Car-Parrinello method for ab-initio Molecular Dynamics

Francesco Buda

Leiden Institute of Chemistry, Leiden University

About 20 years ago…

Roberto Car and Michele Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985): Unified Approach for Molecular Dynamics and Density Functional Theory

References

- R. Car, M. Parrinello , Phys. Rev. Lett. **55** , 2471 (1985)
- D. K. Remler, P. A. Madden , Mol. Phys. **70** , 921 (1990)
- G. Pastore, E. Smargiassi and F. Buda, Phys. Rev. A **44** , (1991)
- Review paper: D. Marx and J. Hutter (2000), in http://www.fz-juelich.de/nic-series/Volume1
- CPMD code distributed at: www.cpmd.org

Publication analysis on CPMD
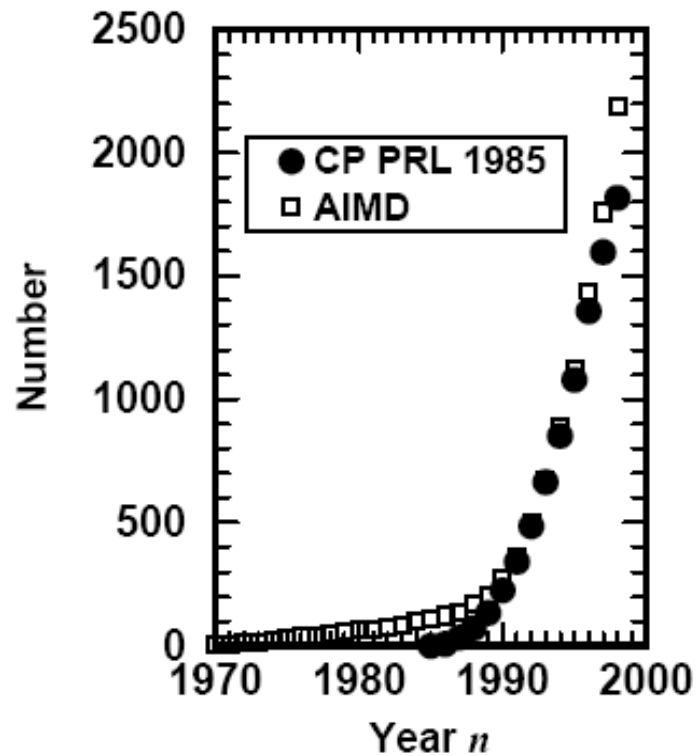
Outline

- Introduction
- Molecular Dynamics
- Density Functional Theory
- Car-Parrinello MD
- Recent developments
- Applications

The Hamilton operator for a general system with n nuclei and N electrons

- The Schrödinger equation is:

$$\hat{H}\Psi(r,R) = E\Psi(r,R)$$

with the Hamiltonian

nucleus-nucleus interaction

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla^2_{r_i} - \frac{\hbar^2}{2M_I}\sum_I \nabla^2_{R_I} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0\left|r_i - r_j\right|} - \sum_{i,I}\frac{Z_I e^2}{4\pi\varepsilon_0\left|r_i - R_I\right|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{4\pi\varepsilon_0\left|R_I - R_J\right|} \right]$$

Electron kinetic energy

Nuclear kinetic energy

electron-electron interaction

electron-nucleus interaction

I,J label atoms with positions R_I, R_J

i,j label electrons with positions r_i, r_j

The Born-Oppenheimer Approximation

- The large difference between the electronic mass and the nuclear mass allows one to separate the electronic and the nuclear problem (*adiabatic approximation*)

- The interatomic forces and potential energy are determined by the behaviour of the bonding electrons, which itself depends parametrically on the atomic structure

- Within the Born-Oppenheimer approximation:

$$\Psi(r, R) = \psi(r; R)\chi(R)$$

Full wavefunction

Electron coordinates

Atomic (nuclear) positions

Electron wavefunction for given nuclear positions R

Nuclear wavefunction

$$\hat{H}\Psi(r,R) = E\Psi(r,R)$$

R: nuclear coordinates

r: electronic coordinates

General Hamiltonian

Born-Oppenheimer approximation

Nuclear Schrödinger equation

Electronic Schrödinger equation

$$[T_n + V_{eff}(R)]\chi(R) = E\chi(R) \Longleftarrow H_e\psi(r;R) = V_{eff}(R)\psi(r;R)$$

Classical Approximation for the nuclei
Newton equation with ab-initio potential

$\Downarrow$

$\Downarrow$

By using DFT:

Car-Parrinello approach $\Longleftarrow$ $V_{eff}(R) = \min_{\rho} E[\rho(r);R] = E[\rho_{GS};R]$

Why *ab initio* Molecular Dynamics ?

Molecular Dynamics:
Classical approximation for the nuclear motion

- Assume the nuclei are heavy enough to be described with classical mechanics

  ➔ The quantum aspects of the nuclear motion, such as tunneling and zero-point motion, are neglected.

- Instead of solving the Schrödinger equation for the nuclei we solve the Newton equation for N particles moving on the *Potential Energy Surface* (PES) $V_{eff}(R)$

$$M_I \frac{d^2 R_I}{dt^2} = -\nabla_I V_{eff}(\{R\})$$

Force Field Methods: empirical potentials

- Capture very simple interactions between atoms
- Predefined functional form for the interatomic potential
- Contain many parameters to be fixed according to experimental data or theoretical calculations
- Usually work in situations where it is easy to identify individual `atomic' charge distributions, and these do not vary strongly as the atoms move around
- Some popular Force Fields for treating bio-molecules:
    - AMBER
    - CHARMM
    - GROMOS
    - SYBYL

Force Field Energy

The force field energy (PES) is written as a sum of terms describing bonded and non-bonded interatomic interaction

$$V_{eff} \equiv E_{FF} = E_{bond} + E_{non-bond}$$

- bonded terms

$$E_{bond} = E_{stretch} + E_{bending} + E_{torsion}$$

- non-bonded terms

$$E_{non-bond} = E_{vdw} + E_{el} \qquad \text{van der Waals and Electrostatic}$$

- Each term contains a number of empirical fitting parameters

The Stretch Energy

- The energy function for stretching a bond between two atoms A and B can be written as a Taylor expansion around the equilibrium bond length

$$E_{str} = E_0 + \frac{dE}{dR}(R^{AB} - R_0^{AB}) + \frac{1}{2}\frac{d^2E}{dR^2}(R^{AB} - R_0^{AB})^2 + \ldots$$

- In the harmonic approximation

$$E_{str} = k^{AB}(R^{AB} - R_0^{AB})^2$$

- Fitting parameters: k^{AB}, R_0^{AB}

Non-bonded energy terms

Van der Waals term: Lennard-Jones potential

$$E_{vdw} = \varepsilon \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^{6} \right]$$

Electrostatic energy: Coulomb potential

$$E_{el} = \frac{Q^A Q^B}{\varepsilon R_{AB}}$$

Molecular Dynamics (1)

- Basic idea: simply follow the dynamical evolution according to Newton's equations of motion for the atoms

- Break time into discrete `steps' Δt, compute forces on atoms from their positions at each timestep

- Evolve positions by, for example, Verlet algorithm:

$$R(t + \Delta t) = R(t) + [R(t) - R(t - \Delta t)] + \frac{(\Delta t)^2}{M} F(t)$$

- or the equivalent `velocity Verlet' scheme

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

$$R(t + \Delta t) = R(t) + v(t)\Delta t + \frac{\Delta t^2}{2M} F(t)$$

Molecular Dynamics (2)

- Follow the `trajectory' and use it to sample the states of the system: The system samples the 'microcanonical' (constant-energy) thermodynamic ensemble, provided that the trajectory eventually passes through all states with a given energy (ergodicity)

Ensemble Averages and Time Averages (ergodic hypothesis)

$$\langle A \rangle = \iint A(q, p) P(q, p) dq dp$$

Where the probability $P(q,p)$ is given by

$$P(q, p) = \frac{e^{-E(q,p)/k_B T}}{\iint e^{-E(q,p)/k_B T} dq dp}$$

$$\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0+t} A(\tau) d\tau$$

Time-correlation functions and transport coefficient

- They give a clear picture of the dynamics in a fluid
- Their time integral may be related directly to macroscopic transport coefficients (e.g. the diffusion coefficient)
- Their Fourier transform may be related to experimental spectra (e.g., vibrational DOS, infrared spectra)

Molecular Dynamics (3)

- Assuming forces are conservative, the total energy will be conserved with time (to order $(\Delta t)^2$ in the case of Verlet)

$$E = K + V = \sum_I \frac{1}{2} M_I \dot{R}_I(t)^2 + V(\{R(t)\}) = \text{constant}$$

- Note: the energy conservation along the dynamics is also a test on the accuracy and stability of the numerical integration

Molecular Dynamics (4)

- Refinements exist to allow simulations with
  - Constant temperature (an additional variable is connected to the system which acts as a 'heat bath')
  - Constant pressure (the volume of the system is allowed to fluctuate)
  - Constant stress (the shape, as well as the volume, of the system is allowed to fluctuate)
  - Geometrical constraints

Technical details

Choice of time step:

- The time step Δt must be smaller compared to the shortest oscillation period of the normal modes of the system

Periodic boundary conditions (to overcome surface effects):

- The box is replicated throughout space to form an infinite lattice

Advantages and Limitations of Force Field Methods

- Advantages
  - speed of calculations
  - large systems can be treated (several thousands atoms with a PC)
  - easy to include solvent effects and crystal packing
- Limitations
  - Lack of good parameters (for molecules which are out of the ordinary)
  - The predicting power is very limited
  - Transferability limited
  - Cannot simulate bond breaking and forming

References on classical MD

- Allen MP and Tildesley DJ (1987) Computer Simulation of Liquids, Clarendon Press, Oxford

- Frenkel D and Smit B (1996) Understanding Molecular Simulation – From Algorithms to Applications, Academic Press, San Diego

Ab initio Molecular Dynamics

- Why AIMD ? Overcome limitations of (force-field) MD, specifically in simulating bond breaking and forming.

- How can we obtain the *Potential Energy Surface* (V_{eff}) ?

  - By fitting *ab initio* results to a suitable functional form. This is very demanding and can be done only for extremely small systems; furthermore it is difficult to design a well-behaved fitting function

  - The fitting step can be bypassed and the dynamics performed directly by calculating the interatomic forces (obtained from the electronic structure calculated *on-the-fly*) at each time-step of an MD simulation

Born-Oppenheimer Molecular Dynamics

- Calculate interatomic forces in Molecular Dynamics by solving the electronic structure problem for each nuclear configuration in the MD trajectory:

$$M_I \frac{d^2 R_I}{dt^2} = -\nabla_I V_{eff}(R)$$

$$H_e \Psi_0 = V_{eff}(R) \Psi_0$$

- Density Functional Theory is mostly used to solve the electronic structure (self-consistent solution of the Kohn-Sham equations). However, in principle other methods can be used (HF, MCSCF, …)

- the direct BO-MD involves a SCF calculation of the wave functions at each time step

Density Functional Theory
(Hohenberg and Kohn, 1964)

- The ground-state electronic energy (E) of a N-electron system can (in principle) be uniquely determined by the electron charge density $\rho(r)$

$$E = E[\rho(r)]$$

- This is so because two ground states for different potentials cannot have the same charge density

- A variational principle holds for the energy functional:

$$E[\rho] \geq E_{GS}$$

$$E[\rho_{GS}] = E_{GS}$$

Walter Kohn: Nobel Prize in Chemistry, 1998

Density Functional Theory
(Kohn and Sham, 1965)

- Write total energy as

$$E[\rho] = T_{\text{single-particle}}[\rho] + E_{\text{ext}}[\rho] + E_{\text{Hartree}}[\rho] + E_{\text{Exchange-correlation}}[\rho]$$

K.E. of noninteracting particles at this density

Interaction with external potential: nuclei-electrons term

Interaction with Hartree potential (Coulomb energy)

The rest!

- Write density in terms of a set of auxiliary one-electron functions

$$\rho(r) = \sum_{i=1}^{N} \left| \varphi_i(r) \right|^2$$

Density Functional Theory
(Kohn and Sham, 1965)

$$E[\rho; R] = T_{\text{single-particle}}[\rho] + E_{\text{ext}}[\rho; R] + E_{\text{Hartree}}[\rho] + E_{\text{Exchange-correlation}}[\rho]$$

$$T = \sum_i f_i \int dr \, \phi_i^* \left(-\frac{\nabla^2}{2} \right) \phi_i$$

K.E. of noninteracting particles at this density

$$E_{ext} = \sum_I \int dr \, \frac{\rho(r) Z_I}{|r - R_I|}$$

Interaction with external potential: nuclei-electrons term

$$E_H[\rho] = \frac{1}{2} \iint dr_1 dr_2 \, \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$$

Interaction with Hartree potential (Coulomb energy)

E_{xc} contains the exchange energy, the correlation energy and the kinetic terms not included in T

Usually also the nuclear-nuclear term $U\{R_I\}$ is added in the total energy functional

Density Functional Theory
(Kohn and Sham, 1965)

- By applying the variational principle for the functional with the constraint on the total number of electrons we obtain a set of *self-consistent* single-particle (Kohn-Sham) equations

$$\left(-\frac{1}{2}\nabla^2 + V^{KS}(r) \right)\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

- where the effective *local* potential is given by

$$V^{KS}(r) = V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + V_{xc}(r)$$

- with the exchange-correlation potential defined as

$$V_{xc}(r) \equiv \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)}$$

Basis Set approximation

- All calculations use a basis set expansion to express the unknown Kohn-Sham (Molecular) Orbitals
- Mostly used basis set are atom-centered functions that resemble atomic orbitals (Linear Combination of Atomic Orbitals)
- basis set used in practical calculations are
  - STO (exponential: Slater-type orbitals)
  - GTO (Gaussian-type orbitals)
  - Plane waves

Local Density Approximation (LDA)

- The Kohn-Sham approach enables one to derive an *exact* set of one-electron equations

- Problem: all the nasty bits (including exchange) are now included into the unknown exchange-correlation energy

- A simple approximation, the *Local Density Approximation*, is surprisingly good: approximate exchange-correlation energy per electron at each point by its value for a homogeneous electron gas of the same density (known from QMC results)

$$E_{XC}^{LDA} = \int \rho(r) \varepsilon_{XC,\,homogeneous}(\rho(r))dr$$

- Can be generalized to include spin polarization (LSDA)

Generalized Gradient Approximation (GGA)

- Though Local Density Approximation works quite well in many cases (metals and semiconductors), in general underestimates the exchange energy and gives poor results for molecules.

- To improve over the LSDA, the exchange-correlation energy should depend not only on the density, but also on derivatives of the density (gradient corrections) :

$$E_{xc}^{GGA} = \int \rho(r) f(\rho(r), \nabla \rho(r)) dr$$

- GGA, as e.g. the BP (Becke-Perdew) or the BLYP (Becke-Lee-Yang-Parr) functional, can give accuracy of the same or better quality than MP2. Hybrid functionals, such as the B3LYP are also widely used.

- The search for increasingly accurate functionals is a current hot topic in the field:

  – Meta-GGA have been also recently developed

$$E_{xc}^{meta-GGA} = \int f(\rho(r), \nabla \rho(r), \nabla^2 \rho(r)) dr$$

Why DFT is the preferred choice for *ab initio* MD?

- Advantages
  - General accuracy for geometries and vibrational frequencies similar or better than MP2
  - Computational cost scales at most as N^3 (N = number of basis functions)

- Limitations
  - Weak interactions (vdW) are poorly described
  - Lack of a systematic improvability

Born-Oppenheimer Molecular Dynamics

- Molecular Dynamics with interatomic forces obtained using DFT for each nuclear configuration in the MD trajectory:

$$M_I \frac{d^2 R_I}{dt^2} = -\nabla_I V_{eff}(R)$$

$$V_{eff}(R) \equiv E^{KS}[\rho; \{R\}]$$

$$\frac{\partial E^{KS}}{\partial \rho} = 0 \Rightarrow \left(-\frac{1}{2} \nabla^2 + V^{KS}(r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

- the direct BO-MD involves a SCF solution of the Khon-Sham equations at each step
  ➔computationally very demanding

Car-Parrinello Molecular Dynamics

- Car and Parrinello (1985) proposed an approach in which the electronic self-consistent problem has to be solved only for the initial nuclear configuration in the MD

- CPMD evolves in time the nuclear positions and the electronic degrees of freedom using an extended Lagrangian:

$$L_{eI} = K_e + K_I - E^{KS}\left[\{\phi_i\}, \{R_I\}\right] + \sum_{i,j} \lambda_{ij}\left(\langle\phi_i \mid \phi_j\rangle - \delta_{ij}\right)$$

Orthogonalization constraint

$$K_e = \mu \sum_i \int dr \mid \dot{\phi}_i \mid^2$$

Fictitious Elec. Kinetic energy

- This dynamics generates *at the same time* the nuclear trajectory and the corresponding electronic ground state.

Car-Parrinello Molecular Dynamics

- The corresponding equations of motion are:

$$M_I \frac{d^2 R_I}{dt^2} = -\nabla_I E^{KS}[R, \phi]$$

$$\mu \frac{d^2 \phi_i}{dt^2} = -\frac{\delta E^{KS}}{\delta \phi_i^*} + constr.$$

- which can be solved numerically using, for example, the Verlet algorithm

Initial conditions

- The electrons are in the ground state corresponding to the initial nuclear configuration:

  - Electron velocities and accelerations are zero
  - The equations of motion for the electrons are equivalent to the Kohn-Sham equations

Why does the Car-Parrinello method work ?

- CPMD exploits a classical adiabatic energy scale separation between the nuclear and electronic degrees of freedom: By choosing the parameter $\mu << M$ the evolution of the ϕ_i can be decoupled from that of R_I

$$\omega_e >> \omega_I$$

- The electrons oscillate around the instantaneous ground-state BO surface with very low kinetic energy

$$K_e << K_I$$

$$U'_I = K_I + E^{KS} \cong const$$

- The physical total energy U'_I behaves approximately like the strictly conserved total energy in classical MD

- Under these conditions the CPMD trajectories derived from the extended Lagrangian
  - reproduce very closely the *true* (Born-Oppenheimer) nuclear trajectories
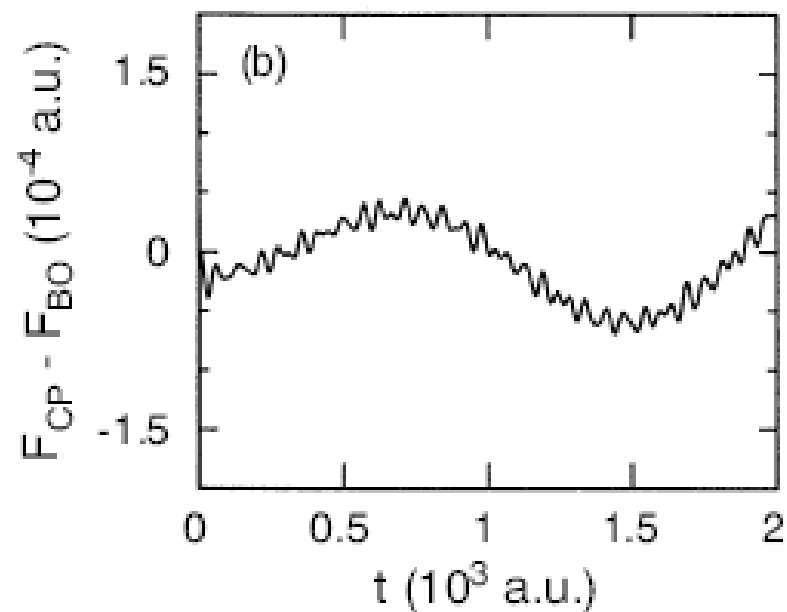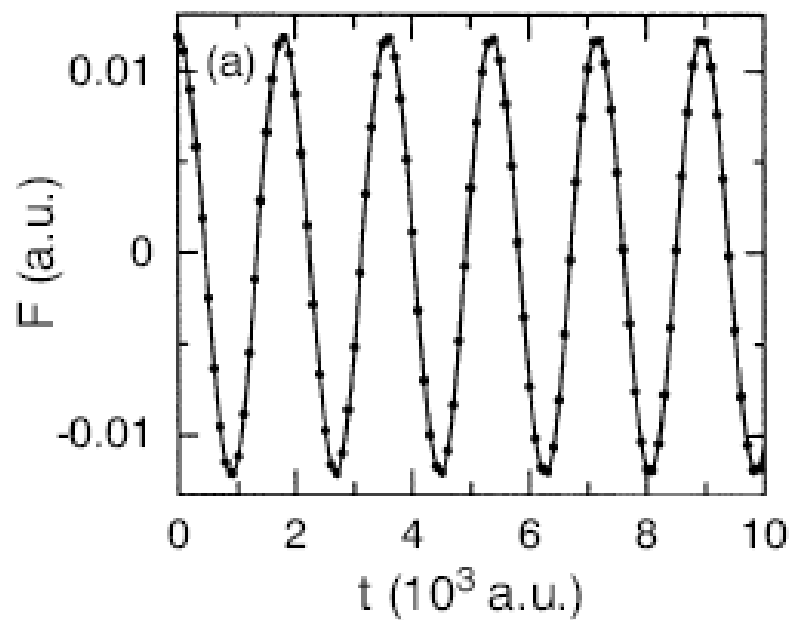 - approximates very closely the microcanonical dynamics

Vibrational density of states
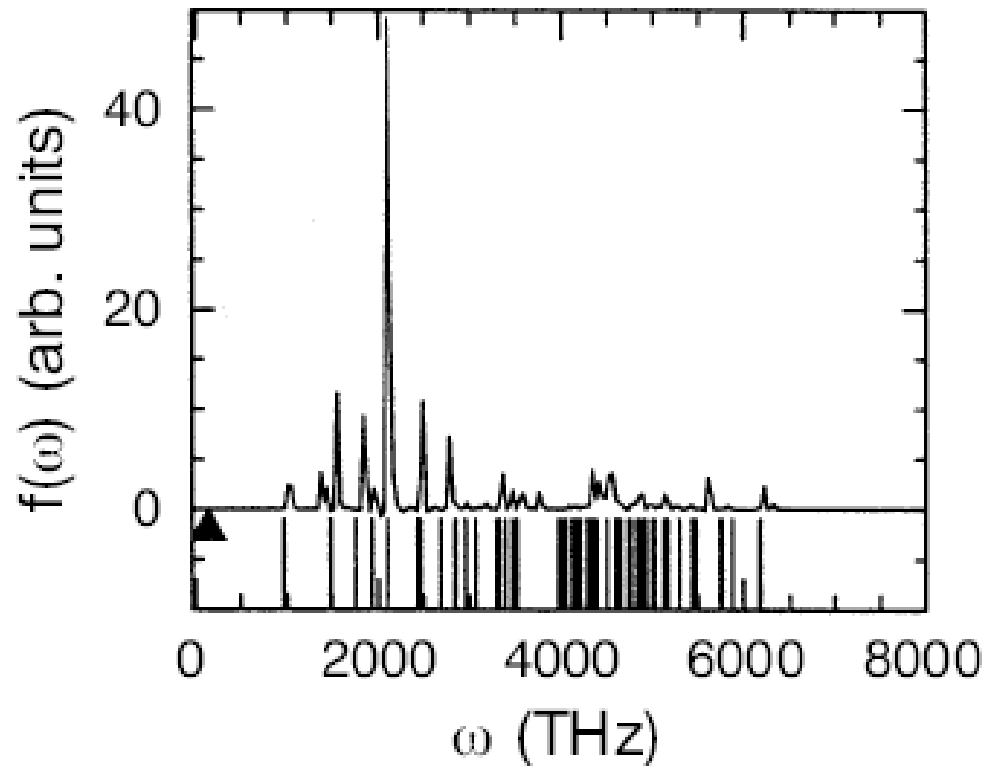
Various energy terms for a model system
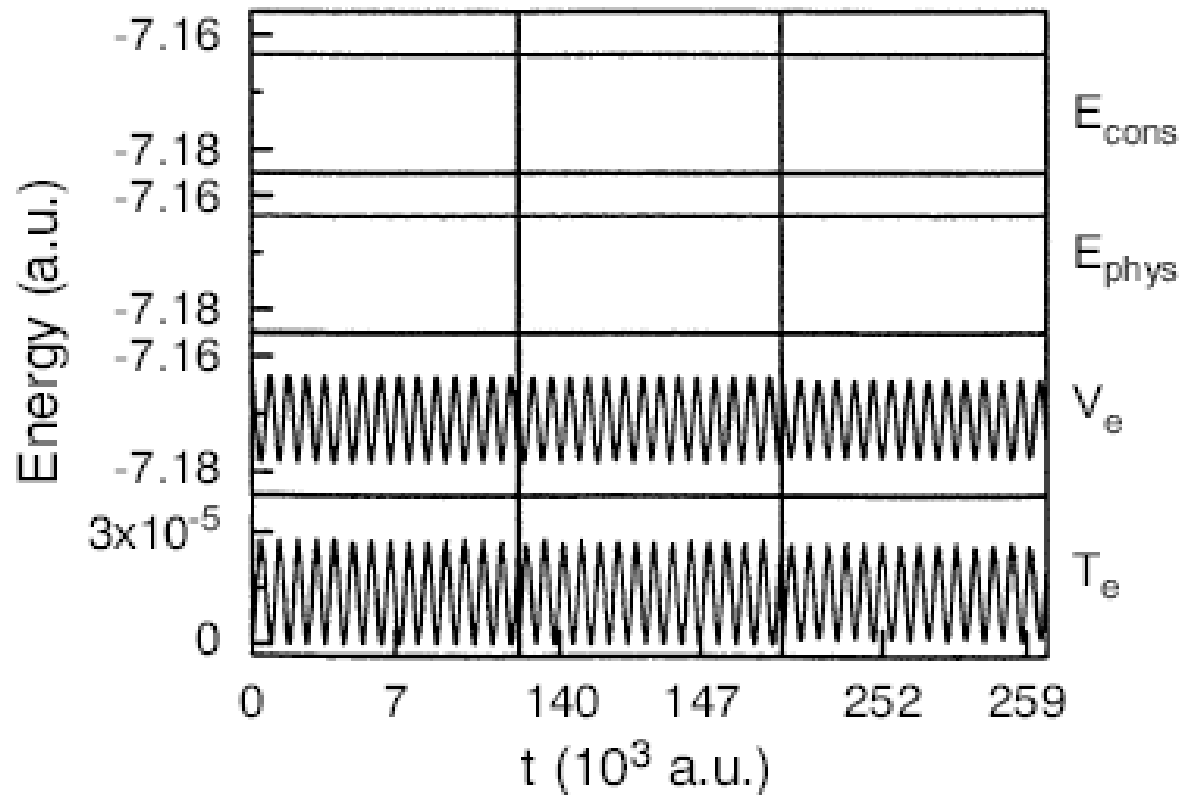
Comparison between
Born-Oppenheimer and Car-Parrinello forces

How to control adiabaticity ?

- The electronic frequencies depend also on the electronic structure:

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

$$\omega_{min}^e \propto \sqrt{\frac{E_{HOMO-LUMO}}{\mu}}$$

- warning: adiabaticity is broken when the gap between occupied and virtual orbitals is too small (problems with metals)

Practical solution to broken adiabaticity

- Couple the electronic subsystem with a thermostat keeping the electron at low temperature

- Couple the nuclear subsystem with a thermostat at the desired physical temperature of the system

Technical details

- Time step Δt
  - Limited by the fast electronic motion
  - Typical value $\Delta t \approx 0.1$ fsec
- Electronic mass μ:
  - Adiabatic evolution if $\mu/M << 1$
  - Typical value $\mu/M = 1/100$

Technical details

- Supercell geometry
  - Periodic boundary conditions
- Plane wave expansion of electronic states

$$\phi_i(r) = \sum_G c_G^i \exp(iG \cdot r)$$

  - more suitable for extended systems: solids, liquids
  - Only one parameter controls the accuracy

$$\frac{1}{2}|k + G|^2 \leq E_{cut}$$

  - Fast Fourier transform (FFT) can be used
  - Evaluation of nuclear forces easy (no Pulay forces)

The Hellman-Feynman theorem

- For a general electron state ψ the electronic energy depends on the state, as well as explicitly on the atomic positions

- In order to find the force on any particular atom, we would therefore have use the chain rule to write

$$\frac{dE_{el}(R)}{dR_I} = \left\langle \psi \left| \frac{\partial \hat{H}_{el}(R)}{\partial R_I} \right| \psi \right\rangle + \frac{\delta \left\langle \psi \left| \hat{H}_{el} \right| \psi \right\rangle}{\delta \left\langle \psi \right|} \frac{\partial \left\langle \psi \right|}{\partial R_I}$$

Explicit dependence of H on R

Implicit dependence of E on R via the change in wavefunction as atoms move

- For the ground state (or indeed any electronic eigenstate) the electronic energy is stationary with respect to variations in ψ and we can therefore ignore the second term.

Pseudopotentials

- To minimize the size of the plane wave basis
  - only valence electrons are included explicitly
  - core electrons are replaced by pseudopotentials
- First-principles pseudopotentials are built to
  - correctly represent the long range interactions of the core
  - produce pseudo-wavefunctions that approach the full wavefunction outside a core radius r_c

Car-Parrinello Molecular Dynamics

- ## Advantages:
  - – More general applicability and predictive power compared to MD using "predefined potentials"
  - – In comparison with static quantum chemistry approaches allows for the inclusion of dynamical, entropic effects, and the possibility of treating disordered systems (e.g. chemical reactions in solution)

- ## Limitations:
  - – approximation in the exchange-correlation functional
  - – size: 100-1000 atoms
  - – time scale : 10 ps

Current developments

- QM/MM extension

- Excited state (TDDFT coupled with CPMD)

- Extension to localized basis set (Gaussians): more suitable for molecules, clusters

Hybrid QM/MM approaches: quantum-mechanics/molecular-mechanics

- Systems of interest in computational biology are too large for a full quantum-mechanical treatment
- Need to integrate various computational chemistry methodologies with differing accuracies and cost.
- In QM/MM approaches this is done by embedding a QM calculation in a classical MM model of the environment

- Review paper: P. Sherwood, (2000), in
  - http://www.fz-juelich.de/nic-series/Volume1

QM/MM scheme

- The system is divided in two subsystems: an inner region (QM) where quantum-mechanics is used and an outer region (MM) where a classical field is used, interacting with each other
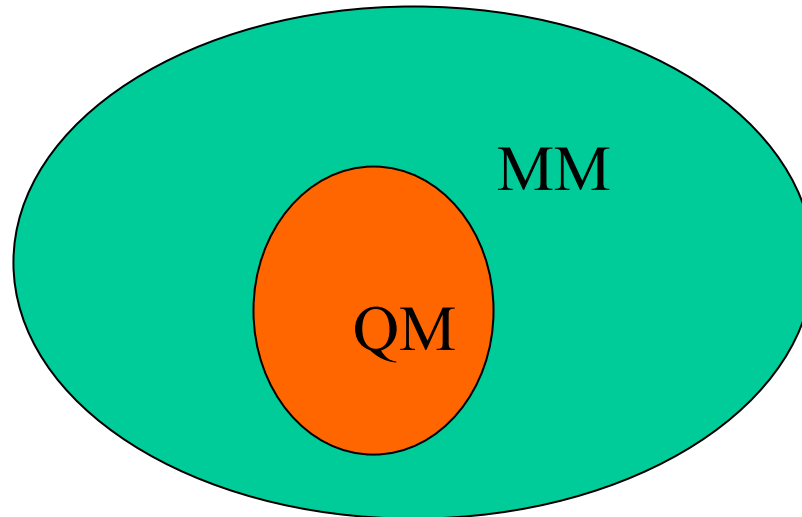
Why and when QM/MM ?

- Interest in active sites of proteins / enzymes
- Geometry and Functionality of active site influenced by the protein environment
- Proteins still too large to be handled completely by quantum chemistry &
  high quality (QM) description only needed for place of interest (*active site*)
- QM/MM schemes aim to incorporate environmental effects at an atomistic level, including mechanical constraints, electrostatic perturbations and dielectric screening

QM-MM Hamiltonian

- We can in general write a total Hamiltonian of the QM-MM system as follows:

$$H = H_{QM} + H_{MM} + H_{QM/MM}$$

- H_{QM} includes all the interactions between the particles treated with QM,

- H_{MM} includes all the interactions between the classical particles,

- $H_{QM/MM}$ accounts for all the interactions between one quantum particle and one classical particle

The choice of the QM method

- The choice of the QM method within a hybrid approach depends on the accuracy required and on the size of the QM region.

- Implementation of QM-MM methods have been reported with almost any QM approach:

  – The first application of Warshel and Levitt (1976) employed a semiempirical method.

  – More recently several implementation involving DFT and Car-Parrinello MD have been reported. This is a very interesting development since DFT can deal with relatively large QM regions and can be used also in combination with Molecular Dynamics.

The choice of the MM model

- The H_{MM} term is determined by the specific classical force field used to treat the MM part.
- The most popular force fields for hybrid QM-MM simulations are the same force fields mostly used for biomolecules:
  - CHARMM
  - AMBER
  - GROMOS96

Handling the hybrid term

- The third term of the Hamiltonian, $H_{QM\text{-}MM}$, is the most critical and the details of this interaction term may differ substantially in different implementations.

- In terms of classification, we can distinguish two possibilities:

- (i) the boundary separating the QM and MM region, does not cut across any chemical bond;

- (ii) the boundary cuts across at least one chemical bond.

Handling the hybrid term

- (i) the QM-MM coupling term in the Hamiltonian contains the non-bonded interactions, i.e., electrostatic and short-range (van der Waals) forces.

- The treatment of the electrostatic interactions varies for different implementations, but the most common is the **electrostatic embedding**, in which the classical part appears as an external charge distribution (e.g. a set of point charges) in the QM Hamiltonian.

Handling the hybrid term

(ii) If there are bonds between the QM and MM regions, it is necessary to introduce some termination of the QM part.

For termination of sites where a covalent bond has been broken, addition of a so-called **link atom** is the most common approach: An extra nuclear centre is introduced together with the electrons required to form a covalent bond to the QM dangling valences that will mimic the bond to the MM region.

The simplest and most used choice is to add a hydrogen atom as link atom. Of course there are chemical differences between hydrogen and the chemical group it replaces. One possible approach to adjust the link atom interaction is to place a pseudopotential at the MM site to mimic the electronic properties of the replaced bond.

Applications:
From Materials Science to Biochemistry

- Semiconductors: silicon in crystalline and disordered phases
- Structural phase transitions of materials under pressure
- Diffusion of atoms in solids
- Surface reconstruction, chemisorption on surfaces
- Simulations of liquids, water, ions in water
- Clusters, fullerenes, nanostructures
- Chemical reactions (in gas phase or in solution)
- Polymerization reactions – Ziegler-Natta catalysts
- Zeolites, metallocenes
- Rhodopsin, enzymatic reactions, drug-DNA interactions