Introduction to Electronic Structure Methods

http://lcbc.epfl.ch/ teaching

Fall Semester 2018

18 September - 18 December
Course: BCH 4119
Computer Exercises: BCH 1113

Lecturer:

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Demos/Exercises:

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LCBC
Lab. of Computational Biochemistry and Chemistry

Group of Computational Chemistry and Biochemistry
http://lcbcpc21.epfl.ch

Exams

- written exam about first half of script (1/3)
- oral exam at the end of the semester about 2nd half of the script (1/3)
- computer exercises (1/3)

Course Support

Documentation:

-script: **Introduction to Electronic Structure Methods**

http://lcbc.epfl.ch/ **teaching**

Illustrations:

- **exercises (analytical and computational)**
- **copy of the slides**
- **supplementary literature (optional):**

Szabo and Ostlund: *Modern Quantum Chemistry*
(pdfs available online)
DFT: R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford (1989).

Time Table

• First 7 weeks (≤ 6 Nov) :	4h course (BCH4119) (Tue&Fri) 2h exercises (BCH4119/BCH1113) (Fri)
• 2nd 7 weeks (6 Nov – 4 Dec):	2h exercises (BCH113) (Tue)

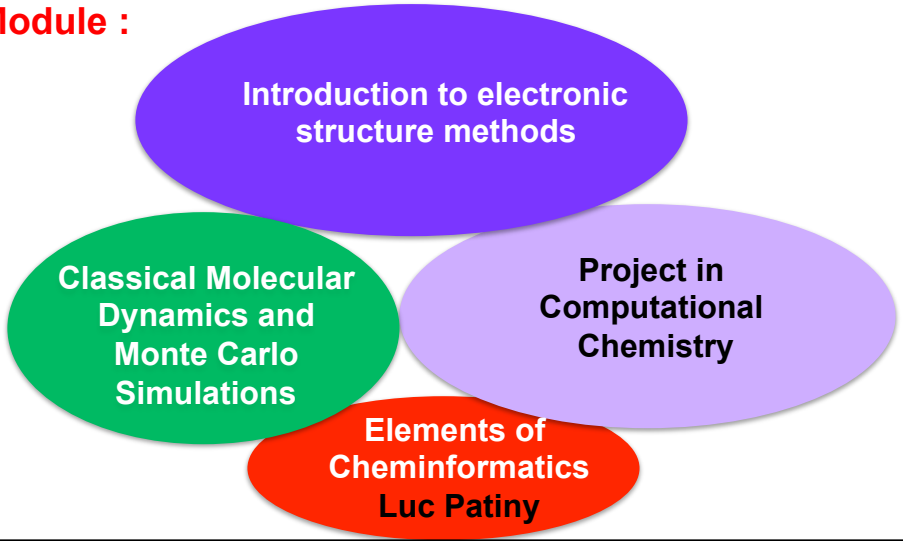
Written Exam: Tue 16 Oct: 15-17:00
Oral Exams: Tue 11 & 18 Dec

Time Table for the Course 'Introduction to Electronic Structure Methods' Fall Semester 2018

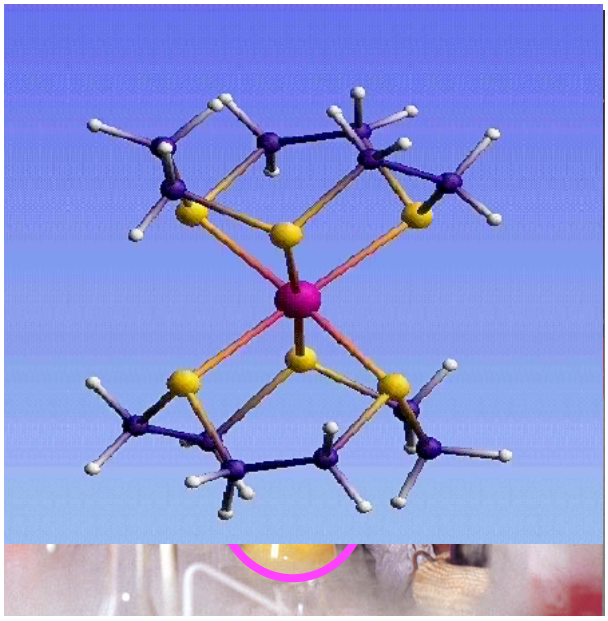
18.9.	Tue	course	practical info, repetition basic QM concepts
21.9.	Fri (morn)	course	repetition linear algebra
	Fri(aftern)	exercises	Exercise 1: Linear Algebra in Quantum Mechanics
25.9.	Tue	course	Basis Sets
28.9.	Fri	course	Hartree-Fock I & Demo Hartree-Fock/Basis Sets
	Fri	exercises	Exercise 2: H Atom: HF calcs in G09
2.10.	Tue	course	Hartree-Fock II
5.10.	Fri	exercises	Exercise 3: Basis sets, De, geom opt.
	Fri	course	HF&CI
09.10.	Tue	course	Configuration Interaction
12.10.	Fri	course	Many-Body Perturbation Theory
	Fri	exercises	Questioning hour & old exams
16.10.	Tue	course	Written Exam
19.10.	Fri	exercises	Exercise 4: Post HF: MPn & CI
	Fri	course	Coupled Cluster
23.10.	Tue	course	Density Functional Theory I
26.10	Fri	course	Solutions Written Exam
	Fri	exercises	Exercise 5 & 6.1: Trouble Shooting, Pitfalls, traps
30.10	Tue	course	Density Functional Theory II (CP, QM/MM & Demos)
02.11	Fri	course	Properties & Summary
	Fri	Exercises	Exercise 6.2: DFT vs HF/MP2
8.11	Tue	exercises	Exercise 6.2 (continued)
13.11	Tue	exercises	Exercise 7: PES scans & traj visualization
20.11	Tue	exercises	Exercise 8.1: TS & Barrier Heights
27.11	Tue	exercises	Exercise 8.2
4.12	Tue	exercises	Question hour
11.12	Tue	exercises	oral exams
18.12	Tue	exercises	oral exams

Basis: mathematics I&II, physics I&II, Informatics I, applied mathematics, probability & statistics, Quantum mechanics

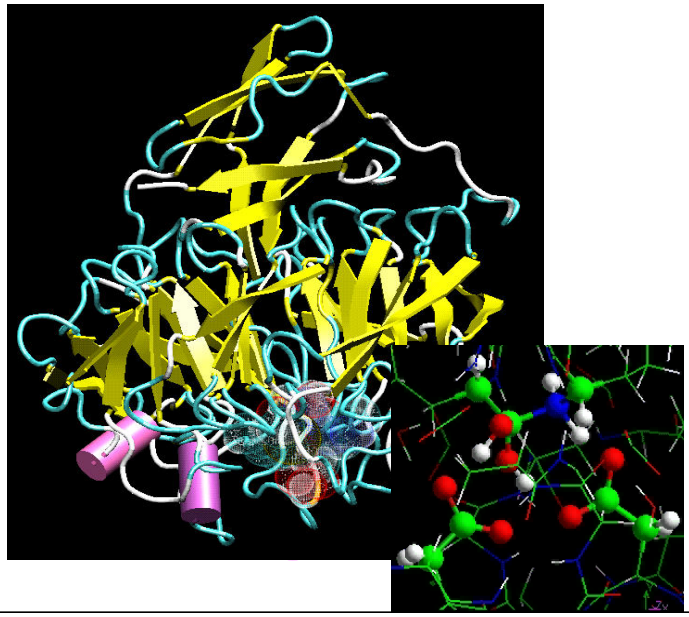
Cheminformatics Module :



Goal:
Description of complex chemical systems with quantum mechanics



Goal:
Description of complex chemical and biochemical systems with quantum mechanics



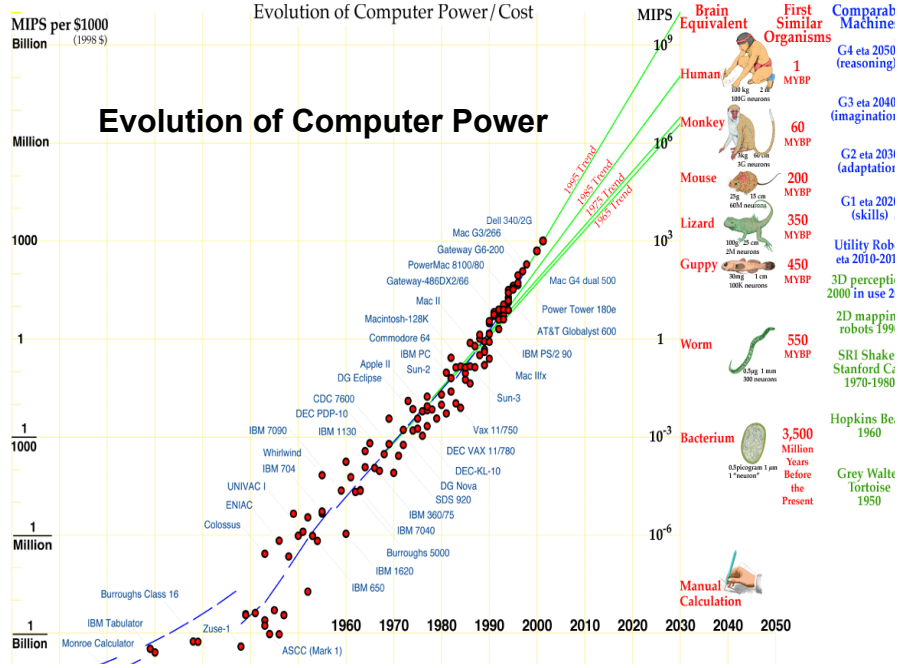
Course Objectives:

- **Extend quantum mechanical description to many-electron systems**
- **Get to know most frequently used quantum chemical methods**
  - **Underlying theory and approximations**
  - **Capabilities and limitations**
  - **Accuracy and applicability**
- **Get to know one of the most frequently used quantum mechanical software packages (GAUSSIAN)**
  - **How to generate inputs**
  - **How to run calculations**
  - **How to interpret outputs**

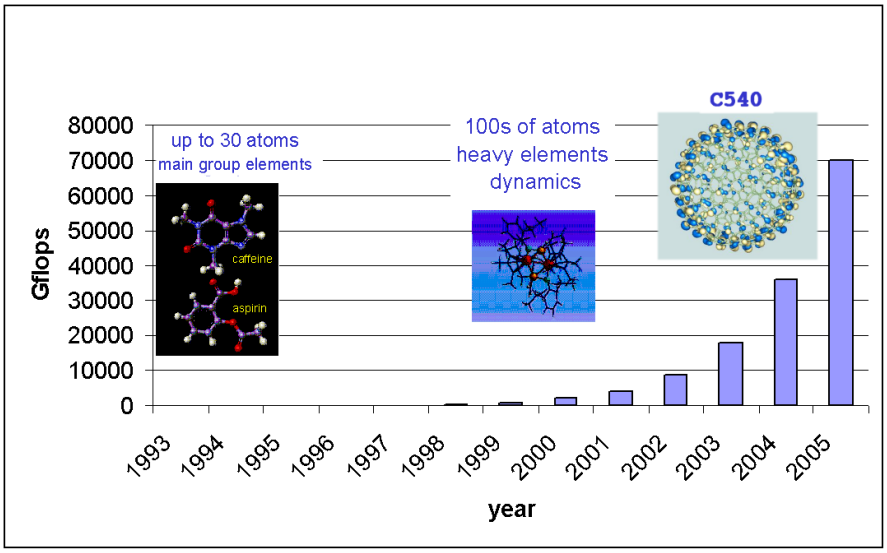
Electronic Structure Calculations of Many-Electron Systems

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Paul Dirac (1902-1984)



Evolution in Quantum Chemistry

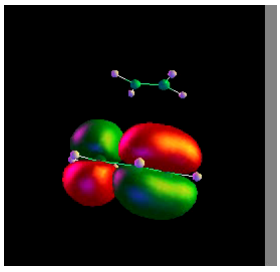


Chapter 1:

Introduction to computational quantum chemistry

Computational Quantum Chemistry

Goal: to calculate (predict) all properties of chemical systems



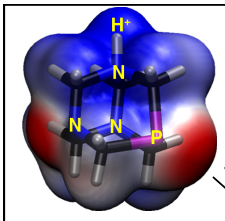
QC

- Lowest energy structure(s)?
- Vibrational properties (IR and Raman spectra)
- Dipole and quadrupole moments
- Proton affinity, pK_a, electron affinity
- Electronically excited states (UV-VIS spectra: Absorption, fluorescence, photochemistry)
- Chemical shifts and NMR coupling constants
- Thermodynamic properties
- Reaction enthalpies, activation energies
- Reaction mechanisms etc..

Theoretical Chemistry
develops mathematical models to describe chemical systems

Computational Chemistry
uses computers to find numerical solutions for these mathematical models

Quantum Chemistry
applies quantum mechanics to describe chemical systems



system:
n electrons
N nuclei with positive charge Z_I
(dimensionless point charges)

Erwin Schrodinger
(1887-1961)

quantum mechanics

Ψ

wavefunction of this system

Once Ψ is known, all properties of the system can be calculated

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n,\vec{R}_1,\vec{R}_2,\ldots\vec{R}_N,t)$$

many-body wavefunction
electron coordinates $\mathbf{r}_i$, nuclear position $\mathbf{R}_I$

Problem separated in electronic and nuclear parts: Born-Oppenheimer Approx.

$$\Psi_{elec}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n,t)=\Psi_{elec}\left(\vec{r},t\right)$$

many-electron wfct
for fixed nuclear position

$$\Psi_{nucl}(\vec{R}_1,\vec{R}_2,\ldots\vec{R}_N,t)=\Psi_{nucl}\left(\vec{R},t\right)$$

nuclear wfct

The wavefunction is determined through the Schrödinger equation:
Electronic Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi_{elec}(t)=\hat{H}_{elec}(t)\Psi_{elec}(t)$$

For time-dependent case

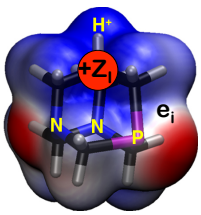
$$\hat{H}_{elec}\Psi_{elec}=E\Psi_{elec}$$

time independent

Hamilton operator

$$\hat{H}_{elec}=\hat{E}_{kin}+\hat{V}_{elec}=-\frac{\hbar^2}{2m_e}\sum_n\vec{\nabla}_n^{\,2}+\hat{V}_{elec}$$

Ex.1



$\hat{V}_{elec}$ **? What fundamental forces?**

→ only Coulomb forces! Ex.2

$$\hat{H}_{elec}=-\frac{\hbar^2}{2m_e}\sum_n\vec{\nabla}_n^{\,2}-\frac{1}{4\pi\varepsilon_0}\sum_n\sum_I\frac{e^2Z_I}{\left|\vec{R}_I-\vec{r}_n\right|}+\frac{1}{4\pi\varepsilon_0}\sum_{n<m}\frac{e^2}{\vec{r}_m-\vec{r}_n}$$

Exact description ! only input: number and type of atoms in the system
Exact solution of this equation gives access to all the properties of the system => ab initio

Les forces fondamentales

		Strength	Range (m)	Particle
Strong	Force which holds nucleus togeher	1	10^{-15} (diameter of a medium sized nucleus)	π, others mass > 0.1 GeV
Electro-magnetic		$\frac{1}{137}$	Infinite	photon mass = 0 spin = 1
Weak	neutrino interaction induces beta decay	10^{-5}	10^{-17} (0.1% of the diameter of a proton)	Intermediate vector bosons W^+, W^-, Z_0, mass > 80 GeV spin =1
Gravity		6×10^{-39}	Infinite	graviton ? mass = 0 spin = 2

http://hyperphysics.phy-astr.gsu.edu/hbase/forces/funfor.html

Exercises

Ex2. Calculate the Coulomb force between an electron and the positively charged nucleus of the hydrogen atom for the case where the electron is at a distance of 1 A from the nucleus. How large is the gravitational force between the two? How large would you estimate that the strong and the weak force between electron and nucleus are?

Exercises

Ex1. Derive the general form of the Hamilton operator starting from the classical description.

Approximate Solutions of the Many-Electron Schrödinger Equation

- Ab initio methods: 'from the beginning', only based on physical laws, no parameterization with experimental data

- semiempirical methods: some terms are approximated or parameterized by empirical data

Possible approximations:

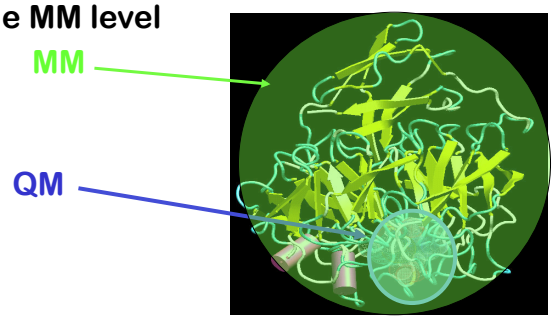
- approximate description of the Hamiltonian (density functional theory (DFT), semiempirical methods)

- approximate description of the wavefunction (Hartree-Fock (HF, SCF), Møller-Plesset perturbation theory (MP2, MP4 etc.), configuration interactio (CIS, CISD etc..), coupled Cluster methods (CCSD, CCSD(T) etc..), quantum Monte Carlo (QMC))

Further possible approximations to describe chemical systems

- No explicit treatment of electrons → use classical mechanics to describe the motion of atoms (classical molecular dynamics (MD) or molecular mechanics methods (MM))

- Mixed quantum mechanical/molecular mechanical (QM/MM) methods → treat a part of the system at the QM level and the rest at the MM level



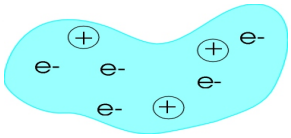
Software Packages

Package	MM	Semi-Empirical	HF	Post-HF	DFT	Ab-inito MD	Periodic	QM/MM
ACES	N	N	Y	Y	N	N	N	N
ADF	N	N	N	N	Y	N	Y	Y
CPMD	Y	N	N	N	Y	Y	Y	Y
DALTON	N	N	Y	Y	Y	N	N	N
GAUSSIAN	Y	Y	Y	Y	Y	Y(?)	Y	Y
GAMESS	N	Y	Y	Y	Y	N	N	Y
MOLCAS	N	N	Y	Y	N	N	N	N
MOLPRO	N	N	Y	Y	Y	N	N	N
MOPAC	N	Y	N	N	N	N	Y	N
NWChem	Y	N	Y	Y	Y	Y(?)	Y	N
PLATO	Y	N	N	N	Y	N	Y	N
PSI	N	N	Y	Y	N	N	N	N
Q-Chem	?	N	Y	Y	Y	N	N	N
TURBOMOL	N	N	Y	Y	Y	Y	Y	N

Problem to solve:

Solution of the

- electronic
- time-independent
- non relativistic



Schrödinger equation for many electron systems:

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

$$\mathcal{H} = \sum_i^N (-1/2\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}}) + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$$

Concepts that you know already and that we are going to use:

Quantum Mechanics (Chapter 2 script):

- basic postulates of quantum mechanics
- antisymmetric wavefunctions and Slater determinants
- Dirac bra – ket notation
- Born-Oppenheimer approximation
- Variational principle and secular equation

Linear Algebra (Appendix A script):

- vector spaces and scalar products
- Representation of a vector in a general basis
- operators in matrix representation
- Eigenvalues and eigenstates

Chapter 2: Repetition of Basic Concepts of Quantum Mechanics

Atomic Units

https://en.wikipedia.org/wiki/Atomic_units