Tutorial 1

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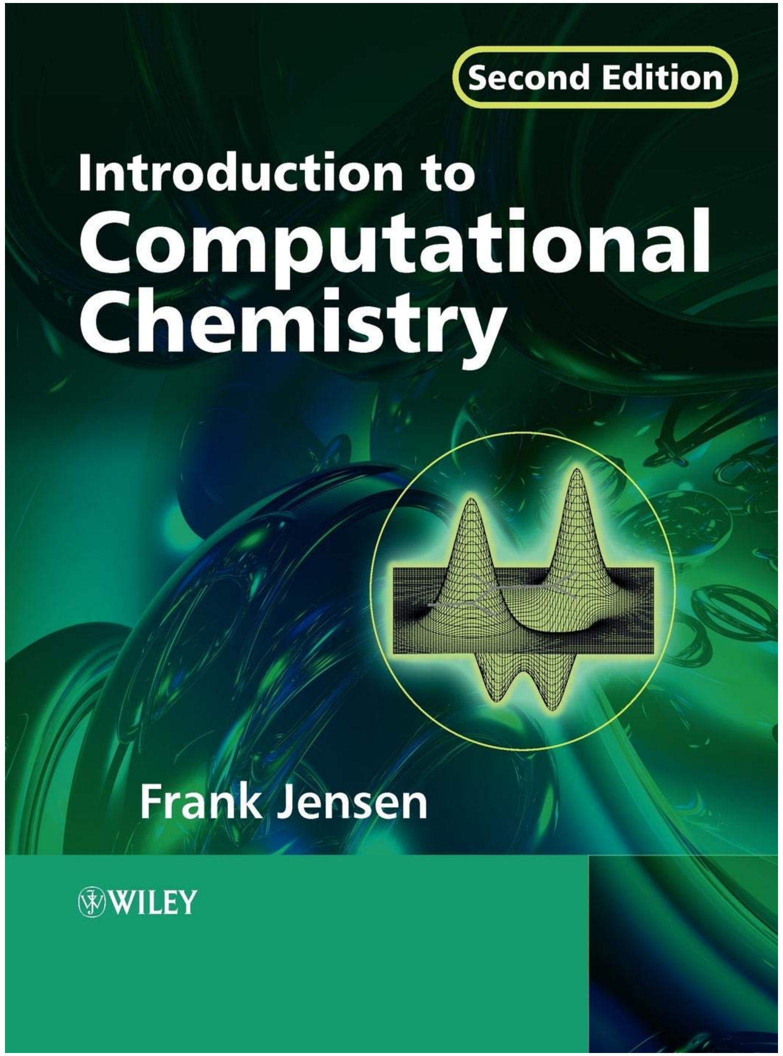
Recommended reading

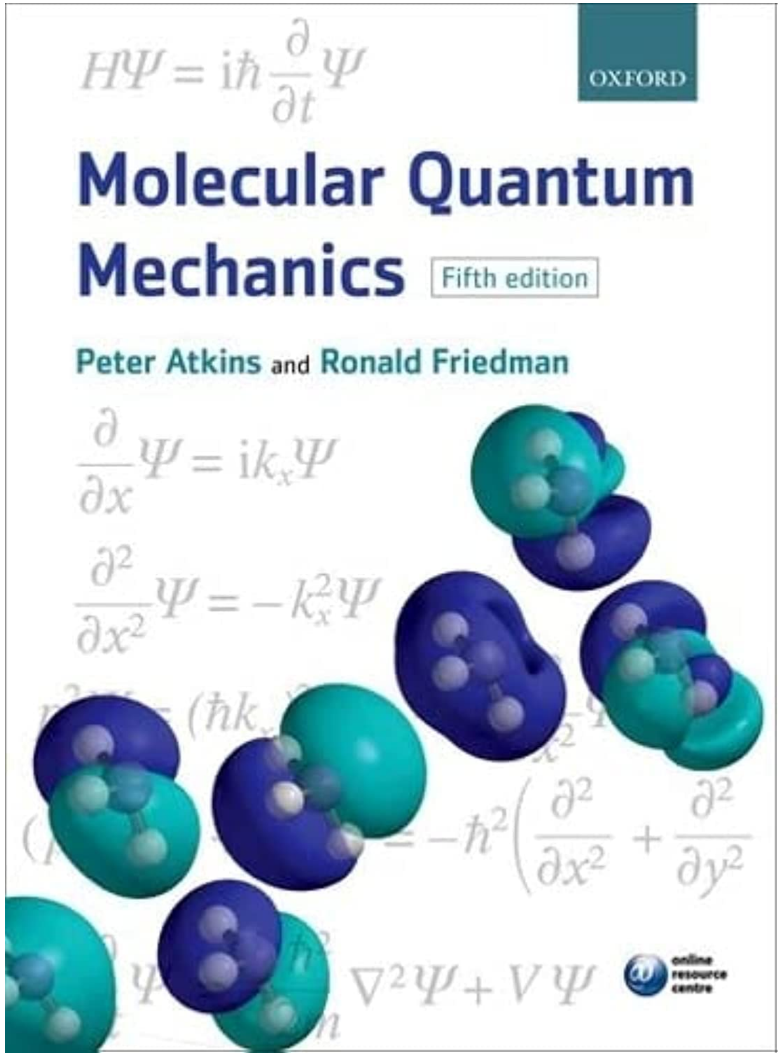


Second Edition

Introduction to Computational Chemistry

Frank Jensen

WILEY



OXFORD

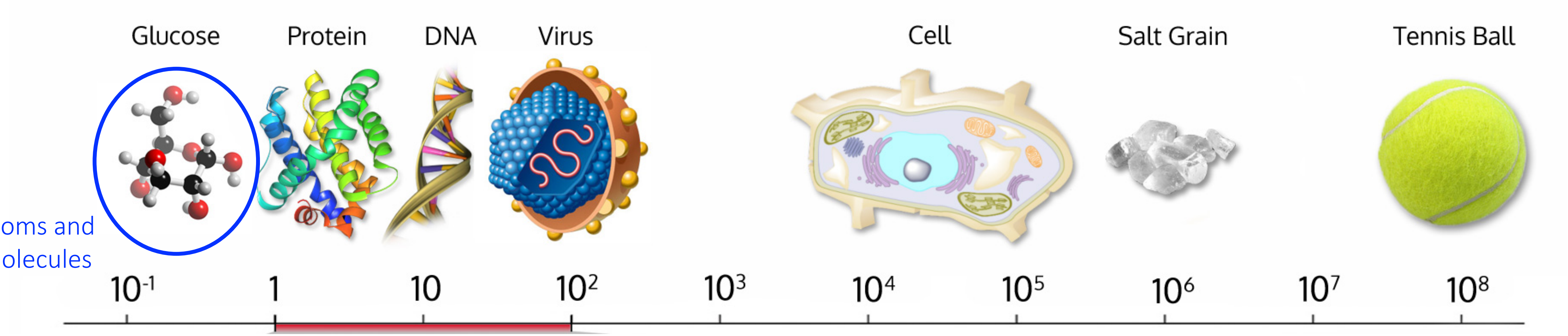
Molecular Quantum Mechanics

Fifth edition

Peter Atkins and Ronald Friedman

online resource centre

How to understand molecular structures and their properties?



Atoms and molecules

Microscopic

Macroscopic

Quantum mechanics

Classical mechanics

- Molecular structures are difficult to determine.

  => Challenging to visualize.

  => Complex arrangements of atoms and bonds.

  => Exhibit dynamic behavior. (e.g., ps scale)

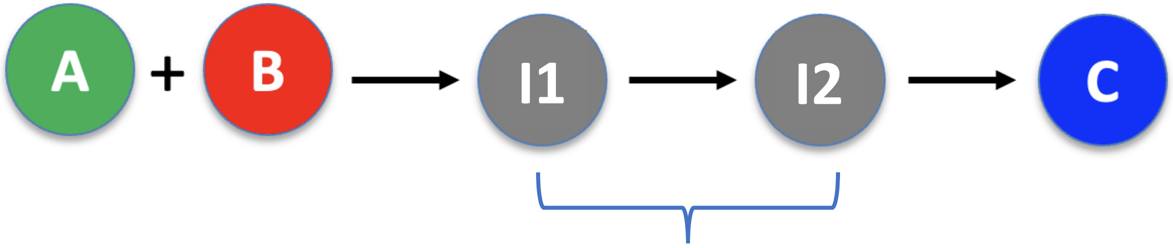
How to understand molecular structures and their properties?

Reactions between
ethylene (C_2H_2) molecules

Microscopic

Quantum mechanics

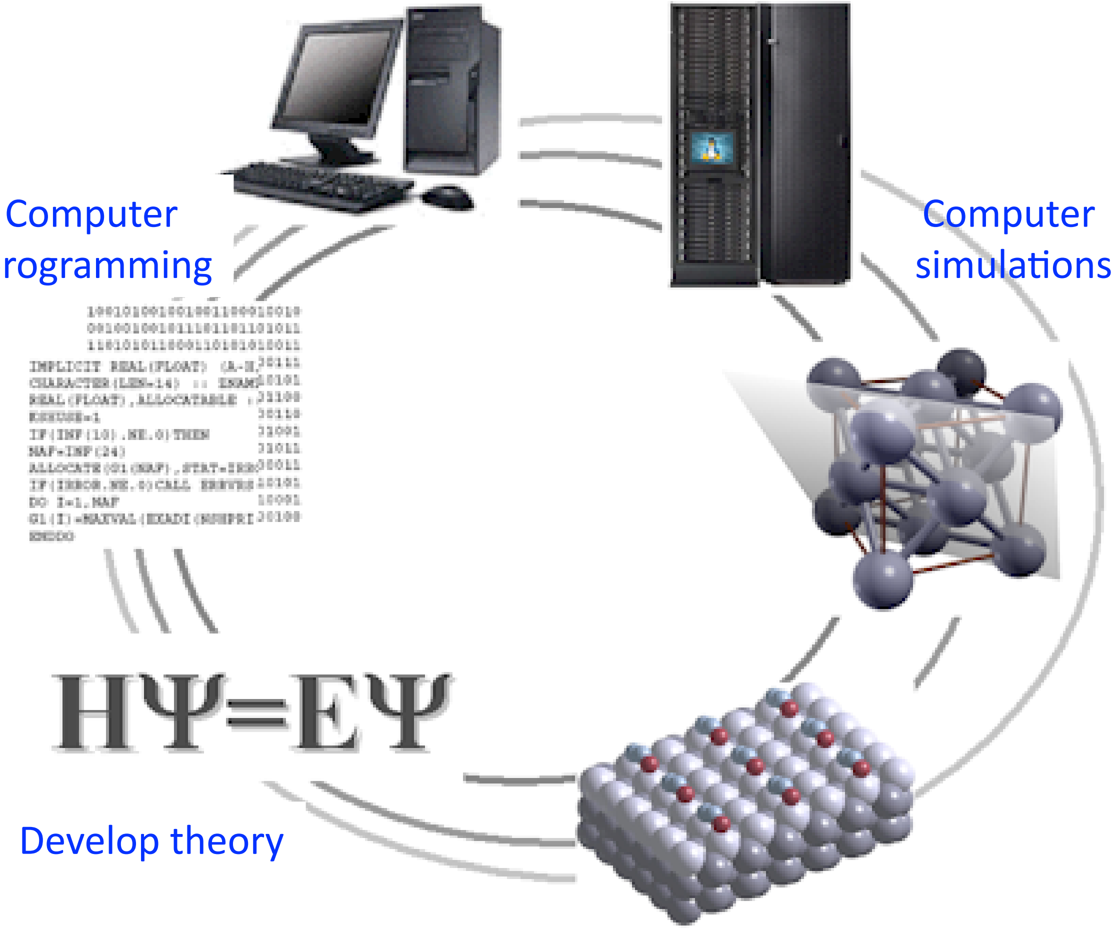
How to understand molecular structures and their properties?



Intermediates are difficult to determine

Experimental observations

Quantum Chemical Methods

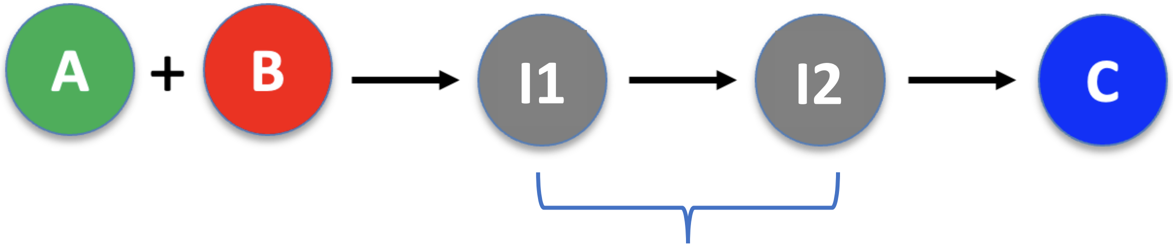


Computer programming

Computer simulations

Develop theory

Quantum chemical computations



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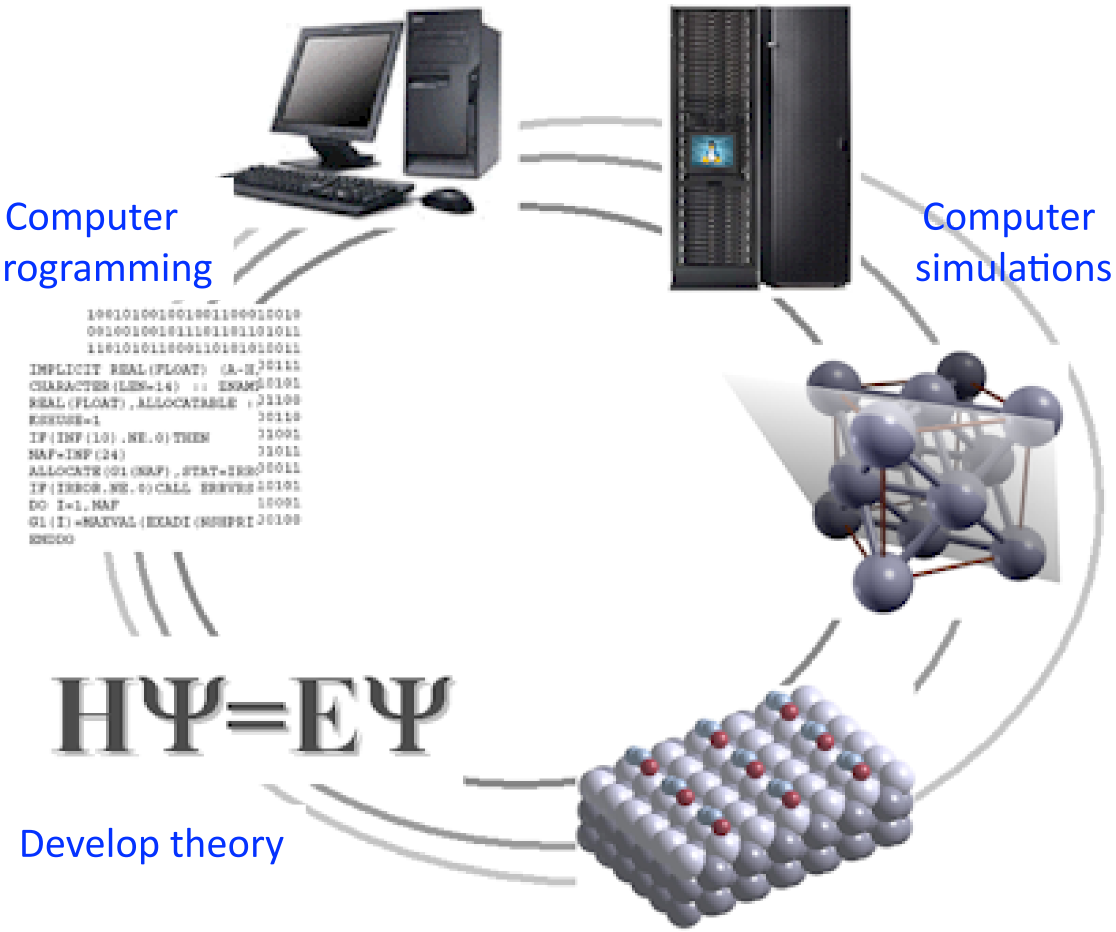

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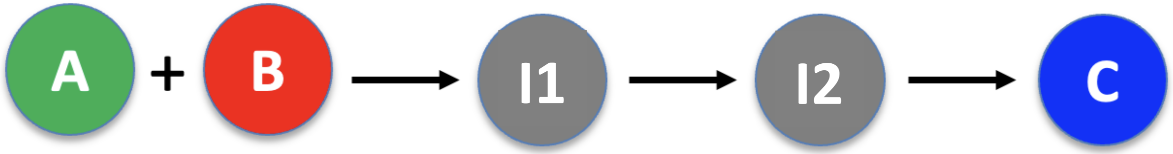
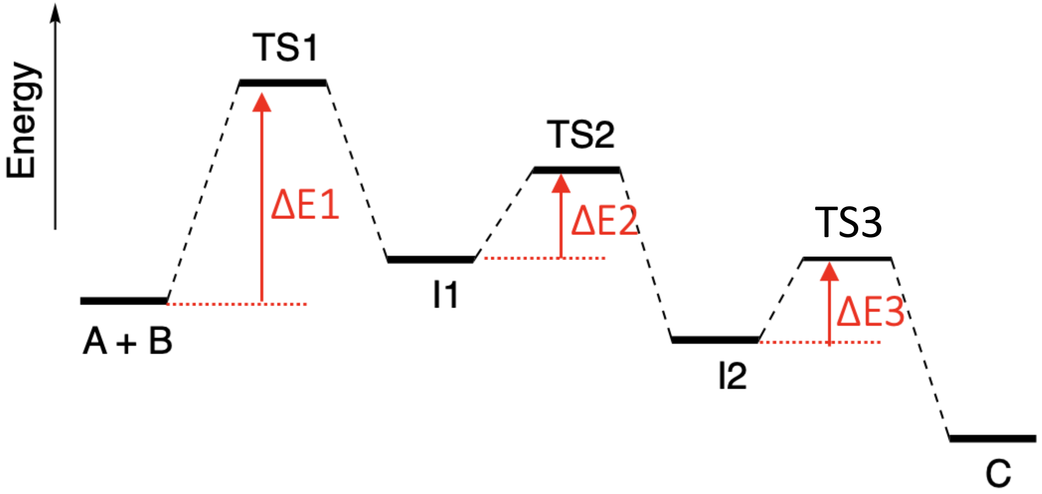
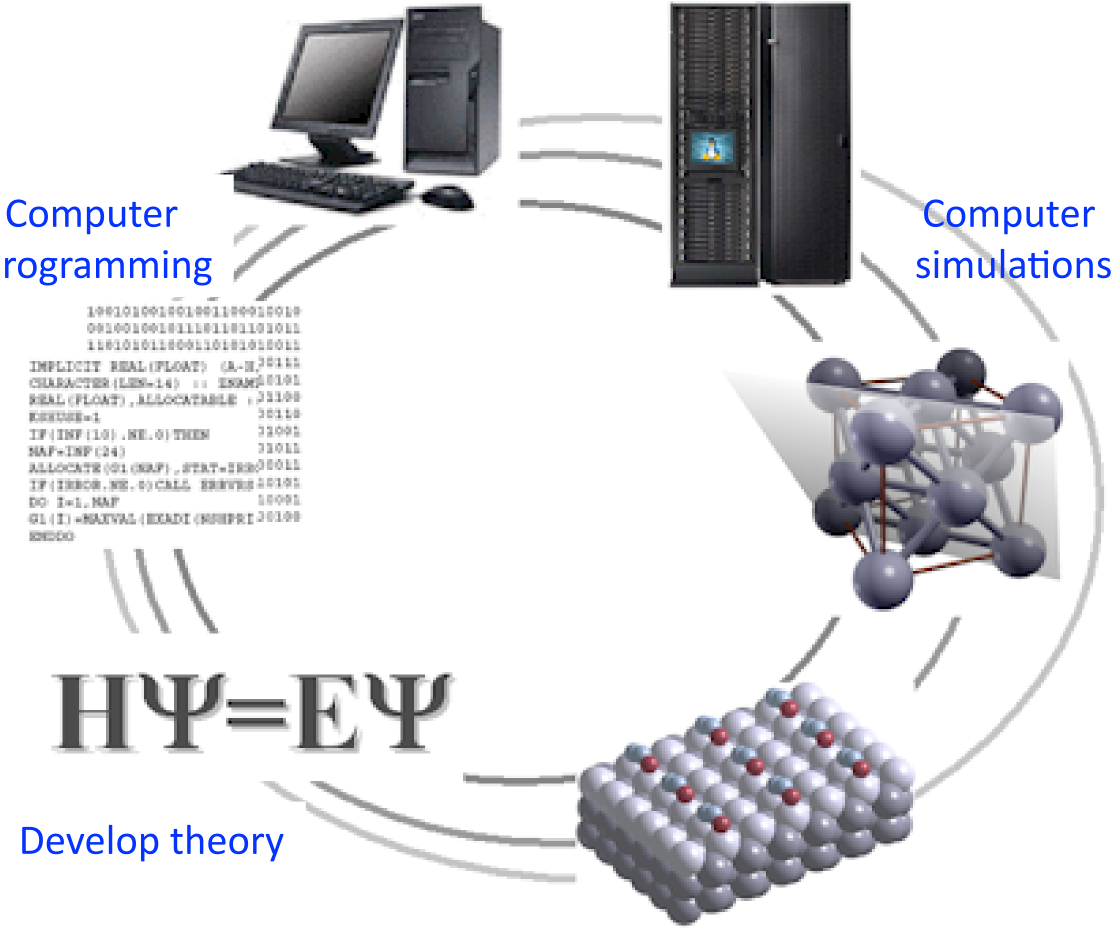




Quantum chemical methods can determine:

Reaction intermediates | Reaction barriers | Rate constants | Branching ratios | Tunneling effects | Binding energies | Diffusion barrier | Desorption energies | Spectroscopy | Many more …

Quantum Chemical Methods



Computer programming

Computer simulations

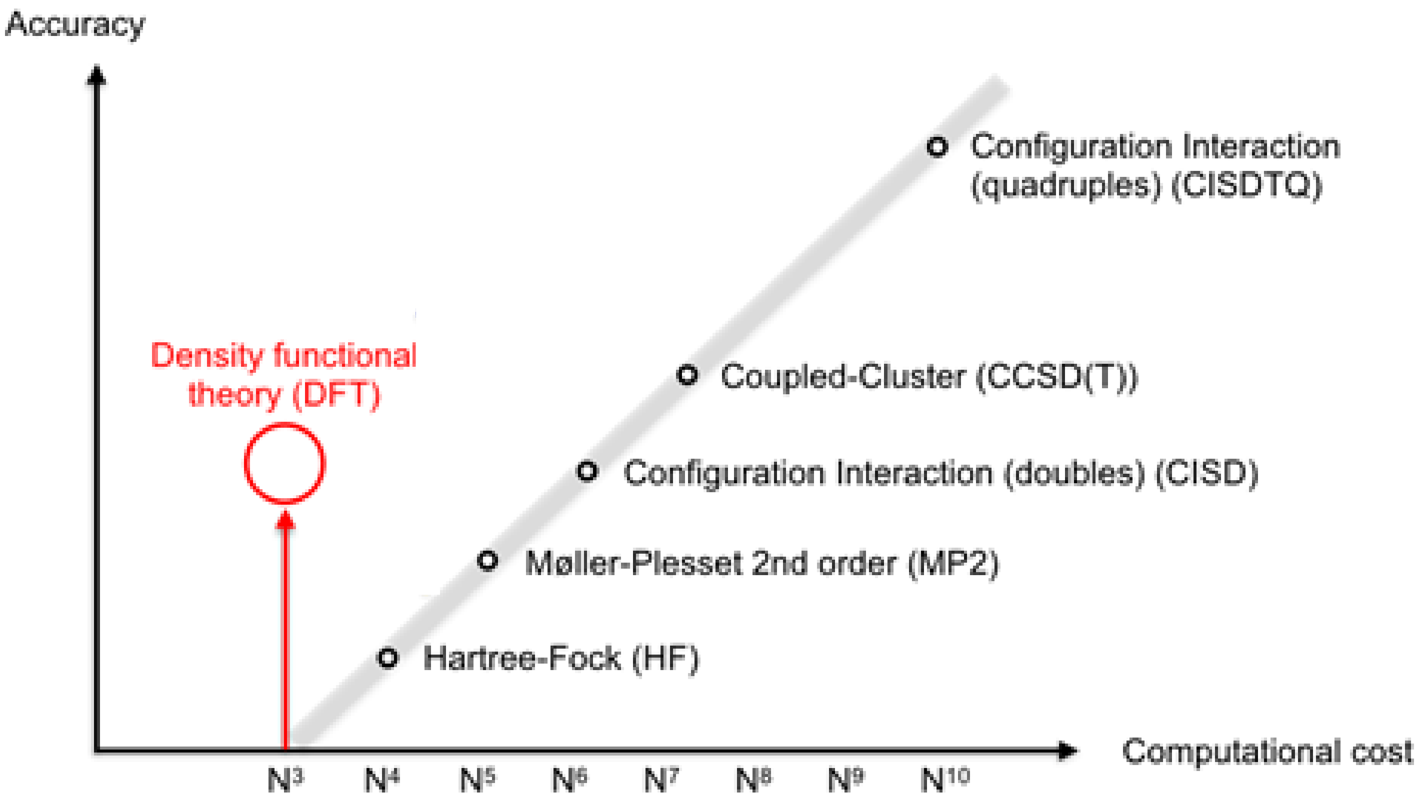
Develop theory

Quantum chemical computations

- The Schrödinger equation governs the behavior of quantum systems but is too complex to solve exactly for most real-world problems.

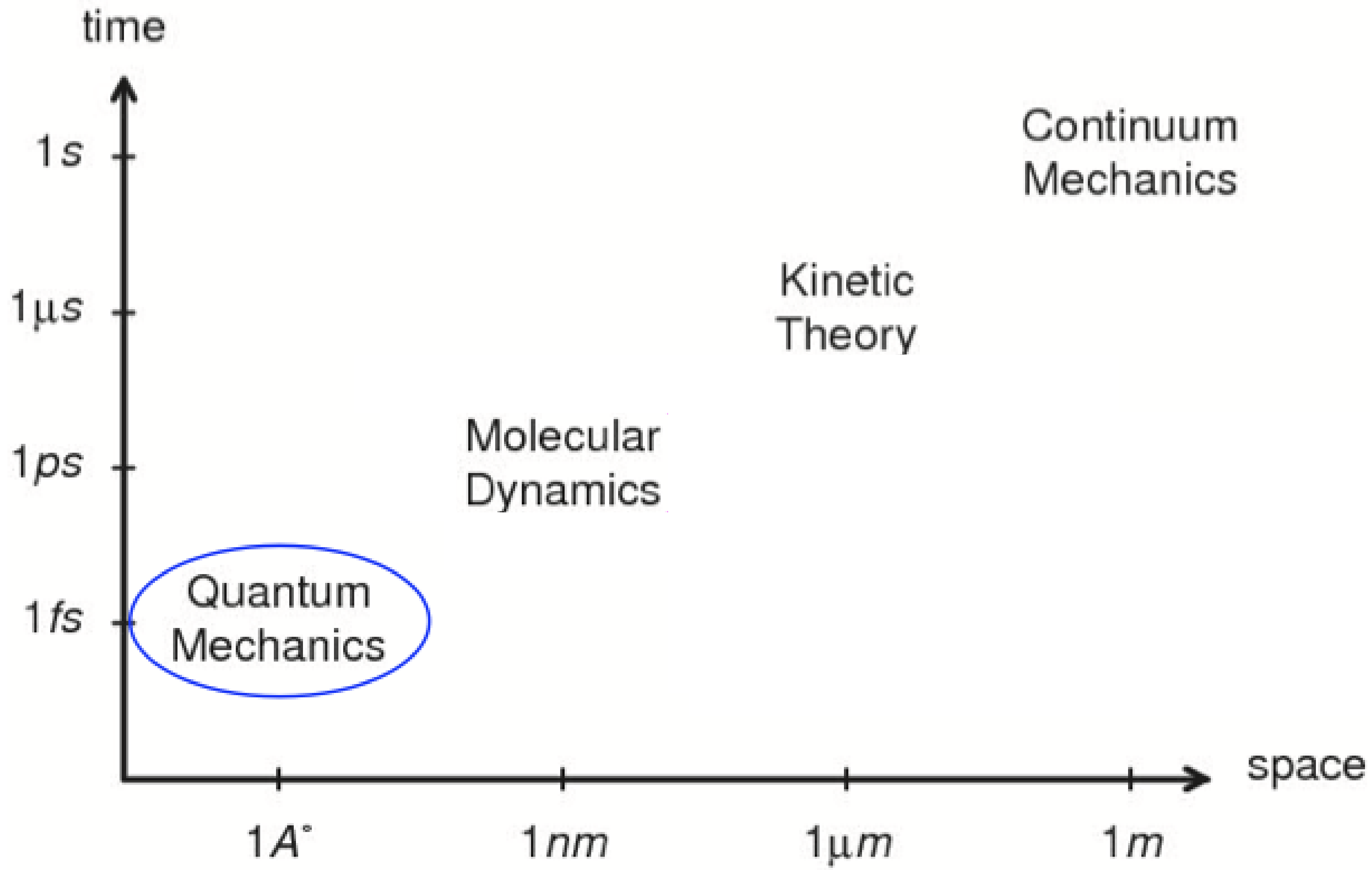
Quantum Chemical Methods

$$\boxed{\hat{H}\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

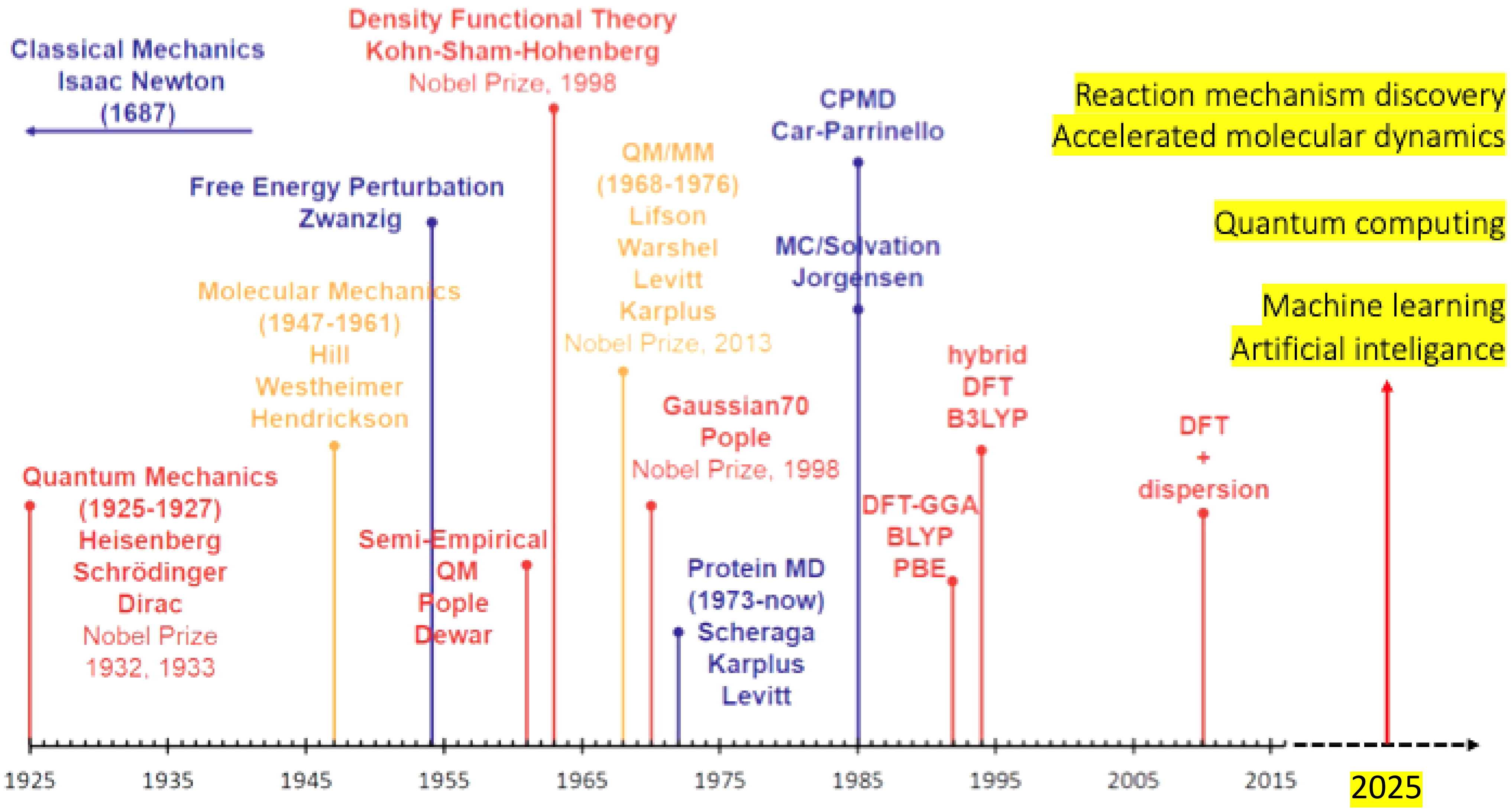


- The Schrödinger equation governs the behavior of quantum systems but is too complex to solve exactly for most real-world problems.
- Density Functional Theory (DFT) is a powerful approximation
- DFT replaces the many-electron wavefunction with the electron density, significantly reducing computational cost.
- DFT is efficient for predicting molecular and material properties.

Modelling approaches and their scales



Milestones in Theoretical and Computational Chemistry



Classical Mechanics
Isaac Newton
(1687)

Quantum Mechanics
(1925-1927)
Heisenberg
Schrödinger
Dirac
Nobel Prize
1932, 1933

Molecular Mechanics
(1947-1961)
Hill
Westheimer
Hendrickson

Free Energy Perturbation
Zwanzig

Semi-Empirical
QM
Pople
Dewar

Density Functional Theory
Kohn-Sham-Hohenberg
Nobel Prize, 1998

QM/MM
(1968-1976)
Lifson
Warshel
Levitt
Karplus
Nobel Prize, 2013

Gaussian70
Pople
Nobel Prize, 1998

Protein MD
(1973-now)
Scheraga
Karplus
Levitt

CPMD
Car-Parrinello

MC/Solvation
Jorgensen

DFT-GGA
BLYP
PBE

hybrid
DFT
B3LYP

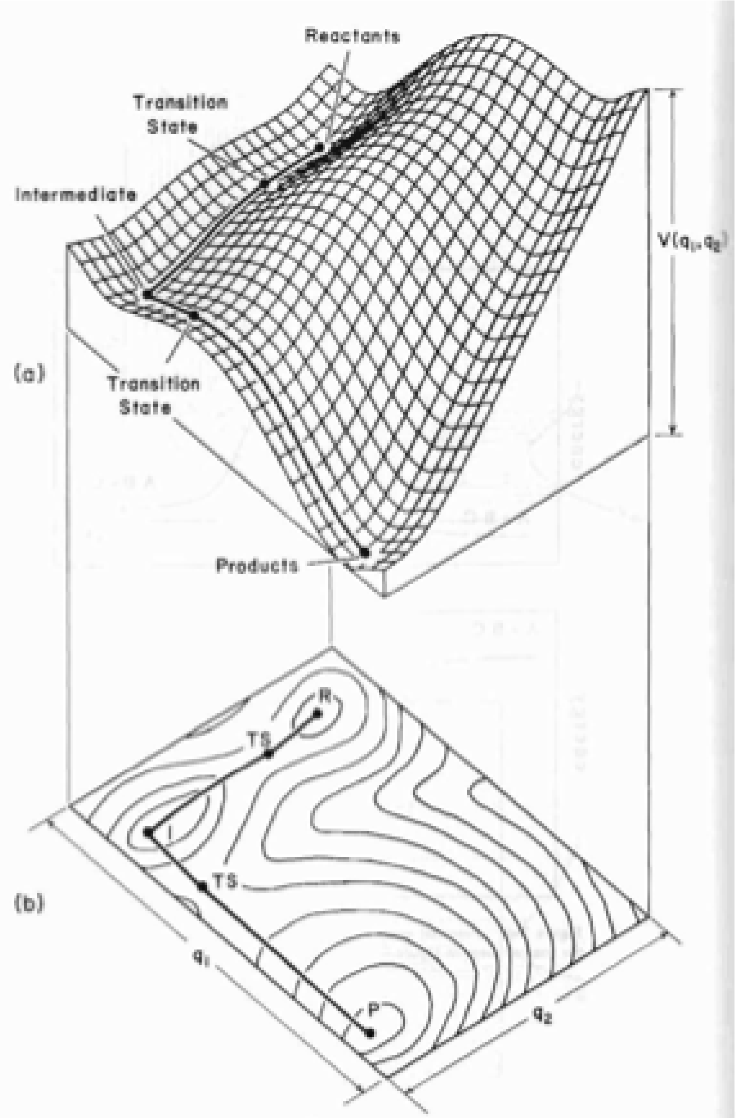
DFT
+
dispersion

Reaction mechanism discovery
Accelerated molecular dynamics

Quantum computing

Machine learning
Artificial inteligance

Potential energy surface (PES)



A three-dimensional perspective (a) and contour map (b) for a model chemical reaction. The solid line is the reaction path. [Adapted from G. M. Maggiora and R. E. Christofferson, in *Transition States of Biochemical Processes*, ed. R. D. Gandour and R. L. Schowen (New York: Plenum, 1978).]

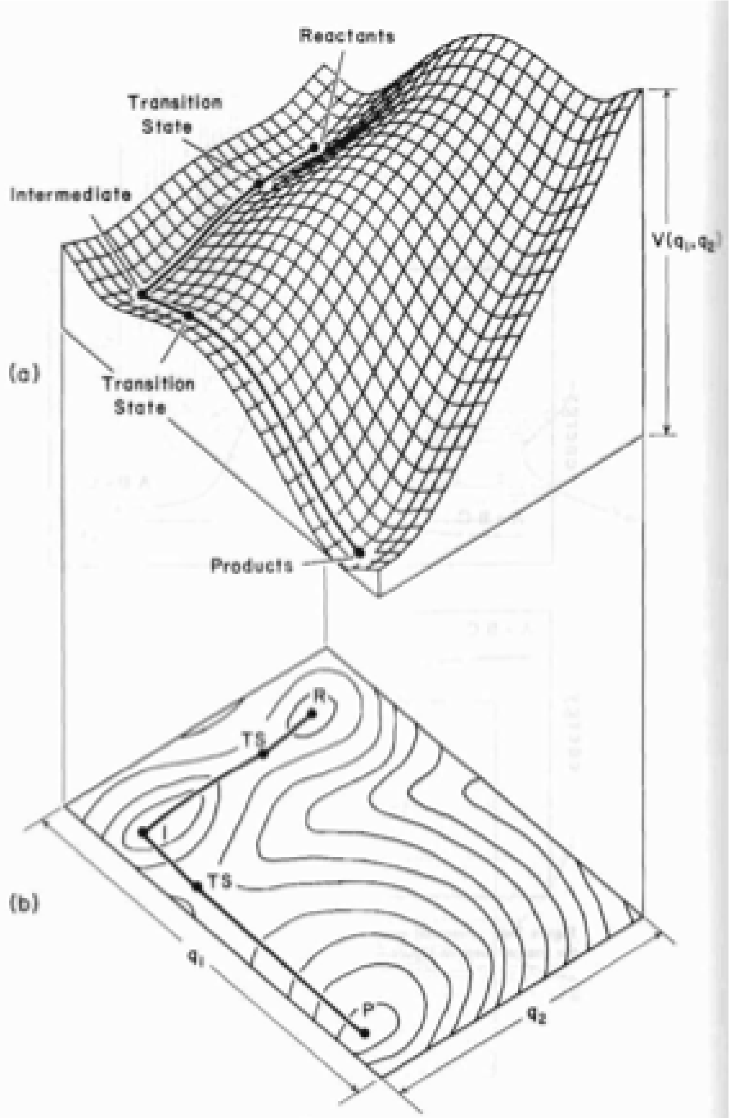
- PES is a geometric hypersurface on which the potential energy of the molecular system is plotted as a function of the coordinates representing the molecular geometry.

- Quantum mechanics can be used for calculating PESs.

- PES is important to understand the molecular structure and properties.

- Thus, calculating the PES of the molecular systems is a primary step in computational chemistry.

Potential energy surface (PES)



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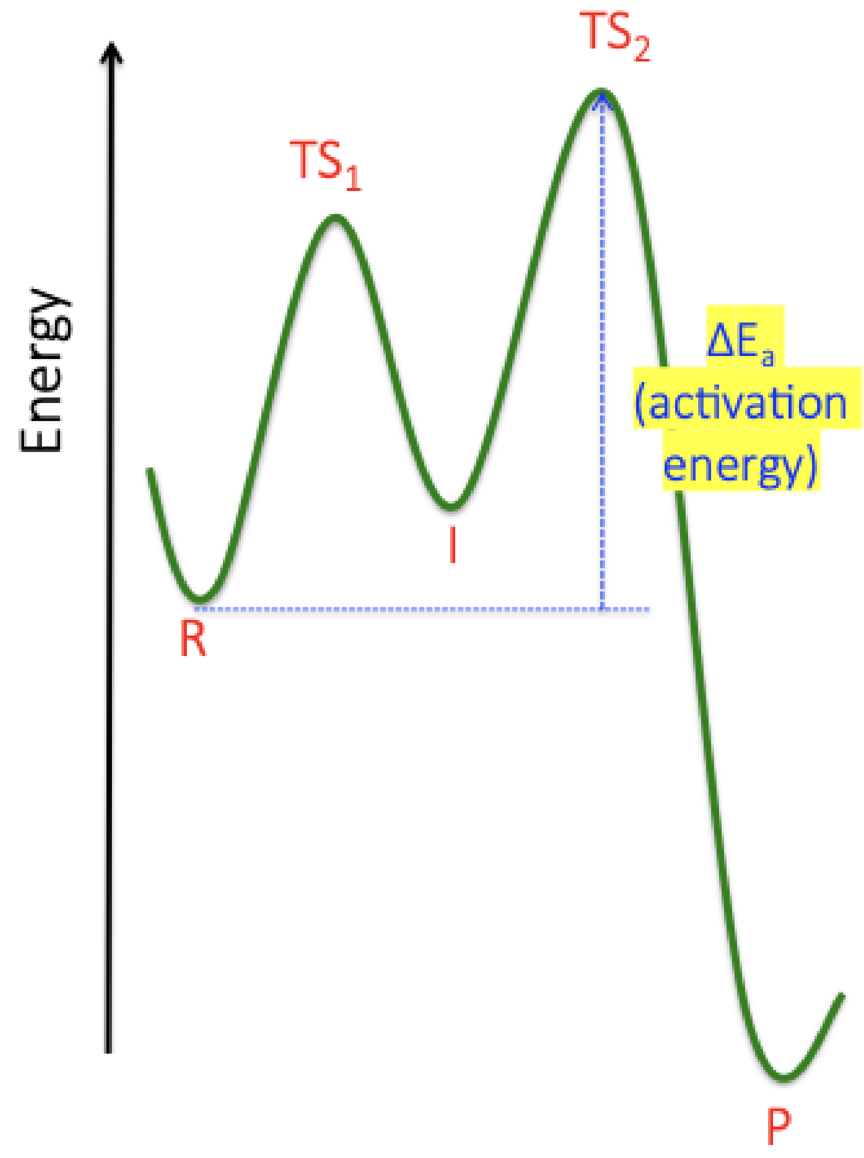

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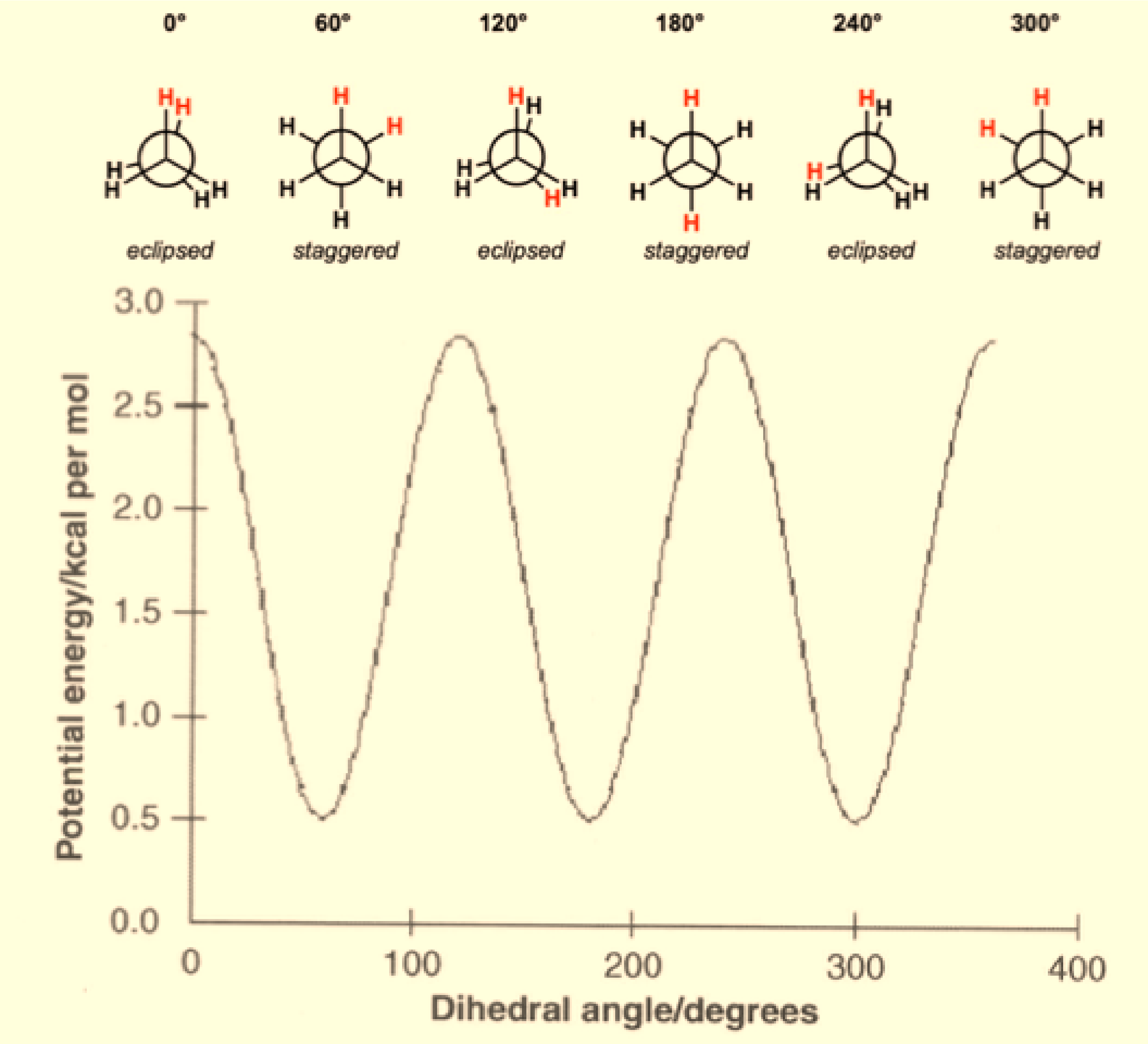
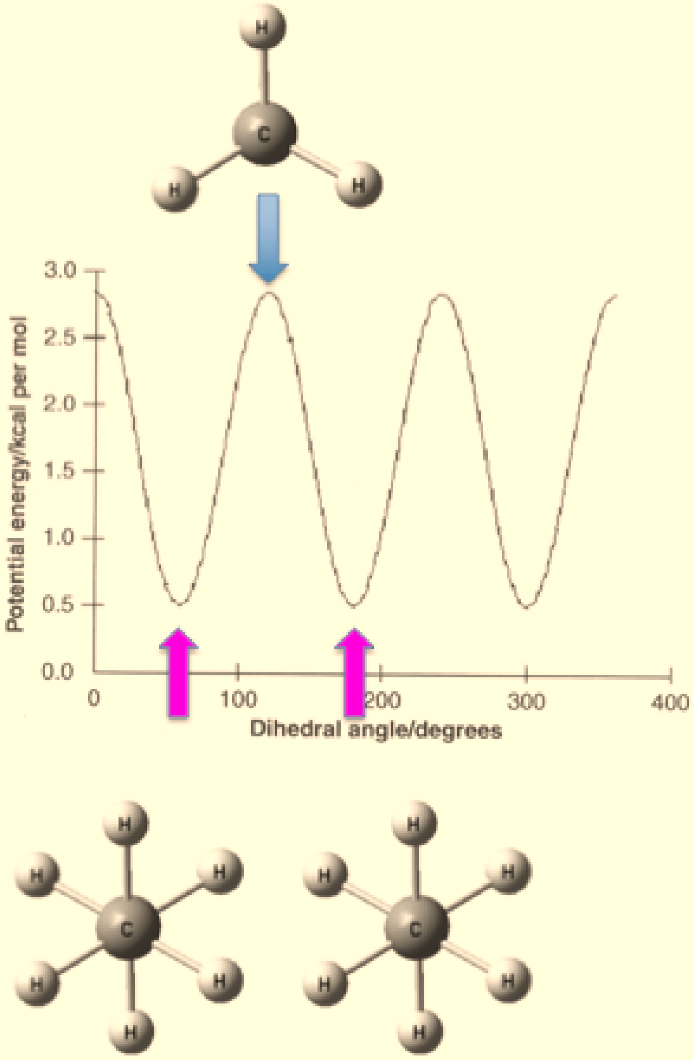
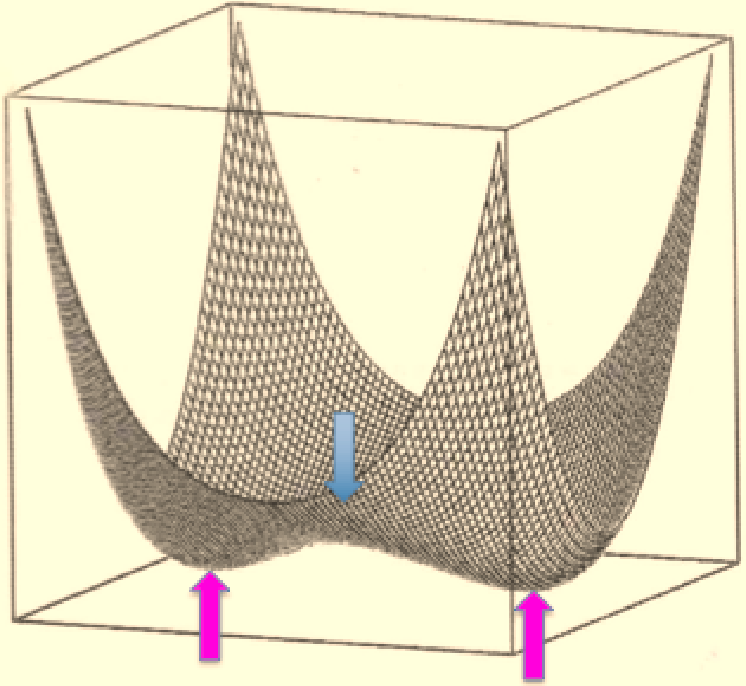
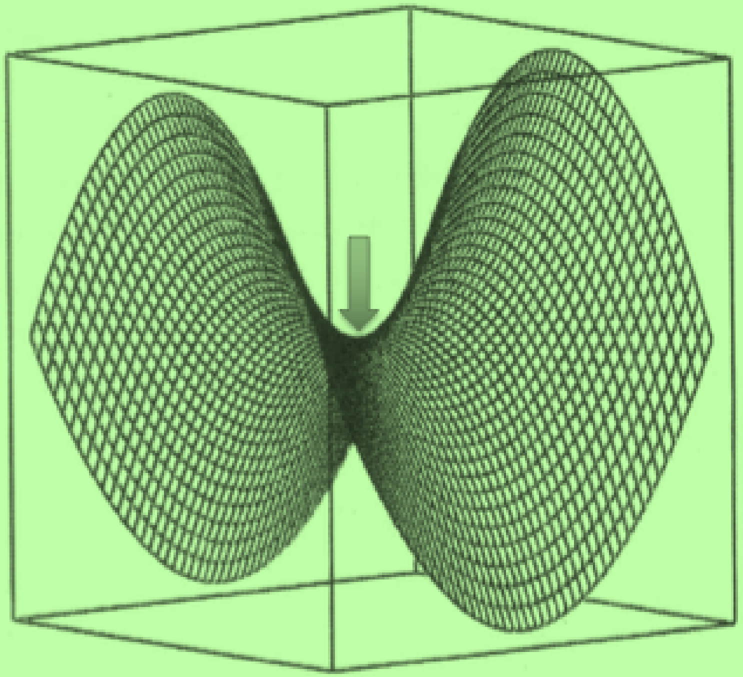


Potential energy surface (PES)



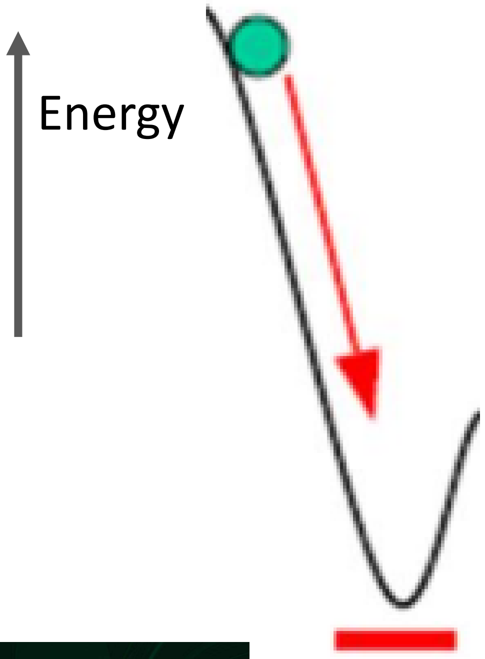


Two minima and a saddlepoint



Saddlepoint
=transition state

Optimization Techniques – locate a local minimum



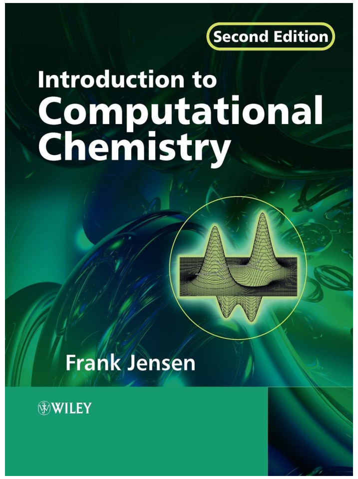
Multivariate Grid Search

- Choose a starting point A.
- For each variable $q_1, q_2, \ldots, q_p$ evaluate the molecular potential energy U at the two points surrounding A (as determined by the grid size).
- Select the new point for which U is a minimum, and repeat above steps until the local minimum is found.

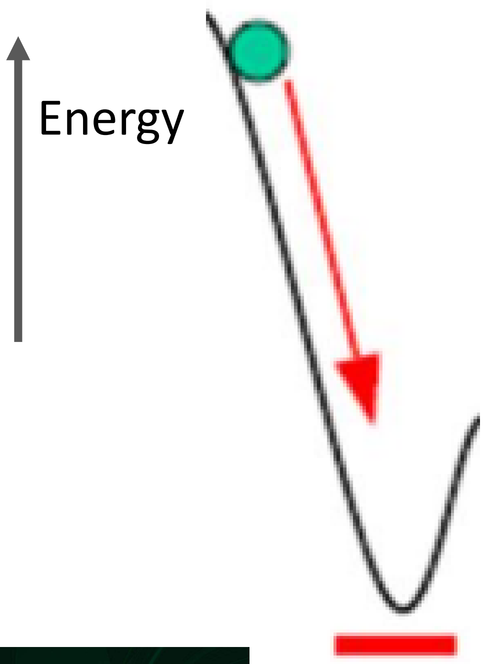
Univariate search

- Choose a starting point A.
- Minimize U(q) for each variable $q_1, q_2, \ldots, q_p$ in turn.
- Repeat the cycle as necessary.

Neither of the two methods makes use of derivatives (gradients and hessians).



Optimization Techniques – locate a local minimum



First-Order Methods

Steepest descent

Conjugate gradients

Second-Order Methods

Second-order methods use not only the gradient but also the hessian to locate a minimum.

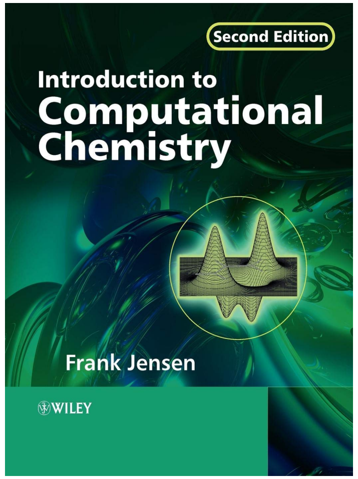
Newton–Raphson

There are a number of variations on the Newton–Raphson method, many of which aim to eliminate the need to calculate the full hessian.

Block diagonal Newton–Raphson.

Quasi-Newton–Raphson.

The Fletcher–Powell algorithm.



ORCA 6.0 TUTORIALS

SEARCH

FIRST STEPS
- How to cite
- Installing ORCA
- Hello water! Your first ORCA calculation
- Input and Output
- Running a calculation in parallel
- Graphical User Interfaces (GUI)
- Solving common issues

WORKFLOWS
- Compound Jobs
- Extrapolation Techniques

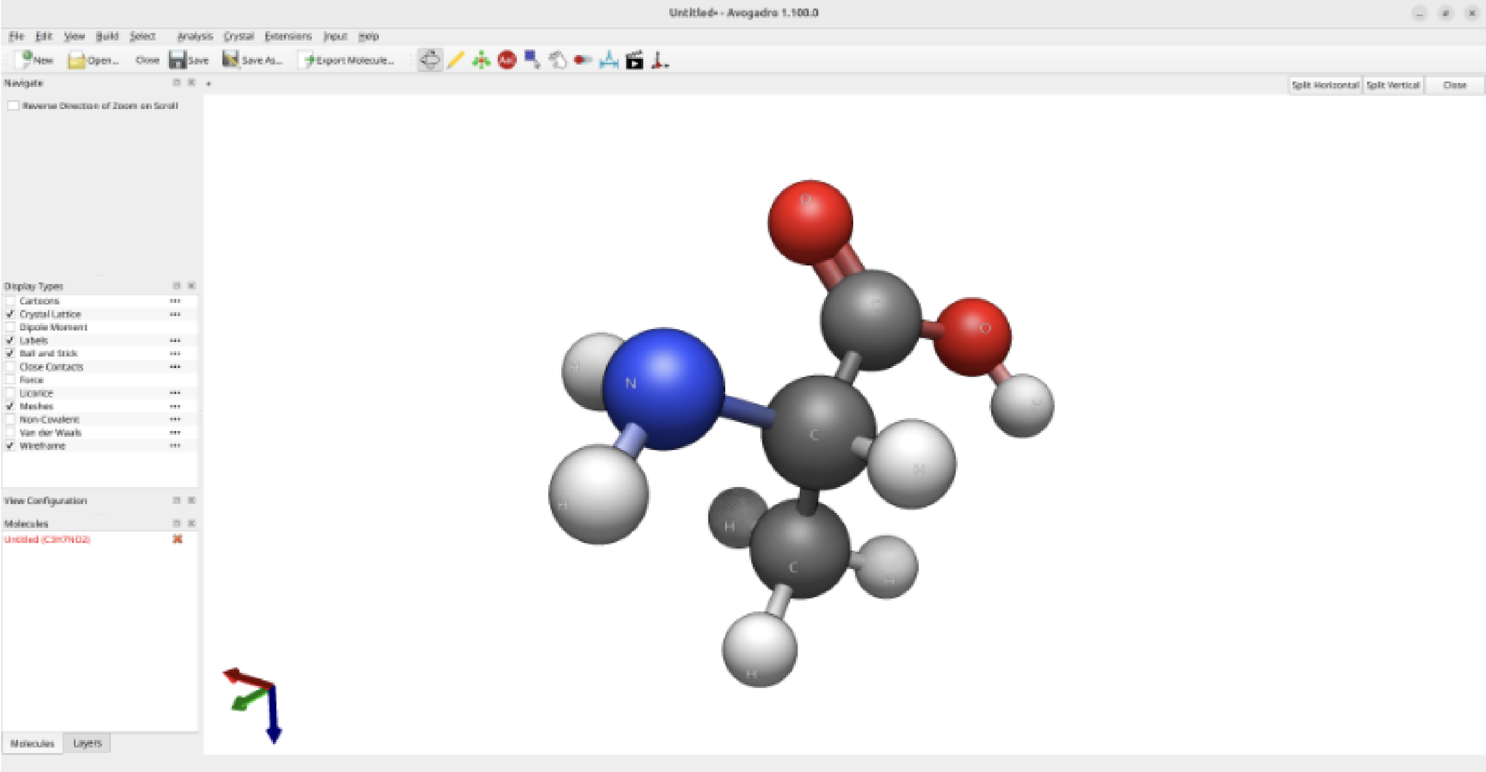
PROPERTIES
- Single point energies
- **Geometry optimization**
- Vibrational frequencies
- Thermodynamics

Geometry optimization

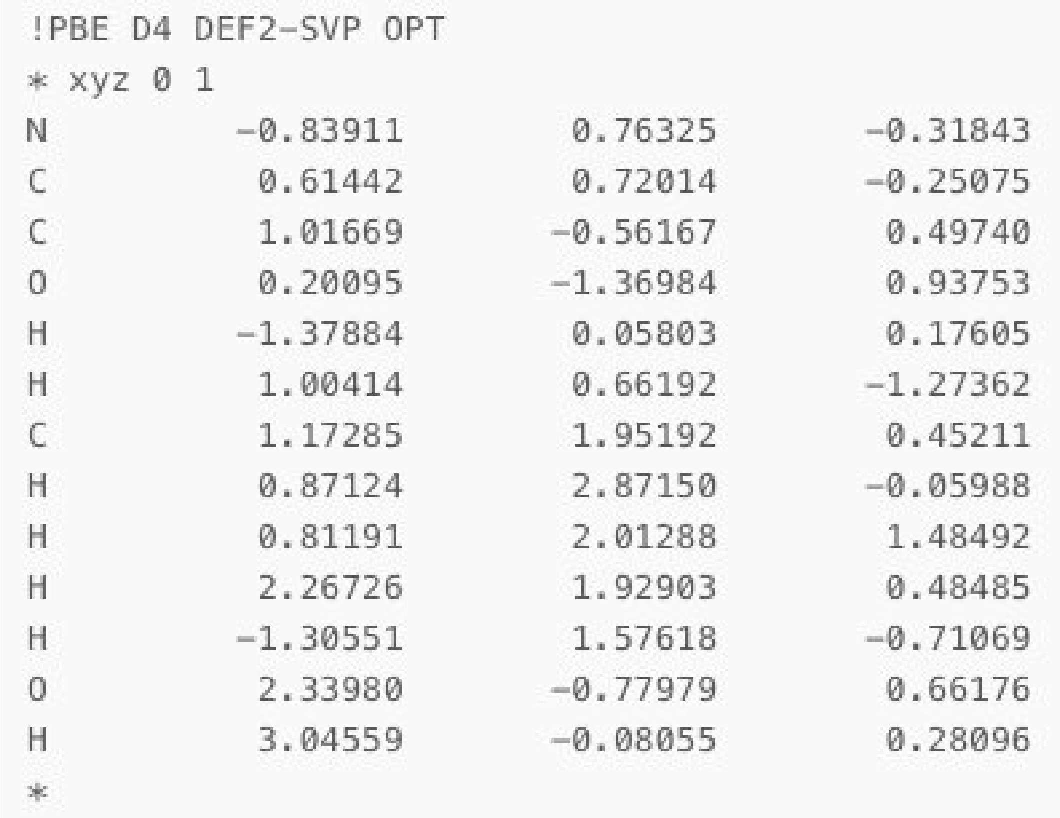
Basic usage

Optimizing a geometry means finding the geometry that minimizes the total energy for a given method.

Now, suppose you want to calculate the optimized geometry of the amino acid alanine for a given method. The first step is to have some kind of guess geometry. You can use Avogadro 2 to draw its structure and run the Open Babel optimizer (via `Extensions` → `Open Babel` → `Optimize Geometry`) to get a reasonable atom arrangement:



Input file



```
!PBE D4 DEF2-SVP OPT
* xyz 0 1
N          -0.83911       0.76325      -0.31843
C           0.61442       0.72014      -0.25075
C           1.01669      -0.56167       0.49740
O           0.20095      -1.36984       0.93753
H          -1.37884       0.05803       0.17605
H           1.00414       0.66192      -1.27362
C           1.17285       1.95192       0.45211
H           0.87124       2.87150      -0.05988
H           0.81191       2.01288       1.48492
H           2.26726       1.92903       0.48485
H          -1.30551       1.57618      -0.71069
O           2.33980      -0.77979       0.66176
H           3.04559      -0.08055       0.28096
*
```

PBE: The Perdew–Burke–Ernzerhof generalized gradient approximation (GGA).

D4: The Grimme D4 dispersion correction.

DEF2-SVP: Thebasis set (a split-valence polarized basis set by Ahlrichs et al.).

OPT: Perform a geometry optimization.

xyz: The coordinate format (Cartesian coordinates in Ångströms).

0: The total charge of the molecule (neutral).

1: The spin multiplicity (singlet; all electrons paired).

Atomic Coordinates

ORCA 6.0
TUTORIALS

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WORKFLOWS

Compound Jobs

Vibrational frequencies

After performing a Geometry optimization, you might want to compute the vibrational frequency of your system and plot normal mode animations. Here is how to do it, using the acetic acid as an example:

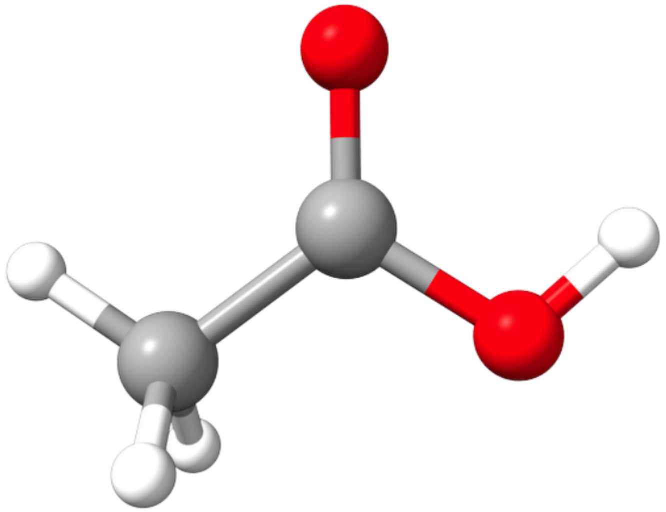
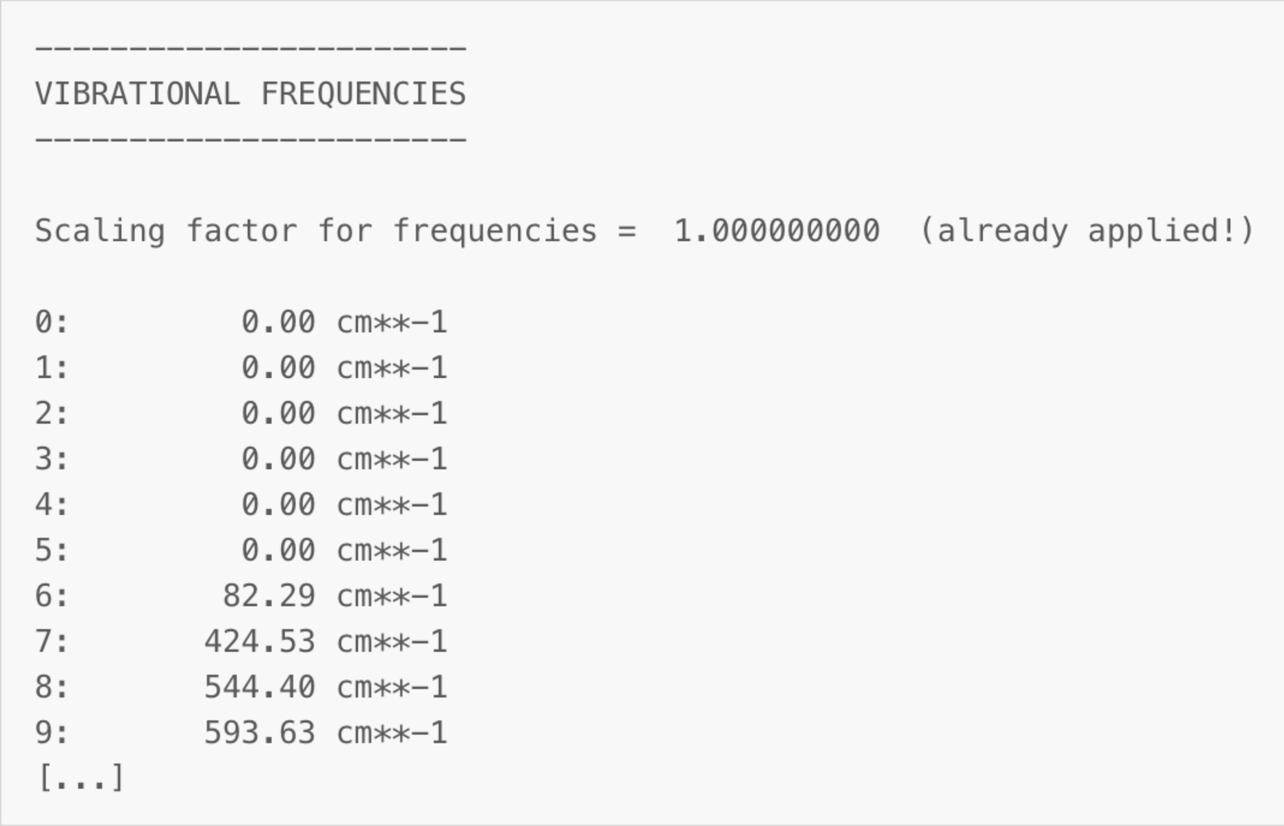


Figure: Molecular structure of acetic acid.

Frequencies

In order to first compute the frequencies, e.g. using DFT and the B3LYP functional use:

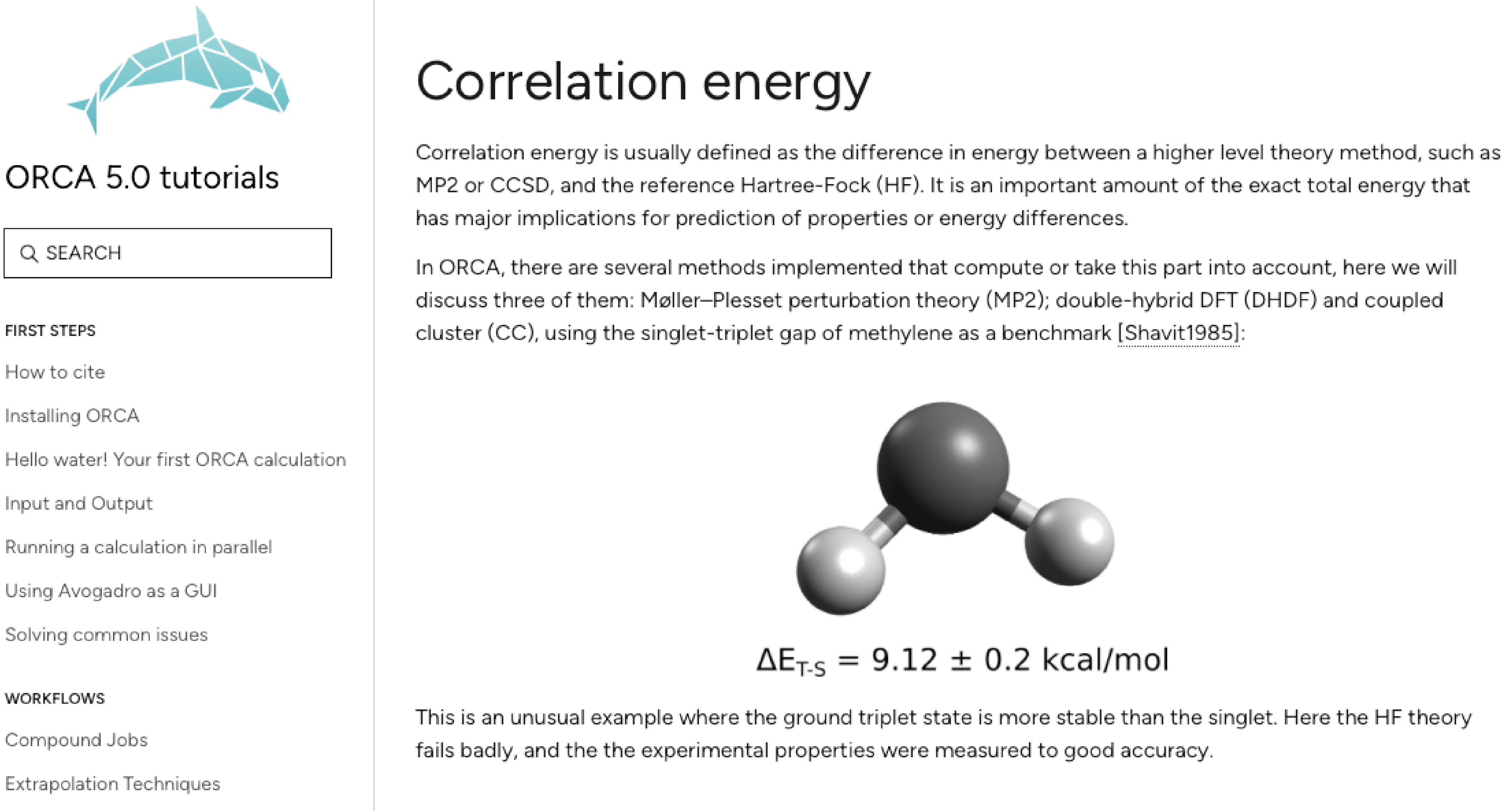
```
!B3LYP D4 DEF2-SVP FREQ
* XYZ 0 1
C         -0.81589      -0.51571      -0.02512
C          0.30690       0.49327      -0.06114
H         -0.42809      -1.56713      -0.28060
H         -1.26914      -0.51520       1.06962
H         -1.64631      -0.14518      -0.75104
O          0.16587       1.68279      -0.21470
O          1.51380      -0.07303       0.21899
H          2.16801       0.64625       0.13143
*
```



```
-----------------------
VIBRATIONAL FREQUENCIES
-----------------------

Scaling factor for frequencies =  1.000000000  (already applied!)

0:         0.00 cm**-1
1:         0.00 cm**-1
2:         0.00 cm**-1
3:         0.00 cm**-1
4:         0.00 cm**-1
5:         0.00 cm**-1
6:        82.29 cm**-1
7:       424.53 cm**-1
8:       544.40 cm**-1
9:       593.63 cm**-1
[...]
```



Correlation energy

Correlation energy is usually defined as the difference in energy between a higher level theory method, such as MP2 or CCSD, and the reference Hartree-Fock (HF). It is an important amount of the exact total energy that has major implications for prediction of properties or energy differences.

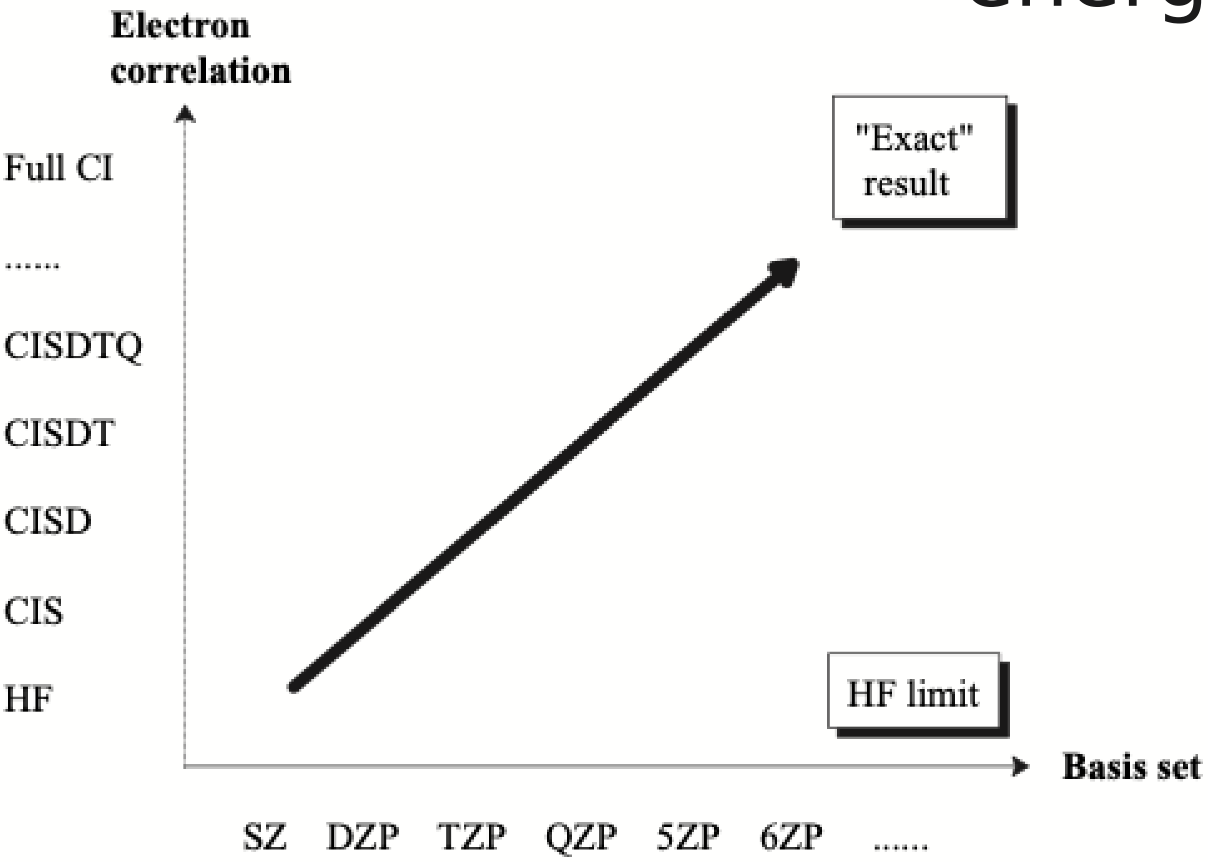
In ORCA, there are several methods implemented that compute or take this part into account, here we will discuss three of them: Møller–Plesset perturbation theory (MP2); double-hybrid DFT (DHDF) and coupled cluster (CC), using the singlet-triplet gap of methylene as a benchmark [Shavit1985]:

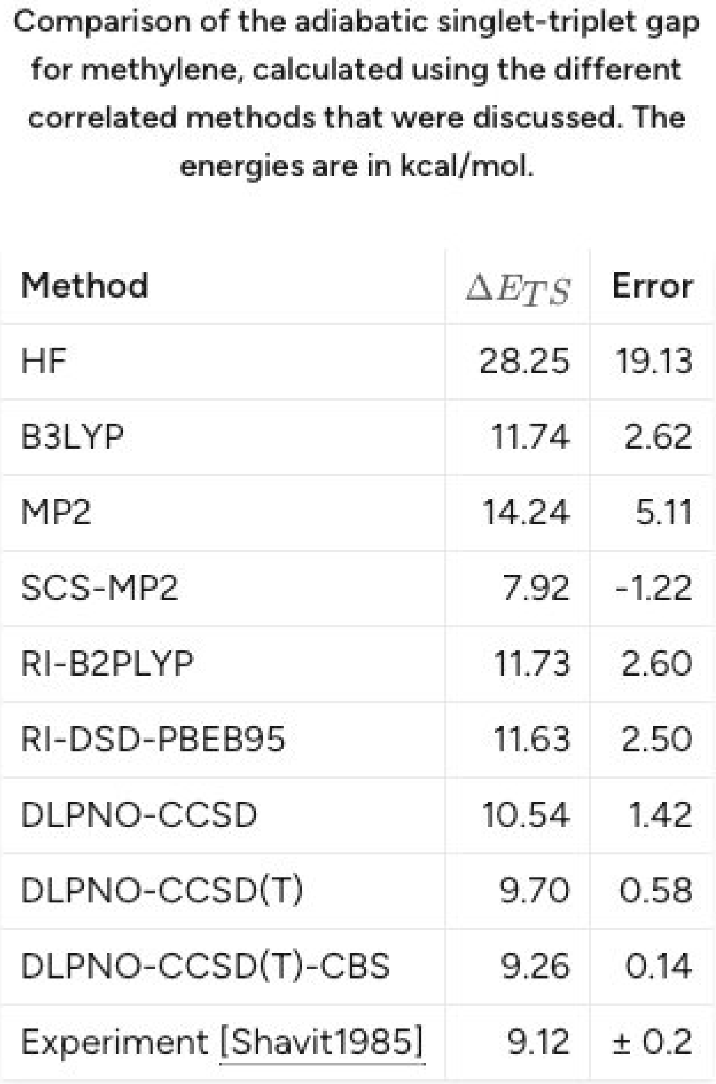
$$\Delta E_{T\text{-}S} = 9.12 \pm 0.2 \text{ kcal/mol}$$

This is an unusual example where the ground triplet state is more stable than the singlet. Here the HF theory fails badly, and the the experimental properties were measured to good accuracy.

https://www.faccts.de/docs/orca/5.0/tutorials/prop/corren.html

Correlation energy





Comparison of the adiabatic singlet-triplet gap for methylene, calculated using the different correlated methods that were discussed. The energies are in kcal/mol.

Method	ΔE_{TS}	Error
HF	28.25	19.13
B3LYP	11.74	2.62
MP2	14.24	5.11
SCS-MP2	7.92	-1.22
RI-B2PLYP	11.73	2.60
RI-DSD-PBEB95	11.63	2.50
DLPNO-CCSD	10.54	1.42
DLPNO-CCSD(T)	9.70	0.58
DLPNO-CCSD(T)-CBS	9.26	0.14
Experiment [Shavit1985]	9.12	± 0.2

In order to calculate total energies with a "chemical accuracy" of ~4kJ/mol (~1 kcal/mol), it is necessary to use a sophisticated methods for including electron correlation and large basis sets.