

CHM 673

Computational Quantum Chemistry

Instructor: Prof. Lyudmila Slipchenko lslipchenko@purdue.edu, WTHR 265H

Office hours: Th 12:00-1:00 pm & by appointment, WTHR 265H

Brightspace: Lecture materials, Assignments, Scores, Grades

Zoom: <https://purdue-edu.zoom.us/j/97501886261>

Passcode: chm673

Quizzes, Labs, Homeworks and Exams

Weekly quizzes on Tuesdays in class

Labs, Homeworks, Python exercises:

due Tuesday midnight on BrightSpace or on paper in class

Midterm: week 8 (March 1st or March 3rd)

Independent computational project:

- Draft of the idea (due week 4)
- Finalized plan (due week 6)
- Report of original calculations (due week 10)
- Final report
- Project presentation in class (week 15)

No final exam!

Grades:

- Lab and homework assignments: 40%
- Midterm: 20%
- Project: 30%
- Weekly quizzes and class participation: 10%

Textbooks

Required

- F. Jensen, *Introduction to Computational Chemistry*, (Wiley, New York, 2017)
- A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*, 1st ed., revised (Dover, 1996)

Optional

- J. Schrier, *Introduction to Computational Physical Chemistry*, (University Science Books, 2017)

Molecular simulations

Dedicated Purdue RCAC resource: “Scholar” cluster

Software:

- Q-Chem (<https://www.q-chem.com>) via iQmol (<http://iqmol.org>) molecular viewer and job editor
- Psi4 (<https://psicode.org/>)

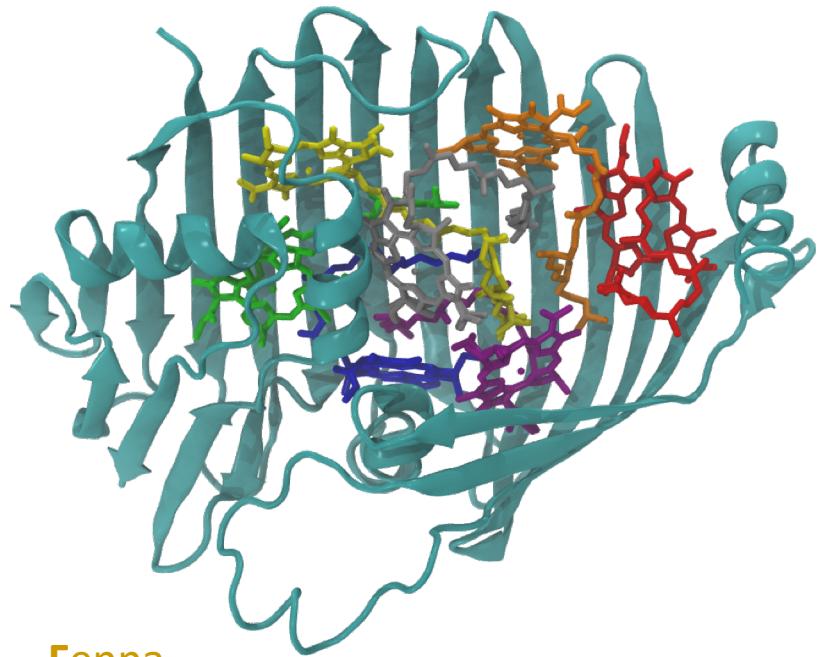
Other software packages can be used/recommended for working on independent project

Course content

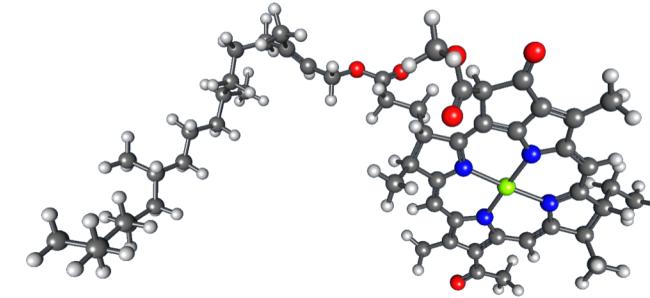
- Fundamentals of molecular simulations:
 - Schrodinger equation, Born-Oppenheimer approximation
- Molecular potential energy surfaces; modeling chemical reactions
- Basic approximation: Hartree-Fock theory
- Toward chemical accuracy: taking care of electron correlation:
 - Configuration interaction, perturbation theory, coupled cluster methods
- Density functional theory
- Chemistry of open-shells and excited states:
 - multireference methods, methods for excited states, TD-DFT
- Modeling large and periodic systems:
 - Solvation models, QM/MM, fragmentation methods

Who am I?

Photochemistry of plants



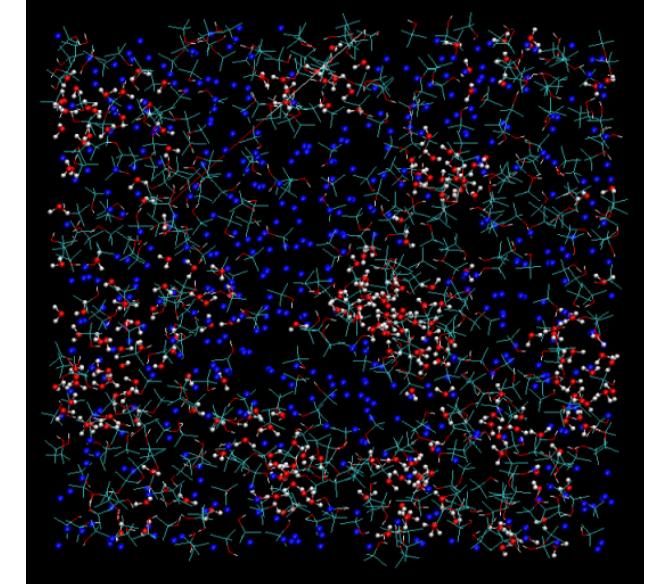
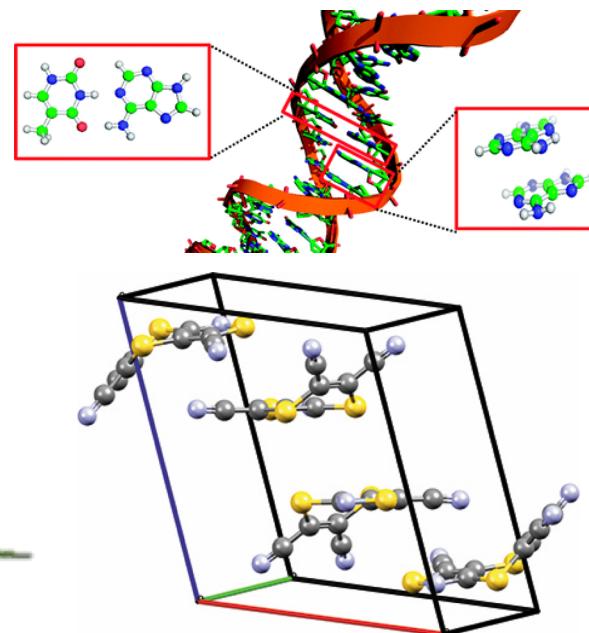
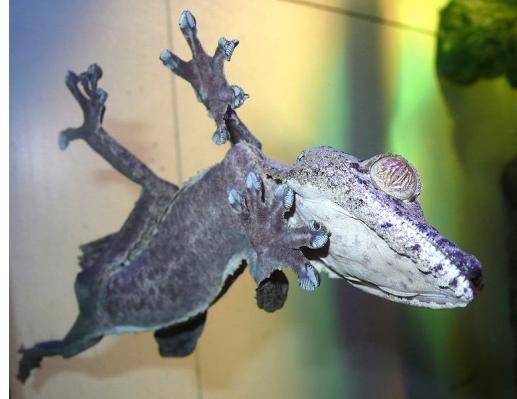
Fenna-
Matthews-
Olson
protein



- How the light is absorbed? - absorption of chlorophylls and carotenoids in specific protein environment
- How the absorbed photon is transferred to the reaction pair? - energy transfer along a chain of chlorophylls
- How the excitation energy is converted to electron-proton pair? - water splitting reactions
- How a plant is protected against excess of solar radiation? - excitation energy dissipation

Who am I?

Intermolecular interactions



- Structure and binding in molecular clusters
- Structure and dynamics in complex liquids
- Crystal structure prediction for pharma

Who are you? (Quiz 0)

- Name
- Department / year / group
- Research interests
- Describe your experience in quantum mechanics / relevant coursework
- Describe your experience in programming (computer languages, coursework, fulfilled tasks, typical usage)
- Are you familiar with Python, and to what extent?
- Describe your experience in molecular simulations
- What do you want to learn from this course / which topics are of particular interest

Course outcomes

After this course you will:

- Know / recognize main notations (electronic structure "soup": names and acronyms of methods and basis sets)
- Understand main challenges and main limitations of electronic structure calculations
- Know expected accuracy of commonly used methods
- Recognize common problems in running electronic structure calculations and be able to resolve them
- Be able to select appropriate methodology for system of interest

I hope that after this course you also learn:

- Be critical about any number the computer produces
- Not to trust any calculations

What is computational quantum chemistry?

Objects of quantum mechanics (QM): atoms, electrons and interactions between them:

- ~~nuclear physics (radiation 10^2 H, annihilation 10^4 H)~~
- Electron ionization, electron excitation, molecular dissociation and chemical reactions ($0.001 - 0.1$ H)
- Molecular vibrations ($10^{-3} - 10^{-2}$ H)
- Molecular rotations ($10^{-6} - 10^{-4}$ H)
- Interactions of electron and nuclear spins ($< 10^{-4}$ H)

1 Hartree (H) = 1 a.u. =
27.212 eV =
627.51 kcal/mol =
 4.36×10^{-18} J =
 2.195×10^5 cm⁻¹ =
 3.158×10^5 K

Energy of H atom: -0.5 Hartree

Energy of ethylene C₂H₄: ~-80 Hartree

We need to capture relatively small changes of total molecular energies:

Electronic structure calculations need to be conducted with extremely high level of accuracy!

Molecular simulations

Electronic structure theory

/ Quantum Chemistry

Solves for motion of electrons in molecules; provides static properties of individual molecules and potential energy surfaces

Molecular dynamics

Solve for motions of molecules on a (quantum or classical) potential energy surface; provides reaction rates

Statistical Mechanics

Solve for bulk properties from properties of individual molecules

Quantum and classical molecular simulations

Molecules consist of nuclei & electrons ->
Laws describing interactions of electrons ->
Quantum mechanics (QM)

Electrons are represented by wave function ->
Schrodinger eqn (1925)

----->
Electronic motion is parameterized :
Force fields (FF)

Molecules consist of atoms (classical particles) ->
Laws describing motion of classical particles ->
Classical or molecular mechanics (MM)

Newton's laws of motion (1687)

Quantum	Classical
More accurate	Less accurate
Equations more complicated	Equations less complicated
Computationally very expensive (typically cannot do dynamics)	Computationally less expensive (can do dynamics)
Can describe motion of electrons: UV/vis spectra, electron transfer, etc	Cannot describe motion of electrons
No empirical parameters or only a few (e.g. DFT)	Involves many empirical parameters

Nobel prizes in computational chemistry

1966



Robert S. Mulliken

“...the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand.”

1998

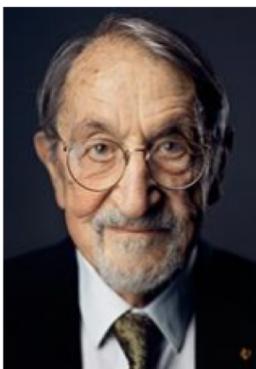


Walter Kohn
for development of
density-functional
theory



John Pople
for development of
computational
methods in quantum
chemistry

2013



Martin Karplus



Michael Levitt



Arieh Warshel

for the development of
multiscale models for
complex chemical systems

Schrödinger equation (1925-1926)

Time-dependent Schrödinger equation (general)

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$$

Time-independent Schrödinger equation (general)

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

Time-independent Schrödinger equation (single non-relativistic particle)

$$E\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r})$$

Analytically solved for few cases:
particle in a box, harmonic oscillator, H atom...
Other systems: numerical solutions



Molecular non-relativistic Hamiltonian

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

$$\hat{H} = \hat{T}_N(R) + \hat{T}_e(r) + \hat{V}_{NN}(R) + \hat{V}_{eN}(r, R) + \hat{V}_{ee}(r)$$

$$\hat{T}_N = - \sum_A^{nuc} \frac{\hbar^2}{2M_A} \nabla_A^2$$

kinetic energy of nuclei

$$\hat{T}_e = - \frac{\hbar^2}{2m} \sum_i^{elec} \nabla_i^2$$

kinetic energy of electrons

$$\hat{V}_{NN} = \sum_{A>B}^{nuc} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

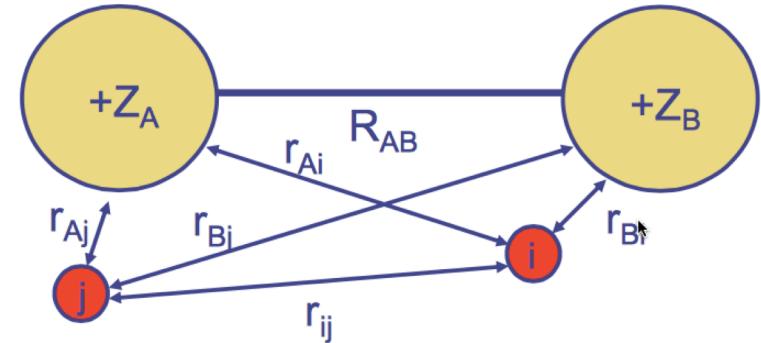
potential energy of nuclei

$$\hat{V}_{eN} = - \sum_i^{elec} \sum_A^{nuc} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}}$$

potential energy of interactions of nuclei and electrons

$$\hat{V}_{ee} = \sum_{i>j}^{elec} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

potential energy of electrons



Atomic units (a.u. or au)

Reduced Planck constant: $\hbar = 1$ also known as the **atomic unit of action**

Elementary charge: $e = 1$ also known as the **atomic unit of charge**

Bohr radius: $a_0 = 1$ also known as the **atomic unit of length**

Electron mass: $m_e = 1$ also known as the **atomic unit of mass**

Energy: $E_h = 1$ **Hartree energy**

Molecular non-relativistic Hamiltonian in atomic units

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

$$\hat{H} = \hat{T}_N(R) + \hat{T}_e(r) + \hat{V}_{NN}(R) + \hat{V}_{eN}(r, R) + \hat{V}_{ee}(r)$$

$$\hat{T}_N = -\sum_i \frac{1}{2M_A} \nabla_A^2$$

kinetic energy of nuclei

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2$$

kinetic energy of electrons

$$\hat{V}_{NN} = \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}$$

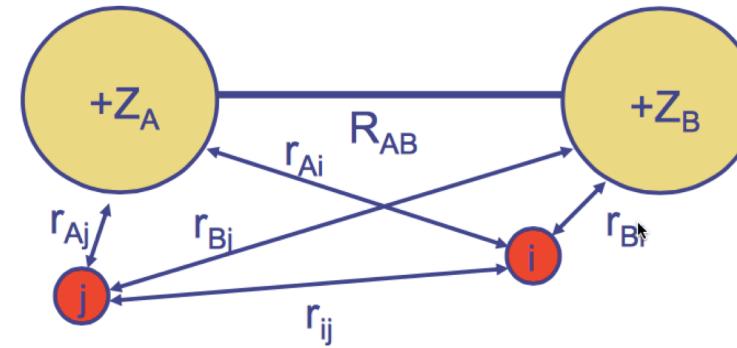
potential energy of nuclei

$$\hat{V}_{eN} = -\sum_{A,i} \frac{Z_A}{r_{Ai}}$$

potential energy of interactions of nuclei and electrons

$$\hat{V}_{ee} = \sum_{i>j} \frac{1}{r_{ij}}$$

potential energy of electrons



What can we learn from solving SE?

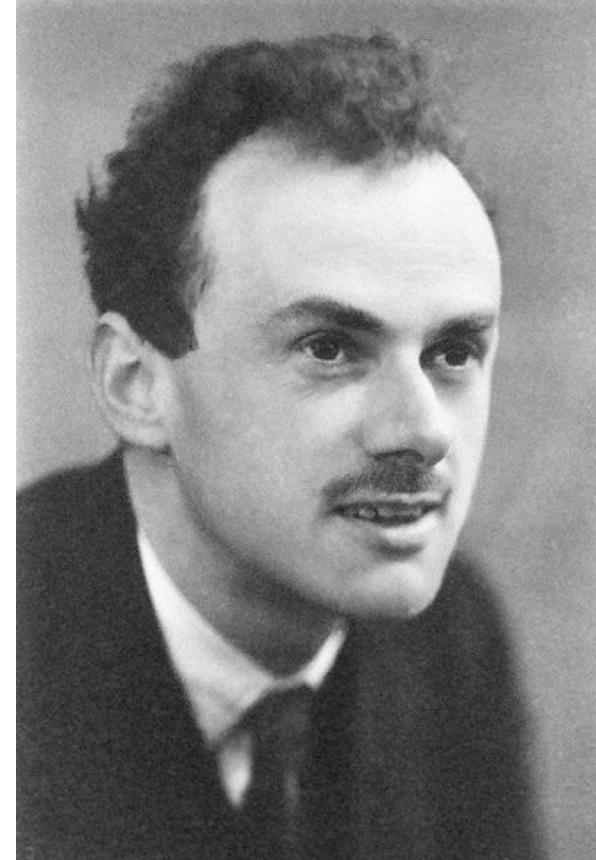
- Geometrical structures (rotational spectra)
- Rovibrational energy levels (infrared and Raman spectra)
- Electronic energy levels (UV and visible spectra)
- Quantum Mechanics + Statistical Mechanics → Thermochemistry (ΔS , ΔH , ΔG , C_v , C_p)
- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics → reaction rates and mechanisms
- Ionization potentials (photoelectron and X-ray spectra)
- Electron affinities
- Franck-Condon factors (transition probabilities, vibronic intensities)
- IR and Raman intensities
- Dipole moments
- Polarizabilities
- Electron density maps and population analyses
- Magnetic shielding tensors → NMR spectra

All structural and energetic information
on a molecular system

Good news / bad news

“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.”

P.A.M. Dirac,
Proc. Roy. Soc. (London), 123 714 (1929)



Numerical solution of SE: art of approximations

Approximations:

- Born-Oppenheimer approximation
- Representation of wave function in a basis set
- Approximate treatment of electron correlation (interactions between electrons)