Computer Simulations in Chemistry: Molecular Dynamics and Monte Carlo

http://lcbc.epfl.ch/page-89186-en.html

Spring Semester 2019

22 February – 31 June
Fri 08:15 - 10:00
Course: BCH 4119
Computer Exercises: BCH 1113

Lectures:

(BCH 4119)

Computer Exercises:

(BCH 1113)

2h every other week

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Time Table

22.2.19	Course: intro & Chapter 1 (From QM to MM)
01.3.19	Exercise I
08.3.19	Chapter 2 (Statistical Mechanics)
15.3.19	Exercise II
22.3.19	Course: Chapter 3 (Monte Carlo Simulations)
29.3.19	Exercise III
05.4.19	Course: Chapter 4 (MD Simulations 1)
12.4.19	Exercise IV
19.4.19	**Good Friday (no course)**
26.4.19	**Easter Break (no course)**
03.5.19	Exercise V
10.5.19	Course: Chapter 5 (MD Simulations 2)
17.5.19	Exam Preparation: Previous Exam & Question Hour
24.5.19	**Written Exam**

Control Continue

- **computer exercises (1/2)**
- **written exam 24.5. (1/2)**

Course Support

Documentation:

- handouts
- copies of slides

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Supplementary Literature:

- M.P. Allen and D.J. Tildesley, *Computer Simulations of Liquids*, Oxford University Press (2002) (MD)
- D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press (2001) (MC)
- David Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press (1987) (Statistical Mechanics)

Molecular Dynamics (MD) and Monte Carlo (MC) Simulations

Aim:

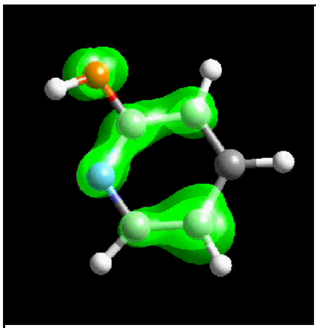
Study the properties of physical, chemical and biological systems by recreating them on the computer as realistically as possible.

Molecular Dynamics & Monte Carlo Simulations:

- Simulate a system in microscopic detail to predict the macroscopic (dynamic) and thermodynamic properties of an ensemble
- The two main numerical simulations techniques in the study of condensed phase and macromolecular systems

MD&MC & Electronic Structure Methods (Quantum Chemistry):

- **Make up the three main pillars of modern Computational Chemistry!**



Matter: system of N atoms (N nuclei with positive charges Z_I and masses M_I and n electrons with negative charges e and masses m_e) (atomic units: $e = m_e = 1$ a.u.)

Quantum Mechanics:

System is described by (electron-nuclear) wavefunction

$$\boxed{\begin{array}{l}\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,\vec{R}_1,\vec{R}_2,\ldots\vec{R}_N,t)\\ \Psi\left(\{\vec{r}_i\},\{\vec{R}_I\},t\right)=\Psi\left(r,R,t\right)\end{array}}$$

Quantum chemical electronic structure methods:

(HF, CI, MPn, CC, DFT etc.)

- Stationary states (no time dependence)
- Born-Oppenheimer approximation to separate electronic and nuclear problem

$$\boxed{\Psi\left(r,R\right)\approx\Psi_{elec}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\Psi_{nuc}(\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N)=\Phi\left(r\right)\chi\left(R\right)}$$

- Solve electronic Schrodinger Equation for fixed nuclear positions (no dynamics of the nuclei, no temperature)

$$\boxed{\hat{H}_{elec}\Psi_{elec}=E\Psi_{elec}} \quad \boxed{\hat{H}_{elec}=\hat{E}_{kin}+\hat{V}_{elec}} \quad \boxed{\hat{H}_{elec}=-\frac{1}{2}\sum_n\vec{\nabla}_n^2-\sum_n\sum_I\frac{Z_I}{\left|\vec{R}_I-\vec{r}_n\right|}+\sum_{n<m}\frac{1}{\vec{r}_m-\vec{r}_n}}$$

Atoms are never at rest!

- *Classical limit T>>0:*

Kinetic theory: temperature T proportional to kinetic energy of particles E_{kin}

$$\boxed{T=\frac{2}{3}\frac{E_{kin}}{N^{DOF}k_B}} \quad \boxed{E_{kin}=\frac{1}{2}\sum_I M_I v_I^2}$$

N^{DOF}: number of degrees of freedom (3N)

k_B: Boltzmann constant

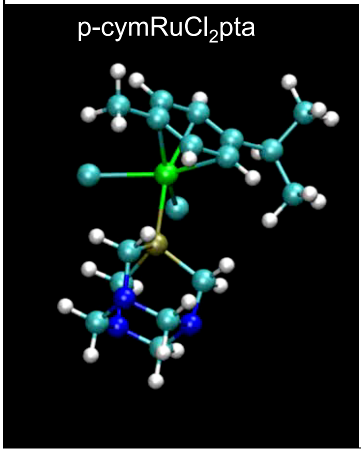
- *T = 0:*

Zero point motion

Quantum Harmonic Oscillators:

Zero point energy E^{ZP}

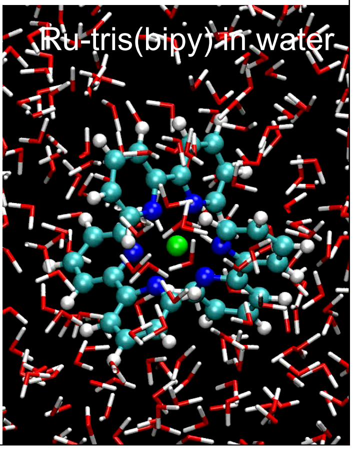
$$\boxed{E^{ZP}=\frac{1}{2}\sum_{k=1}^{3N-6}\hbar\omega_k}$$



How do we incorporate finite T effects?

How do we take into account all relevant configurations to describe the thermodynamic ensemble?

-> Molecular Simulations (MD & MC)



Chapter 1:

From Quantum Mechanics to Classical Mechanics

Semiclassical approximation: treat electrons at the QM level and move nuclei classically

2) Most atoms are heavy enough so that their motion can be described with classical mechanics

- ratio of the deBroglie wavelength $\lambda = \frac{h}{\sqrt{2mE}}$ of an electron and a proton: $\frac{\lambda_{el}}{\lambda_p} = \left(\frac{m_p}{m_{el}}\right)^{1/2} \approx 40$

⇒ classical approximation is better: m↑, n↑, E↑, T↑

⇒ Works surprisingly well in many cases!

⊘ what cannot be described:
- zero point energy effects
- (proton) tunneling

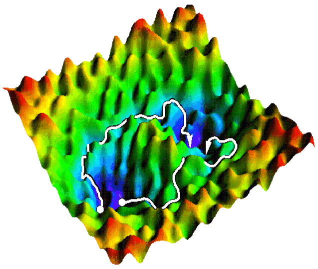
⇒ quantum corrections to classical results (Wigner&Kirkwood)

⇒ classical MD extended to quantum effects on equilibrium properties and to some extend also to quantum dynamics

⇒ path integral MD and centroid dynamics

Solve electronic Schrödinger Eq. for each set of nuclear coordinates

$R = (\vec{R}_1, \vec{R}_2, \vec{R}_3, \ldots \vec{R}_N) \Rightarrow E(R)$ **potential energy surface (PES) V(R)**



Nuclear Schrödinger Eq.

$$H_{nu}\Psi_{nu}(\vec{R}_1, \vec{R}_2, \vec{R}_3 \ldots \vec{R}_N) = E_{tot}\Psi_{nu}(\vec{R}_1, \vec{R}_2, \vec{R}_3 \ldots \vec{R}_N)$$

Nuclear Hamilton operator:

$$\mathrm{H}_{nu} = -\sum_I \frac{1}{2M_I}\nabla_I^2 + V(R) + \sum_{I,J}\frac{Z_I Z_J}{R_{IJ}}$$

$\Rightarrow$ **Nuclear Quantum Dynamics**

(review: Makri, Ann. Rev. Phys. 50, 167 (1999)