

Introduction to Electronic Structure Methods

Fall Semester 2024

Course webpage: <https://moodle.epfl.ch/course/view.php?id=14818>

Exercises: <https://lcbc-epfl.github.io/iesm-public/intro.html>



09 September - 17 December

Recorded lectures 2021:

<https://mediaspace.epfl.ch/channel/CH-353+Introduction+to+electronic+structure+methods/29640>

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Lecturer:

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Marks

- computer exercises (1/3)
- written exam at mid semester (1/3)
- written exam at the end of the semester (1/3)

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Course Support

Format:

- powerpoint slides & blackboard
- (Recorded lectures from 3 years ago available online)

Documentation:

script: Introduction to Electronic Structure Methods
<https://moodle.epfl.ch/course/view.php?id=14818>

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).

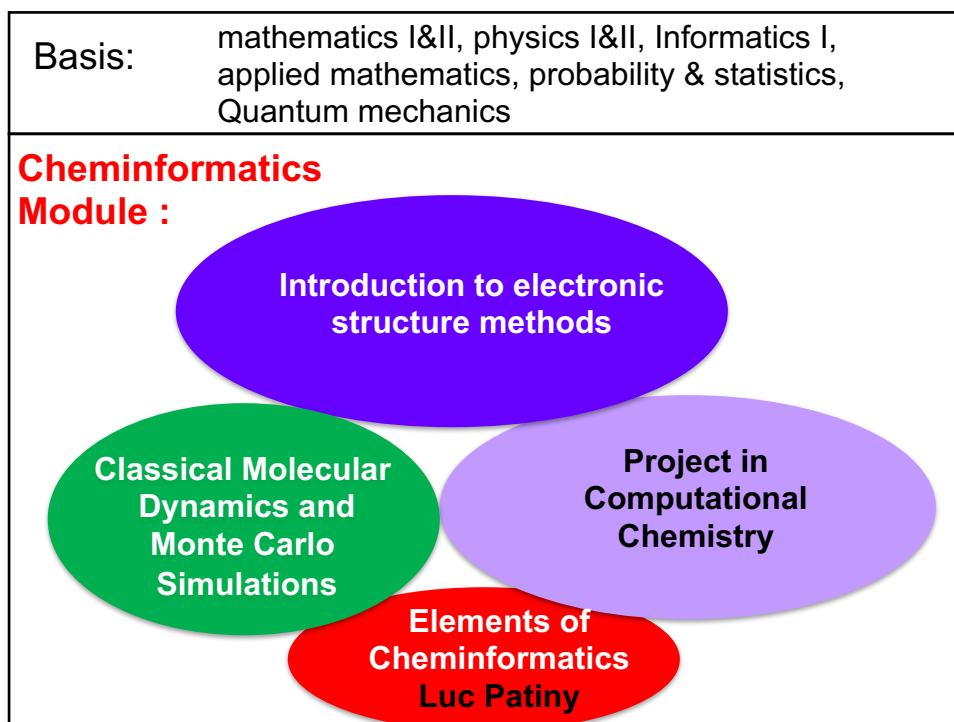
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Time Table
2h course/ 2h exercises (Mon& Tue 10:15-12h) courses BCH 3303/ exercises BCH 1113
Written Exam I: Mon 28 Oct 10:15-12h (about 1st half of material: script chapters ≤ 4) Written Exam II: Mon 16 Dec 10:15-12h (about 2nd half of material: script chapters ≥ 5)

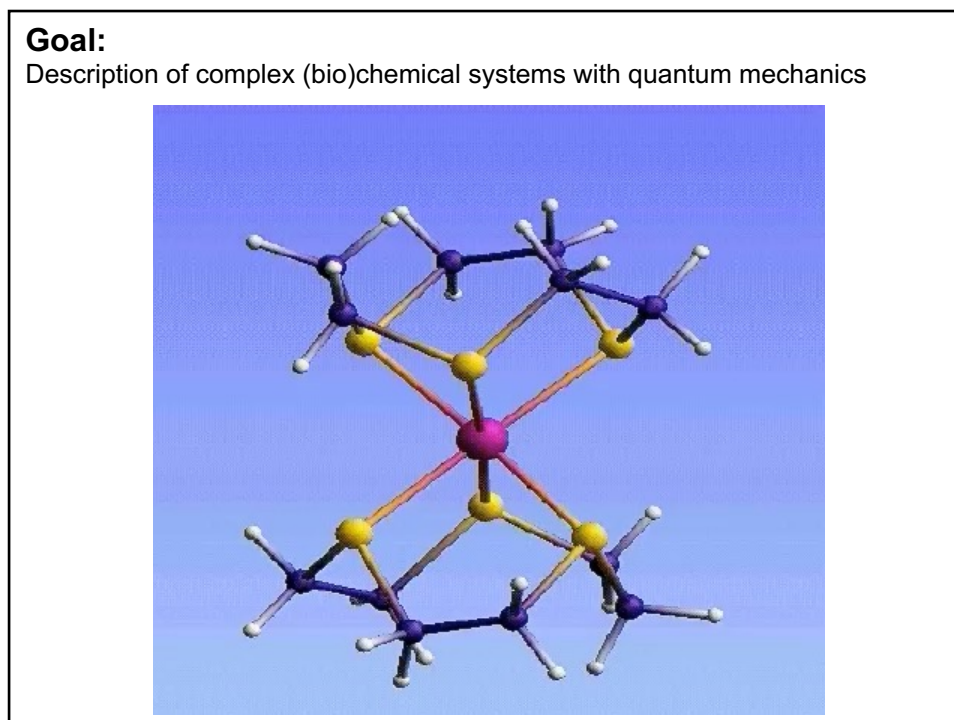
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Time Table for the Course 'Introduction to Electronic Structure Methods' Fall Semester 2024			
09.09.	Mon	exercises	Exercise 1: Linear Algebra in Quantum Mechanics
10.09	Tue	course	practical info
16.09.	Mon	--	jeûne fédéral
17.09.	Tue	course	Basis Sets I
23.09.	Mon	course	Basis Sets II
24.09.	Tue	exercises	Exercise 2: Intro Linux/Noto.epfl.ch & Psi4: H Atom: HF calcs in Psi4
30.09	Mon	course	Hartree-Fock I
01.10.	Tue	exercises	Exercise 3: Basis sets, De, geom opt.
07.10.	Mon	course	Hartree-Fock II
08.10.	Tue	exercises	Exercise 4: Hartree Fock procedure in detail
14.10.	Mon	exercises	mock exam with old written exam
15.10.	Tue	exercises	solutions of mock exam & questioning hour
21.10.	Mon		fall break – no classes
22.10.	Tue		fall break – no classes
28.10.	Mon		written exam I
29.10	Tue	course	Configuration Interaction
04.11.	Mon	course	Many-Body Perturbation Theory
05.11	Tue	exercises	Exercise 5: Post HF: MPn & CI
11.11.	Mon	course	Coupled Cluster Theory
12.11.	Tue	exercises	Exercise 6: DFT vs HF/MP2
18.11	Mon	course	Multireference Methods
19.11.	Tue	course	Density Functional Theory I
25.11	Mon	exercises	Exercise 7: Trouble Shooting, Pitfalls, traps
26.11.	Tue	course	DFT II
02.12.	Mon	exercises	Exercise 8: PES Scans
03.12.	Tue	course	DFT III (CP, QM/MM, Demos) & Summary
09.12.	Mon	exercises	Exercise 9: Transition States
10.12	Tue	exercises	Q&A session
16.12	Mon		written exam II

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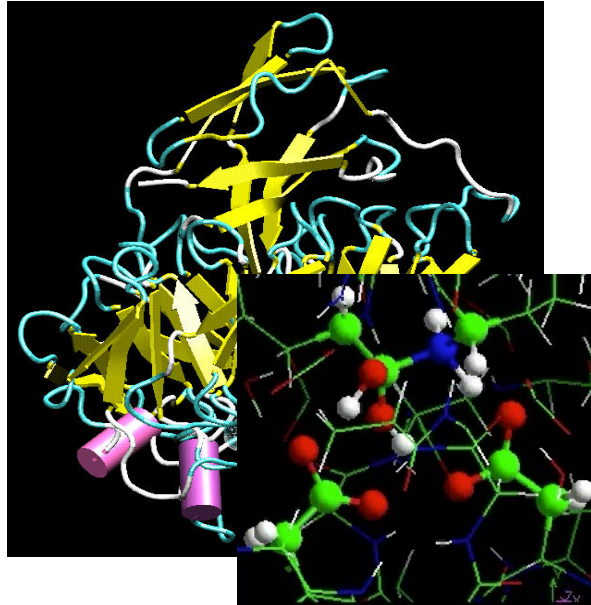
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Goal:

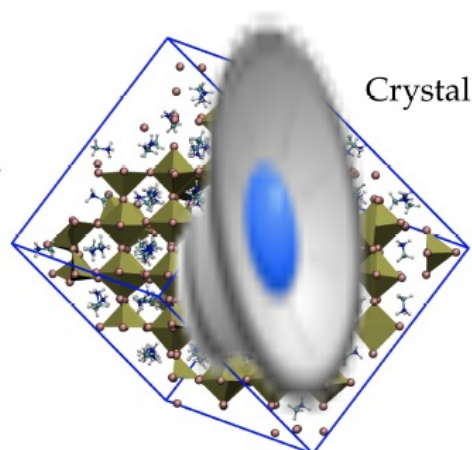
Description of complex (bio)chemical systems with quantum mechanics



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Goal:

Description of complex materials with quantum mechanics



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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
 - What method/basis set should be used for a given problem?
- Get to know one open-source quantum chemical software package (PSI4)
 - How to generate inputs
 - How to run calculations
 - How to interpret outputs
- Computational Chemistry as standard tool in Chemistry

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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.



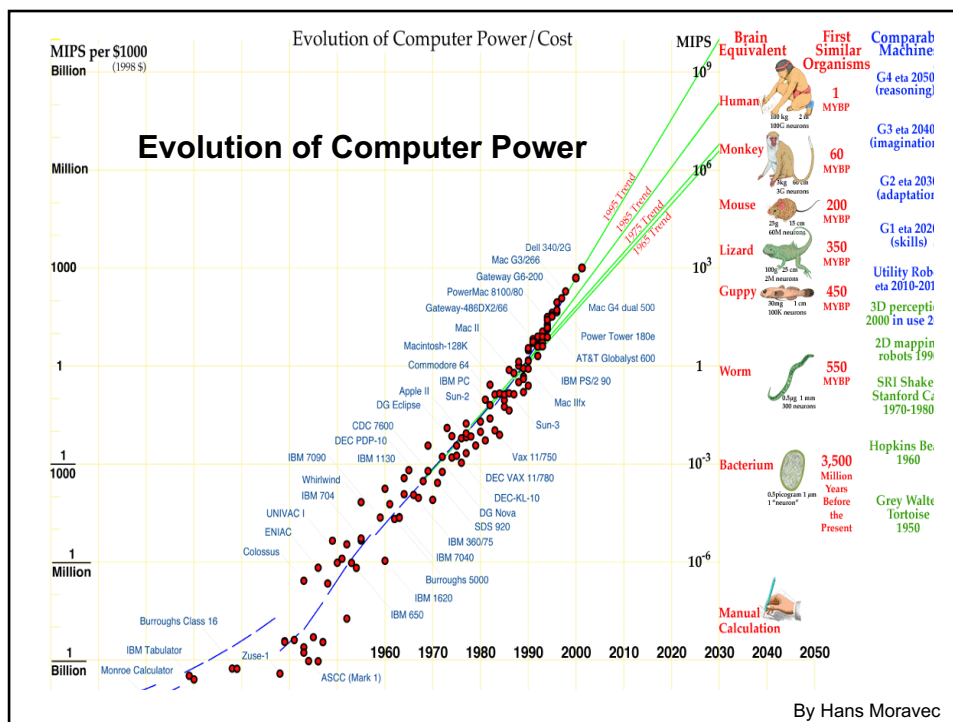
Paul Dirac (1902-1984)

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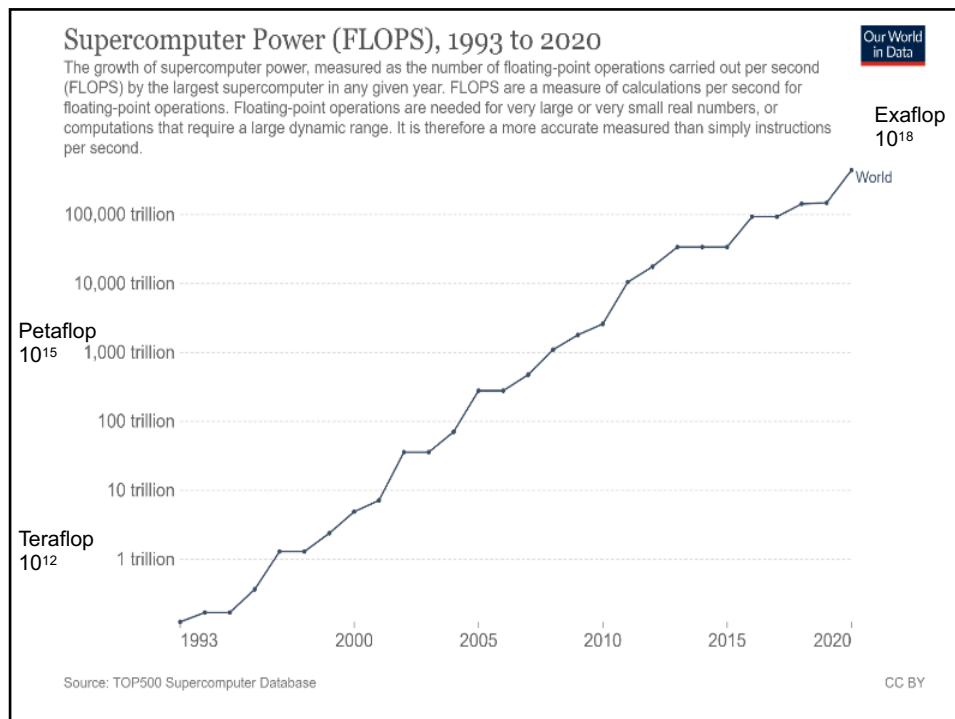
Quiz I: Exactly Solvable Quantum Systems

- 1) Which exactly solvable quantum systems do you know?
- 2) For each system:
 - a) What is the Hamiltonian?
 - b) What is the general form of the wavefunction?
 - c) How do the energy eigenvalues depend on the quantum numbers?

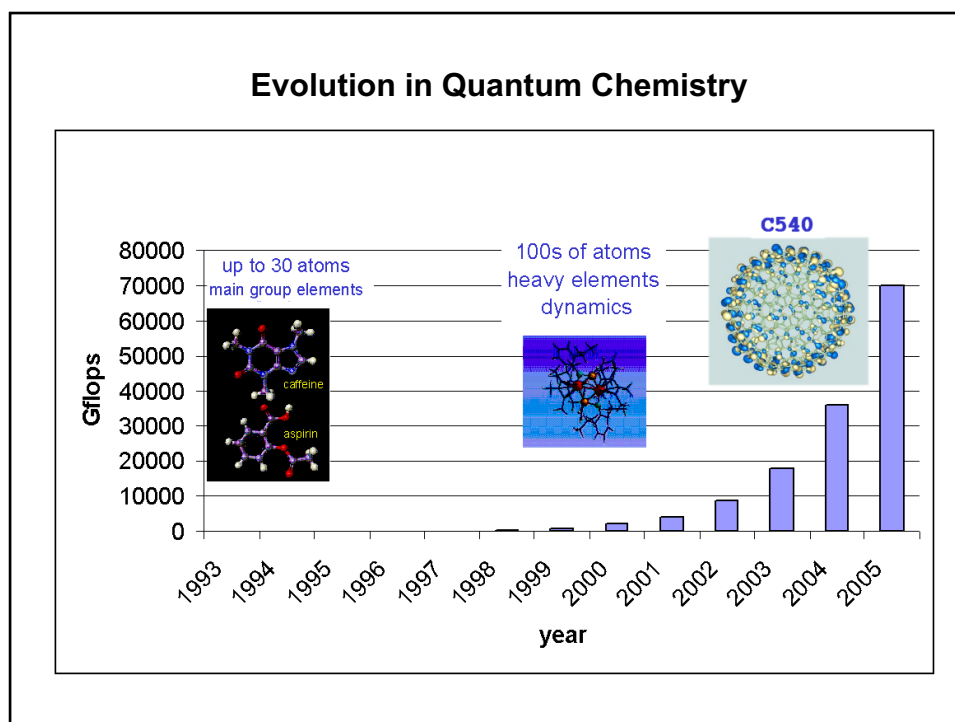
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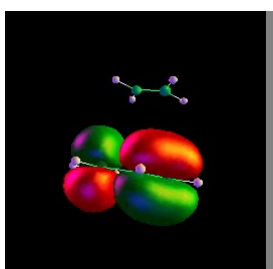
Chapter 1:

Introduction to computational quantum chemistry

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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

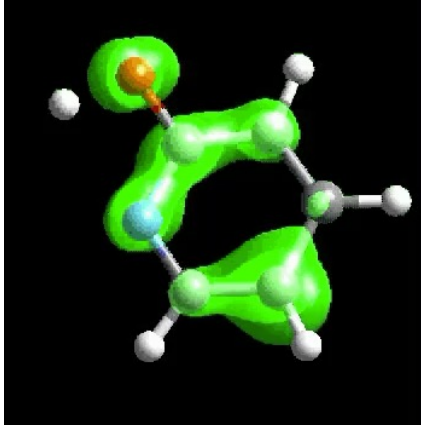
Quantum Chemistry

applies quantum mechanics to describe chemical systems

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Chemical Properties are Determined by Electronic Structure

- wave nature determined by de Broglie wavelength λ



$$\lambda = \frac{h}{\sqrt{2mE}}$$

h: Planck constant
m: mass
E: Energy

$$\frac{\lambda_{el}}{\lambda_p} = \left(\frac{m_p}{m_{el}} \right)^{1/2} \approx 40$$

Examples:

- Photon with 1eV $\Rightarrow$ 1000nm = 1 μ m
- Electron with 1eV energy $\Rightarrow$ ca. 1nm = 10⁻⁹m
- Proton with 1eV energy $\Rightarrow$ 1/40nm = 0.25Å
- Person 80kg walking with 1m/s $\Rightarrow$ 10⁻³⁵m

$\Leftrightarrow$ Compared to typical interatomic distances
1Å = 0.1nm

$\Rightarrow$ Need quantum mechanics to describe electrons!

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quantum mechanics

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

Erwin Schrodinger
(1887-1961)

Ψ

wavefunction of this system

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

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

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

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

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

many-electron wfct
for fixed nuclear position

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

nuclear wfct

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

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

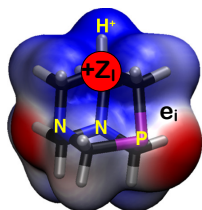
For time-
dependent
case

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

time independent

Hamilton operator

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



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Quiz II: Molecular Hamiltonian

- 1) What kind of fundamental forces do you know? What is their interaction range and approximate relative strength?
- 2) 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?
- 3) Derive the general form of the Hamilton operator starting from the classical description.

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Fundamental Forces					
Strong		Force which holds nucleus together	Strength 1	Range (m) 10^{-15} (diameter of a medium sized nucleus)	Particle π , others mass > 0.1 GeV
Electro-magnetic			Strength $\frac{1}{137}$	Range (m) Infinite	Particle 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			Strength 6×10^{-39}	Range (m) Infinite	Particle graviton ? mass = 0 spin = 2

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

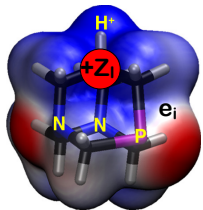
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The wavefunction is determined through the **Schrödinger equation**:
Electronic Schrödinger equation

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

For time-dependent case

Hamilton operator



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

$\hat{V}_{elec}$?

→ **only Coulomb forces!**

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

time independent

$$\hat{H}_{elec} = -\frac{\hbar^2}{2m_e} \sum_n \vec{\nabla}_n^2 - \frac{1}{4\pi\epsilon_0} \sum_n \sum_I \frac{e^2 Z_I}{|\vec{R}_I - \vec{r}_n|} + \frac{1}{4\pi\epsilon_0} \sum_{n < m} \frac{e^2}{|\vec{r}_m - \vec{r}_n|}$$

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 or from first-principles

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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

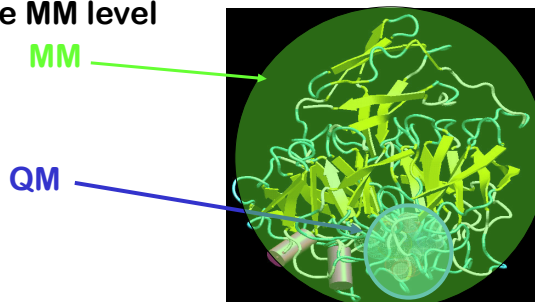
Possible approximations:

- **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 interaction (CI, 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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QC Software packages

	Written in	License	MM	Semi-empirical	Post-HF	Ab initio MD	Periodic	QM/MM
Psi4	C, C++, Python	Free, GPL	✗	✗	✓	✗	✗	(✓)
Gaussian	Fortran	\$2,420	✓	✓	✓	✗	✓	✓
Cp2k	Fortran	Free, GPL	✓	✓	✓	✓	✓	✓
CPMD	Fortran	Free for academics	✓	✗	✗	✓	✓	✓
Orca	C++	Free for academics	✓	✓	✓	✓	✗	✓
Gamess-US	Fortran	Free, GPL	✗	✓	✓	✗	✗	✓
Q-Chem	Fortran, C, C++	\$ 3899	✓	✓	✓	✓	✗	✓
Mopac7	Fortran	Free, Public domain	✗	✓	✗	✗	✗	✗
Turbomole	Fortran	500 Euro	✗	✗	✓	✓	✓	✓

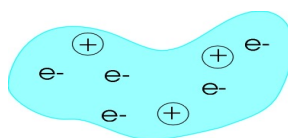
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Problem to solve:



Solution of the

- **electronic**
- **time-independent**
- **non relativistic**



Schrödinger equation for many electron systems:

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

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

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

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

Quantum Mechanics (script Chapter 2):

- 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 (script Appendix A):

- 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 from Quantum Mechanics

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

Quantum Mechanics (script Chapter 2):

- atomic units
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Quiz III: Atomic Units

- 1) What are the atomic units for
 - a) mass?
 - b) charge?
 - c) length?
 - d) energy?
 - e) time?
 - f) What is the value of the reduced Planck constant in atomic units?
 - g) What is the expression $4\pi\epsilon_0$ in atomic units?
- 1) Write down the molecular Hamiltonian given in Slide 23 in atomic units

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Chapter 2: Repetition of Basic Concepts of Quantum Mechanics

1) Atomic Units

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

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

Quantum Mechanics (script Chapter 2):

- 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 (script Appendix A):

- vector spaces and scalar products
- Representation of a vector in a general basis
- operators in matrix representation
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Quiz IV: Operators and Matrices

- 1) What is a Hermitian operator/matrix?
- 2) What is a Unitary operator/matrix?
- 3) What is the equivalent of 1) and 2) in real numbers?
- 4) Why are the eigenvalues of a Hermitian operator real?
- 5) Repetition:
 - a) Write down a projection operator to a basis function ϕ_i
 - b) Write down the completeness relation in the basis ϕ_i

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Quiz V: Vector Spaces

- 1) What are the mathematical rules that define a vector space
 - a) For addition?
 - b) For scalar multiplication?
- 2) Do you know any mathematical functions that form a complete basis?

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