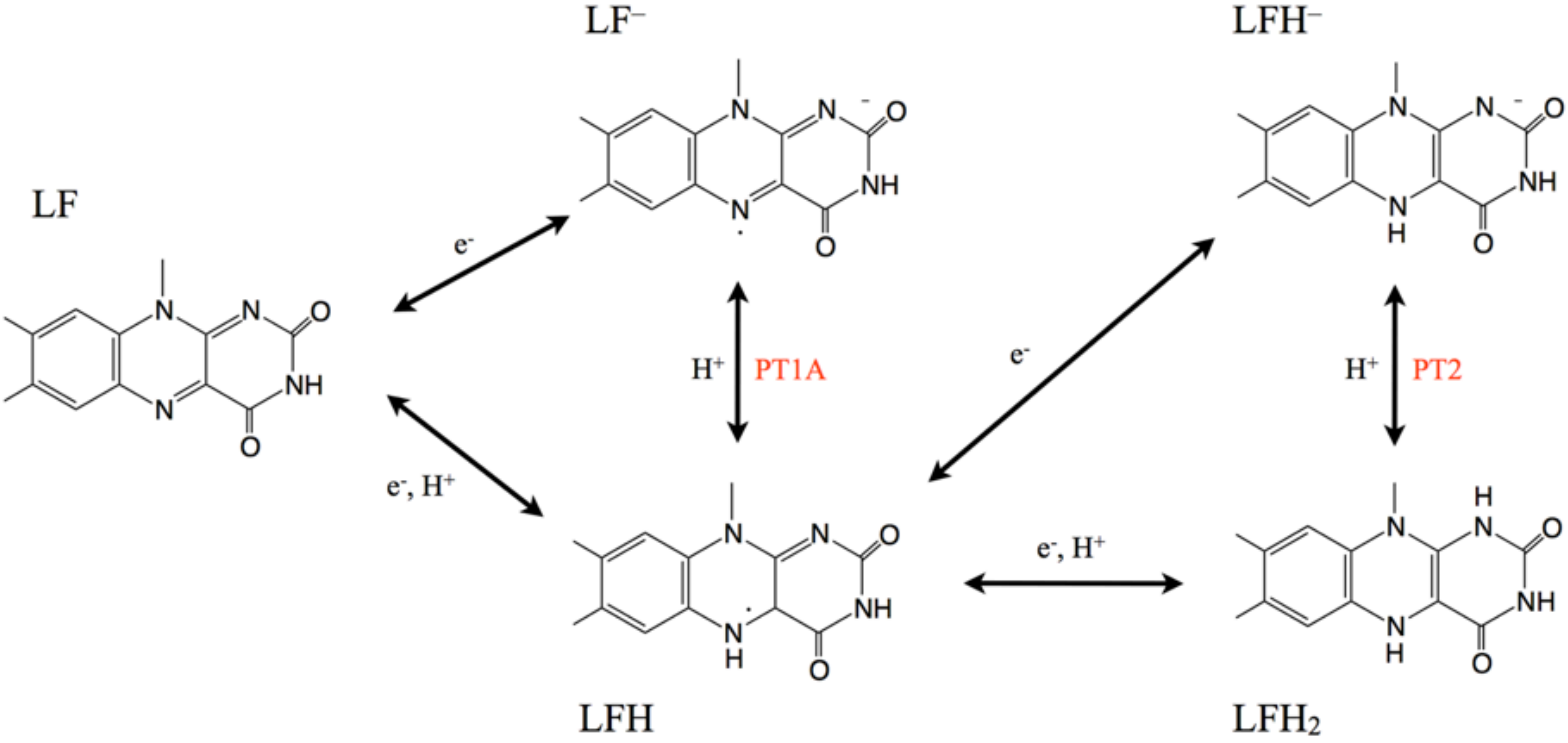
The vertical energy gap quantifies the polarization by the environment.

- reaction coordinate:

$$\Delta E = E_R(\mathbf{r}^N) - E_O(\mathbf{r}^N).$$

Lumiflavin

oxidation and protonation states

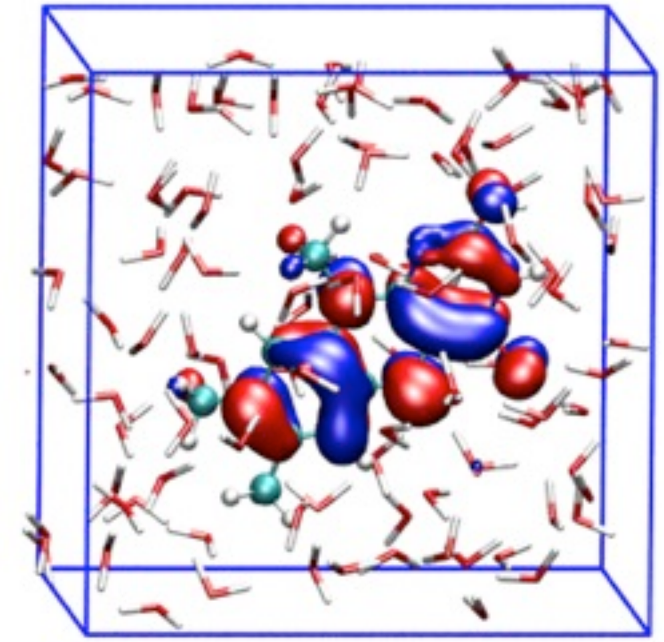


Redox potentials

$$\Delta E = E_R(\mathbf{r}^N) - E_O(\mathbf{r}^N).$$

We can histogram dE during an MD simulation:

$$P_\eta(\Delta E') = Z^{-1} \int d\mathbf{r}^N e^{-\beta E_\eta} \delta(\Delta E - \Delta E')$$
$$= \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \delta(\Delta E(\mathbf{r}^N(t)) - \Delta E')\, dt$$



DFT-MD (BO simulations)
CP2K program
PBE + DZVP/300Ry

lumiflavin + 102 H2O
Lbox=15 A (PBCs)
NVT ensemble
sim. time: 30-50 ps

Redox potentials

$$\Delta E = E_R(\mathbf{r}^N) - E_O(\mathbf{r}^N).$$

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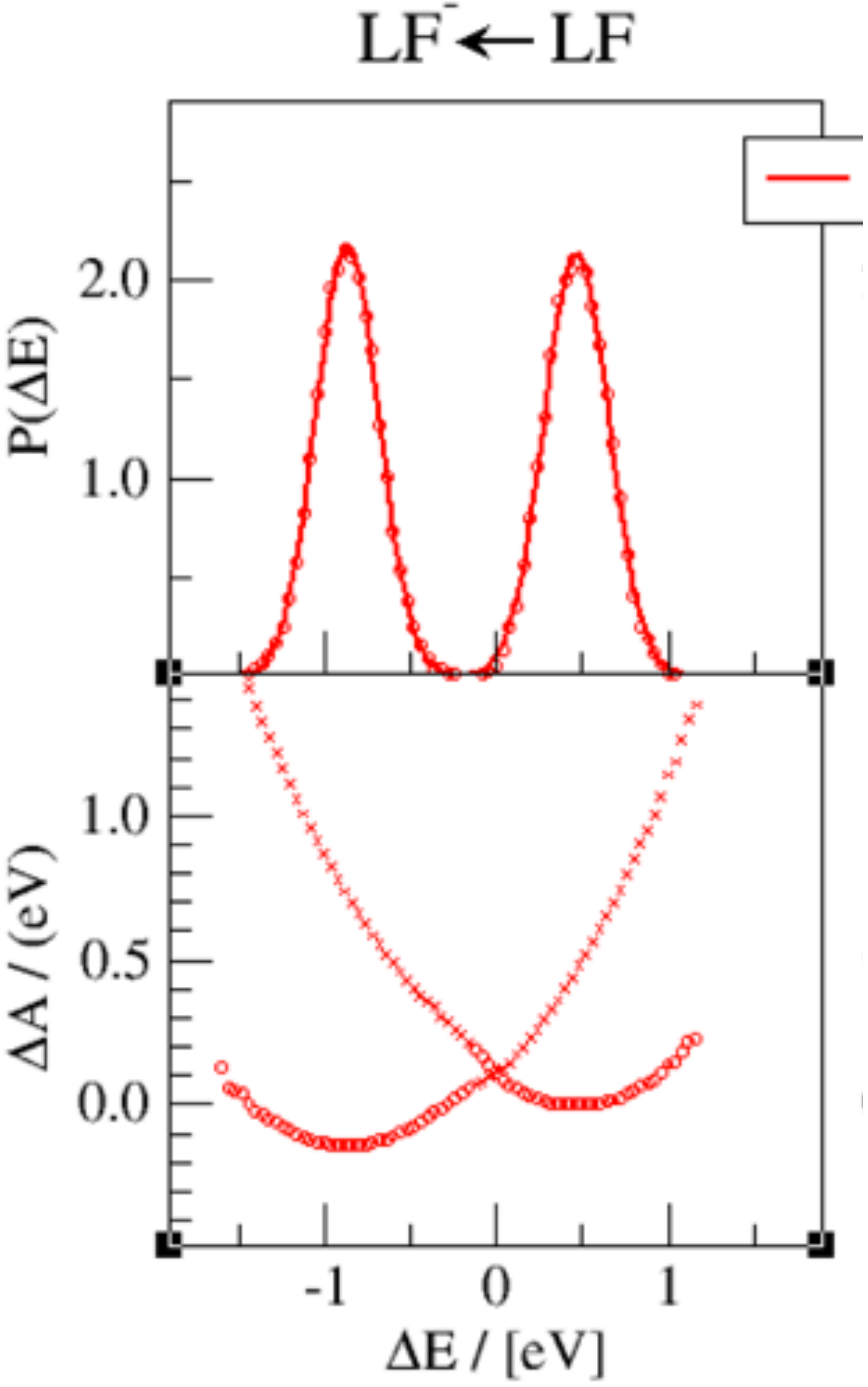
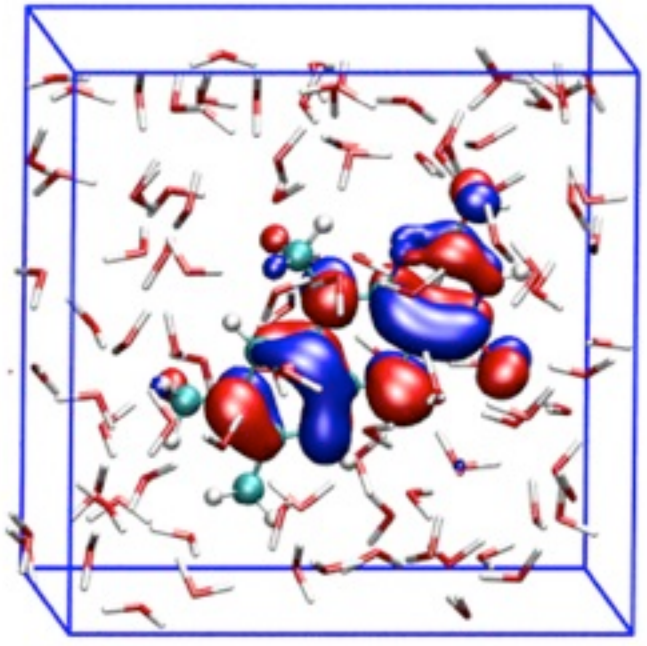
$$= \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \delta(\Delta E(\mathbf{r}^N(t)) - \Delta E')\, dt$$

And make the free energy profiles:

$$A_\eta(\Delta E) = -k_B T \ln [P_\eta(\Delta E)]$$





DFT-MD (BO simulations)
CP2K program
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lumiflavin + 102 H2O
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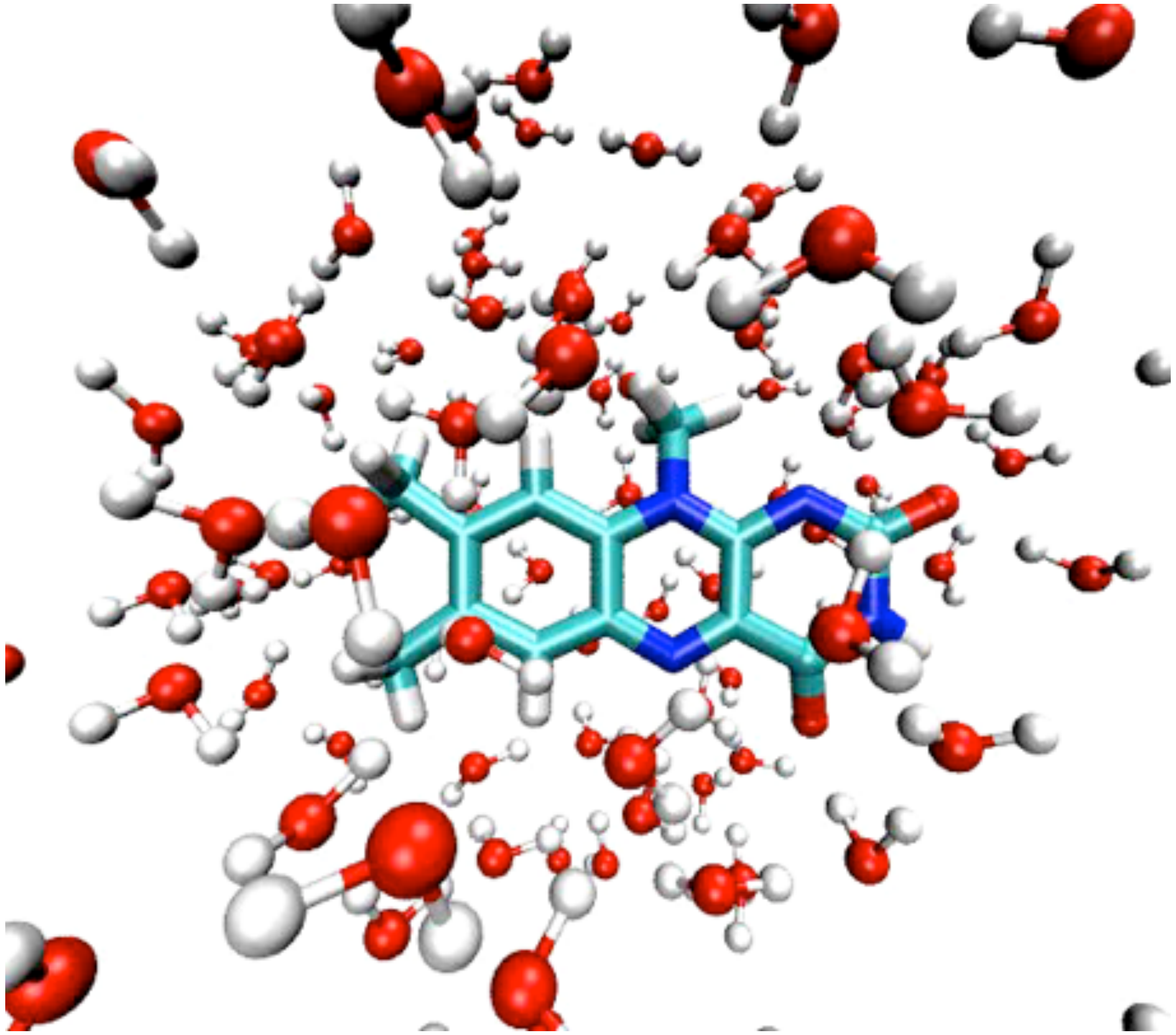
NVT ensemble
sim. time: 30-50 ps

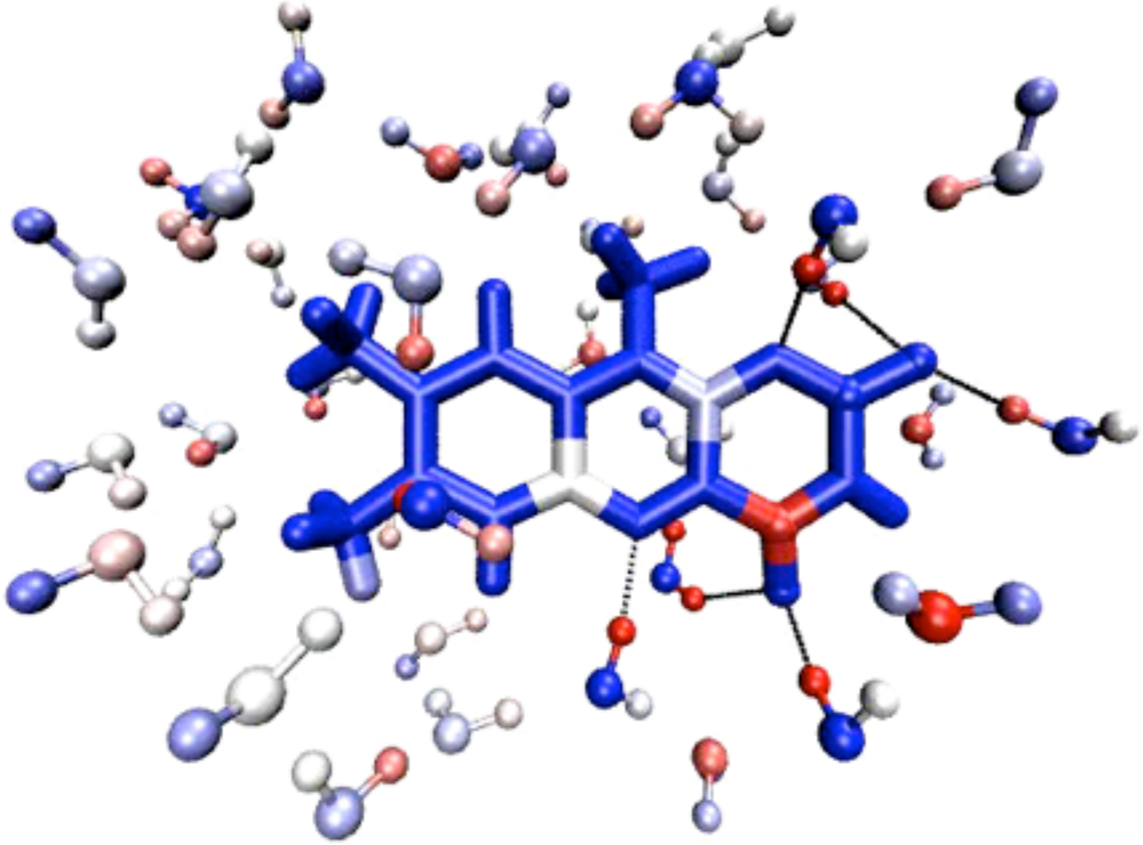
Redox potentials

What is the reorganization?
(which changes correlate with dE?)



Redox potentials

What is the reorganization?
(which changes correlate with dE?)



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AIMD implementations

CPMD
PAW
VASP
quantum-espresso
Siesta
CP2K
...

ADF
Gaussian
...

Extensions

extension to DFT-based AIMD (CPMD, BOMD)

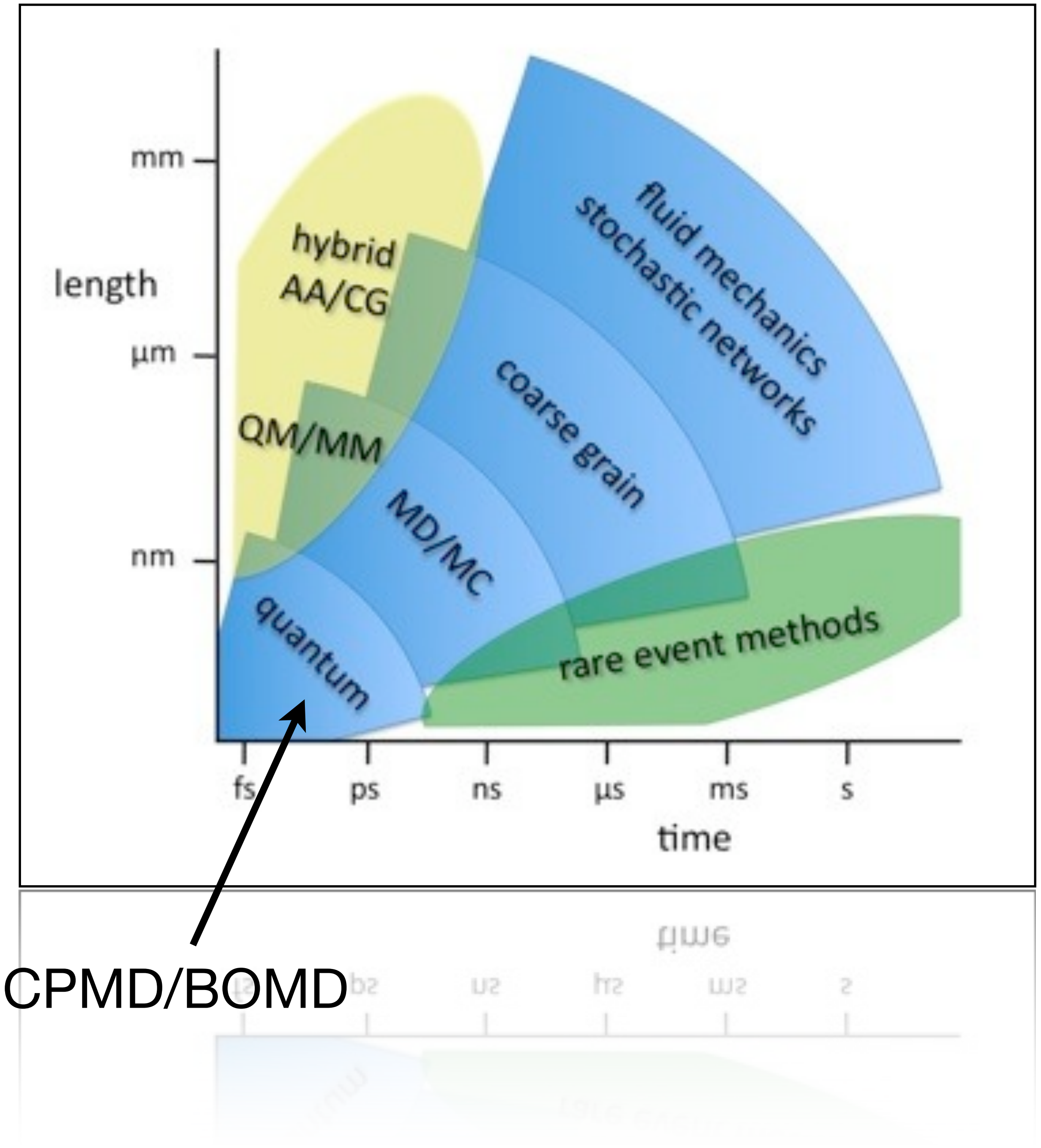
- combined CP/BO MD, wave function propagation + minimization (CP2K)
- Brillouin zone sampling, k-space integration
- TD-DFT MD, ROKS-MD excited state molecular dynamics
- Ehrenfest, Tully’s minimum hops approach, ...
- PIMD, path-integral, ring-polymer dynamics
- HF, B3LYP, MP2 – MD
- enhanced sampling methods
    - constrained MD, steered MD, metadynamics, transition path sampling
- QM/MM

Longer time scales

The rare event problem:

chemical reactions take place on a time scale that as much longer than can be simulated with AIMD

Enhanced sampling methods:
- constrained MD
- umbrella sampling
- steered MD
- metadynamics
- transition path sampling



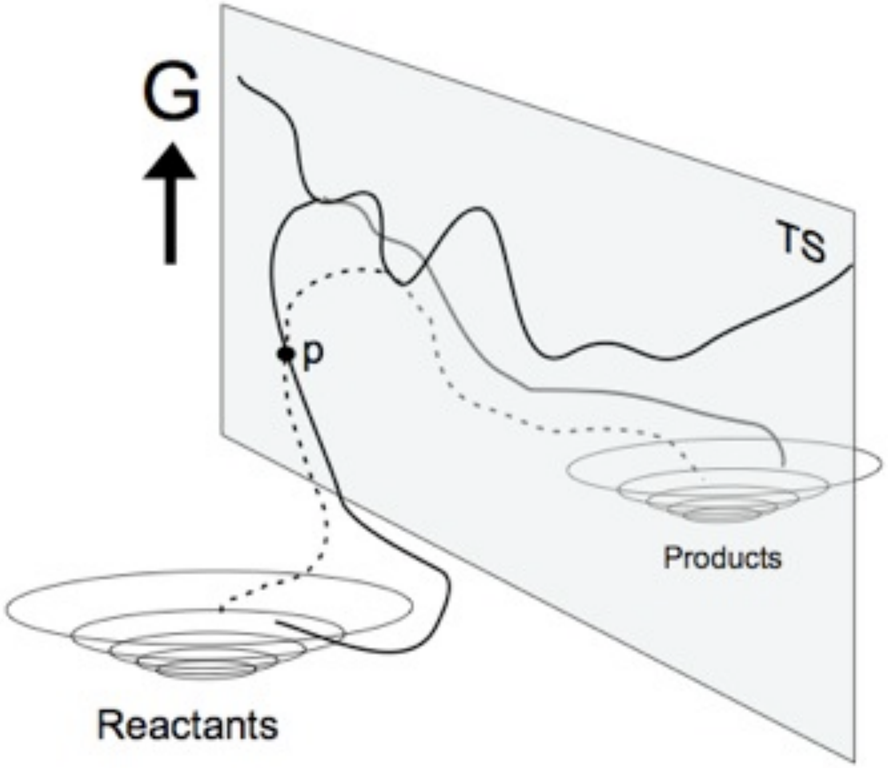
CPMD/BOMD

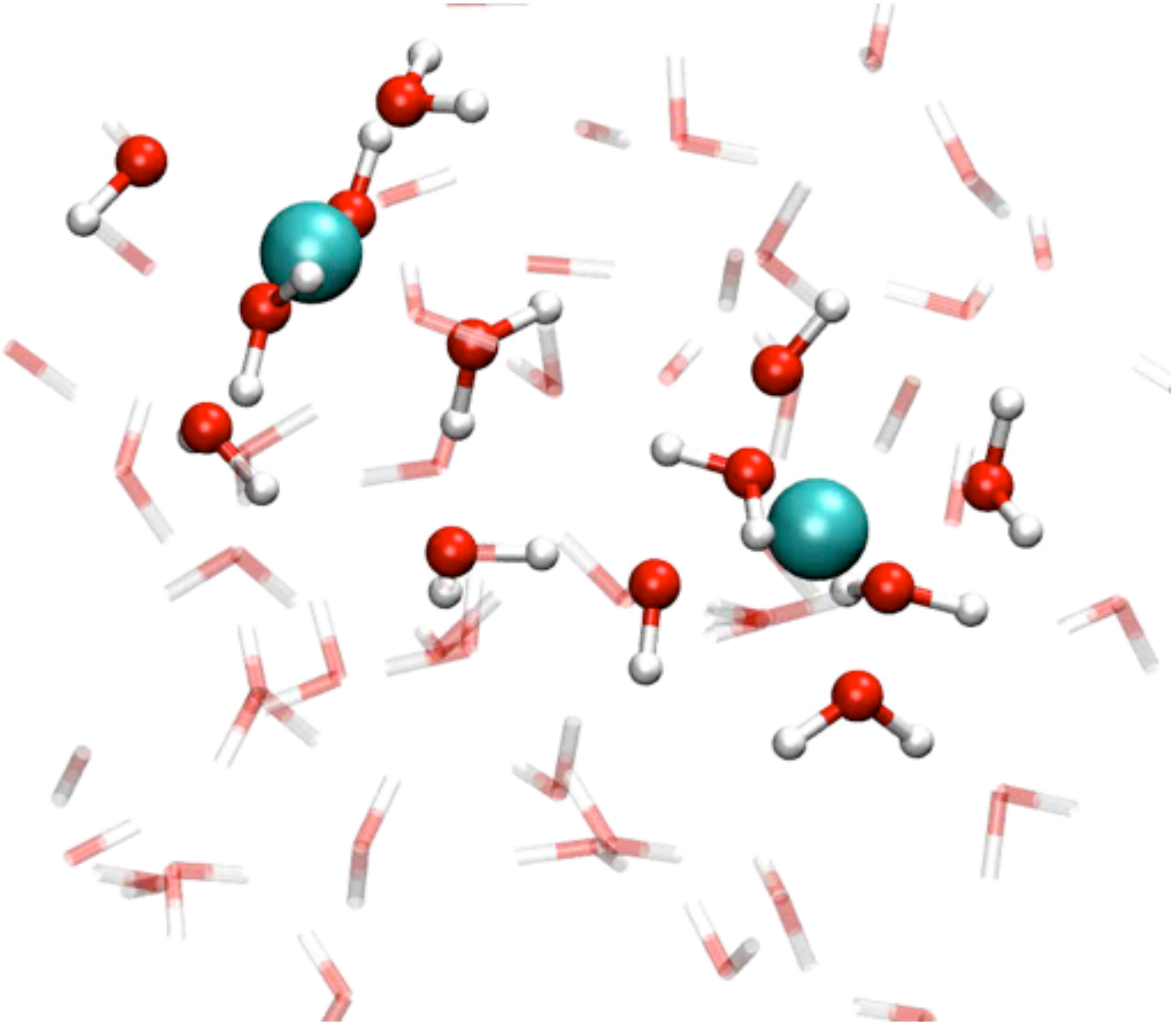
Longer time scales

Transition path sampling of electron transfer
self-exchange between Ru^{2+} and Ru^{3+} in water

Sampling ensemble of transition paths

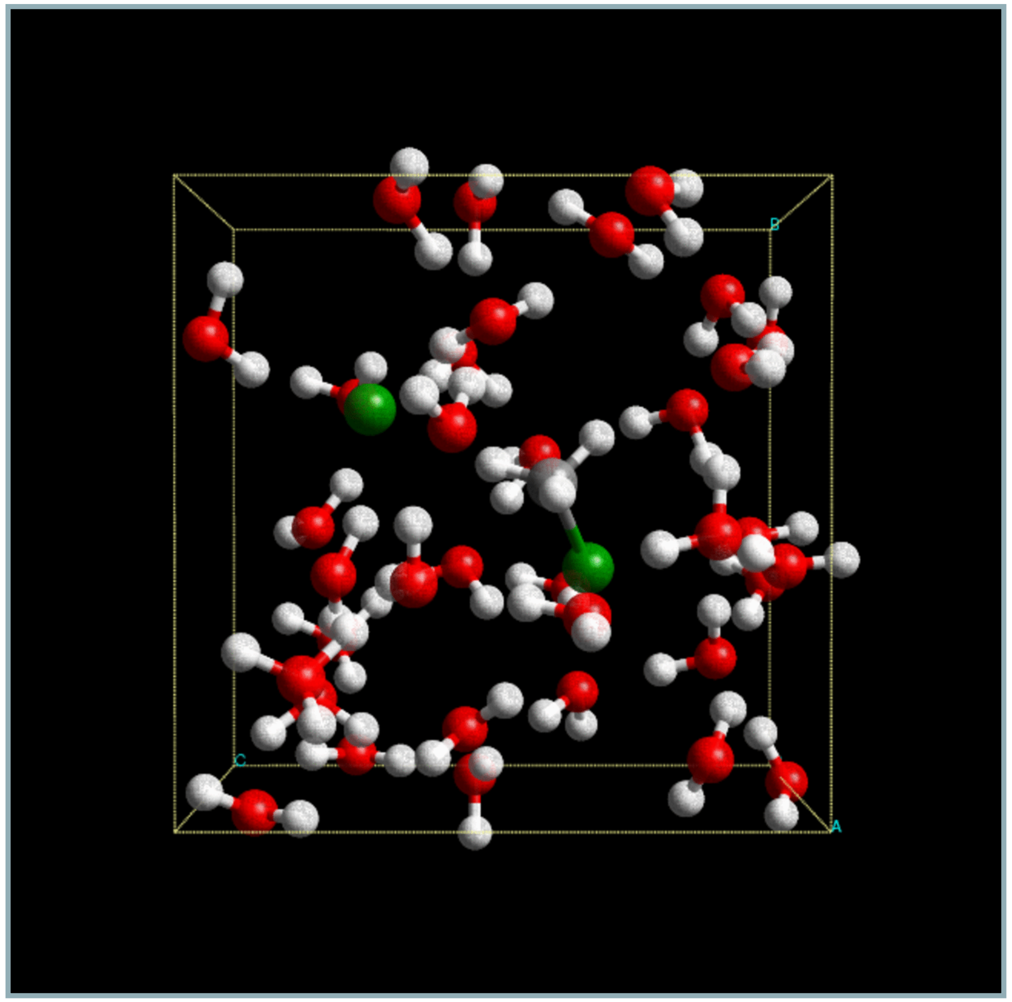
- Monte Carlo scheme
- No reaction coordinate needed
- description of stable states
- Needs initial path
- Can relax an unphysical (enforced) path

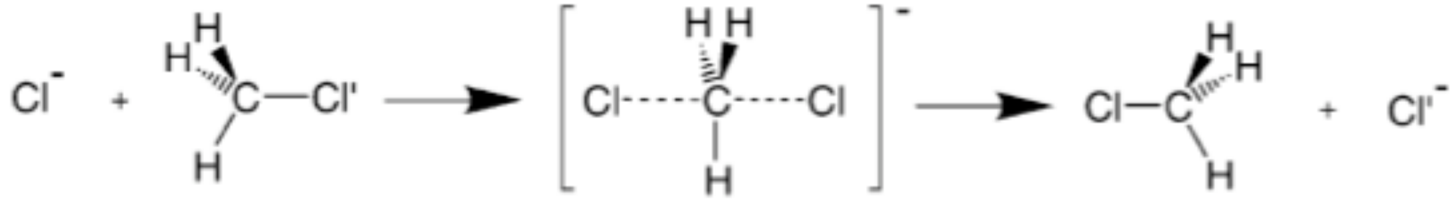


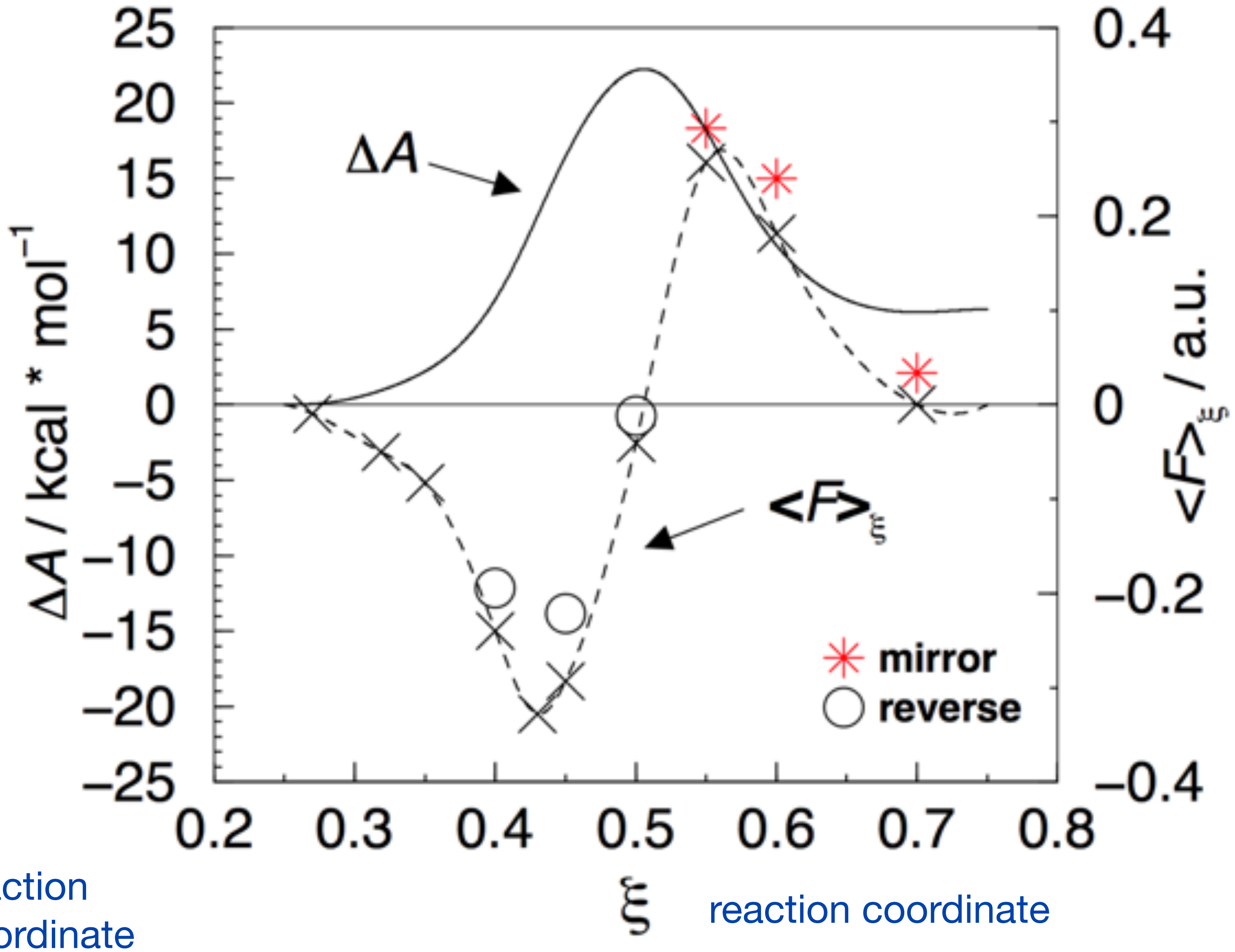


Free energy calculations

Constrained Molecular Dynamics







reaction coordinate

Landau free energy

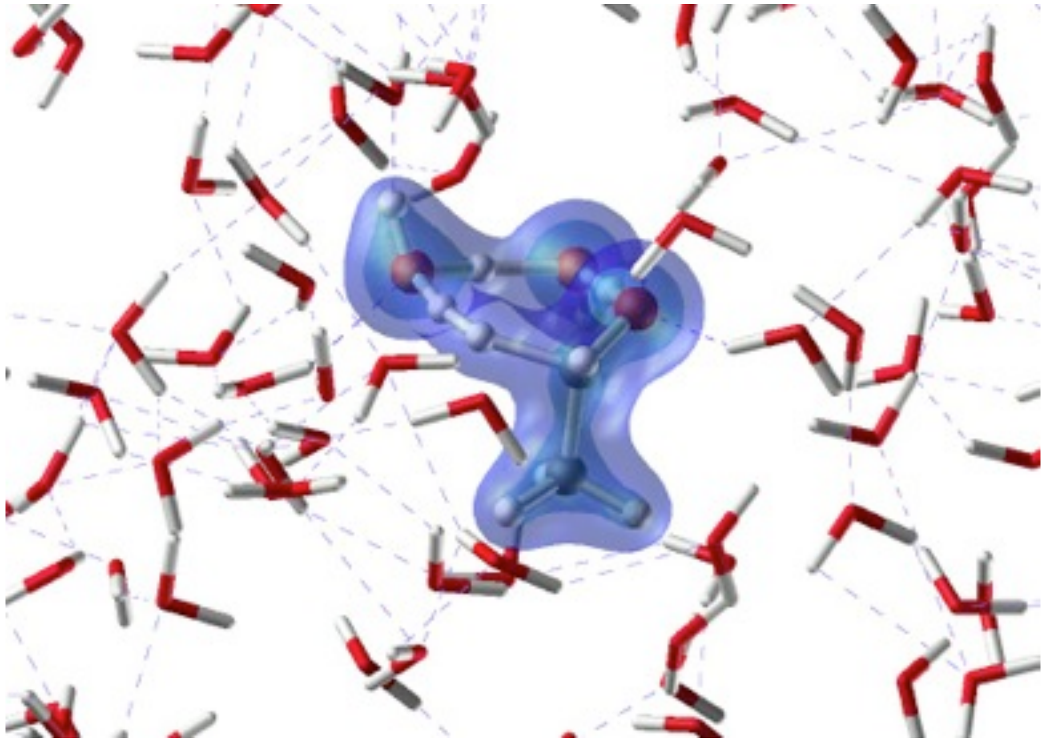
$$\Delta A(\lambda) = \int \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{T,V,\lambda} d\lambda$$

force of constraint

reaction coordinate

Larger length scales

QM/MM
- important part of the system with QM (semi-empirical, HF, DFT,...
- environment included with MM (empirical force field)



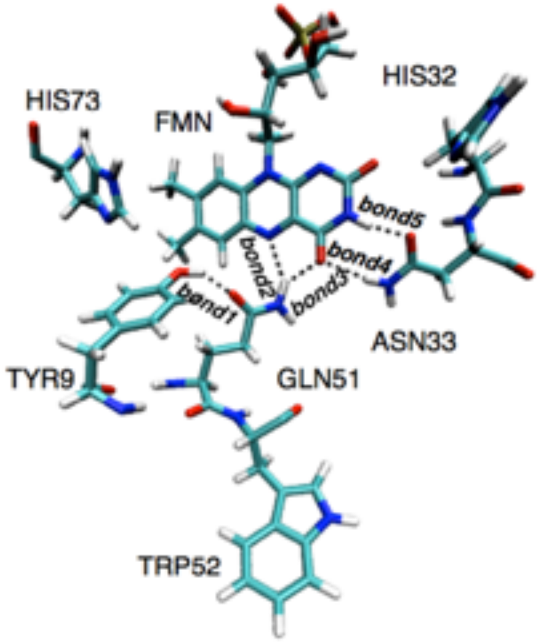
QM-MM coupling
- Mechanical coupling: bonds, angles, VdW
- Electrostatic coupling to include environment interaction into the QM system.
  - polarization of electron density

- Link atom/pseudo potential at hybrid (QM/MM) bonds

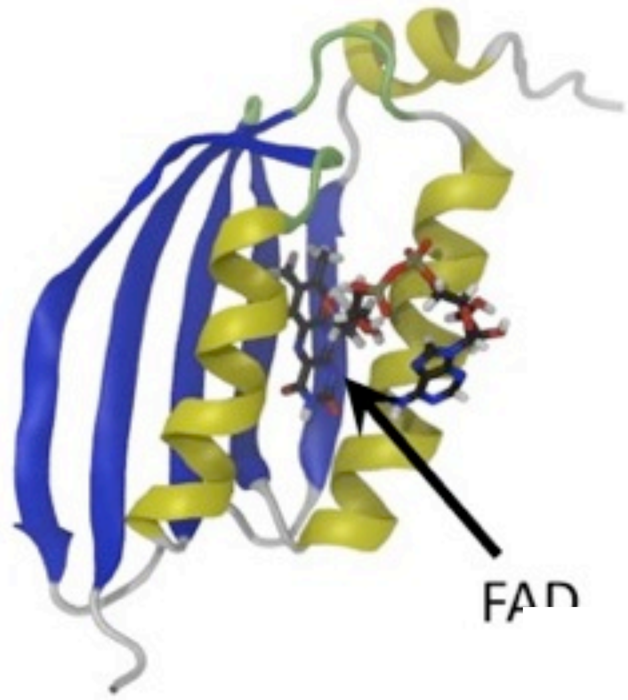
Karplus, Levitt, Warshel
Chemistry Nobelprize 2013

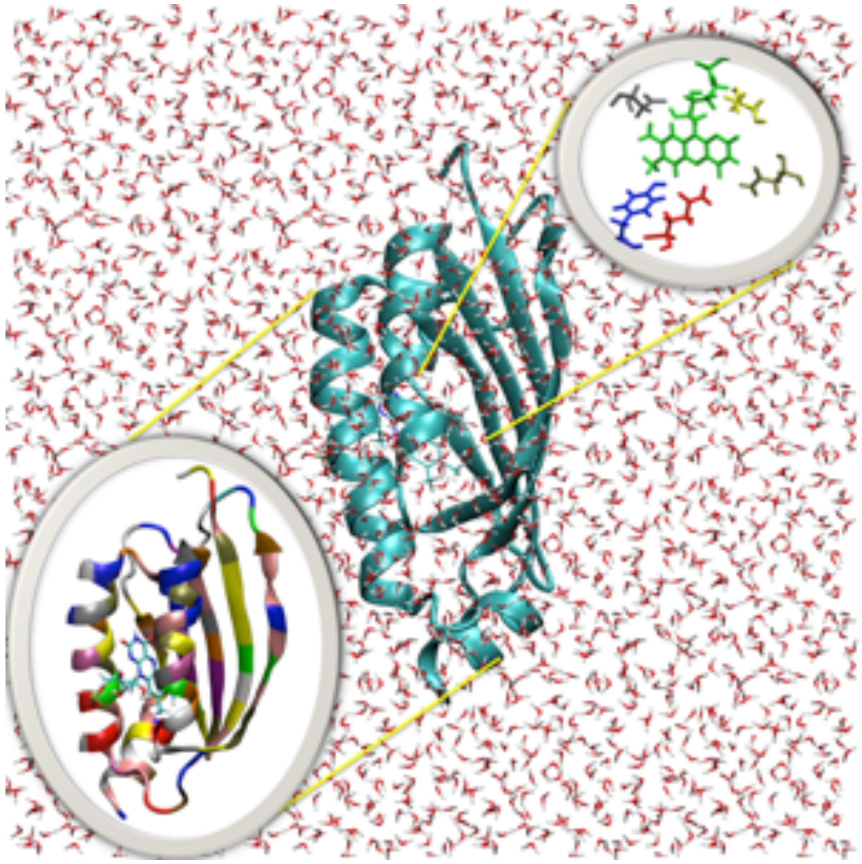
QM/MM

embedded flavin



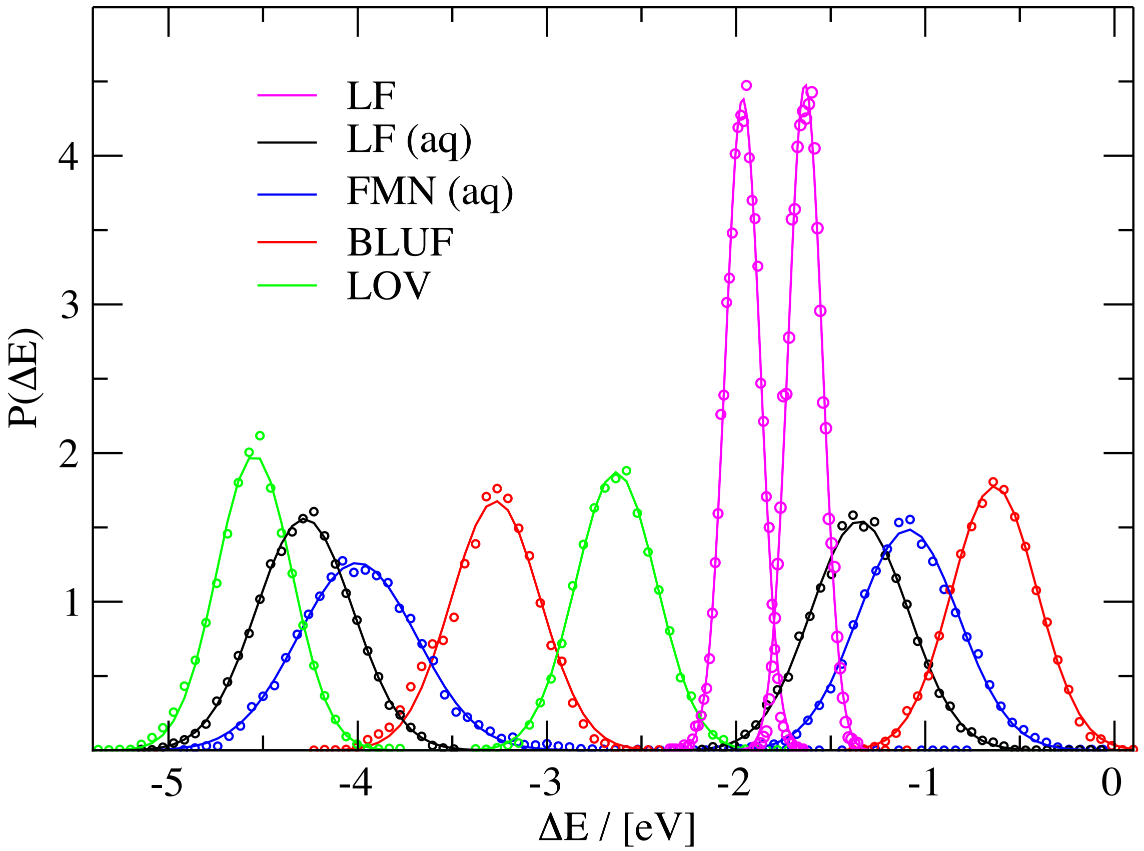
Appa (BLUF)





QM/MM Redox potential calculation
- flavin molecule in different environments (water, BLUF, LOV photo-receptor proteins)

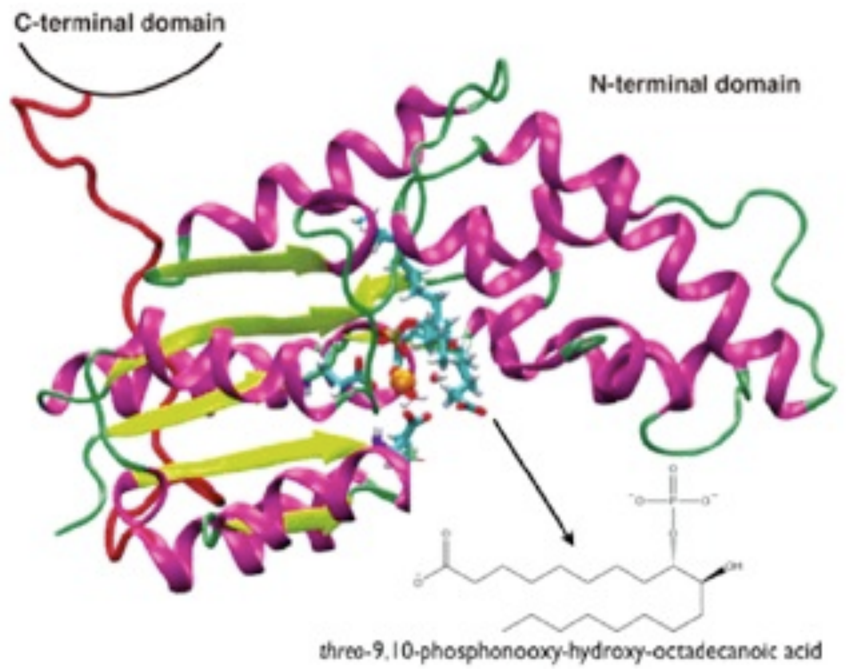
- CP2K
- flavin: QM, protein+water+ions: MM
- Sim. time: ~25 ps

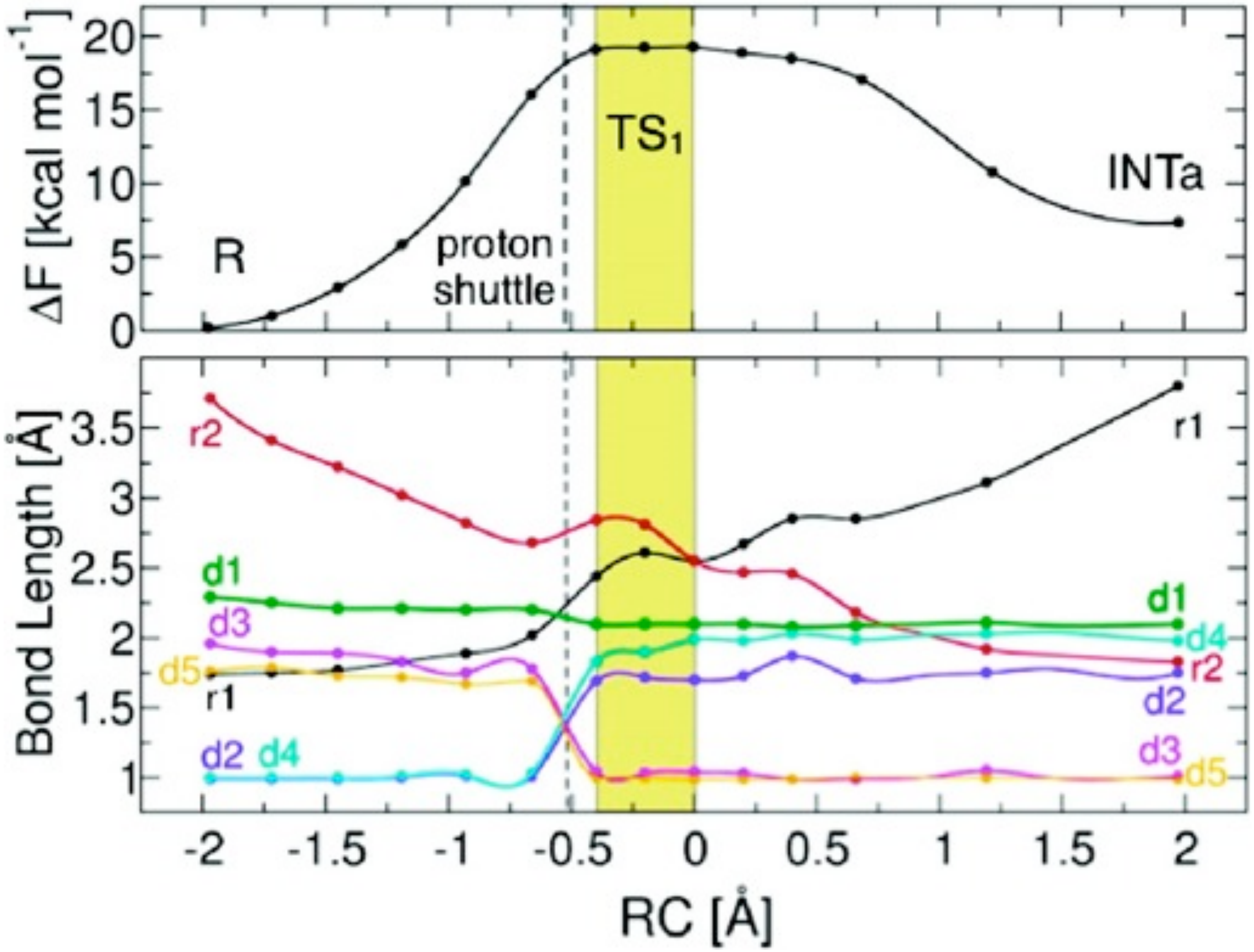


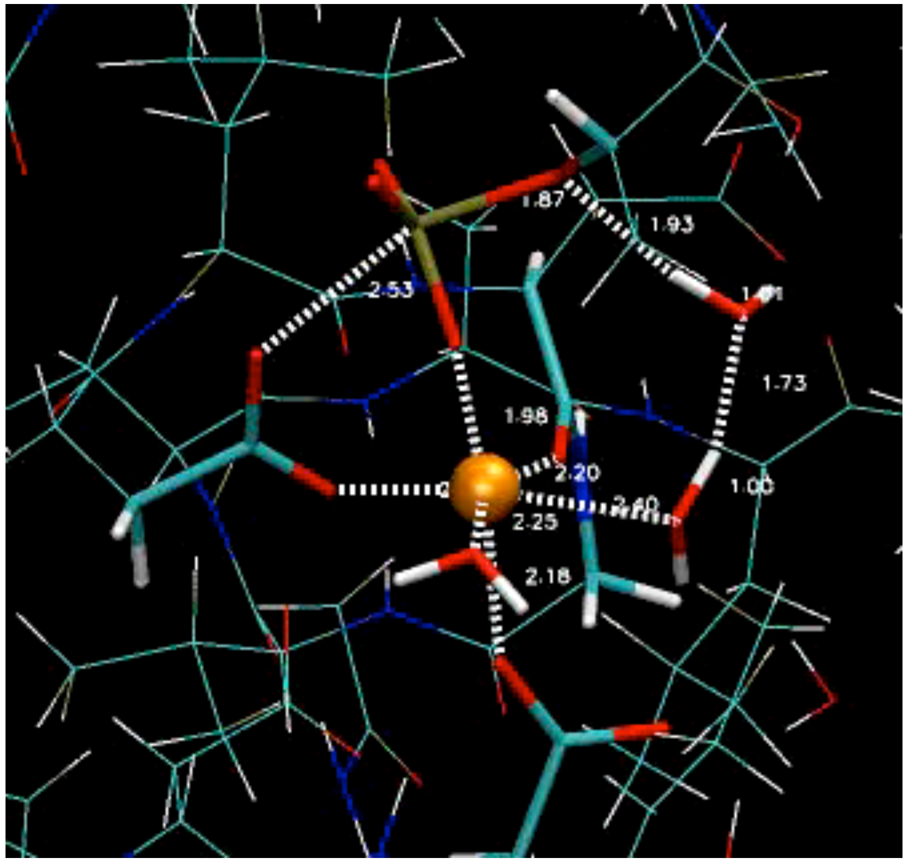
QM/MM + enhanced sampling

Proton Shuttles and Phosphatase Activity in Soluble Epoxide Hydrolase

- CPMD QM/MM
- constrained MD



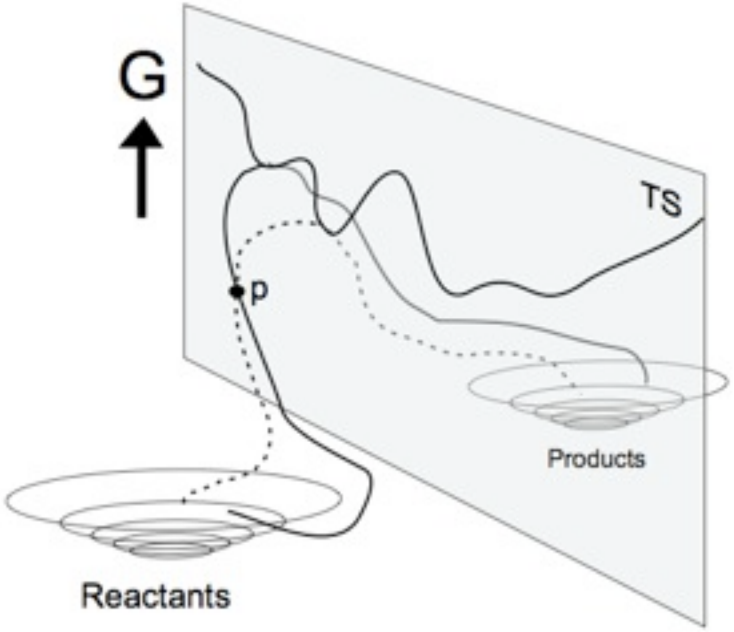


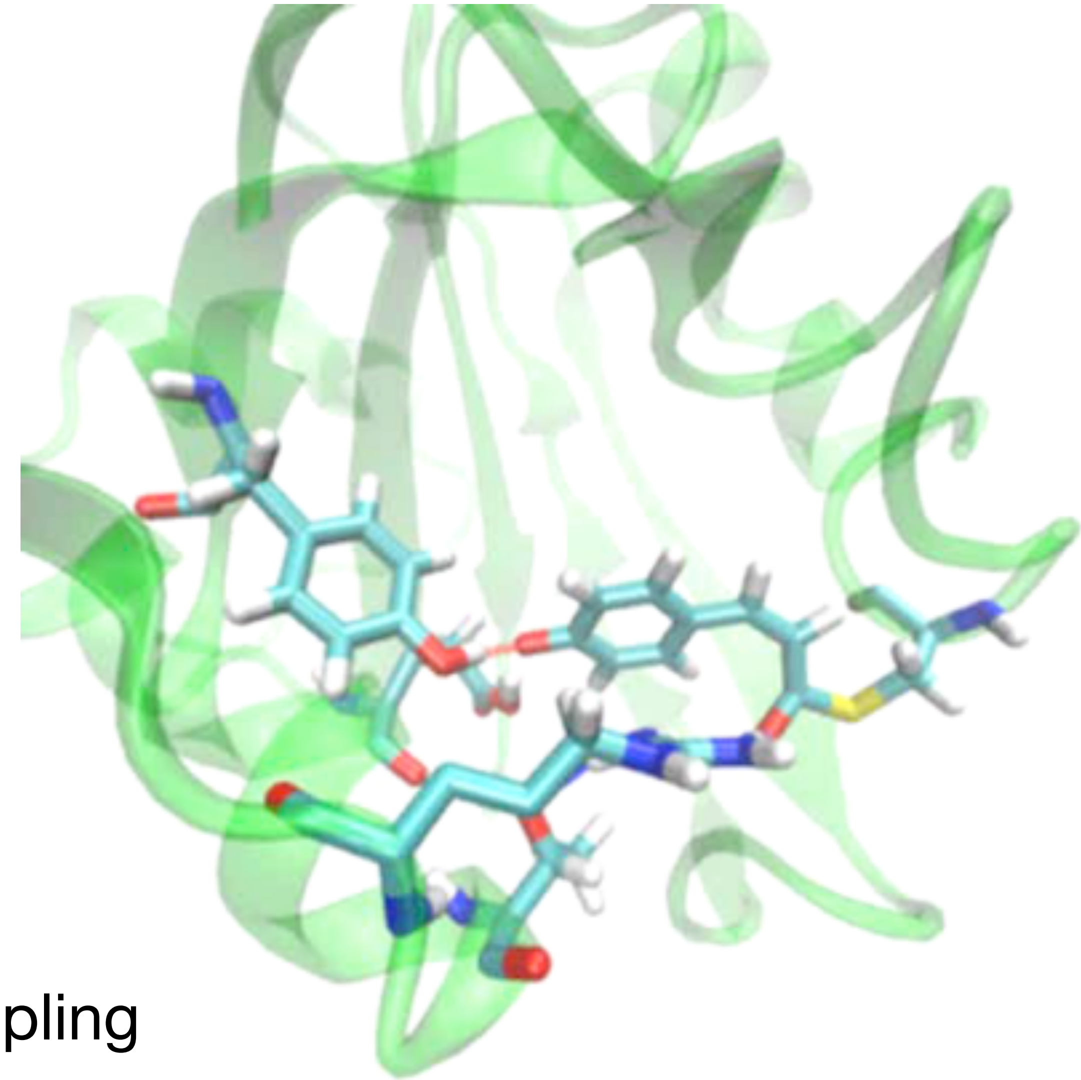


Computational study of phosphatase activity in soluble epoxide hydrolase: high efficiency through a water bridge mediated proton shuttle.
Marco De Vivo, Bernd Ensing, and Michael L. Klein
Communication in *J. Am. Chem. Soc.* **127** (2004), 11226-11227

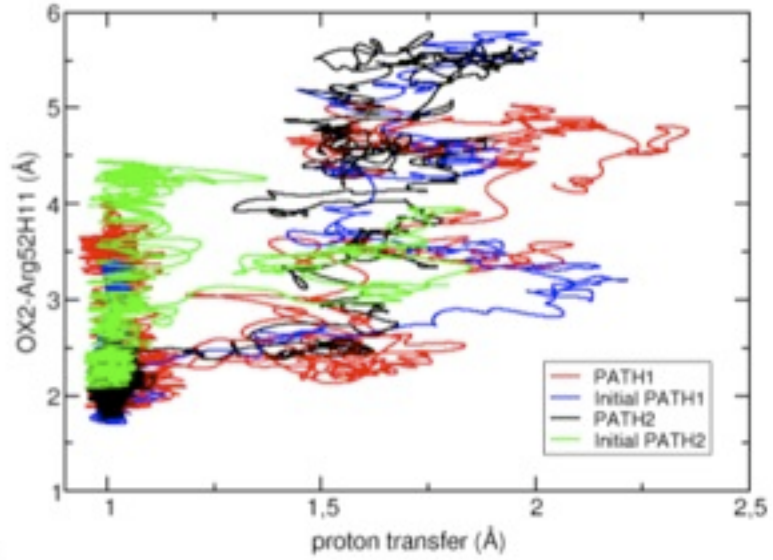
QM/MM + enhanced sampling

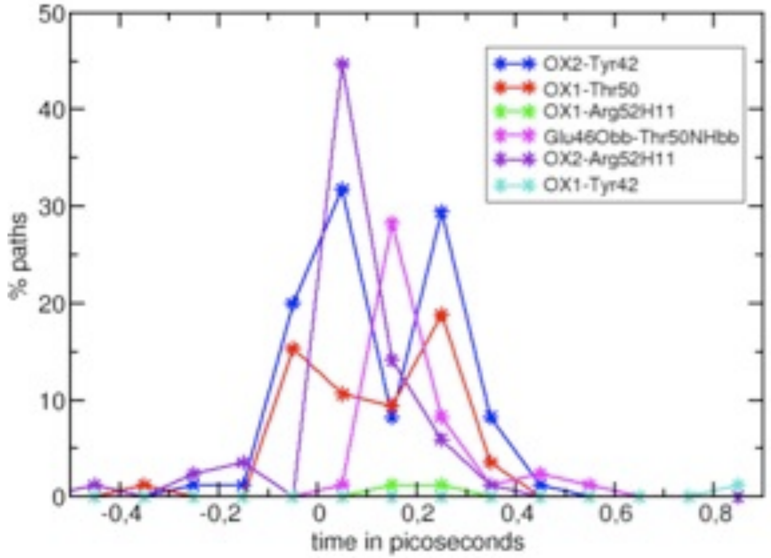
Proton transfer during signal propagation in Photoactive Yellow Protein

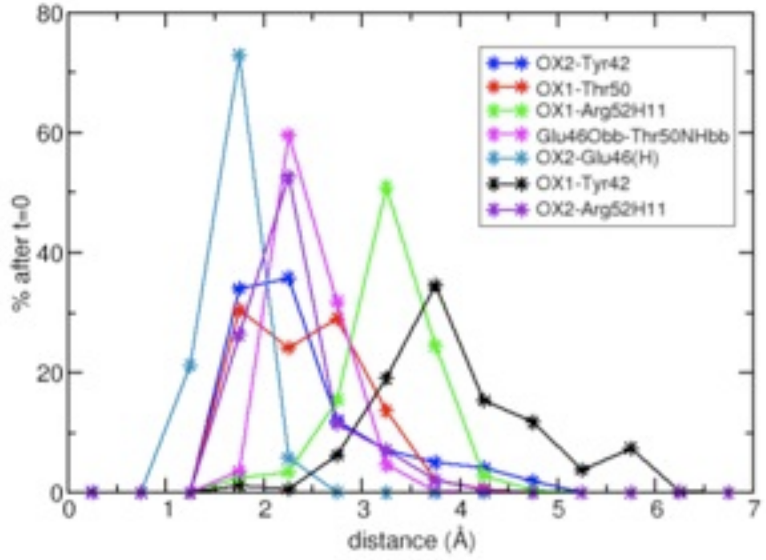




- CPMD QM/MM
- transition path sampling







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