Introduction to
Electronic Structure Methods

http://lcbc.epfl.ch/
Teaching

Fall Semester 2019

17 September - 17 December
Course: BCH 3303/4310
Computer Exercises: BCH 1113

Lecturer:
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BCH 4109
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Demos/Exercises:
Matthias Dankl
François Mouvet
Justin Villars
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/](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)

Time Table

- First 7 weeks (≤ 5 Nov):
  - 4h course (BCH3303/4310) (Tue&Fri)
  - 2h exercises (BCH1113) (Fri)
- 2nd 7 weeks (5 Nov – 3 Dec):
  - 2h exercises (BCH1113) (Tue)

Written Exam: Tue 15 Oct: 8:15-10:00
Oral Exams: Tue 10 & 17 Dec
<table>
<thead>
<tr>
<th>Date</th>
<th>Day</th>
<th>Time</th>
<th>Course/Exercise</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.9</td>
<td>Tue</td>
<td>17.00</td>
<td>practical info, repetition basic QM concepts</td>
</tr>
<tr>
<td>20.9</td>
<td>Fri</td>
<td>17.00</td>
<td>repetition linear algebra</td>
</tr>
<tr>
<td>24.9</td>
<td>Tue</td>
<td>17.00</td>
<td>Enhancement of basic QM concepts</td>
</tr>
<tr>
<td>27.9</td>
<td>Fri</td>
<td>17.00</td>
<td>Exercise 1: Linear Algebra in Quantum Mechanics</td>
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<tr>
<td>01.10</td>
<td>Tue</td>
<td>17.00</td>
<td>Hartree-Fock I &amp; Demo Hartree-Fock/Basis Sets</td>
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<tr>
<td>04.10</td>
<td>Fri</td>
<td>17.00</td>
<td>Exercise 2: Hartree-Fock II</td>
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<tr>
<td>08.10</td>
<td>Tue</td>
<td>17.00</td>
<td>Hartree-Fock II &amp; Basis Sets</td>
</tr>
<tr>
<td>11.10</td>
<td>Fri</td>
<td>17.00</td>
<td>Questioning hour &amp;旧 papers</td>
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<tr>
<td>15.10</td>
<td>Tue</td>
<td>17.00</td>
<td>Written Exam</td>
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<tr>
<td>18.10</td>
<td>Fri</td>
<td>17.00</td>
<td>Coupled Cluster</td>
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<tr>
<td>22.10</td>
<td>Tue</td>
<td>17.00</td>
<td>Density Functional Theory I</td>
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<tr>
<td>25.10</td>
<td>Fri</td>
<td>17.00</td>
<td>DFT II (CP QM/MM &amp; Demos)</td>
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<tr>
<td>29.10</td>
<td>Tue</td>
<td>17.00</td>
<td>Exercise 5.1: Trouble shooting, pitfalls, traps</td>
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<tr>
<td>01.11</td>
<td>Fri</td>
<td>17.00</td>
<td>Exercise 4.2: HF vs MPn &amp; CI</td>
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<tr>
<td>05.11</td>
<td>Tue</td>
<td>17.00</td>
<td>Exercise 6.2 (continued)</td>
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<tr>
<td>12.11</td>
<td>Tue</td>
<td>17.00</td>
<td>Exercise 7: PES scans &amp; trajectory visualization</td>
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<tr>
<td>19.11</td>
<td>Tue</td>
<td>17.00</td>
<td>Exercise 8.1: TS &amp; Barrier heights</td>
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<tr>
<td>26.11</td>
<td>Tue</td>
<td>17.00</td>
<td>Exercise 8.2 (assistants)</td>
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<tr>
<td>03.12</td>
<td>Tue</td>
<td>17.00</td>
<td>Question hour</td>
</tr>
<tr>
<td>10.12</td>
<td>Tue</td>
<td>17.00</td>
<td>Oral exams</td>
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<tr>
<td>17.12</td>
<td>Tue</td>
<td>17.00</td>
<td>Oral exams</td>
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</tbody>
</table>

**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
- Elements of Cheminformatics Luc Patiny
- Project in Computational Chemistry

**Chemistry:**

- Chemistry I
- Chemistry II
- Informatics I
- Applied mathematics
- Probability & Statistics
- Quantum mechanics
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 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, $pK_a$, 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
Chemical Properties Determined by Electronic Structure

- wave nature determined by de Broglie wavelength

\[ \lambda = \frac{h}{\sqrt{2mE}} \]

\[ \frac{\lambda_{el}}{\lambda_p} \approx 40 \]

\[ \Psi (\vec{r}_1, \vec{r}_2, ..., \vec{r}_n, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N, t) \]

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

\[ \Psi_{\text{elec}} (\vec{r}_1, \vec{r}_2, ..., \vec{r}_n, t) = \Psi_{\text{elec}} (\vec{\bar{r}}, t) \]

many-electron wavefunction for fixed nuclear position

\[ \Psi_{\text{nuc}} (\vec{R}_1, \vec{R}_2, ..., \vec{R}_N, t) = \Psi_{\text{nuc}} (\vec{\bar{R}}, t) \]

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

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

For time-dependent case

Hamilton operator

\[ \hat{H}_{\text{elec}} = \hat{\mathbf{E}} + \hat{V}_{\text{elec}} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \hat{V}_{\text{elec}} \]

Ex. 1

Ex. 2

What fundamental forces?

→ 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>
<thead>
<tr>
<th>Force</th>
<th>Strength</th>
<th>Range (m)</th>
<th>Particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td></td>
<td>1</td>
<td>π, others ( m &gt; 0.1 \text{ GeV} )</td>
</tr>
<tr>
<td>Electro-magnetic</td>
<td></td>
<td>1/137</td>
<td>photon ( m = 0 ), spin = 1</td>
</tr>
<tr>
<td>Weak</td>
<td></td>
<td>( 10^{-5} )</td>
<td>intermediate ( m &gt; 80 \text{ GeV} ), spin = 1</td>
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<tr>
<td>Gravity</td>
<td></td>
<td>( 6 \times 10^{-39} )</td>
<td>graviton? ( m = 0 ), spin = 2</td>
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</table>

http://hyperphysics.phy-astr.gsu.edu/hbase/forces/funfor.html
<table>
<thead>
<tr>
<th>Exercises</th>
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<tbody>
<tr>
<td>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 Å 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?</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exercises</th>
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</thead>
<tbody>
<tr>
<td>Ex1. Derive the general form of the Hamilton operator starting from the classical description.</td>
</tr>
</tbody>
</table>
**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))

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**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

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![Image of molecular structure]
### Software Packages

<table>
<thead>
<tr>
<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>
<th>Periodic</th>
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<td>Y</td>
<td>Y</td>
<td>Y</td>
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<td>N</td>
</tr>
</tbody>
</table>

### Problem to solve:

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

  **Schrödinger equation for many electron systems:**

  \[ \mathcal{H}\Psi = E\Psi \]

  \[ \mathcal{H} = \sum_i^N (-1/2\nabla_i^2 - \sum_j Z_j) + \sum_i^N \sum_{j>i}^{N} \frac{1}{r_{ij}} \]

  \[ \mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \]
Concepts that you know already and that we are going to use:

**Quantum Mechanics (Chapter 2 script):**
- atomic units
- 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

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**Chapter 2: Repetition of Basic Concepts of Quantum Mechanics**

**Atomic Units**