Introduction to
Electronic Structure Methods

http://lcbc.epfl.ch/roethlisberger

Fall Semester 2017

19 September - 19 December
Course: BCH 4119
Computer Exercises: BCH 1113

Lecturer:

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Demos/Exercises:

Ariadni Boziki
Thibaud von Erlach
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/roethlisberger](http://lcbc.epfl.ch/roethlisberger) teaching

Illustrations:
- exercises (analytical and computational)
- copy of the slides

- supplementary literature (optional):
  Szabo and Ostlund: *Modern Quantum Chemistry*  
  (pdfs available online)

Time Table

<table>
<thead>
<tr>
<th>Time Frame</th>
<th>Activities</th>
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<tbody>
<tr>
<td>First 7 weeks (≤ 7 Nov)</td>
<td>4h course (BCH4119) (Tue&amp;Fri)</td>
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<tr>
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<td>2h exercises (BCH4119/BCH1113) (Fri)</td>
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<tr>
<td>2nd 7 weeks (7 Nov – 5 Dec)</td>
<td>2h exercises (BCH1113) (Tue)</td>
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Written Exam: Tue 17 Oct: 15-17:00  
Oral Exams: Tue 12 & Tue 19 Dec
<table>
<thead>
<tr>
<th>Date</th>
<th>Day</th>
<th>Time</th>
<th>Topic</th>
<th>Exercises</th>
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<tbody>
<tr>
<td>10.9</td>
<td>Tue</td>
<td>course</td>
<td>practical info, repetition basic QM concepts</td>
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<tr>
<td>22.9</td>
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<td>course</td>
<td>repetition linear algebra</td>
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<td>Hartree-Fock I</td>
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<td>Exercise 2: H Atom: HF calcs in G09</td>
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<td>Demo Hartree-Fock/Basis Sets</td>
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<td>Exercise 3: Basis sets, De, geom opt.</td>
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<td>Configuration Interaction</td>
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<td>Many-Body Perturbation Theory</td>
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<td>Coupled Cluster</td>
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<td>Density Functional Theory I</td>
<td>Exercise 5 &amp; 6.1: Trouble Shooting, Pitfalls, traps</td>
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<td>Exercise 8.1: TS &amp; Barrier Heights</td>
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**Basis:**
- mathematics I&II, physics I&II, Informatics I, applied mathematics, probability & statistics, Quantum mechanics

**Cheminformatics Module:**
- Introduction to electronic structure methods
- Classical Molecular Dynamics and Monte Carlo Simulations
- Project in Computational Chemistry
- Cheminformatics
  - Luc Patiny
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 package (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 of Computer Power

Evolution in Quantum Chemistry
Chapter 1:

Introduction to computational quantum chemistry

**Computational Quantum Chemistry**

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

- Lowest energy structure(s)?
- Vibrational properties (IR and Raman spectra)
- Dipole and quadrupole moments
- Proton affinity, pK<sub>a</sub>, 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
Erwin Schrödinger (1887-1961)

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

quantum mechanics

$\Psi$

Once $\Psi$ is known, all properties of the system can be calculated

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

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

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

$\Psi_{\text{nuc}}(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N, t) = \Psi_{\text{nuc}}(\vec{R}, t)$

The wavefunction is determined through the Schrödinger equation:

Electronic Schrödinger equation

Ex. 1

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

Ex. 2

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

$\rightarrow$ only Coulomb forces!

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

<table>
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<th>Force Type</th>
<th>Strength</th>
<th>Range (m)</th>
<th>Particle</th>
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<td>Strong</td>
<td>1</td>
<td>$10^{-15}$</td>
<td>$\pi$, others mass &gt; 0.1 GeV</td>
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<tr>
<td>Electro-magnetic</td>
<td>$\frac{1}{137}$</td>
<td>Infinite</td>
<td>Photon mass = 0 spin = 1</td>
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<tr>
<td>Weak</td>
<td>$10^{-5}$</td>
<td>$10^{-17}$</td>
<td>Intermediate vector bosons W^+, W^-, Z^0, mass &gt; 60 GeV spin = 1</td>
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<tr>
<td>Gravity</td>
<td>$6 \times 10^{-39}$</td>
<td>Infinite</td>
<td>Graviton? mass = 0 spin = 2</td>
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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
- semiemirical methods: some terms are approximated or parameterized by empirical data

Possible approximations:

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

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<th>Package</th>
<th>MM</th>
<th>Semi-Empirical</th>
<th>HF</th>
<th>Post-HF</th>
<th>DFT</th>
<th>Ab-initio MD</th>
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<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
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</table>
Problem to solve:

Solution of the
- electronic
- time-independent
- non relativistic

Schrödinger equation for many electron systems:

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

$$\mathcal{H} = \sum_{i}^{N}(-\frac{1}{2}\nabla_{i}^{2} - \sum_{I} Z_{I} \frac{1}{r_{ii}}) + \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$

$$\mathcal{H} = \mathcal{H}_{1} + \mathcal{H}_{2}$$

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