Computational Modeling of Nanosystems

TD5 – DFT & TDDFT Tutorial

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Theoretical Chemistry

- Quantum Chemistry / Electronic Structure Theory:

Solve for motions of electrons in molecules; provide static properties of individual molecules and potential energy surfaces

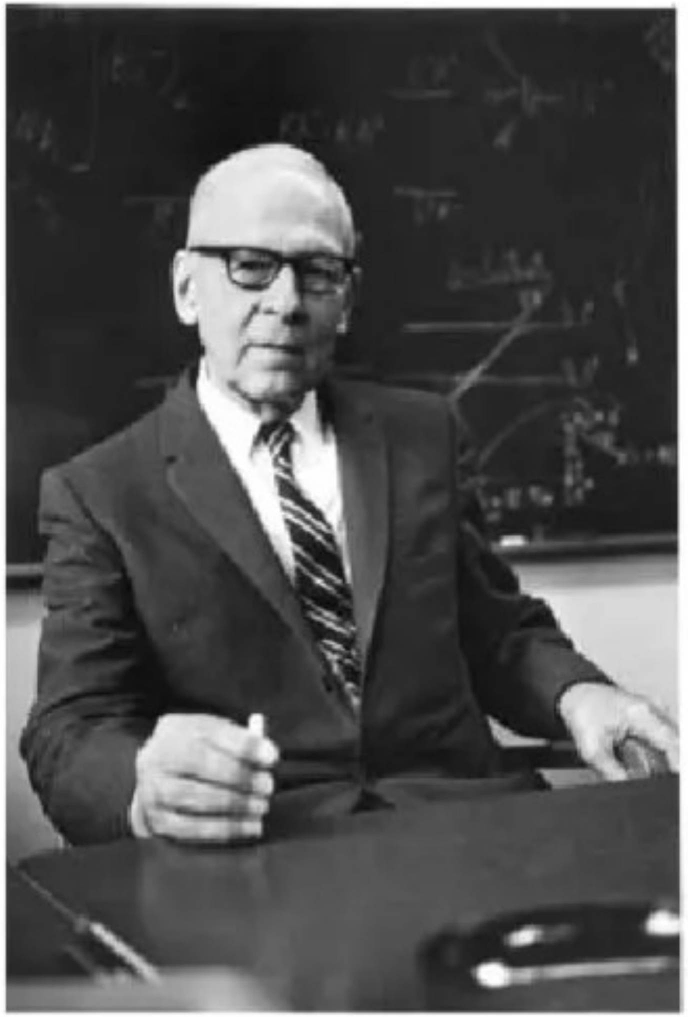
- Dynamics:

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

- Statistical Mechanics:

Solve for bulk properties from properties of individual molecules.

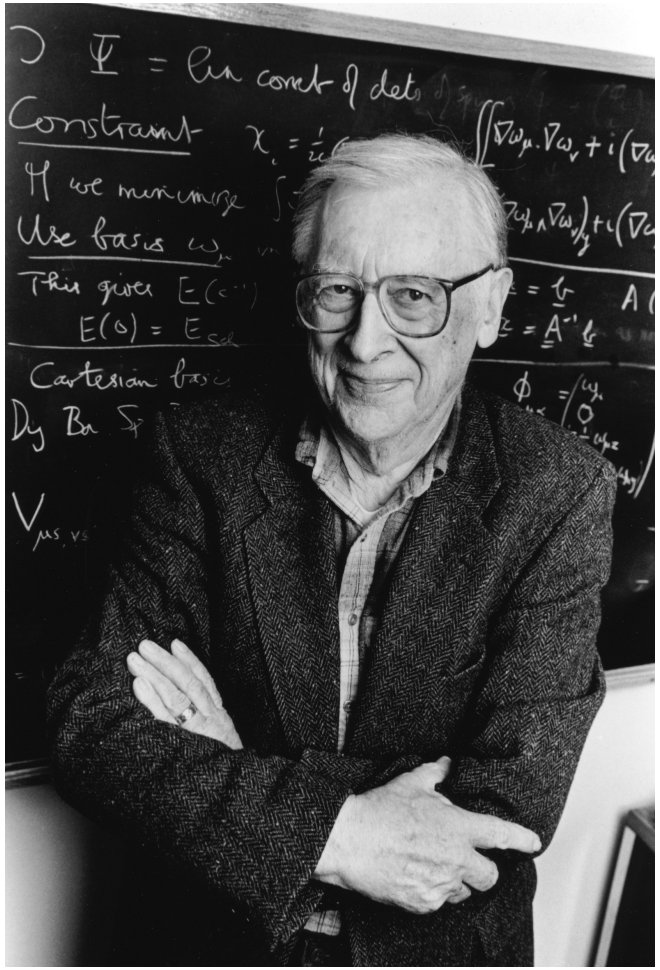
Robert S. Mulliken:
“What are the Electrons Really Doing in Molecules?”

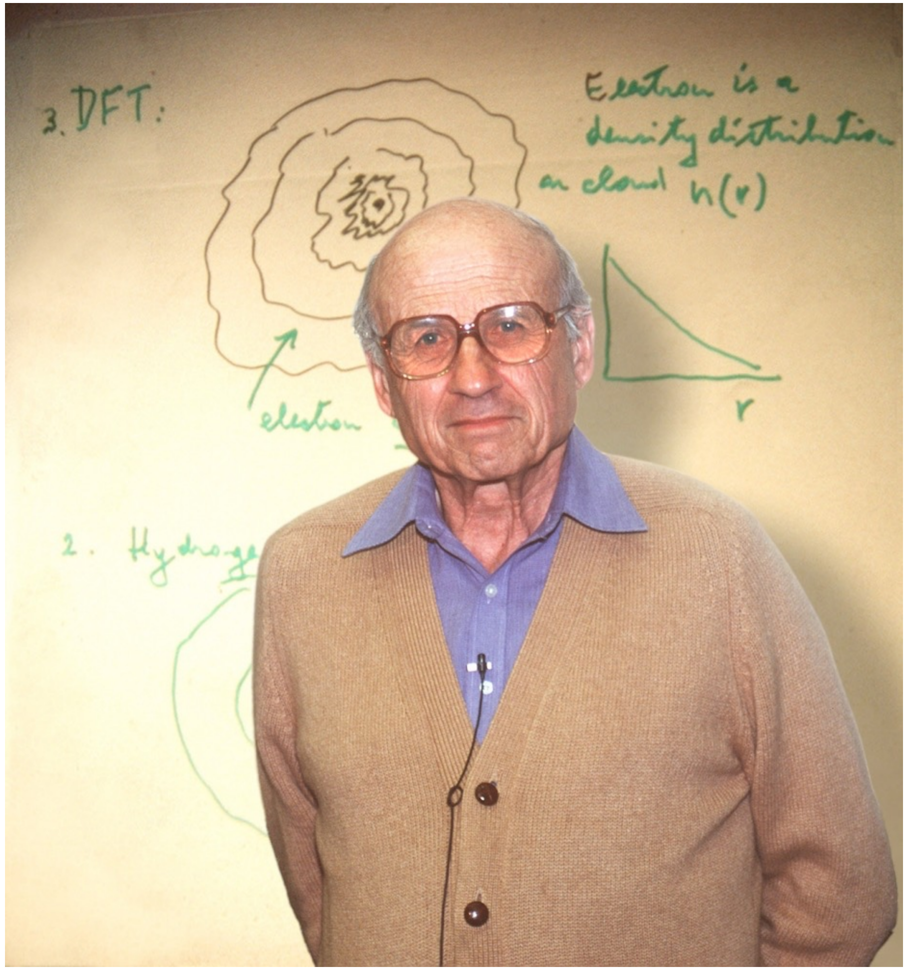


Robert S. Mulliken
1966 Noble Prize in Chemistry

"… the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory … is already at hand. There is only one obstacle, namely, that someone must pay for the computing time.”

John Pople & Walter Kohn
1998 Noble Prize in Chemistry



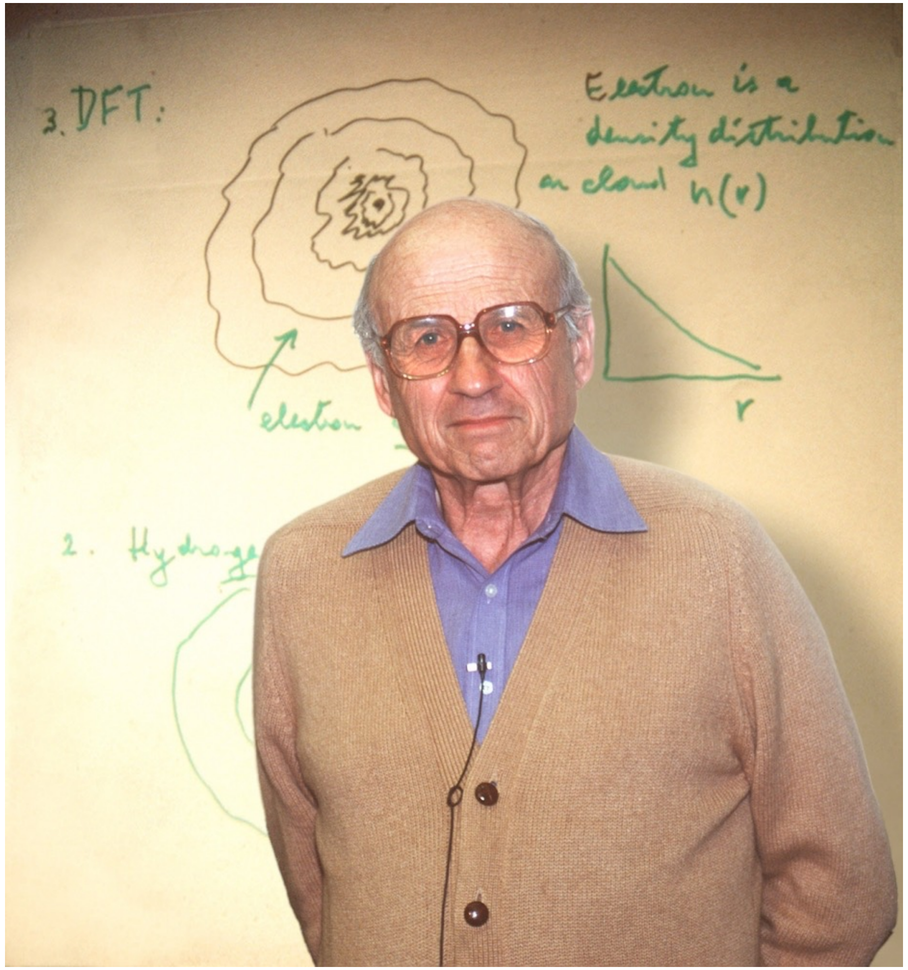


John Pople: for development of computational methods in quantum chemistry

Walter Kohn: for development of the density functional theory

John Pople & Walter Kohn
1998 Noble Prize in Chemistry

"… The fact that I got the Noble Prize in Chemistry reflects the fact that, at a certain theoretical level, **chemistry and physics are very close to each other**."



Walter Kohn: for development of the density functional theory

Electronic Structure Theory

- Equilibrium Geometries (microwave spectra)
- Vibrational Frequencies (IR spectra)
- Excited States (UV/VIS Spectra)
- Ionization Potentials (Photoelectron and X-ray Spectra)
- Electron affinities
- Magnetic Shielding Tensors (NMR Spectra)
- Dipole moment, Polarizibility, …
- Reaction Pathways and barrier heights
- Reaction rate (with statistical or dynamical studies)
- Thermodynamic properties (statistical mechanics)

The Schrödinger Equation for Molecules

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

$$\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{R}_1, \boldsymbol{r}_2, \boldsymbol{R}_2, \cdots, \boldsymbol{r}_n, \boldsymbol{R}_n)$$

$$\hat{H} = \cancel{\hat{T}_N(\boldsymbol{R})} + \hat{T}_e(\boldsymbol{r}) + V_{eN}(\boldsymbol{r}; \boldsymbol{R}) + V_{NN}(\boldsymbol{R}) + V_{ee}(\boldsymbol{r})$$

$$\widehat{H_{el}} = \hat{T}_e(\boldsymbol{r}) + V_{eN}(\boldsymbol{r}; \boldsymbol{R}) + V_{NN}(\boldsymbol{R}) + V_{ee}(\boldsymbol{r})$$

$$\hat{H}_{el}(\boldsymbol{r}; \boldsymbol{R})\Psi(\mathbf{r}; \mathbf{R}) = E_{el}\Psi(\mathbf{r}; \mathbf{R})$$

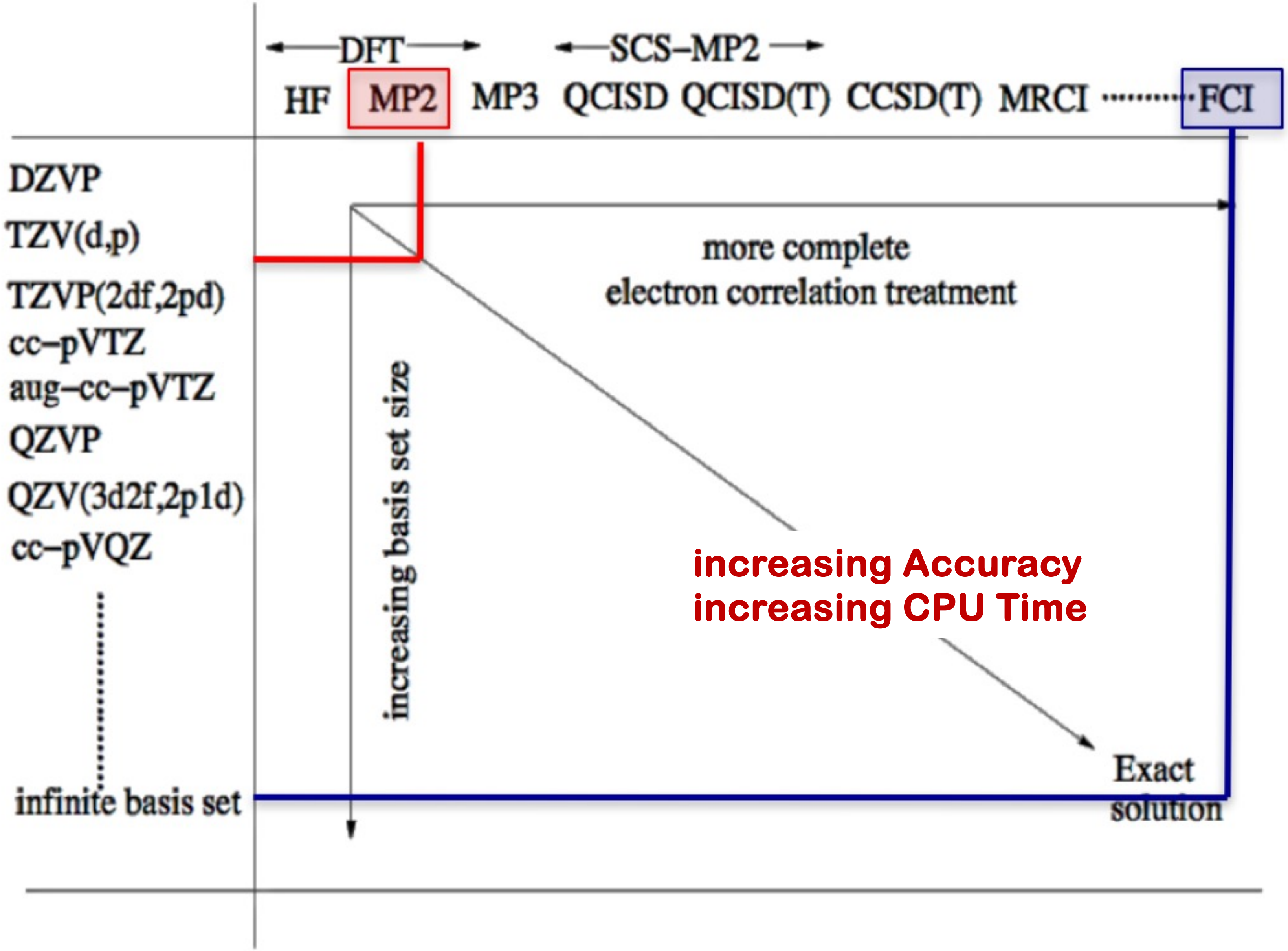
The Electronic Schrödinger Equation

"… 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)

Quantum Chemistry approximately solves $\widehat{H}_{el}(\boldsymbol{r};\boldsymbol{R})\Psi(\mathbf{r};\mathbf{R}) = E_{el}\Psi(\mathbf{r};\mathbf{R})$

Pople Diagram: Level of Theory



Electronic Structure Methods

Method	Accuracy	Max atoms
Semi-empirical	Low	~5000
Hartree-Fock	Medium	~500
(Standard) DFT	Medium-High	~500
MP2	High	~100
CISD	High	~40
CCSD, CCSD(T)	Very High	~30
Multireference CI, CC	Ultra High	~15

David Sherrill, YouTube video on Intro to Electronic Structure Theory:
https://www.youtube.com/watch?v=srL6i7zwzu4

Density Functional Theory

- Use the electron density (3 dimensions) as the fundamental quantity instead of complicated many-electron wavefunctions (3N dimensions).
- Introducing “Functional” (function of a function) as the relationship of the energy to the density, $E[\varrho(x,y,z)]$.
- Employing the variational principle minimizes the energy with respect to the density.
- The true functional is unknown uses various approximations.
- Efficient and low computational cost.

Szabo and Ostlund, modern Quantum Chemistry, Dover Publications, NY 1996.

Density Functional Theory

- First Hohenberg-Kohn Theorem: The ground state properties of a many-electron system depend only on the electron density ϱ(x,y,z).
- Second Hohenberg-Kohn Theorem: The correct ground state density for a system is the one that minimizes the total energy through the functional E[ϱ(x,y,z)].
- Coulomb interaction for a given electron density interacting with the nuclei and interaction between the electron densities with itself (J).
- Exchange terms (K) account for electron antisymmetry and electron correlation effects.
- The kinetic energy of electron density is computed by assuming that the density corresponds to a wavefunction consisting of a Slater determinant (same as Hartree-Fock Theory) ➔ Kohn-Sham DFT.

Density Functional Theory: Exchange Correlation Functionals

- Local density approximation (LDA): Functional depends only on the local density at a given point; S-VWN
- Gradient-corrected approximation (GGA): Functional depends on the local density and its gradient; PBE, LYP correlation functionals, B88 exchange functional
- Meta-GGA: Functional depends on density, its gradient and its second derivative; M06-L.
- Hybrid DF: Mixes in Hartree-Fock exchange; B3LYP (hybrid GGA), M05-2X and M06-2X (hybrid meta-GGA).
- Double-Hybrid DF: Hybrid DFT also mixes in some MP2 correlation, B2-PLYP.

Time-Dependent Density Functional Theory

- Linear Response-TDDFT calculates excitation energies in the response of the ground state density to a time-varying applied electric field.
- Runge-Gross-Kohn Theorem: The external potential is time-dependent (static ionic potential + external perturbation via electromagnetic field).

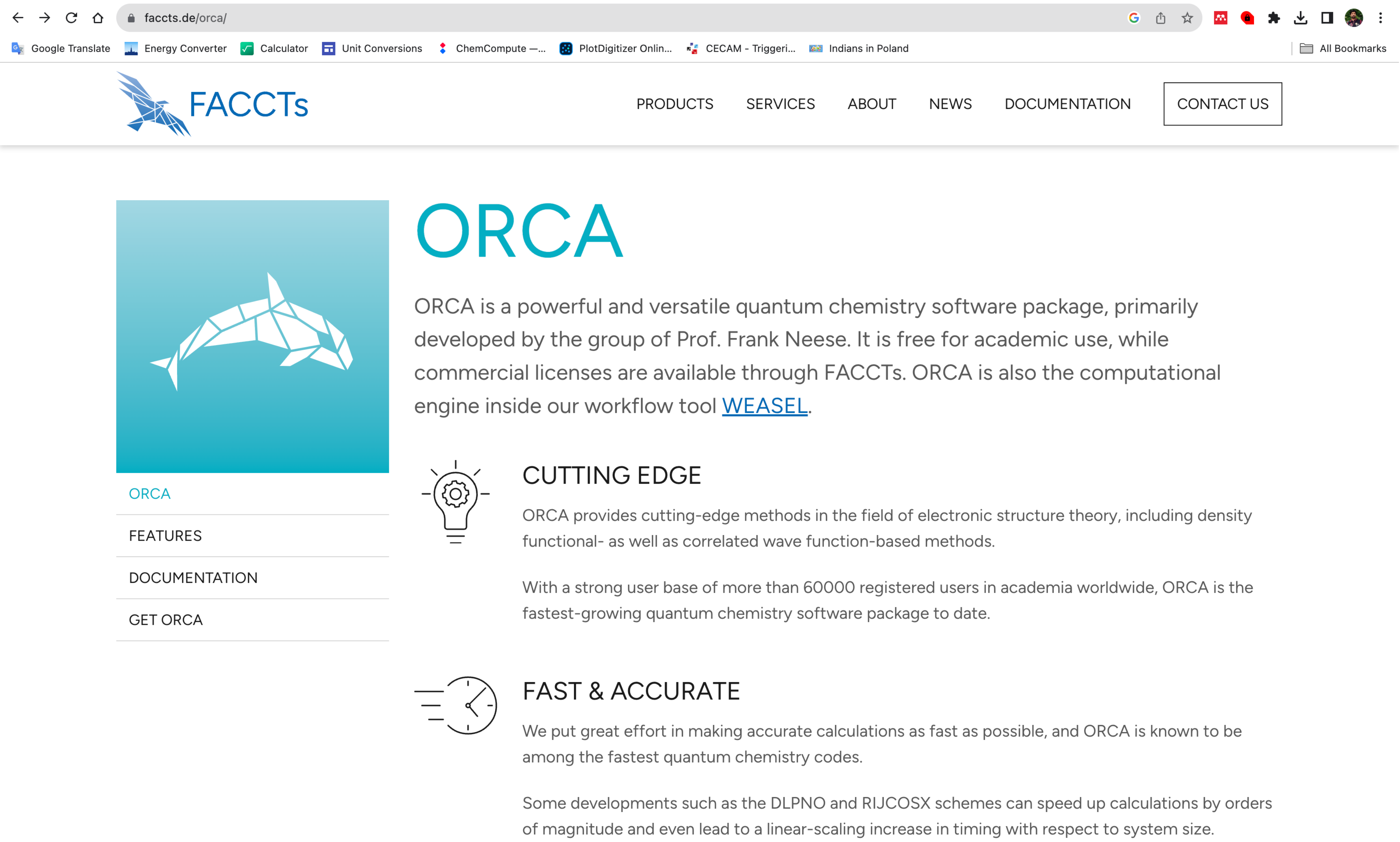
E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

Fundamentals of Time-Dependent Density Functional Theory, Lecture Notes in Physics 837, M. A. L. Marques, N. Maitra, F. Nogueira, E. K. U. Gross, A. Rubio (eds.), Springer (2012).

M. E. Casida, Time-Dependent Density Functional Response Theory for Molecules, Singapore, World Scientific (1995).

ORCA Quantum Chemistry Package – Prof. Frank Neese, MPI Mulheim

https://www.faccts.de/orca/



ORCA

ORCA is a powerful and versatile quantum chemistry software package, primarily developed by the group of Prof. Frank Neese. It is free for academic use, while commercial licenses are available through FACCTs. ORCA is also the computational engine inside our workflow tool WEASEL.

CUTTING EDGE

ORCA provides cutting-edge methods in the field of electronic structure theory, including density functional- as well as correlated wave function-based methods.

With a strong user base of more than 60000 registered users in academia worldwide, ORCA is the fastest-growing quantum chemistry software package to date.

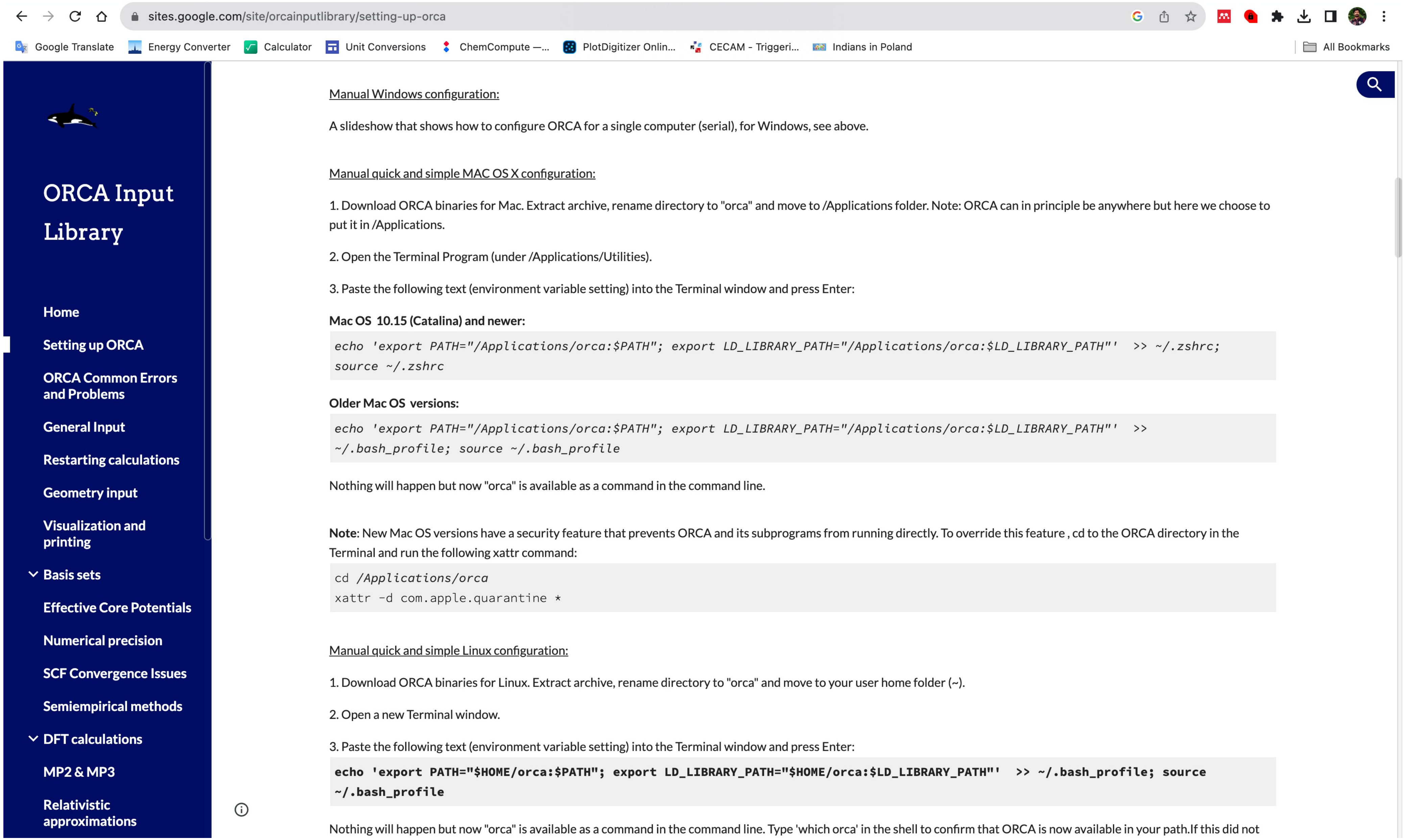
FAST & ACCURATE

We put great effort in making accurate calculations as fast as possible, and ORCA is known to be among the fastest quantum chemistry codes.

Some developments such as the DLPNO and RIJCOSX schemes can speed up calculations by orders of magnitude and even lead to a linear-scaling increase in timing with respect to system size.

ORCA Quantum Chemistry Package – Prof. Frank Neese, MPI Mulheim

https://sites.google.com/site/orcainputlibrary/setting-up-orca



Manual Windows configuration:

A slideshow that shows how to configure ORCA for a single computer (serial), for Windows, see above.

Manual quick and simple MAC OS X configuration:

1. Download ORCA binaries for Mac. Extract archive, rename directory to "orca" and move to /Applications folder. Note: ORCA can in principle be anywhere but here we choose to put it in /Applications.

2. Open the Terminal Program (under /Applications/Utilities).

3. Paste the following text (environment variable setting) into the Terminal window and press Enter:

Mac OS 10.15 (Catalina) and newer:

```
echo 'export PATH="/Applications/orca:$PATH"; export LD_LIBRARY_PATH="/Applications/orca:$LD_LIBRARY_PATH"'  >> ~/.zshrc;
source ~/.zshrc
```

Older Mac OS versions:

```
echo 'export PATH="/Applications/orca:$PATH"; export LD_LIBRARY_PATH="/Applications/orca:$LD_LIBRARY_PATH"'  >>
~/.bash_profile; source ~/.bash_profile
```

Nothing will happen but now "orca" is available as a command in the command line.

Note: New Mac OS versions have a security feature that prevents ORCA and its subprograms from running directly. To override this feature , cd to the ORCA directory in the Terminal and run the following xattr command:

```
cd /Applications/orca
xattr -d com.apple.quarantine *
```

Manual quick and simple Linux configuration:

1. Download ORCA binaries for Linux. Extract archive, rename directory to "orca" and move to your user home folder (~).

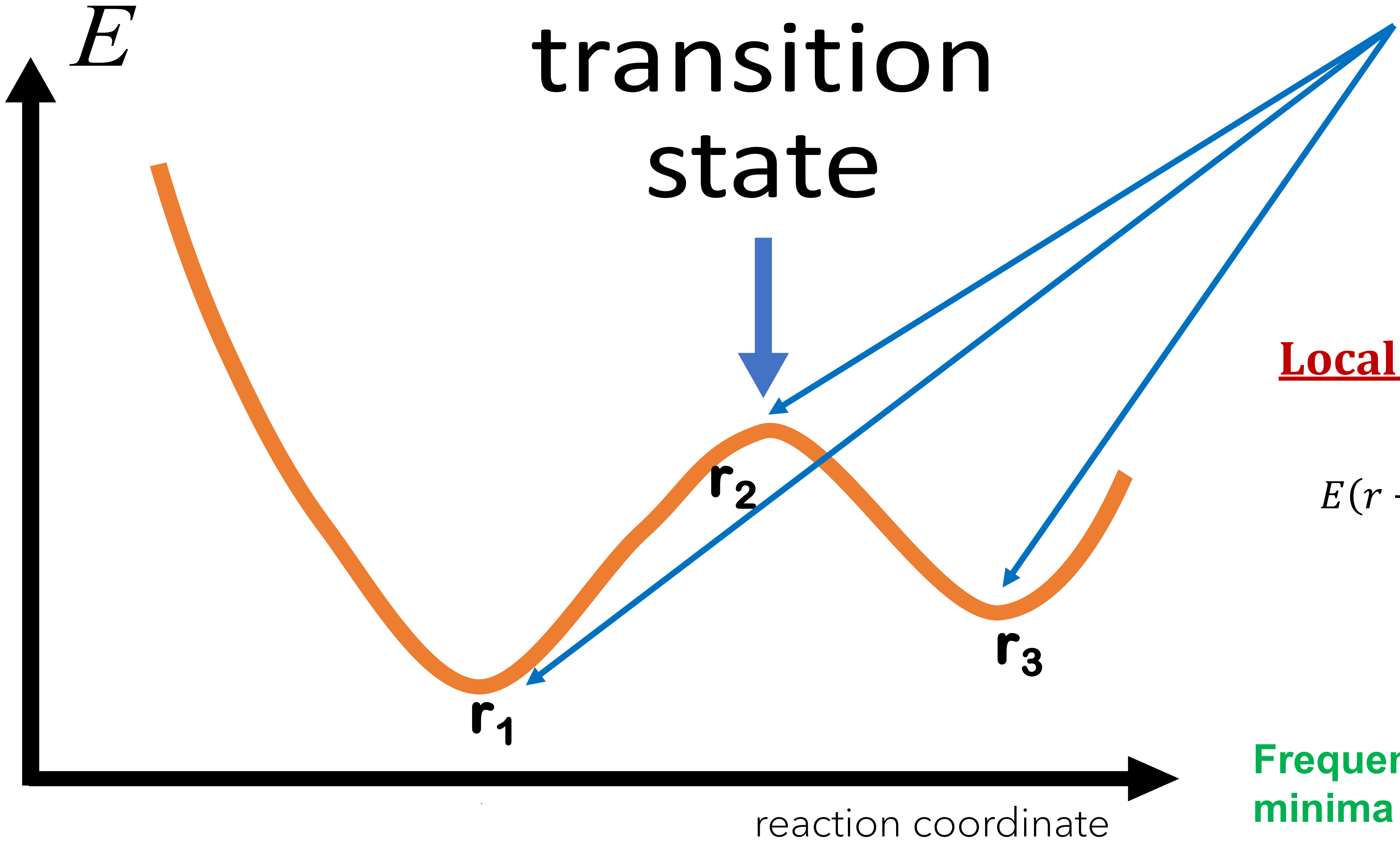
2. Open a new Terminal window.

3. Paste the following text (environment variable setting) into the Terminal window and press Enter:

```
echo 'export PATH="$HOME/orca:$PATH"; export LD_LIBRARY_PATH="$HOME/orca:$LD_LIBRARY_PATH"'  >> ~/.bash_profile; source
~/.bash_profile
```

Nothing will happen but now "orca" is available as a command in the command line. Type 'which orca' in the shell to confirm that ORCA is now available in your path.If this did not

Geometry Optimization



stationary points

$$\left.\frac{dE}{dr}\right|_{r=r_i} = 0$$

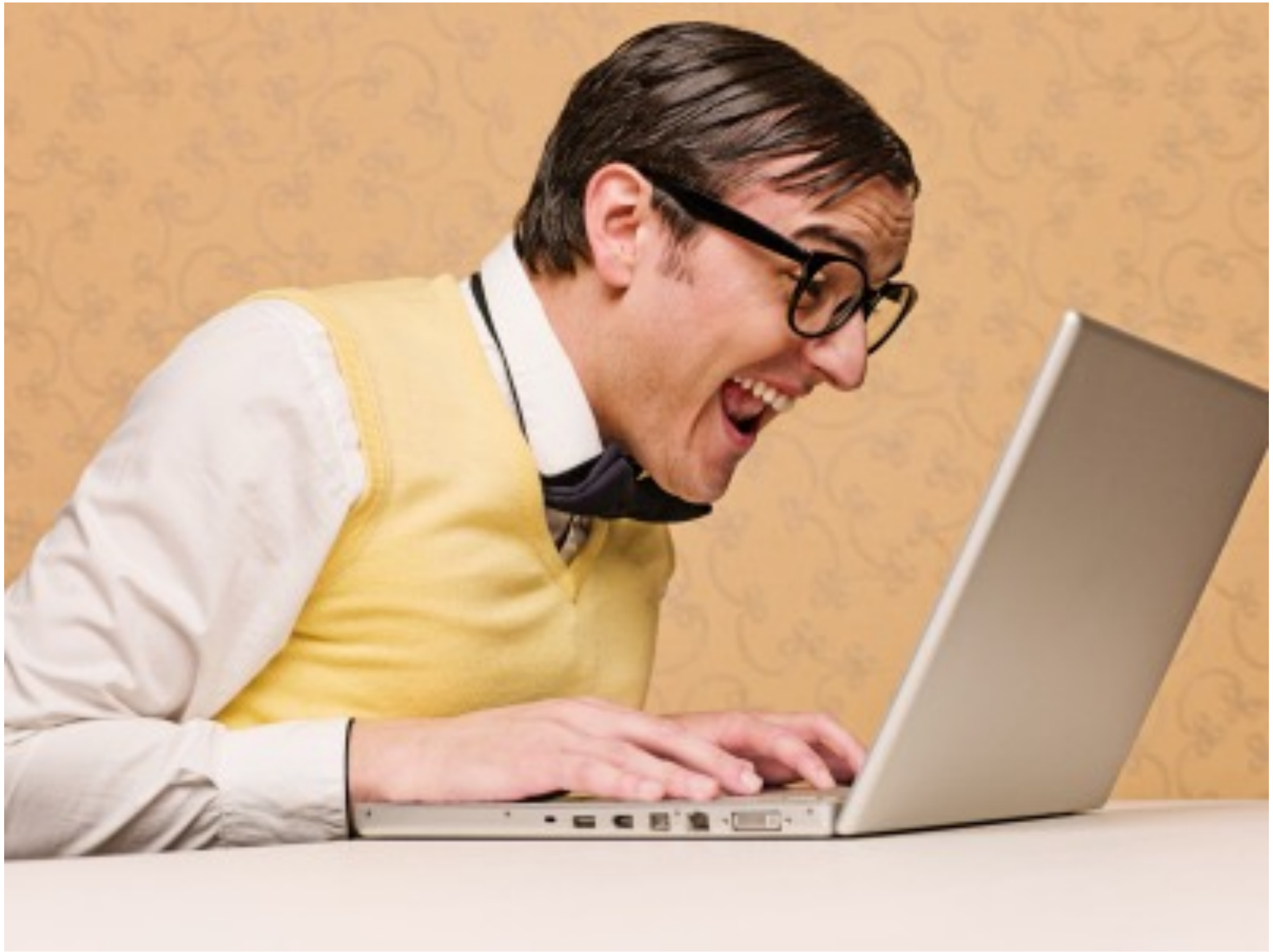
Local Parabola

$$E(r-r_i) \approx \frac{1}{2}k_i(r-r_i)^2$$

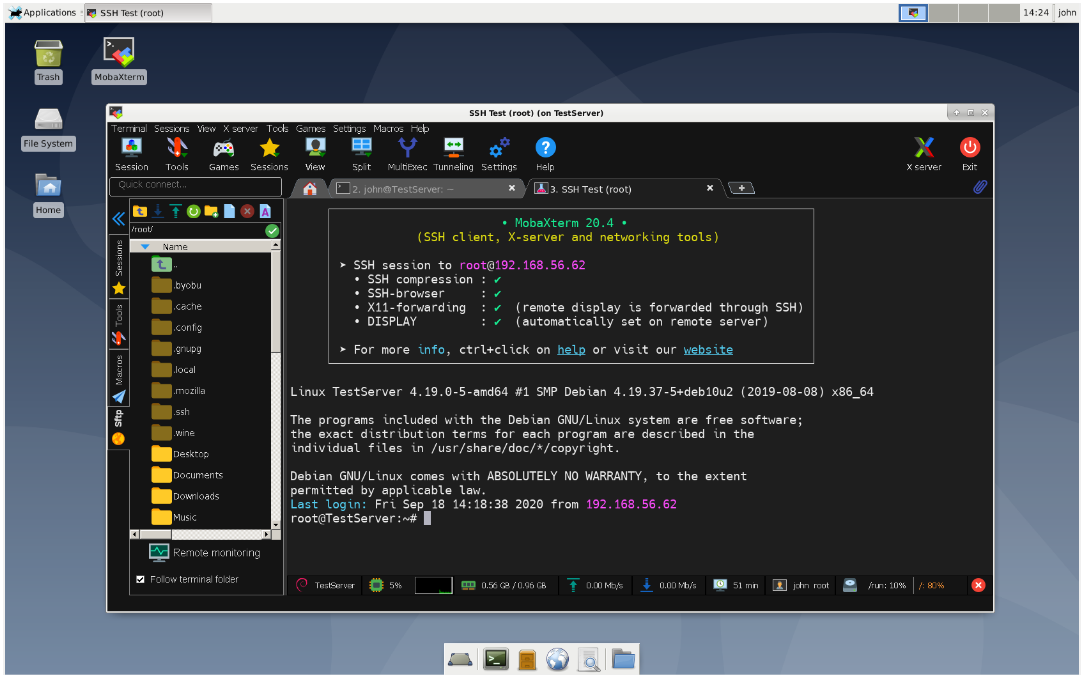
$$\omega_i \approx \sqrt{\frac{k_i}{\mu}}$$

Frequencies are real for minima and imaginary for TS

Let’s do Quantum Chemistry



Windows User: MobaXterm

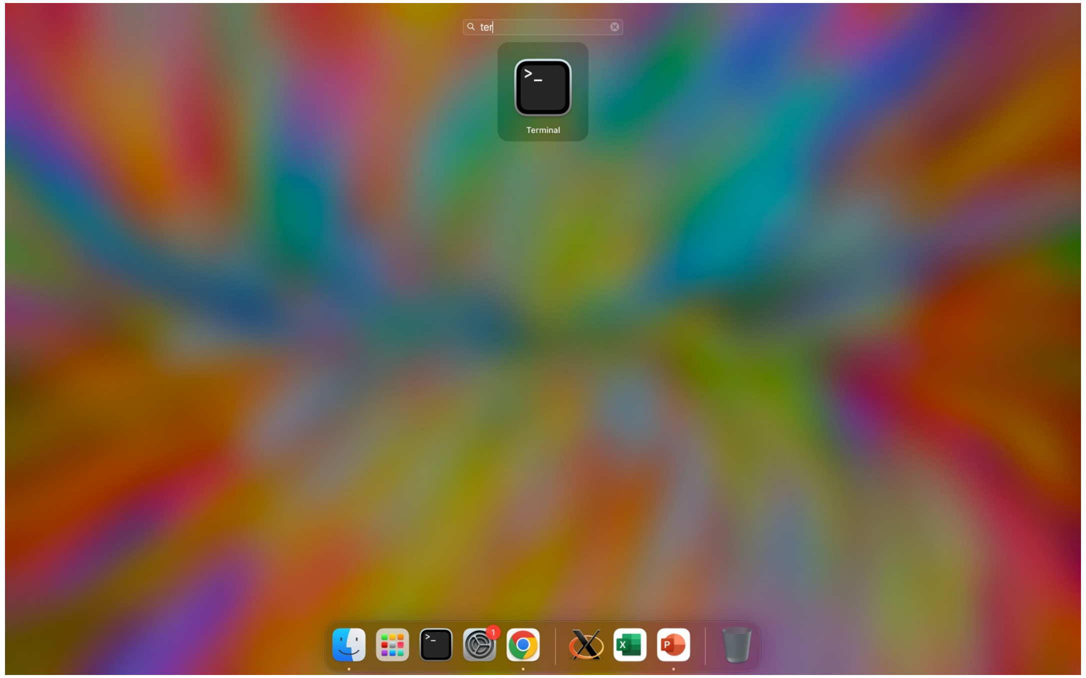


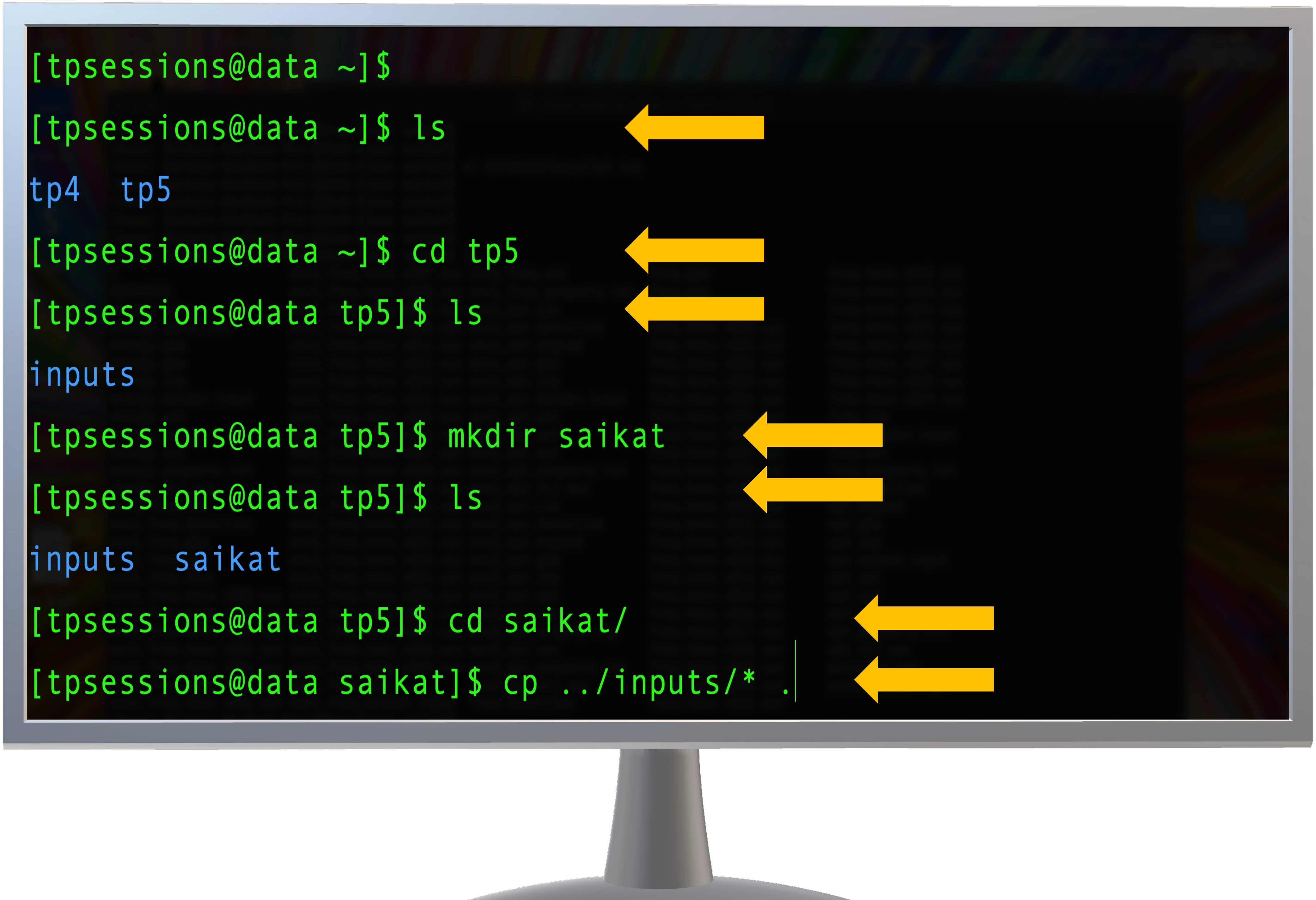
```
                 • MobaXterm 20.4 •
      (SSH client, X-server and networking tools)

 ➤ SSH session to root@192.168.56.62
   • SSH compression : ✔
   • SSH-browser     : ✔
   • X11-forwarding  : ✔  (remote display is forwarded through SSH)
   • DISPLAY         : ✔  (automatically set on remote server)

 ➤ For more info, ctrl+click on help or visit our website

Linux TestServer 4.19.0-5-amd64 #1 SMP Debian 4.19.37-5+deb10u2 (2019-08-08) x86_64

The programs included with the Debian GNU/Linux system are free software;
the exact distribution terms for each program are described in the
individual files in /usr/share/doc/*/copyright.

Debian GNU/Linux comes with ABSOLUTELY NO WARRANTY, to the extent
permitted by applicable law.
Last login: Fri Sep 18 14:18:38 2020 from 192.168.56.62
root@TestServer:~#
```

Mac User: Terminal

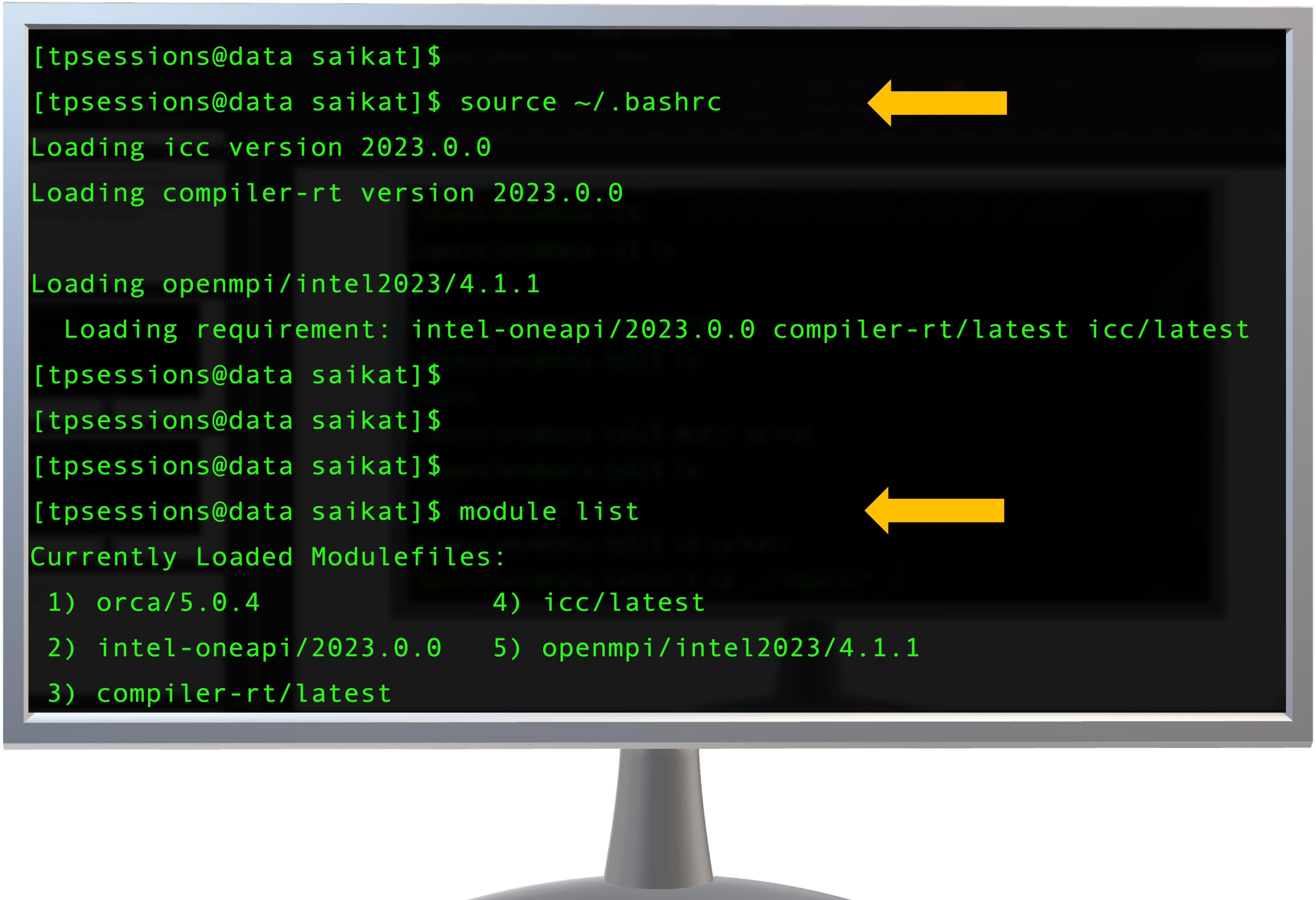
Go to "Launchpad"

→ look for "Terminal"





```
[tpsessions@data ~]$
[tpsessions@data ~]$ ls
tp4   tp5
[tpsessions@data ~]$ cd tp5
[tpsessions@data tp5]$ ls
inputs
[tpsessions@data tp5]$ mkdir saikat
[tpsessions@data tp5]$ ls
inputs   saikat
[tpsessions@data tp5]$ cd saikat/
[tpsessions@data saikat]$ cp ../inputs/* .
```



```
[tpsessions@data saikat]$
[tpsessions@data saikat]$ source ~/.bashrc
Loading icc version 2023.0.0
Loading compiler-rt version 2023.0.0

Loading openmpi/intel2023/4.1.1
  Loading requirement: intel-oneapi/2023.0.0 compiler-rt/latest icc/latest
[tpsessions@data saikat]$
[tpsessions@data saikat]$
[tpsessions@data saikat]$
[tpsessions@data saikat]$ module list
Currently Loaded Modulefiles:
 1) orca/5.0.4              4) icc/latest
 2) intel-oneapi/2023.0.0   5) openmpi/intel2023/4.1.1
 3) compiler-rt/latest
```

Geometry Optimization

Prepare and Run Input

- starting geometry
- level of theory (method and basis sets)
- convergence criteria
- run:

```
orca opt.inp > opt.out &
```

Revision: Basis Sets
Lecture2 – Quantum Mechanics 2: Quantum Chemistry

Geometry Optimization: Few Specifics

- Convergence Criteria

NORMALOPT
TIGHTOPT
VERYTIGHTOPT
Geometry

NORMALSCF
TIGHTSCF
VERYTIGHTSCF
SCF

- RI Approximations (need auxiliary basis sets)

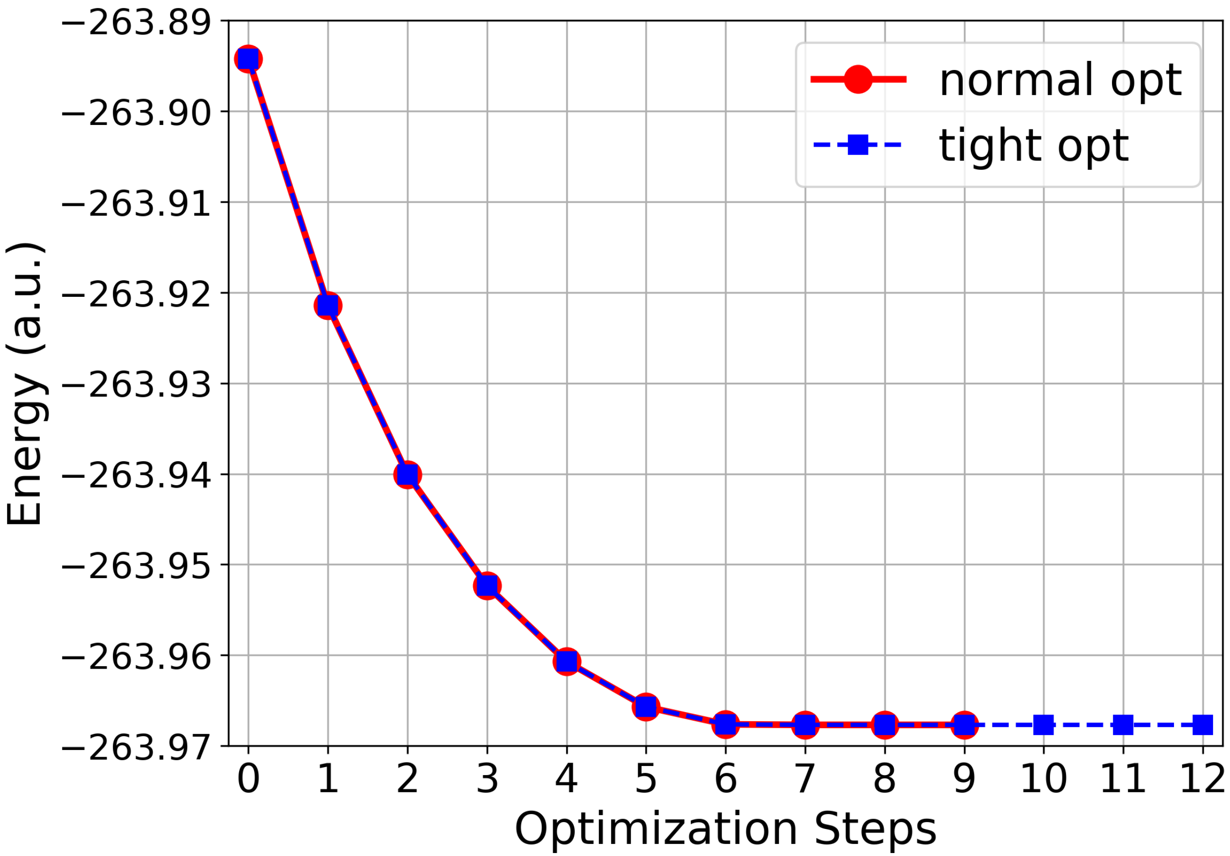
NORI	! no approximation
RIJONX	! RI-J for the Coulomb integrals only; no approximations applied to HF exchange
RIJK	! RI for both Coulomb integrals and HF exchange integrals
RIJCOSX	! RI-J for Coulumb integrals and COSX numerical integration for HF exchange

Geometry Optimization

Analysis

- Look for success
- optimized geometry
- energy minimization
- orbitals

`orca_2mkl opt -molden`



Frequencies and normal modes

Frequencies

$$f_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}}$$

Force constants

$$k_i = 4\pi^2 f_i^2 c^2 \mu_i$$

Revision: Lecture6

Classical Mechanics 2: Molecular Normal Modes

Cartesian displacements

$$Q_{ni}^{(Cart)} = \sum_{j=1}^{3N} \left(\frac{D_{nj} L_{ji}}{\sqrt{M_n}} \right)$$

Reduced masses

$$\mu_i = \left(\sum_{n}^{3N} \left(Q_{ni}^{(Cart)} \right)^2 \right)^{-1}$$

Vibrational Frequency

Workflow

- start with optimized geometry
- level of theory (same as optimization)
- run:

```
orca freq.inp > freq.out &
```

- identify normal mode vibrations

```
orca_pltvib freq.hess all vibrations
```

Vibrational Frequency

Frequency calculation with not optimized geometry

↓

imaginary frequency

Single-Point excitation Energies

Workflow

- starting geometry
- level of theory (ground state & electronic excited states)
- run:

```
orca energy.inp > energy.out &
```

- identify the electronic excited states

```
orca_2mkl energy -molden
```

- see the oscillator strengths

Reaction Pathways

- **Ground-State Optimization**

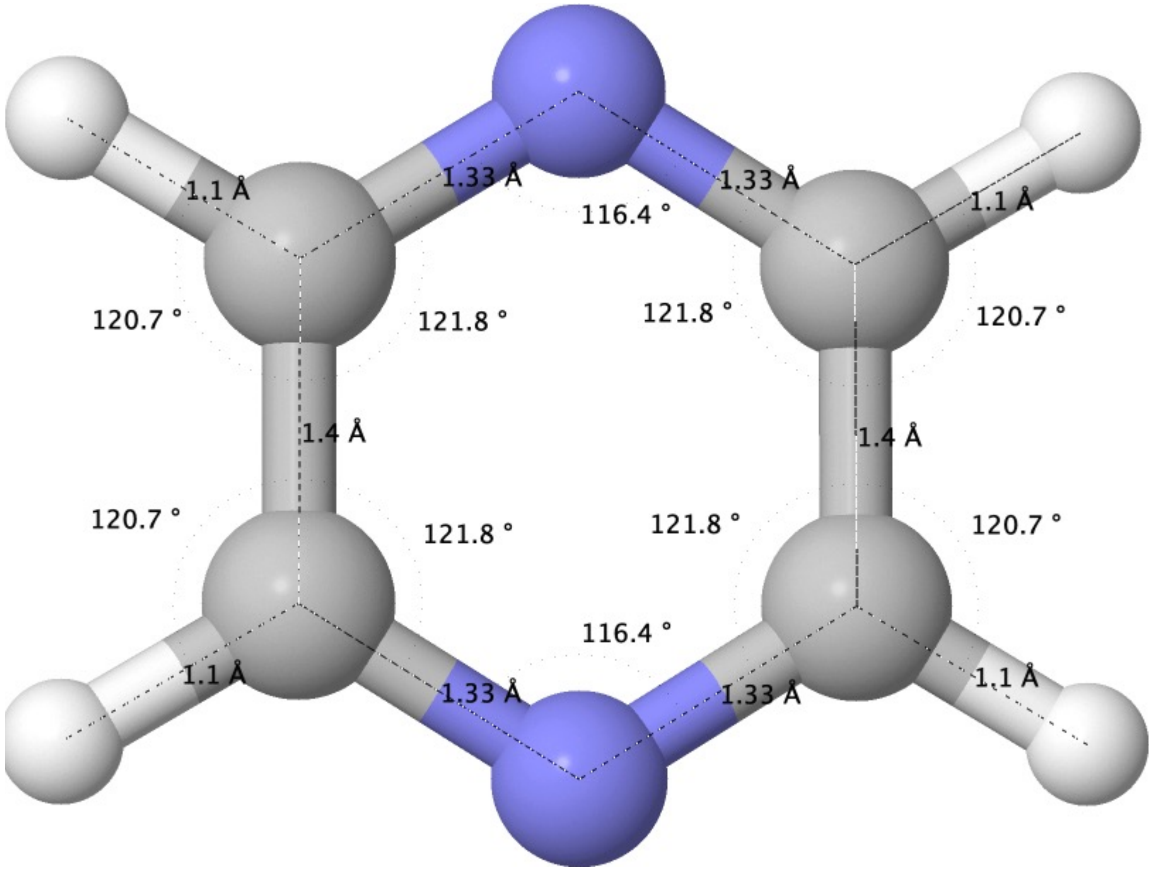
  confirmed by frequency calculation

- **Excited-States Optimization**

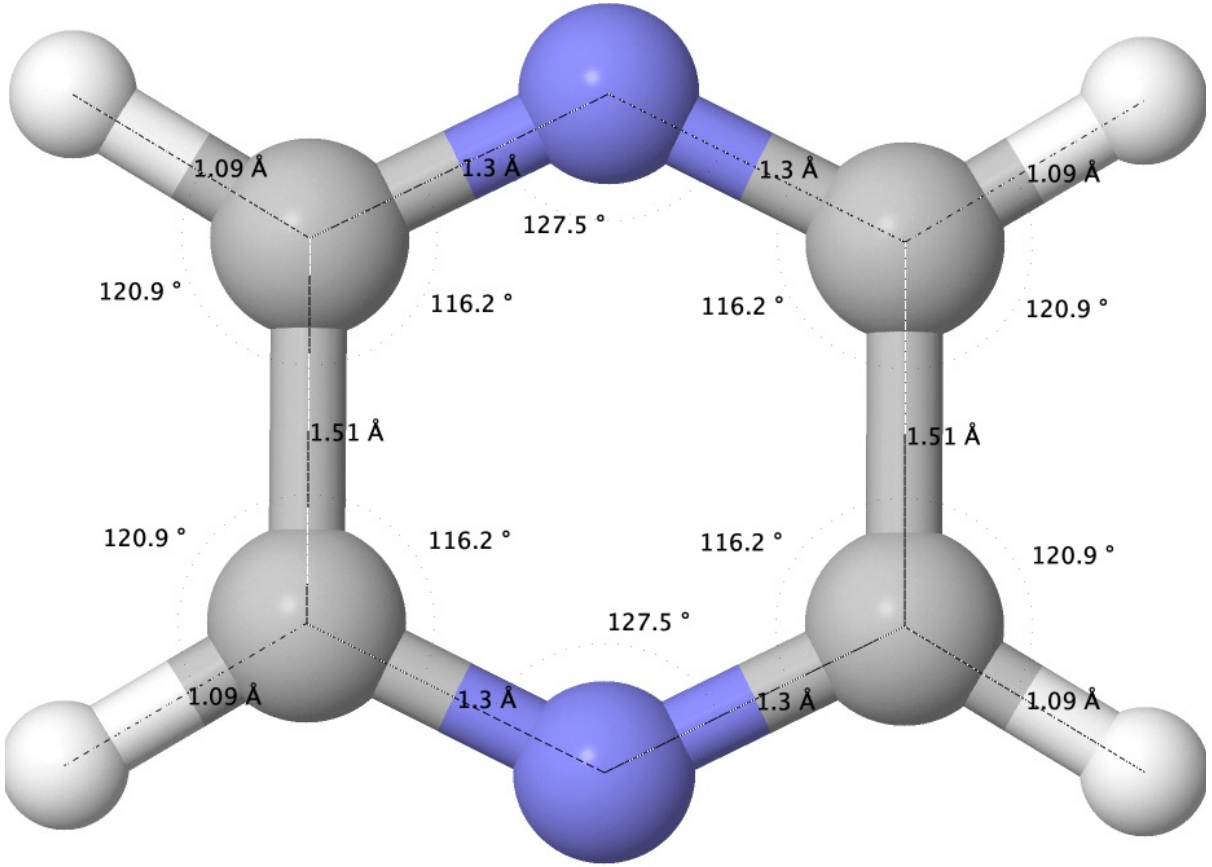
  confirmed by frequency calculation

- **Conical Intersection search between excited states**

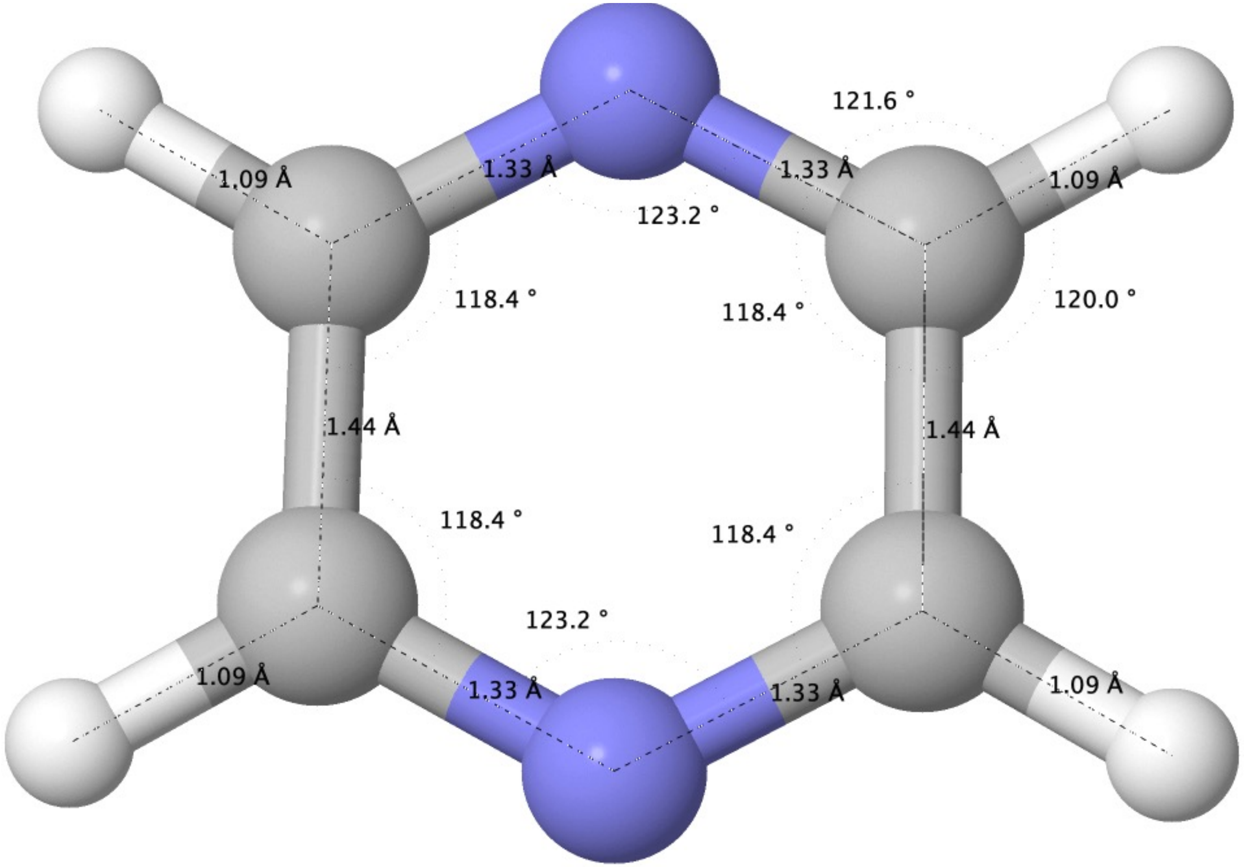
S_0 min - Planar



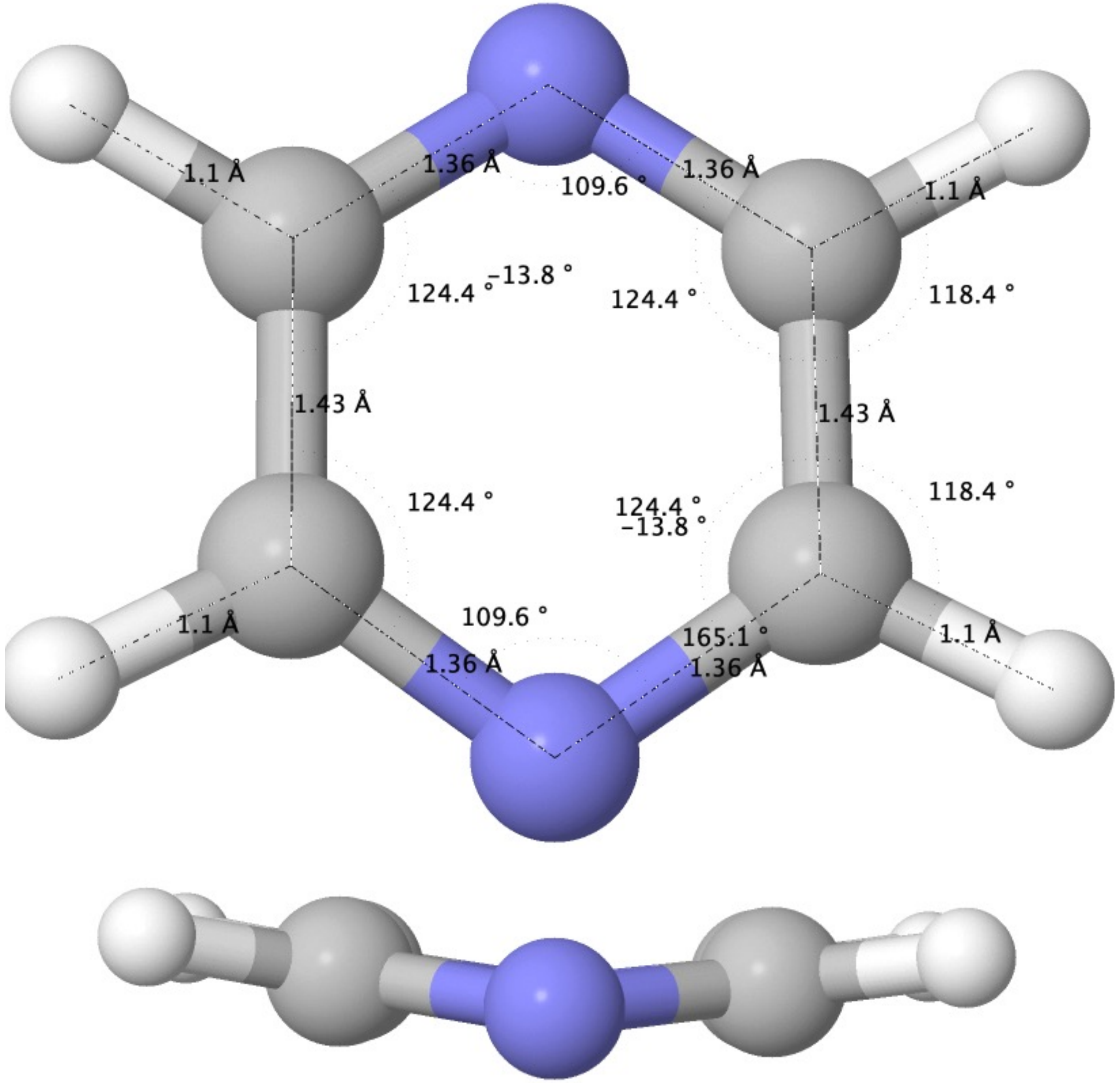
S_1 min - Planar



S_1/S_2 CI - Planar



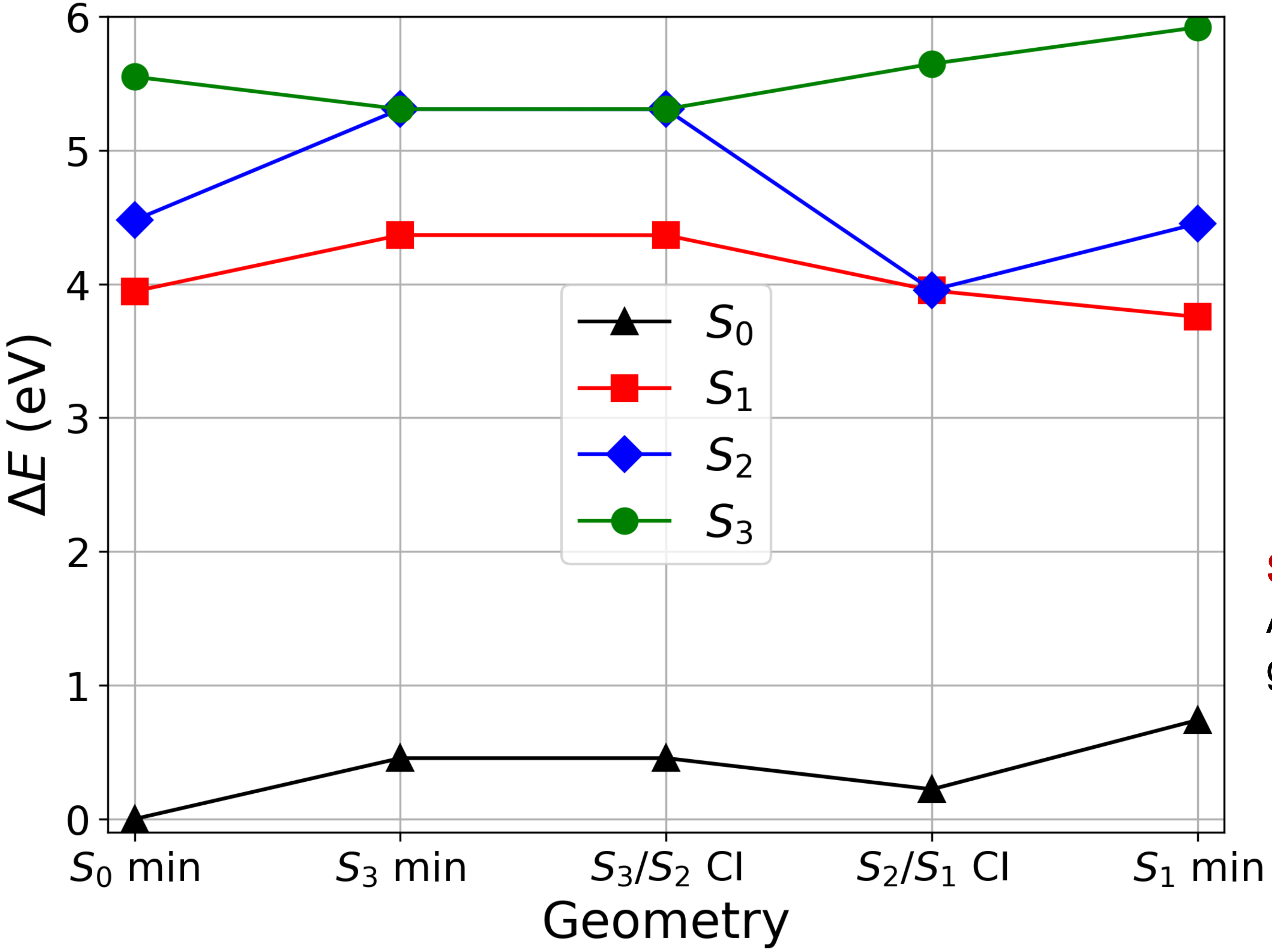
S_3/S_2 CI - Bent



Geometry Parameters

	S_0 min	S_1 min ($n\pi^\star$)	S_2 min	S_3 min ($\pi\pi^\star$)	S_3/S_2 CI	S_2/S_1 CI
C-N (ang)	1.33	1.34		1.37	1.36	1.33
C-C (ang)	1.4	1.51		1.43	1.43	1.44
C-H (ang)	1.1	1.09		1.1	1.1	1.09
C-N-C (°)	116.4	127.5		110.4	109.6	123.2
C-C-N (°)	121.8	116.2		124.8	124.4	118.4
H-C-C (°)	120.7	120.9		118.3	118.4	120.0
N-C-C-N (°)	0	0		0	13.8	0
H-C-N-C (°)	0	0		0	165.1	0
	Planar	Planar		Planar	Bent	Planar

Reaction Pathways



Special Note:
All energies are referenced to the ground state equilibrium energy.

Implicit Solvent Models

Revision: Lecture7

Classical Mechanics 3: Continuum models

➢ Conductor-like Polarizable Continuum Model (CPCM)

the bulk solvent is treated as a conductor-like polarizable continuum and the main parameters to define are the refractive index and the dielectric constant of the medium

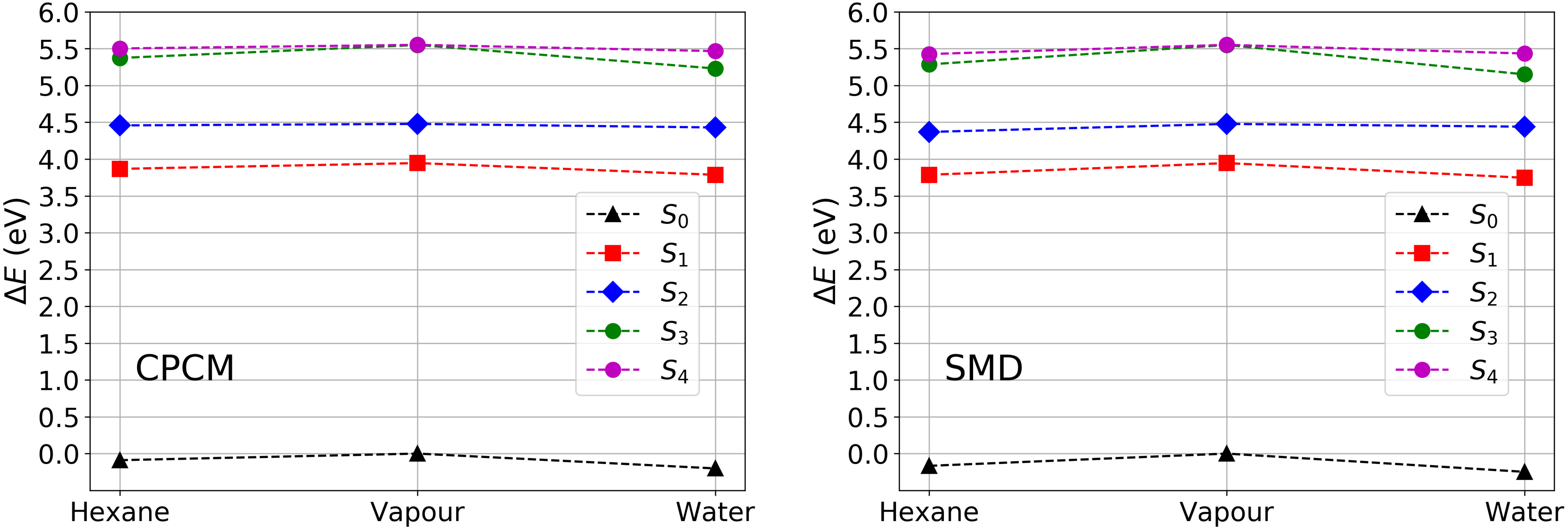
Solvent Name	Dielectric constant	Refractive index
Water	80.4	1.33
Hexane	1.89	1.375

➢ Universal Solvation Model (SMD)

modification on the CPCM scheme. It uses the full solute electron density to compute the cavity-dispersion contribution instead of the area only.

➢ COSMO

Implicit Solvent Models



Appendix

Optimization algorithm

- Gradient descent or Steepest Descent:

A first-order iterative optimization algorithm for finding a local minimum of a differentiable function. The idea is to take repeated steps in the opposite direction of the gradient (or approximate gradient) of the function at the current point.

- Newton-Raphson:

It is an iterative method for finding the roots of a differentiable function F, which are solutions to the equation F(x) = 0. As such, Newton's method can be applied to the derivative f′ of a twice-differentiable function f to find the roots of the derivative (solutions to f ′(x) = 0), also known as the critical points of f. These solutions may be minima, maxima, or saddle points. This is relevant in optimization, which aims to find (global) minima of the function f.

BFGS:

The algorithm is an iterative method for solving unconstrained nonlinear optimization problems. BFGS determines the descent direction by preconditioning the gradient with curvature information. It does so by gradually improving an approximation to the Hessian matrix of the loss function, obtained only from gradient evaluations (or approximate gradient evaluations) via a generalized secant method.

Conical Intersection Search