Aalto University
School of Chemical
Engineering

Introduction to Quantum Chemistry

CSC Spring School on Computational Chemistry 2024

Antti Karttunen
2024-04-18

Learning outcomes

- After the lectures you are able to describe:
  - What kind of systems can be studied with quantum chemical methods.
  - What kind of properties can be studied with quantum chemical methods.
  - What kind of software is available for quantum chemical modelling of molecules and materials.

- After the lectures, you will be able to use quantum chemical software in the hands-on session.

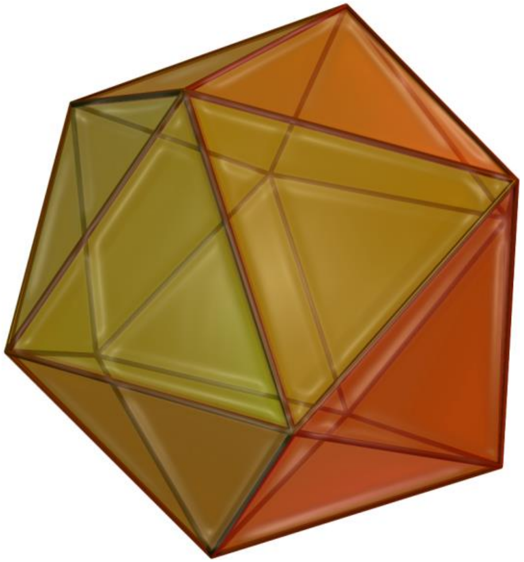


Figure: AJK

Outline of the contents

- Introduction to quantum chemical modelling of molecules and materials.
- Part I
  - Methods based on *ab initio* molecular orbital theory (”wavefunction methods”).
  - Basis sets for molecular quantum chemistry.
- Part II
  - Density Functional Theory
- Part III
  - Models, software, and practical suggestions.

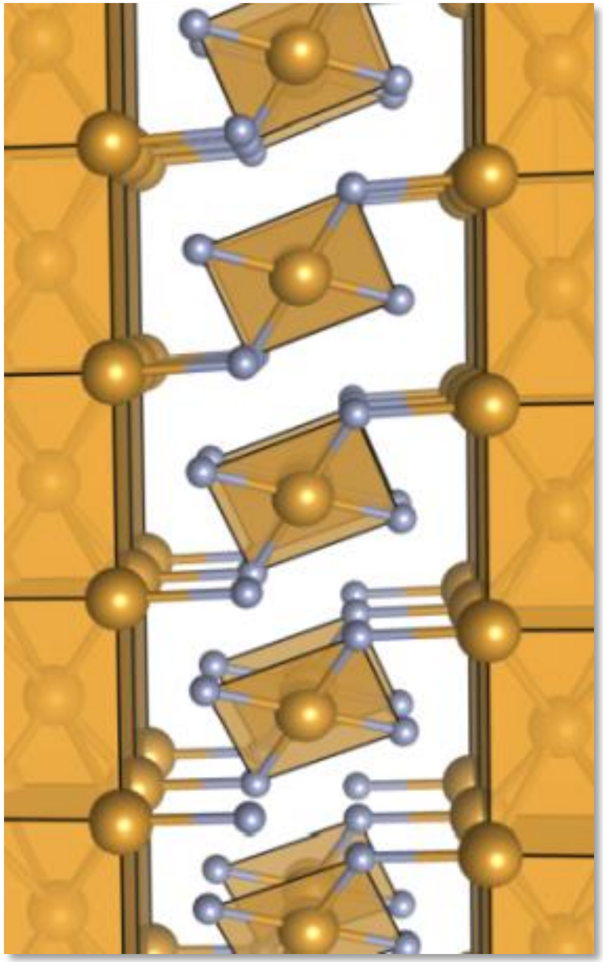
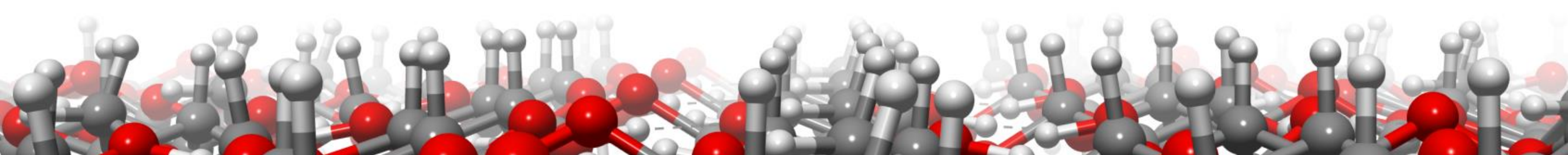


Figure: AJK

Introduction to quantum chemical modelling of molecules and materials.

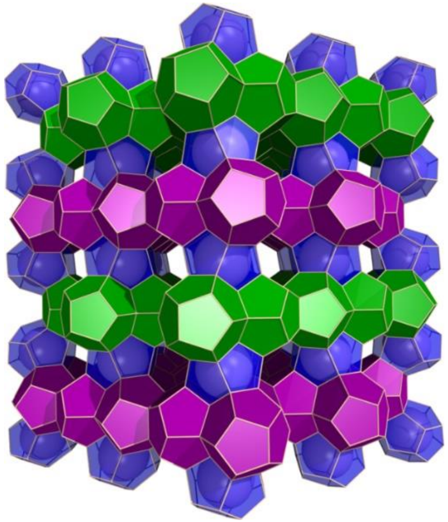


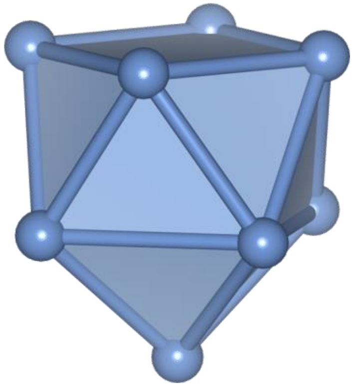
Quantum chemistry for molecules and materials

- Quantum chemical methods allow to study chemical systems at the level of individual electrons.

- Quantum chemical methods can be used for gas-phase molecules, liquids, and solids.

- Quantum chemical materials modelling techniques can be used to:
  1. Assist in the interpretation and explanation of experimental results
  2. Predict the existence and properties of new materials and molecules



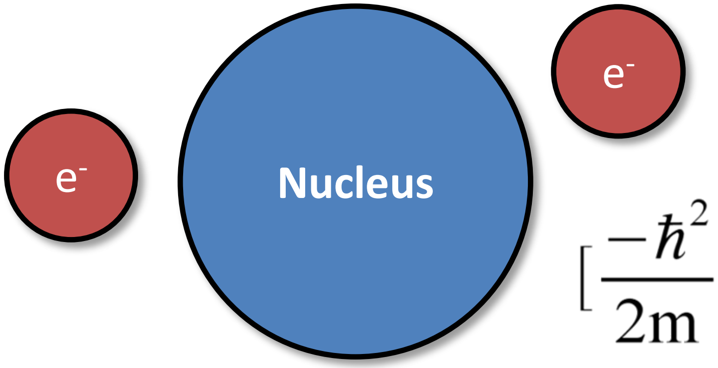


Figures: AJK

Quantum chemical methods

- In principle, quantum mechanics provides the mathematical machinery to describe all chemical phenomena exactly.
- We can study chemical systems at the level of individual electrons.
  - In practice, exact solutions are not feasible.
- We need approximate methods and computational power.
- Understanding the limitations of the approximations is a crucial skill for any computational chemist.
  - Choosing the right **level of theory** for a chemical problem.

$$F_e = \frac{k\,q_1 q_2}{r^2}$$



$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

Time-dependent Schrödinger equation

Figure: AJK

Level of theory

- The **level of theory** determines the reliability of the results:
  1. How the electron-electron interactions are described (=”**method**”)
  2. How a single electron is described (=”one electron **basis set**”)

- The computational resource requirements depend on
  - The **level of theory**
  - The size of the **model system** (number of atoms)
  - The type of the **model system** (molecular or periodic in 1D/2D/3D)

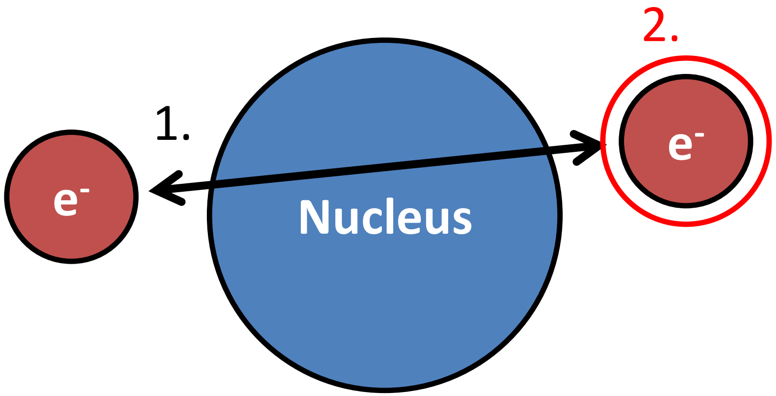


Figure: AJK

Ab initio / first principles methods

- Two major “branches”, which are in fact often combined in practical calculations
  - *Ab initio* molecular orbital theory
  - Density functional theory (DFT)
- **No system-dependent parametrization** required.
- Only the universal physical constants and the atomic-level structure of the system are required to predict the properties of the system.
- Predictions can be made also for non-existing molecules and materials.
  - Most successful in close collaboration with experimentalists.

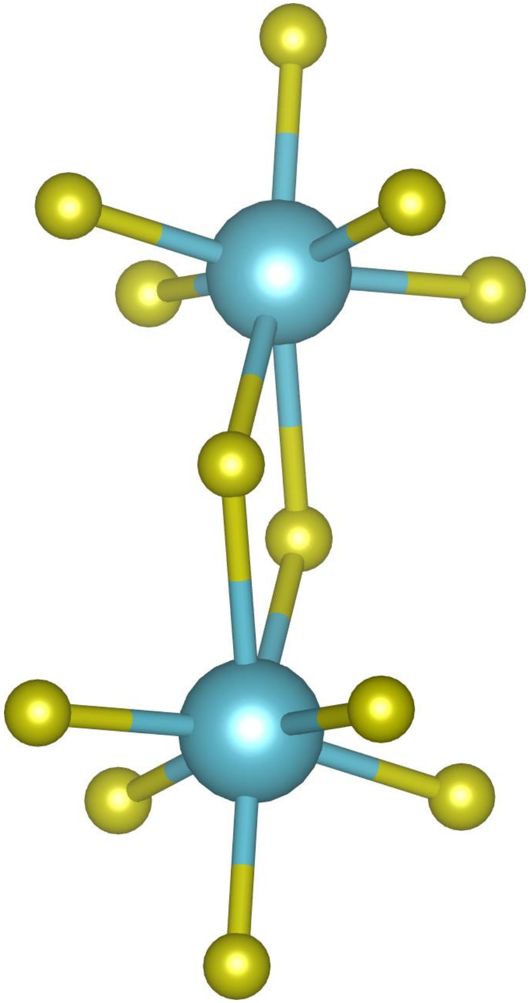


Figure: AJK

Learning material on computational quantum chemistry

- Textbooks
  - F. Jensen, ***Introduction to Computational Chemistry*** (Wiley)
  - C. J. Cramer, ***Essentials of Computational Chemistry*** (Wiley)
  - Helgaker, Jorgensen, Olsen, ***Molecular Electronic-Structure Theory*** (Wiley)
- Lecture notes:
  - European Summerschool in Quantum Chemistry
  - http://vergil.chemistry.gatech.edu/notes/ (Prof. C. David Sherrill)
- YouTube playlists:
  - Introduction to Computational Chemistry (Prof. C. David Sherrill)
  - ComputationalChemistryUMN (Prof. Chris Cramer)
- Orca program package manual (https://orcaforum.kofo.mpg.de/)
  - 1300+ pages in version 5.0.3
  - Lots of discussion on various methods and examples on their performance
  - Practical examples (you can run them by yourself with Orca!)

Recent reviews with emphasis on materials

Nature Materials **2021**, *20*, 728–735. https://doi.org/10.1038/s41563-021-01015-1

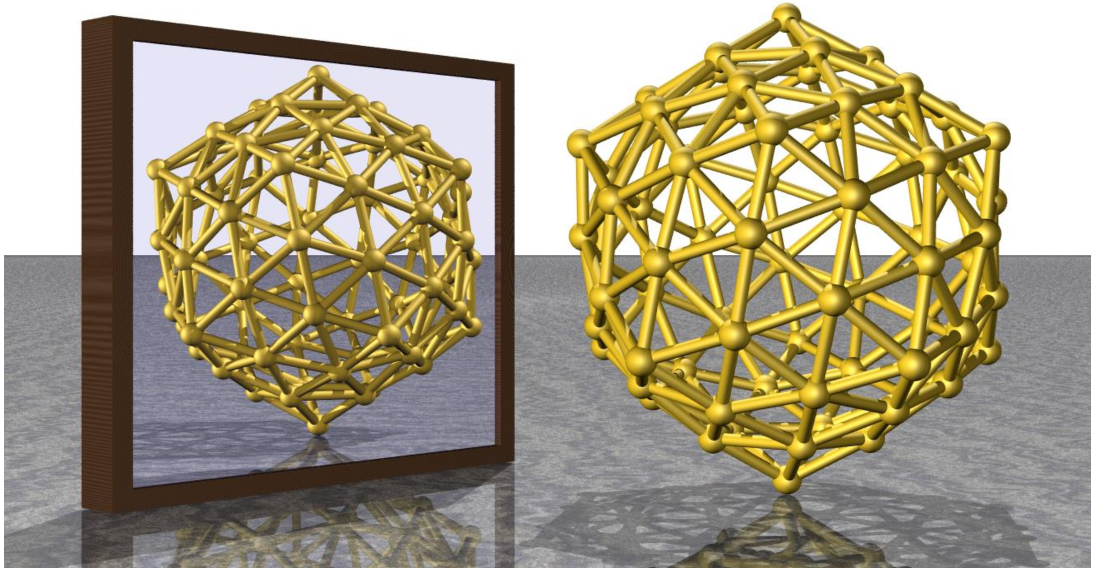
Discovering and understanding materials through computation

Steven G. Louie[1,2]✉, Yang-Hao Chan[1,2,3], Felipe H. da Jornada[4], Zhenglu Li[1,2] and Diana Y. Qiu[5,6]

Nature Materials **2021**, *20*, 736–749. https://doi.org/10.1038/s41563-021-01013-3

Electronic-structure methods for materials design

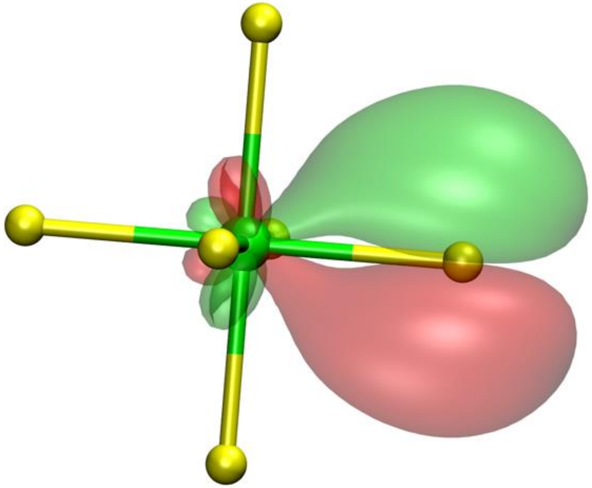
Nicola Marzari[1]✉, Andrea Ferretti[2] and Chris Wolverton[3]

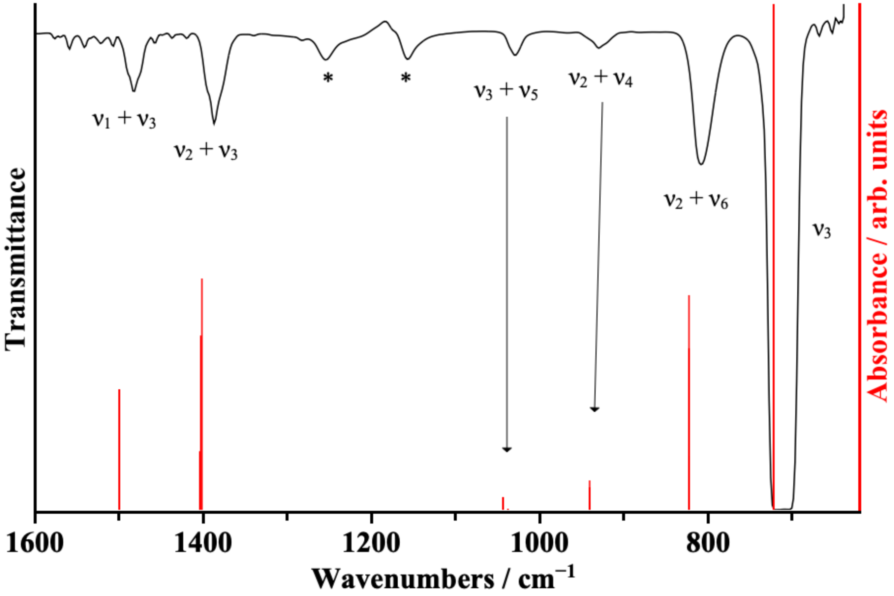


Example 1 (gas-phase)

A Computational Study on Closed-Shell Molecular Hexafluorides MF_6 (M=S, Se, Te, Po, Xe, Rn, Cr, Mo, W, U) – Molecular Structure, **Anharmonic Frequency Calculations**, and **Prediction** of the NdF_6 Molecule

https://doi.org/10.1002/cphc.202200903

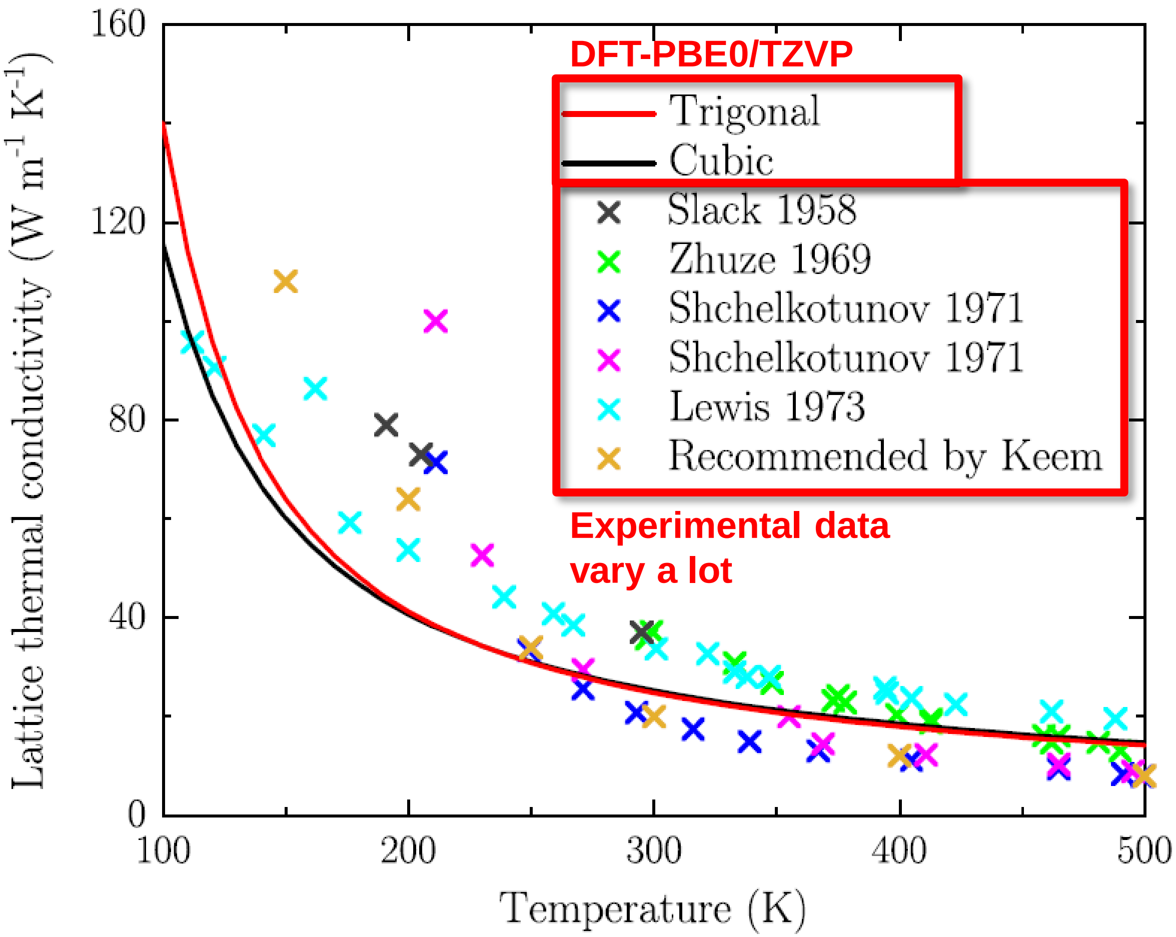




Experimental IR spectrum of WF_6 vapor recorded at 298 K (black curve, top) compared with the calculated wavenumbers and infrared intensities (red lines, bottom). The modes are **combination modes**.

CCSD(T)/cc-pVTZ(-PP) level of theory

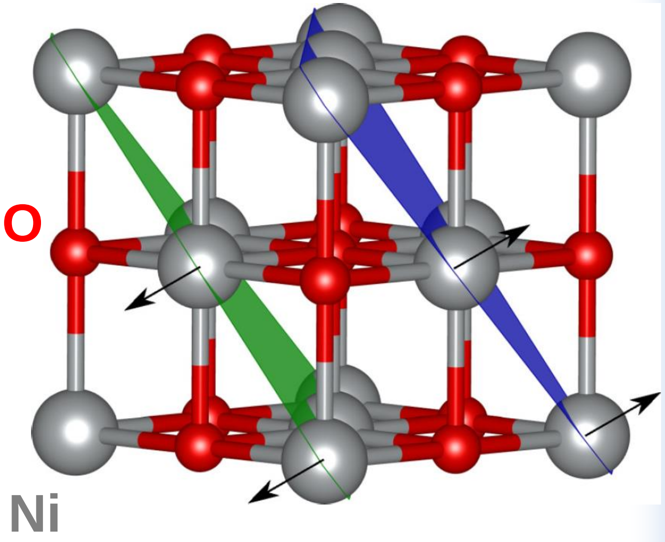
Example 2 (solid-state)
Lattice thermal conductivity of NiO



DFT-PBE0/TZVP

Experimental data vary a lot

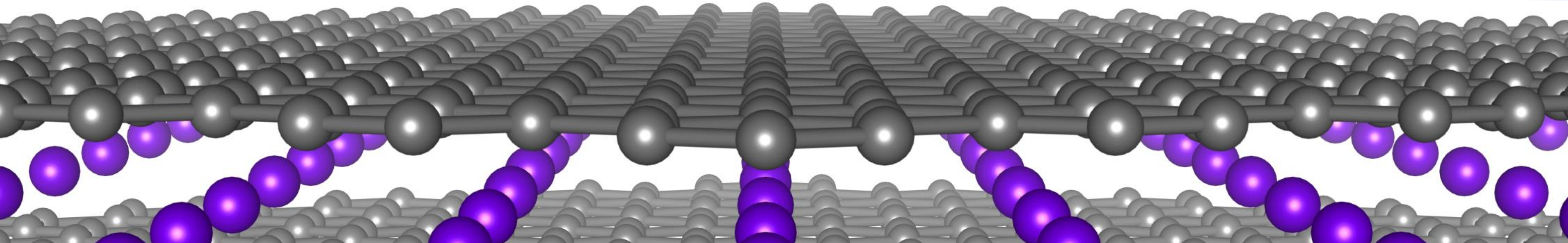
FIG. 4. Lattice thermal conductivity of NiO calculated using both the trigonal (red line) and cubic (black line) primitive cells. Crosses denote the different experimental data points [48–52].



NiO (*Fm*-3*m*)
Antiferromagnetic up to 525 K
Magnetic ordering: *R*-3*m*

J. Linnera, A. J. Karttunen, *Phys. Rev. B* **2019**, *100*, 144307.

Part I: *ab initio* molecular orbital theory



The molecular Hamiltonian

- We would like to solve the time-independent Schrödinger equation ***HΨ* = *EΨ*.**
  - This would yield the wavefunction ***Ψ*** and the total energy ***E***.
- The Hamiltonian operator ***H*** describes
  - The Coulombic interactions between the electrons and nuclei (V_{eN}, V_{ee}, V_{NN})
  - The kinetic energy of the electrons (T_e). The nuclei are so massive in comparison to the electrons that their kinetic energy can be neglected (Born-Oppenheimer approximation)

$$
\begin{aligned}
\hat{H}_{\mathrm{BO}} &= T_e + V_{eN} + V_{ee} + V_{NN} \\
&= -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \\
&\quad + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j \neq \grave{\imath}}}^{N}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \frac{1}{2}\sum_{A=1}^{M}\sum_{\substack{B=1 \\ A \neq B}}^{M}\frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}
\end{aligned}
$$

Electrons at positions $\boldsymbol{r}_i$, $\boldsymbol{r}_j$; Nuclei at positions $\boldsymbol{R}_A$, $\boldsymbol{R}_B$, with charges $\boldsymbol{Z}_A$, $\boldsymbol{Z}_B$

A concise summary of HF/DFT: F. Neese, *Coord. Chem. Rev.* **2009**, 253, 526–563.

Variational principle

- The Hamiltonian operator in $\boldsymbol{H\Psi = E\Psi}$ is known, now we need a way to describe the wavefunction Ψ*:*

$$\hat{H}_{\mathrm{BO}}\Psi(\mathbf{x}_1, \ldots, \boldsymbol{x}_{\mathrm{N}}|\boldsymbol{R}_1, \ldots, \boldsymbol{R}_{\mathrm{M}}) = E\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{\mathrm{N}}|\boldsymbol{R}_1, \ldots, \boldsymbol{R}_{\mathrm{M}})$$

($\boldsymbol{x}_i$ = position and spin of electron *i*; $\boldsymbol{R}_i$ = the nuclear coordinates entering as parameters)

- The key ingredient in the *ab initio* molecular orbital theory is the **variational principle**:

$$E \leq \frac{\langle \Psi_{\mathrm{trial}}|H|\Psi_{\mathrm{trial}}\rangle}{\langle \Psi_{\mathrm{trial}}|\Psi_{\mathrm{trial}}\rangle}$$

- The energy resulting from a (well-defined) trial wavefunction Ψ_{trial} is always higher than the exact energy *E* (only for the true ground-state wavefunction Ψ_0 we reach *E*)
- We can now start to construct trial wavefunctions and improve them with the help of the variational principle

Hartree-Fock method (1)

- In the **Hartree approximation**, the wavefunction Ψ is described as a simple product of single-electron wavefunctions called the **molecular orbitals** ψ_i

$$\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \psi_1(\boldsymbol{x}_1), \ldots, \psi_N(\boldsymbol{x}_N)$$

- The Hartree approximation violates the Pauli principle (wavefunction must be **antisymmetric** with respect to interchange of two sets of electronic variables)
- In the **Hartree-Fock method**, the wavefunction Ψ is described by a **Slater determinant**, which in turn is composed of molecular orbitals ψ_i

$$\Psi_{\mathrm{SD}}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\boldsymbol{x}_1) & \psi_2(\boldsymbol{x}_1) & \cdots & \psi_N(\boldsymbol{x}_1) \\ \psi_1(\boldsymbol{x}_2) & \psi_2(\boldsymbol{x}_2) & \cdots & \psi_N(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\boldsymbol{x}_N) & \psi_2(\boldsymbol{x}_N) & \cdots & \psi_N(\boldsymbol{x}_N) \end{vmatrix}$$

- The Slater determinant obeys the Pauli principle (switching two electronic variables implies switching two rows -> the sign of the wavefunction changes)

Hartree-Fock method (2)

- The molecular orbitals ψ_i of the Slater determinant are formed as **Linear Combinations of Atomic Orbitals** (LCAO):

  $\Psi_i = \Sigma_k c_{ik} \varphi_k$
- The atomic orbitals φ_k constitute the **basis set**
- Now, we can vary the coefficients c_{ik} to improve the Hartree-Fock energy

$$E \leq \frac{\langle \Psi_{\text{trial}} | H | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle}$$

- The expectation value of the molecular Hamiltonian operator over the Slater determinant is

$$\langle \Psi_{\text{SD}} | H_{\text{BO}} | \Psi_{\text{SD}} \rangle = V_{NN} + \sum_i \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \langle \psi_i \psi_j || \psi_i \psi_i \rangle$$

One-electron integrals

Two-electron integrals

One- and two-electron integrals

- The **one-electron integrals** are defined as

$$\langle \psi_i | h | \psi_i \rangle = \int \psi_i^*(\boldsymbol{x}) h(\boldsymbol{x}) \psi_i(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x}$$

- The one-electron hamiltonian *h*(***x***) includes the kinetic energy of the electron and the nuclear-electron attraction
- The **two-electron integrals** are defined as

$$\langle \psi_i \psi_j || \psi_i \psi_j \rangle \quad = \quad \langle \psi_i \psi_j | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \psi_j \psi_i \rangle$$

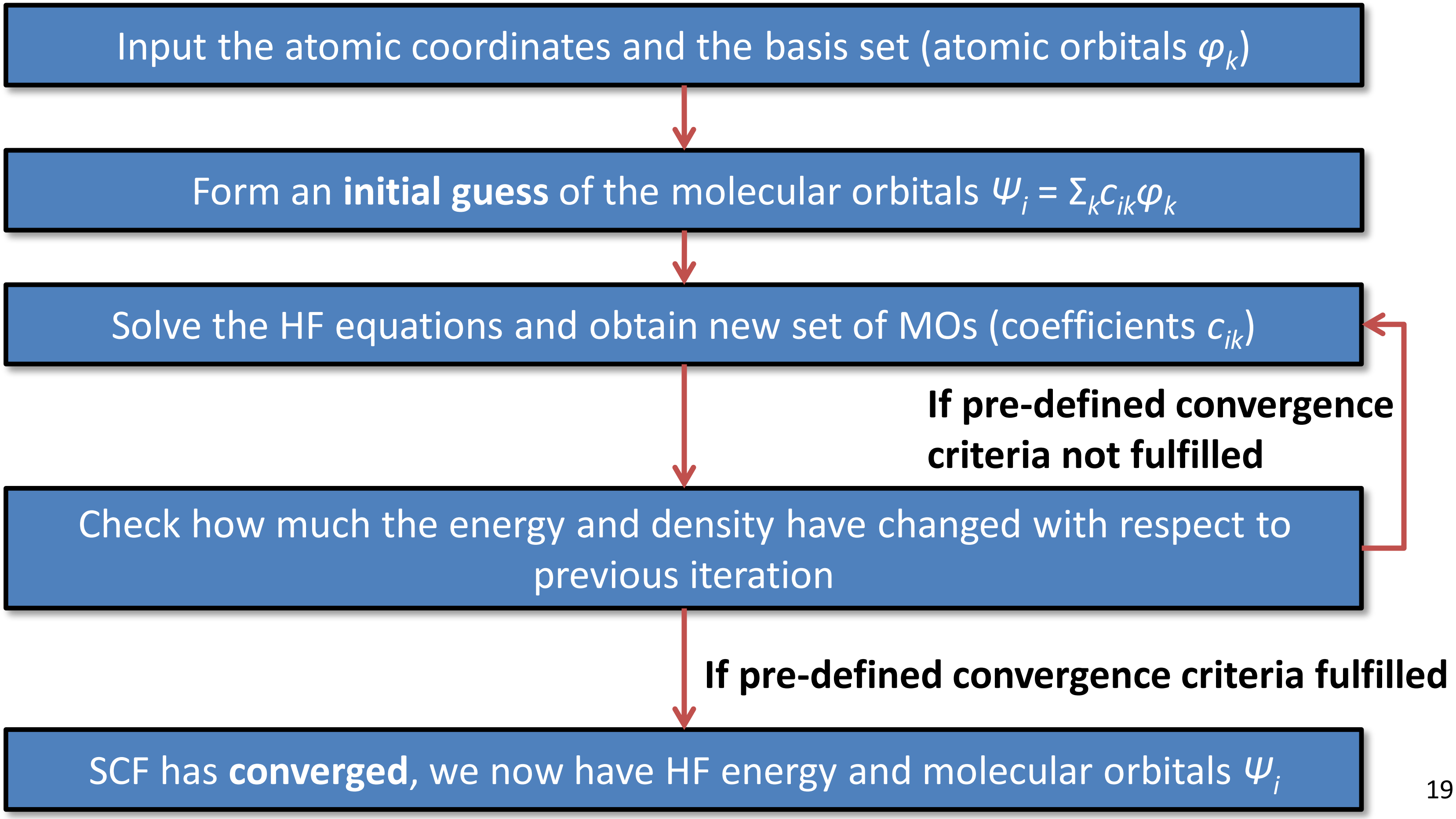
Coublomb integral (=Coulomb repulsion between electrons)

Exchange integral (no classical counterpart, arises from antisymmetry requirement)

- The main challenge in solving the Hartree-Fock equations is related to obtaining the two-electron integrals

Self-Consistent Field (SCF)

- The Hartree–Fock equations constitute a complicated set of nonlinear integro-differential equations that cannot be solved directly
- Instead, they are solved with an iterative **Self-Consistent Field** (SCF) method



Input the atomic coordinates and the basis set (atomic orbitals φ_k)

Form an **initial guess** of the molecular orbitals $\Psi_i = \Sigma_k c_{ik} \varphi_k$

Solve the HF equations and obtain new set of MOs (coefficients c_{ik})

If pre-defined convergence criteria not fulfilled

Check how much the energy and density have changed with respect to previous iteration

If pre-defined convergence criteria fulfilled

SCF has **converged**, we now have HF energy and molecular orbitals Ψ_i

Approximations within HF

1. Mean-field approximation: Each electron moves in an average potential created by the other electrons and the many-body problem is reduced to a one-body problem
    - **Post-HF** methods aim to account for the missing **electron correlation** E_{corr}:

      $E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}}$
2. The wavefunction is described by one Slater determinant only
    - **Multiconfigurational** or **multi-reference** methods account for this.
3. Finite number of basis functions for describing the electrons
    - Increasing the basis set towards the complete basis set is straightforward (but computationally demanding).
4. Relativistic effects are neglected
    - Can be easily partially reintroduced via **Effective Core Potentials**.
    - Nowadays spin-orbit coupling can also be treated in many codes.
5. Born-Oppenheimer approximation
    - Typically used in quantum chemical calculations.

Basis sets for molecular quantum chemistry

Basis sets

- Reminder: we need a basis set to describe the electrons.
- The molecular orbitals ψ_i of the Slater determinant are formed as **Linear Combinations of Atomic Orbitals** (LCAO):

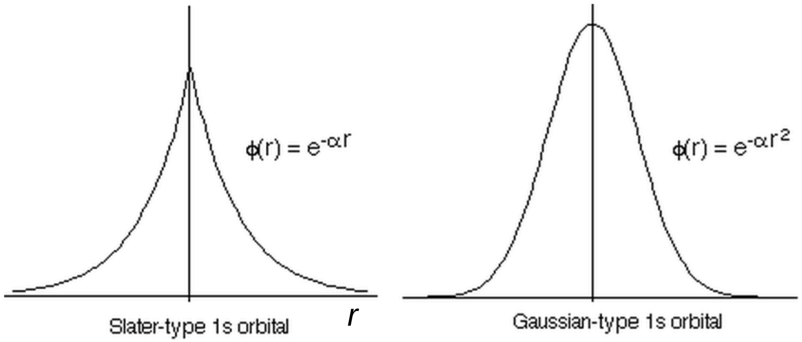
  $$\Psi_i = \Sigma_k c_{ik} \varphi_k$$

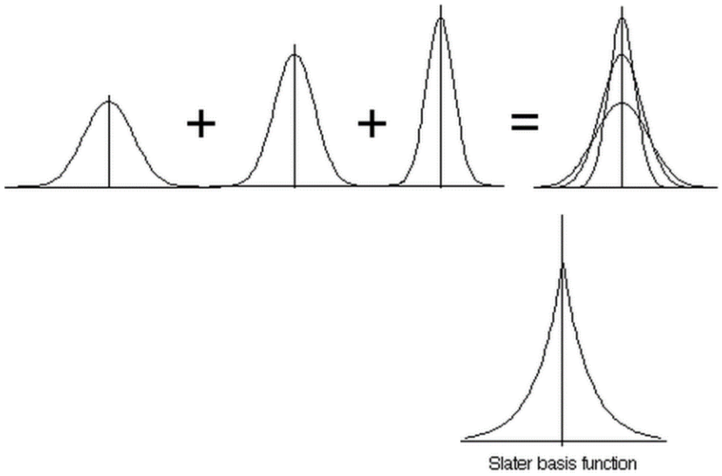
- The atomic orbitals φ_k constitute the **basis set**
  - A basis set comprises of **basis functions**.

- Quantum chemical program packages usually include large number of standard basis sets. Further basis sets are available at: https://www.basissetexchange.org/
- Vast majority of researchers use standard basis sets, developing new basis sets is (a very important) niche field.

Gaussian-type orbitals (GTO)

- Generally, the atomic orbitals are related to the (exact) atomic orbitals of hydrogen
- So-called Slater-type orbitals (STO) would resemble closely the hydrogen-like AOs, but the two-electron integrals become too difficult to handle analytically
- Instead, we normally use linear combinations of **Gaussian-Type Orbitals** (GTOs), which approximately describe the Slater-type orbitals
- The more Gaussian functions we combine in one GTO, the closer to the STO we get
- But there is always a difference in the nucleus (STOs have a cusp, GTOs don't)





Figures: Mike Colvin

Minimal GTO basis set: STO-3G

- Each atomic orbital is described by one **contracted** GTO, which is formed as a linear combination of three **primitive** Gaussian functions
- This basis set is only of historical and conceptual importance, one should never use it in production-level calculations!
- One GTO per atomic orbital is too little, especially for the valence electrons.
- The valence electrons determine the chemistry and require a more flexible description (valence MOs must adjust to difference molecular environments)
- Solution: Use multiple GTOs for the valence electrons
- Split-valence, double-zeta, triple-zeta, quadruple-zeta...

STO-3G for carbon (in TURBOMOLE format)

```
$basis
*
c STO-3G
*          Exponent          Contraction
    3  s
      0.7161683735D+02       0.1543289673D+00
      0.1304509632D+02       0.5353281423D+00    1s
      0.3530512160D+01       0.4446345422D+00
    3  s
      0.2941249355D+01      -0.9996722919D-01
      0.6834830964D+00       0.3995128261D+00    2s
      0.2222899159D+00       0.7001154689D+00
    3  p
      0.2941249355D+01       0.1559162750D+00
      0.6834830964D+00       0.6076837186D+00    2p
      0.2222899159D+00       0.3919573931D+00
*
$end
```

A simple split-valence basis: 3-21G

- Each core orbital is described by one **contracted** GTO consisting of three **primitive** Gaussian functions
- Each valence orbital is described by **two** contracted GTOs consisting of **two** and **one** primitive Gaussian functions, respectively
- This basis set is only of historical and conceptual importance, one should never use it in production-level calculations!

$\underline{3}\text{-}\underline{21}\text{G}$

Core electrons

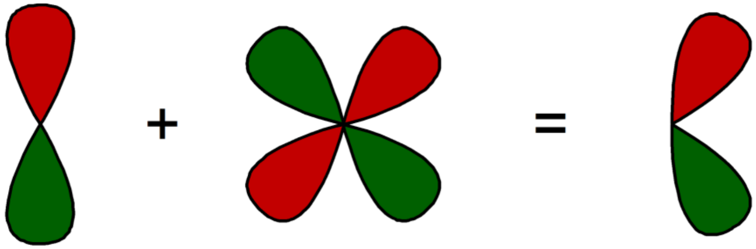
Valence electrons

3-21G for carbon (in TURBOMOLE format)

```
$basis
*
c 3-21G
*
    3   s
      0.1722560000D+03       0.6176690738D-01
      0.2591090000D+02       0.3587940429D+00   1s
      0.5533350000D+01       0.7007130837D+00
    2   s
      0.3664980000D+01      -0.3958951621D+00   2s
      0.7705450000D+00       0.1215834356D+01
    1   s
      0.1958570000D+00       0.1000000000D+01   2s
    2   p
      0.3664980000D+01       0.2364599466D+00   2p
      0.7705450000D+00       0.8606188057D+00
    1   p
      0.1958570000D+00       0.1000000000D+01   2p
*
$end
```

Polarization functions

- Using multiple basis functions for each valence orbital is generally not enough to describe the numerous different bonding situations
- The flexibility of the basis set can be increased by including **polarization functions** that enable the orbitals to further deform from their ”basic” shape
- If the outermost valence electrons are of **s-type** -> add a **p-type** function
- If the outermost valence electrons are of **p-type** -> add a **d-type** function, etc.



p-valence d-polarization more flexible p-valence

- The polarization functions can be denoted in several ways. Examples for (obsolete) Pople-style 6-31G basis set: 6-31G*, 6-31G(d), 6-31G(d,p)

Figure: Wikipedia

Diffuse functions

- For systems with very **diffuse** (dispersed, spread) electron density, it might be important to include a further set of additional, **diffuse** basis functions
- Typically relevant for:
  - Anions
  - Radicals (unpaired electrons)
  - Accurate electron-correlated calculations for systems with weak interactions (dispersion / van der Waals interaction)
- Diffuse functions are Gaussian functions with a very small exponent (”shallow” profile)
- Denoted as 6-31+G for the (obsolete) Pople-style basis sets.

Typical basis sets

- Due to historical reasons, the Pople-type basis sets are still very widely used (3-21G, 6-31G(d), 6-311G(2df), etc.)
  - Limited availability considering the whole periodic table: Not generally available beyond Ar.
- Balanced Karlsruhe **def2-**basis sets (elements H-Rn)
  - def2-SVP, def2-TZVP, def2-QZVP, …: **Recommended choice**
  - Diffuse functions available as def2-SVPD, def2-TZVPD, etc.
  - Latest version called **dhf** (includes modifications for relativistic calculations)
- For electron-correlated methods, the Correlation Consistent basis sets of Dunning are also a widely used alternative (can be computationally very demanding)
  - cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z (correlation consistent polarized valence double/triple/quadruple/5/6 zeta)
  - Diffuse functions available as aug-cc-pVDZ, etc.
- Basis set exchange: https://www.basissetexchange.org/
- Karlsruhe basis sets: http://www.cosmologic-services.de/basis-sets/basissets.php

Electron-correlated post-HF methods

Electron-correlated MO-methods

- **Post-HF** methods aim to account for the missing **electron correlation:**

  $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$
  - E_{corr} may be small in comparison to the total energy, but crucial for chemistry.
- ***Dynamical correlation*** arises because HF is a mean-field approximation (each electron moves in an average potential created by the other electrons)
  - Dynamical electron correlation is dominated by electrons with ***opposite spins***
  - Exchange interaction between ***parallel spins*** is described exactly in HF
- There are three main classes of electron-correlated methods:
  - Configuration interaction (CI)
  - Møller–Plesset perturbation theory (MP)
  - Coupled cluster (CC)
- MP2 is the cheapest way to add electron correlation. It is able to describe weak van der Waals interactions that HF cannot describe.
- CC methods such as CCSD and CCSD(T) are the most robust methods.
- The methods can be improved very systematically, but detailed discussion is left to the appendix slides.

The Big Picture (1)

Basis ↓/ Method →	HF	CCSD	CCSDT	CCSDTQ	…	Full-CI
cc-pVDZ					…	
cc-pVTZ					…	
cc-pVQZ					…	
cc-pV5Z					…	
…	…	…	…	…	…	
∞	HF-limit				…	***Exact SE***

But there are still approximations remaining: We are solving the ***Non-relativistic***, ***time-independent*** Schrödinger equation!

The Big Picture (2)

3rd dimension: The ”physics” included in the Hamiltonian

Quantum Electrodynamics

Full relativity via the Dirac equation $\left(\beta mc^2 + \sum_{k=1}^{3} \alpha_k p_k \, c\right) \psi(\mathbf{x},t) = i\hbar \frac{\partial \psi(\mathbf{x},t)}{\partial t}$

Scalar relativistic effects (when the speed of electrons approaches *c*)

Basis ↓/ Method →	HF	CCSD	CCSDT	CCSDTQ	...	Full-CI
cc-pVDZ					...	
cc-pVTZ					...	
cc-pVQZ					...	
cc-pV5Z					...	
...	...	...	...	...	...	
∞	HF-limit				...	***Exact SE***

4th dimension: time (dynamics), enabling also finite temperature.

Part II: Density functional theory

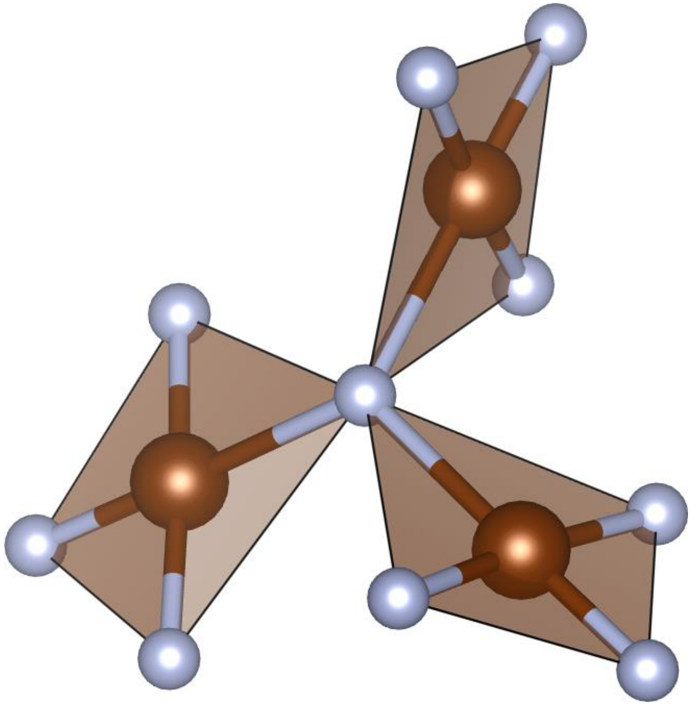


Figure: AJK

Density functional theory (DFT)

- Development began already in the 1930s (but it was not called DFT back then)
- Theoretical framework established in 1960s (Kohn, Hohenberg, Sham)
- Mostly used in solid-state physics in 1970s
- Entered computational chemistry in 1980s

- Different “classes” of density functional methods:
  - *first principles* DFT (no empirical parametrization)
  - Different empirical parametrizations (number of parameters 1-10^2)

- Currently the most widely used approach for large molecules and solids
  - Molecules with hundreds of atoms can be routinely treated with moderate computational resources (multi-core desktop/laptop).
  - Solids with 10^1 – 10^2 atoms in the unit cell can be treated routinely, solids with 10^3 atoms and beyond with supercomputers

What can be studied with DFT?

Structures / thermodynamics / magnetism

Optimized geometries
Relative energies and Gibbs free energies
Reaction energies and Gibbs free energies
Transition states and reaction barriers
Magnetic ground states, magnetic ordering
Crystal structure prediction (e.g. USPEX)

Chemical bonding

Population analyses (*e.g.* partial charges)
Electronic band structures
Electronic density of states
Crystalline orbitals and localized orbitals
Charge densities and band-projected densities
Topological analysis of electron density (e.g. Bader Atoms-in-Molecules analysis)

Spectroscopy

Infrared spectra
Raman spectra
Effects of isotopic substitution
NMR spectroscopy
Optical spectroscopies
Various X-ray spectroscopies
Inelastic neutron scattering spectra
Mössbauer spectroscopy

Physical properties

Dielectric properties (dielectric constant, refractive index, polarizability, SHG)
Spontaneous polarization (e.g. ferroelectricity)
Elastic properties
Piezoelectric proeprties
Photoelastic properties
Thermal expansion
Heat capacities

Transport properties

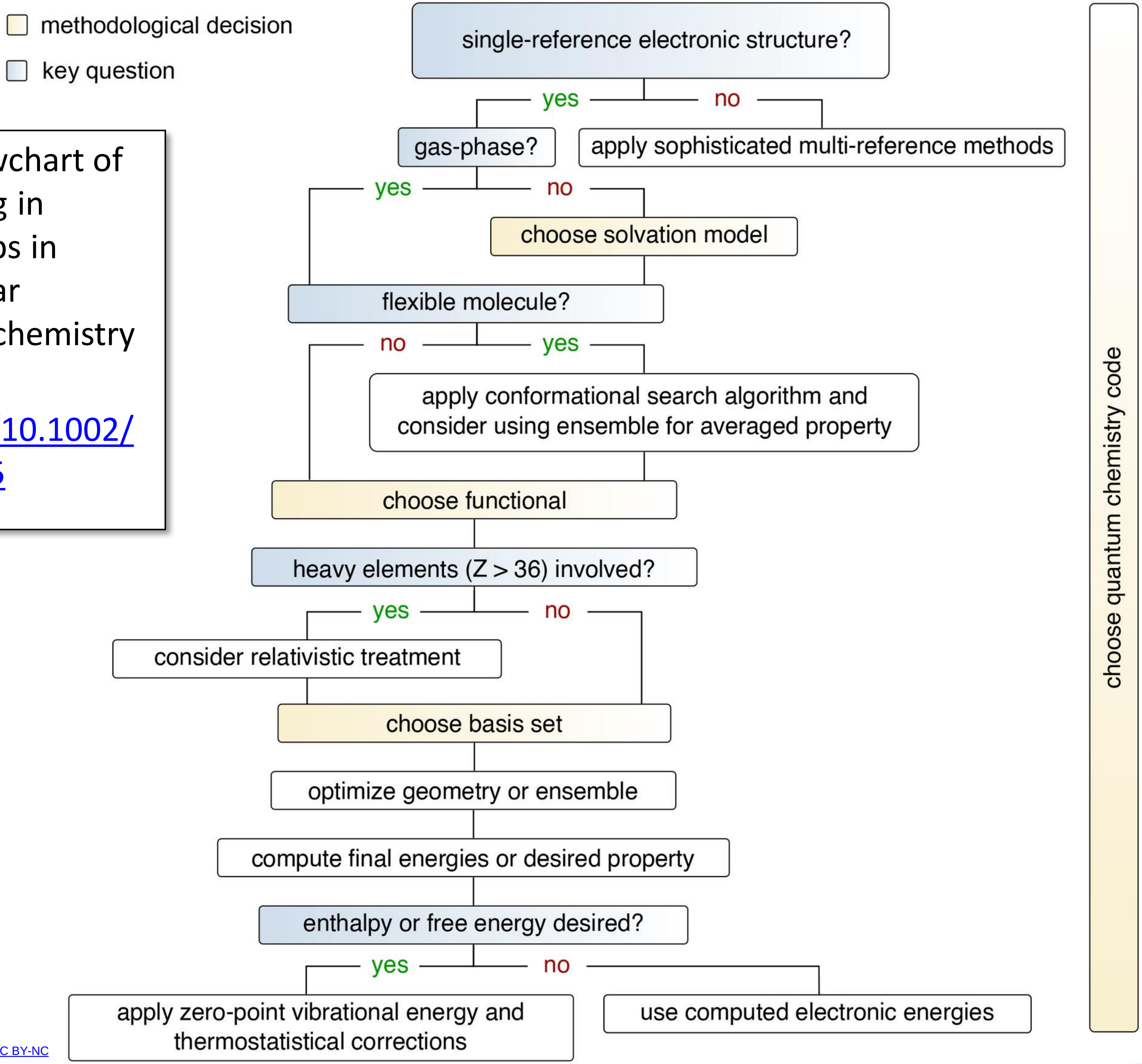
Electronic transport properties (e.g. thermoelectricity)
Thermal conductivity

Further reading on DFT

- A concise summary of DFT: F. Neese, *Coord. Chem. Rev.* **2009**, 253, 526–563.
- A more complete treatise: W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley, **2001** (great for basics, otherwise bit outdated)
- The ABC of DFT by Burke: https://dft.uci.edu/research.php
- Bursch, Mewes, Hansen, and Grimme: Best-Practice DFT Protocols for Basic Molecular Computational Chemistry: https://doi.org/10.1002/anie.202205735
  - Example diagram from the paper on the next slide

Conceptual flowchart of decision-making in elementary steps in typical molecular computational chemistry calculations.

https://doi.org/10.1002/anie.202205735



🟨 methodological decision

🟦 key question

single-reference electronic structure?

yes

gas-phase?

yes

no

choose solvation model

no

apply sophisticated multi-reference methods

flexible molecule?

no

yes

apply conformational search algorithm and consider using ensemble for averaged property

choose functional

heavy elements (Z > 36) involved?

yes

consider relativistic treatment

no

choose basis set

optimize geometry or ensemble

compute final energies or desired property

enthalpy or free energy desired?

yes

apply zero-point vibrational energy and thermostatistical corrections

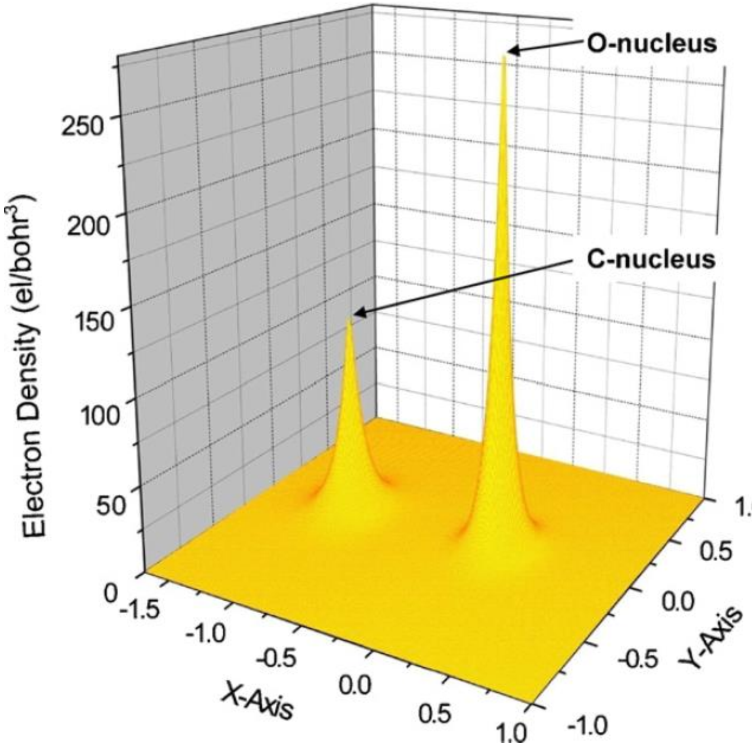
no

use computed electronic energies

choose quantum chemistry code

What can we deduce from the electron density?

- The figure shows the electron density of a CO molecule
- Where are the atoms located?
- What is the nuclear charge?
- How many electrons are there?
- What is the nuclear-electron potential V_{eN}? ('external potential')



From density to exact energy

- Since we know
  - The number of electrons N
  - The nuclear positions and charges
  - The external potential V_{eN}
- We can construct the Hamiltonian operator of the system (H_{BO}) from $\rho(\mathbf{r})$
- Since H_{BO} determines E, Ψ, and all associated properties, it must be possible to construct a ***functional*** $E[\rho]$ that provides the exact E, given the exact ρ
- The first Hohenberg-Kohn theorem:
  - The external potential $v_{ext}(\mathbf{r})$, and hence the total energy E, is a unique functional of the electron density $\rho(\mathbf{r})$

Hohenberg-Kohn theorems

- The universal functional $E[\rho]$ can be written as

$$E[\rho] = V_{NN} + V_{eN}[\rho] + J[\rho] + T[\rho] + E'_{\mathrm{XC}}[\rho]$$

- $J[\rho]$ is the ***classical electron-electron repulsion***
- $T[\rho]$ is (universal but unknown) ***kinetic energy functional***
- $E'_{XC}[\rho]$ is the (universal but unknown) ***exchange-correlation functional***
- The second Hohenberg-Kohn theorem:
  - For any trial density ρ', $E[\rho'] \geq E[\rho]$ (equality holds for $\rho' = \rho$)
  - Minimization of $E[\rho']$ over the range of allowed ρ' would yield the exact ground state density, energy, and all other properties of the system
  - The ***variational theorem*** of DFT.
  - The ground state energy can be obtained variationally: the density that minimizes the total energy is the exact ground state density.

Kohn-Sham construction (1)

- The universal functional described by the Hohenberg-Kohn theorems is not known
- Getting the H_{BO} from ρ does ***not*** actually solve anything yet (like in HF)
- In fact, the next step takes us towards the Hartree-Fock theory
- Kohn and Sham introduced a fictitious system of non-interacting electrons, which is described exactly by a Slater Determinant

$$\psi_{\mathrm{KS}}(\boldsymbol{x}) = |\psi_i \ldots \psi_{\mathrm{N}}|$$

- Now, the ψ_i are the Kohn-Sham orbitals and the electron density is

$$\rho_{\mathrm{KS}}(\boldsymbol{r}) = \sum_i \int |\psi_i(\boldsymbol{x})|^2 \, \mathrm{d}s$$

Kohn-Sham construction (2)

- Let's require that $\rho_{KS}(\mathbf{r}) = \rho(\mathbf{r})$ (the exact density). Now we can write

$$E[\rho] = V_{NN} + T_{\mathrm{s}}[\rho] + V_{eN}[\rho] + J[\rho] + E_{\mathrm{XC}}[\rho]$$

- The ***non-interacting kinetic energy*** T_s can be obtained from the KS orbitals:

$$T_{\mathrm{s}}[\rho] = -\frac{1}{2}\sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle$$

- $T_s[\rho]$ presumably forms the largest contribution to the exact $T[\rho]$
- So where does the kinetic energy of the "interacting" electrons go to?
- Hide it in the exchange-correlation functional, which is anyway unknown!

Kohn-Sham construction (3)

- The exchange-correlation functional can now be redefined as

$$E_{\mathrm{XC}}[\rho] = E'_{\mathrm{XC}}[\rho] + T[\rho] - T_{\mathrm{s}}[\rho]$$

- Now we have a machinery in many ways analogous to the HF-SCF equations!
- The single-particle Kohn-Sham equations (can be varied via the 2nd HK-theorem)

$$\left\{-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\boldsymbol{r})\right\}\psi_i(\boldsymbol{x}) = \varepsilon_i\psi_i(\boldsymbol{x})$$

- The effective potential v_{eff} seen by the electrons:

$$v_{\mathrm{eff}}(\boldsymbol{r}) = -\sum_A Z_A|\boldsymbol{r} - \boldsymbol{R}_A|^{-1} + \int \rho(\boldsymbol{r}')|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\mathrm{d}\boldsymbol{r}' + V_{\mathrm{XC}}(\boldsymbol{r})$$

- Where the exchange-correlation potential V_{xc} is solved via numerical integration

$$V_{\mathrm{XC}}(\boldsymbol{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta\rho(\boldsymbol{r})}$$

- The equations are solved ***self-consistently***!

Exchange-Correlation functionals

- Now, all the hard parts have been hidden into E_{XC}!
  - Electronic exchange
  - Coulomb correlation between the interacting electrons
  - The kinetic energy of the interacting electrons
- A big issue for the contemporary DFT functionals is the ***self-interaction***
- Unlike in the Hartree-Fock theory, we don’t have ***exact exchange*** anymore and the electrons can unphysically interact with themselves
- This must be accounted for in E_{XC}, but so far there is no perfect solution for this
- Let’s have a look at the density functionals available nowadays.

Overview: Jacob's ladder

- John Perdew's vision of five generations of E_{xc} functionals

HEAVEN **(chemical accuracy[*])**		
Rung 5	fully nonlocal	explicit dependence on unoccupied orbitals
Rung 4	hybrid functionals	explicit dependence on occupied orbitals
Rung 3	meta-GGAs	explicit dependence on kinetic energy density
Rung 2	GGAs	explicit dependence on gradients of the density
Rung 1	LDA	local density only
EARTH (Hartree theory)		

[*] 4 kJ/mol (1 kcal/mol) accuracy in atomization energies (very difficult)

Local Density Approximation: E_X

- Derive the E_X for ***Homogeneous (uniform) electron gas***
  - Finite volume with a positive background charge that renders the entire system electrically neutral
  - Constant electron density ($\rho = N/V$)
- ***Local*** density exchange functional:

$$E_x^{\mathrm{LDA}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho(\mathbf{r})^{4/3}\, \mathrm{d}\mathbf{r}$$

- For comparison, Hartree-Fock exchange is ***non-local***
- Developed already before HK theorems by Dirac (1930) and Slater (1951)
- The key points:
  - Apply the ***homogeneous*** electron gas exchange equation ***locally***
  - Assume that in an ***inhomogeneous*** system the same equation still holds ***locally*** at each point in space!

Local Density Approximation: E_C

- First expression for E_C was proposed by Wigner already in 1938

$$E_{\mathrm{C}}^{\mathrm{W}}[\rho] = \int \rho(\boldsymbol{r})\varepsilon_{\mathrm{C}}^{\mathrm{W}}[\rho]\,\mathrm{d}\boldsymbol{r} = -\int \rho(\boldsymbol{r})\frac{0.44}{r_{\mathrm{S}} + 7.8}\,\mathrm{d}\boldsymbol{r}$$

- $r_{\mathrm{S}} = (3/(4\pi\rho))^{1/3}$ is the Wigner-Seitz radius. However, the expression is too simple
- The correlation between electrons of the same spin and of opposite spin is drastically different and this must be accounted for
- Electrons with ***parallel spin*** avoid each other already due to the antisymmetry of the wavefunction (Fermi hole, Pauli principle)
- The same is not true for electrons of ***opposite spin***
- Therefore, ***opposite spin-pairs*** contribute more strongly to the correlation energy than ***parallel spin-pairs***
- Many different parametrizations of E_C for uniform electron gas exist
- For example: Vosko-Wilk-Nusair (VWN)

LDA: Performance

- LDA is generally applicable for metals and other solid-state systems with homogeneous electron density
- For molecules, LDA delivers results that are comparable to or even better than the Hartree-Fock approximation
  - Equilibrium geometries
  - Harmonic frequencies
- However, energetics, such as ***binding energies*** from LDA are poor and therefore it never became that popular in quantum chemistry
- Comparison to experimental atomization energies in the so-called G2 test set shows an average unsigned deviation of 150 kJ/mol for LDA (very large)
- However, the corresponding error for HF is 330 kJ/mol!
- While Hartree-Fock typically underestimates atomization energies, LDA overestimates them (“***LDA overbinding***”)

Generalized Gradient Approx.

- Generalized gradient approximation (GGA) is a logical extension of LDA
- Instead of using just the electron density $\rho(\boldsymbol{r})$ at a particular point in space, use also the information on the ***gradient of the density***, $\nabla\rho(\boldsymbol{r})$ at the same point

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)\, d\vec{r}$$

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA}$$

- $\nabla\rho(\boldsymbol{r})$ describes the non-homogeneity of the true electron density in molecules
- Various GGA E_X and E_C approximations have been developed, but only few of them are really widely used

GGA: E_X

- The most important GGA E_X functionals:
  - ***B88*** (Becke), ***PW91*** (Perdew, Wang), ***PBE*** (Perdew, Burke, Ernzerhof)
- The GGA E_X functionals do include LDA exchange:

$$E_X^{GGA} = E_X^{LDA} - \sum_{\sigma} \int F(s_\sigma)\, \rho_\sigma^{4/3}(\vec{r})\, d\vec{r}$$

- The reduced density gradient s_σ is

$$s_\sigma(\vec{r}) = \frac{|\nabla \rho_\sigma(\vec{r})|}{\rho_\sigma^{4/3}(\vec{r})}$$

- As an example, the functional form used by Becke in ***B88***:

$$F^B = \frac{\beta s_\sigma^2}{1 + 6\beta s_\sigma \sinh^{-1} s_\sigma}$$

- Here, β is an empirical constant (0.0042), which was obtained by a least-squares fit to the exactly known exchange energies of the rare gas atoms He-Rn
- ***PW91*** and ***PBE*** do not include empirical parametrization

GGA: E_C

- The most important GGA E_C functionals:
  - ***P86*** (Perdew), ***PW91*** (Perdew, Wang), ***LYP*** (Lee, Yang, Parr)
- P86 includes one empirical parameter (a fit to the correlation energy of Ne atom)
- PW91 is a parameter-free functional
- LYP includes one empirical parameter
  - Unlike the other functionals, LYP is not based on uniform electron gas, but derived by using an expression for the correlation energy of the He atom
  - This raises some issues in metallic solid state systems (don’t use it there)
- The analytical expressions for the GGA E_C functionals are so complicated that there is not point at investigating them in detail
- In fact, some of the GGA E_C functionals are not based on physical models. Instead, they apply mathematical constructs that yield suitable results

GGA: Performance

- With the introduction of GGA, DFT became a suitable tool for investigating molecules
- Some of the most important GGA E_{XC} combinations:
  - ***BP86***, ***BLYP***, ***PBE*** (PBE_X + PBE_C, a simplified form of ***PW91***)
- For molecular properties such as equilibrium geometries and harmonic frequencies, GGA is usually a further improvement from LDA
- However, the crucial step forward is that the overbinding tendency of LDA is corrected by GGA!
- Comparison to experimental atomization energies in the G2 test set shows errors of 20-30 kJ/mol for GGA functionals
  - Compare with 150 kJ/mol for LDA or 330 kJ/mol for HF!

Meta-GGAs

- The next logical step from GGAs is to include even higher derivatives of the density in the expression of E_{XC}
- One such attempt is the TPSS (Tao, Perdew, Staroverov, Scuseria) functional
- TPSS uses the ***kinetic energy density*** in addition to $\rho(\boldsymbol{r})$ and $\nabla\rho(\boldsymbol{r})$

$$\tau(\boldsymbol{r}) = \frac{1}{2}\sum_i |\nabla \psi_i(\boldsymbol{r})|^2$$

- However, the improvement over GGAs is not as significant as the improvement from LDA to GGA.

Hybrid functionals

- Hybrid functionals incorporate some exact (HF) exchange into the E_{XC}
- The approach was formally justified by Becke by using the ***adiabatic connection***

$$\mathrm{E_{XC}} = \int_0^1 \mathrm{E}_{\mathrm{ncl}}^{\lambda} \mathrm{d}\lambda \, .$$

- Integration over E_{ncl} (non-classical contribution to e-e interaction)
- At λ = 0, we have an interaction free system and E_{ncl} is composed of ***exchange only***
- At λ = 1, we have a fullt interacting system, which we can approximate with any E_{XC}
- The simplest approximation is to assume that E_{ncl} is a linear function of λ:

$$\mathrm{E_{XC}^{HH}} = \frac{1}{2}\mathrm{E_{XC}^{\lambda=0}} + \frac{1}{2}\mathrm{E_{XC}^{\lambda=1}}$$

- This combination is known as Becke's Half-and-Half combination of exact exchange and DFT exchange-correlation
- The approach showed a promising performance (similar errors with respect to experiment as GGAs) and Becke carried on with the idea

Becke's three-parameter hybrid

- Next, Becke took the decisive step and included semi-empirical parametrization in his three-parameter hybrid functional ***B3PW91***:

$$E_{XC}^{B3} = E_{XC}^{LSD} + a(E_{XC}^{\lambda=0} - E_{X}^{LSD}) + bE_{X}^{B} + cE_{C}^{PW91}$$

- The empirical constants *a*, *b*, and *c* are 0.20, 0.72, and 0.81, respectively
- Determined by fitting the results to the atomization and ionization energies and proton affinities with respect to the experimental values in the G2 test set
- The authors of the Gaussian program package proposed another variant, ***B3LYP***

$$E_{XC}^{B3LYP} = (1-a)\ E_{X}^{LSD} + a\ E_{XC}^{\lambda=0} + b\ E_{X}^{B88} + c\ E_{C}^{LYP} + (1-c)\ E_{C}^{LSD}$$

- B3LYP became immensely popular in quantum chemistry
- The most popular ”parameter-free” hybrid functional is ***PBE0*** (PBE with 25% HF exchange). It performs as well as B3LYP/B3PW91.

Hybrid-DFT: performance

- Generally, geometries and vibrational frequencies are improved from GGA
- Comparison to experimental atomization energies in the G2 test set shows errors of 8-12 kJ/mol for hybrid functionals such as B3PW91 or B3LYP
  - Was 20-30 kJ/mol for GGAs
  - Nice improvement and closer to the chemical accuracy of 4 kJ/mol
- Numerous hybrid functionals have been devised by fitting against various data sets, but the community opinion on these is rather divided
- With more extensive fitting
  - The universality of the functional might be lost
  - The physical reasoning behind the functional might be completely lost
  - B3LYP is semi-empirical, but functionals with tens of parameters are more like empirical

Further developments

- ”Rung 5” functionals: Dependence on unoccupied orbitals
- Perhaps the most popular scheme is the Grimme’s ***Double Hybrid*** functionals, where E_{XC} contains two contributions from the ab initio MO theory:
  - Exact exchange from Hartree-Fock (occupied orbitals)
  - Electron correlation from second order perturbation theory (***MP2***) (unoccupied orbitals)
- Accuracy surpasses rung 4 hybrids.
- Inclusion of MP2 makes them computationally more demanding

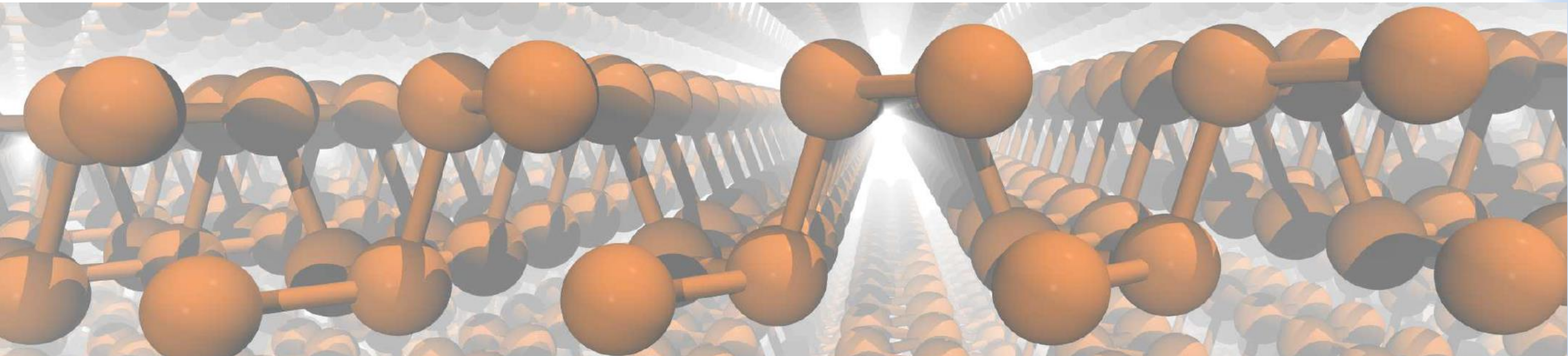
- Overall, systematic improvement of E_{XC} is very difficult.
- Latest developments like SCAN or r^{2}SCAN have further improved the performance, but did not lead in major breakthroughs.
- Bursch, Mewes, Hansen, and Grimme: Best-Practice DFT Protocols for Basic Molecular Computational Chemistry: https://doi.org/10.1002/anie.202205735

Common choices for DFT

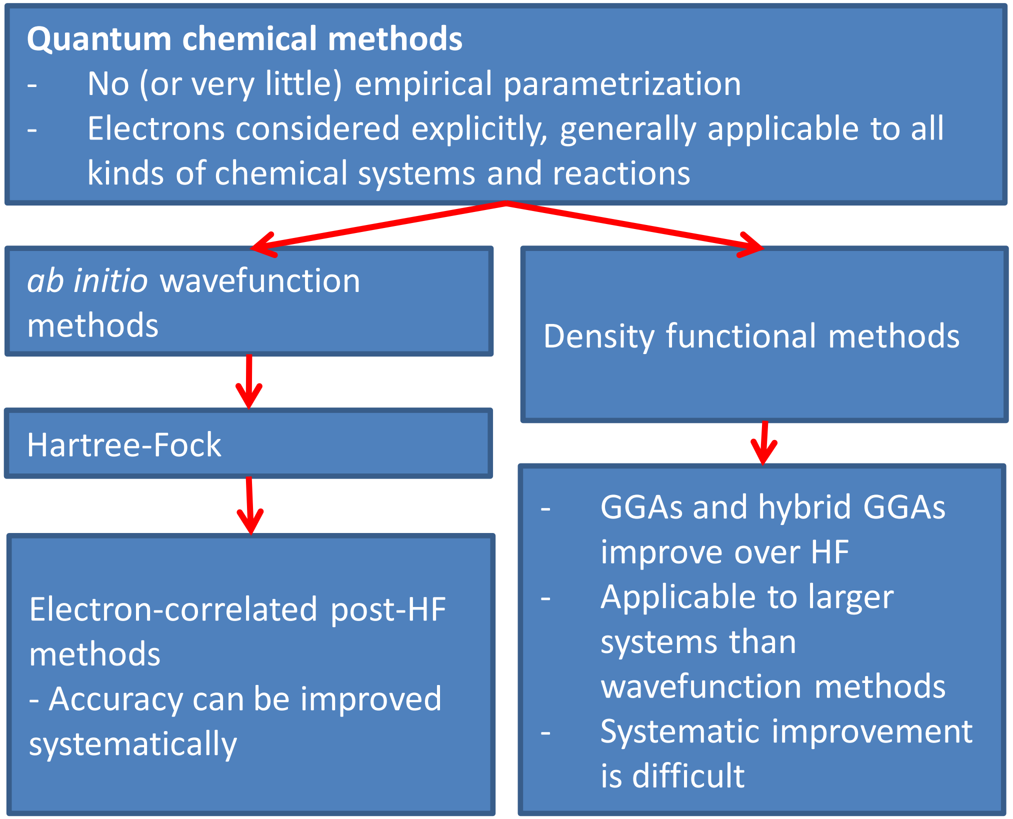
- There is a huge number of DFT functionals available nowadays (too many).
- Recent discussion for example in Bursch, Mewes, Hansen, and Grimme: Best-Practice DFT Protocols for Basic Molecular Computational Chemistry: https://doi.org/10.1002/anie.202205735

- Some suggested DFT methods with as little as possible empirical parametrization:
- LDA: Only consider using LDA for metallic / homoatomic solid state systems and even then, it makes sense to test a GGA functional, too
- GGA: ***PBE*** or ***BP86***
- Meta-GGA: ***TPSS*** or ***SCAN*** and its derivatives (which can be numerically tough)
- Hybrid functionals: ***PBE0*** or ***HSE06*** (latter mainly for periodic systems)
- **Warning**: None of the above functionals can properly describe weak dispersive (van der Waals) interactions! When these are important, use (empirical) dispersion-corrected DFT: DFT-D3 or DFT-D4.

Part III: Models, software, and practical suggestions.



Overview of the discussed methods



Quantum chemical methods
- No (or very little) empirical parametrization
- Electrons considered explicitly, generally applicable to all kinds of chemical systems and reactions

ab initio wavefunction methods

Hartree-Fock

Electron-correlated post-HF methods
- Accuracy can be improved systematically

Density functional methods

- GGAs and hybrid GGAs improve over HF
- Applicable to larger systems than wavefunction methods
- Systematic improvement is difficult

The same **Gaussian-Type basis sets** can be used for both ab initio wavefunction and DFT methods

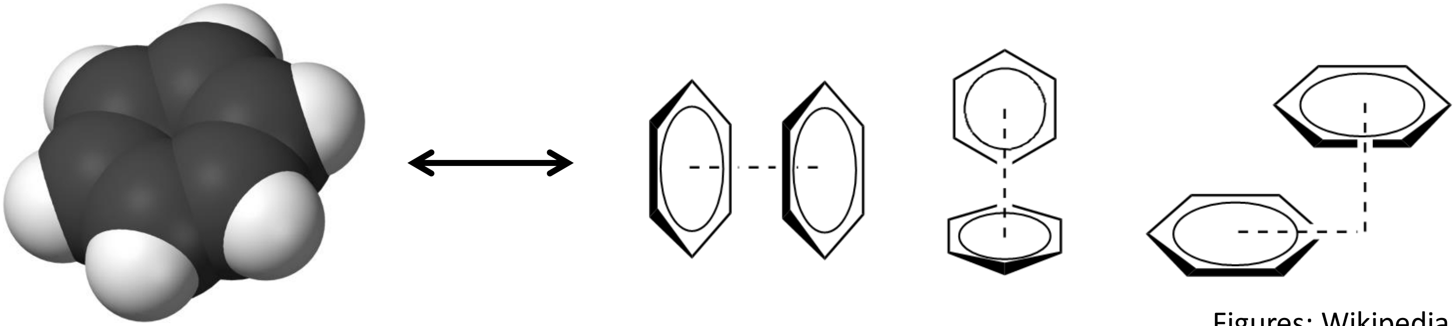
Quantum chemical methods can be combined with **molecular dynamics** to investigate **time-dependent** phenomena in **finite temperatures**

Models: Three states of matter

- Going from left to right:
  - Accurate, non-parametrized molecular modelling research generally becomes more difficult
  - Reliable interpretation of the experiments also often becomes somewhat more difficult
  - Direct comparison between quantum chemical calculations and experiment becomes more difficult
- The main challenge for liquid systems: ***finite temperature*** ($T > 0$)

Gas-phase models

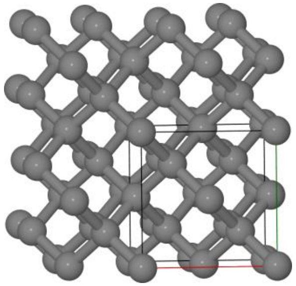
- Dilute gas is the simplest state of matter for molecular modelling research
- The model can consist of a single molecule (neutral or ionic)
- Intermolecular interactions and reactions can be investigated by including several molecules in the model
- In practice, the most accurate quantum chemical methods can currently be applied only in gas phase (but their accuracy can even surpass experimental methods for small molecules!)



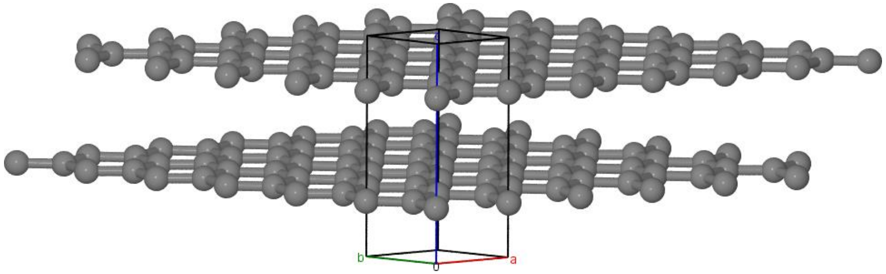
Figures: Wikipedia

Solid state models

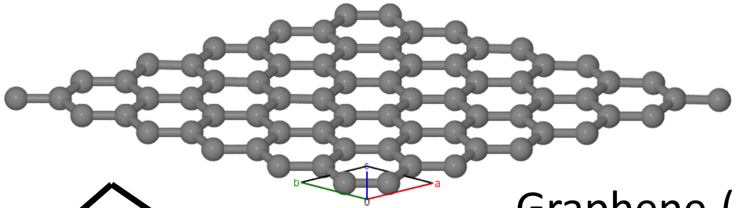
- Bulk (3D), surfaces (2D), polymers (1D)
- Periodic models are defined using a **unit cell** (lattice vectors + atomic positions)
- **Amorphous solids** are much more challenging and comparable to liquids in difficulty!



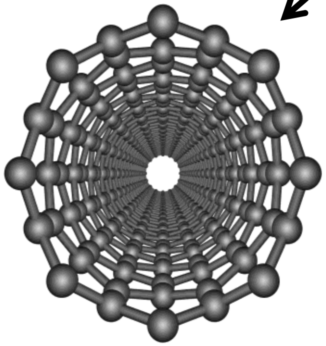
Diamond (3D)



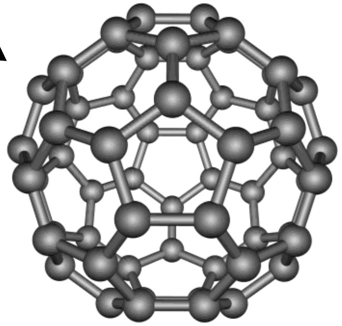
Graphite (3D)



Graphene (2D)



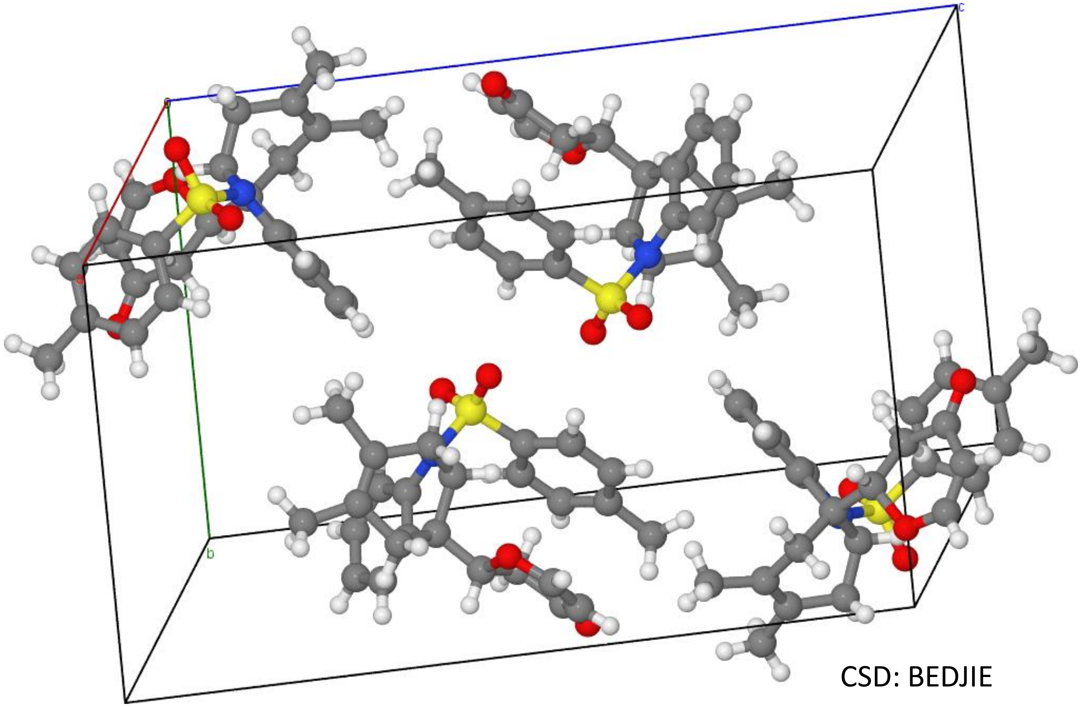
Carbon nanotube (1D)



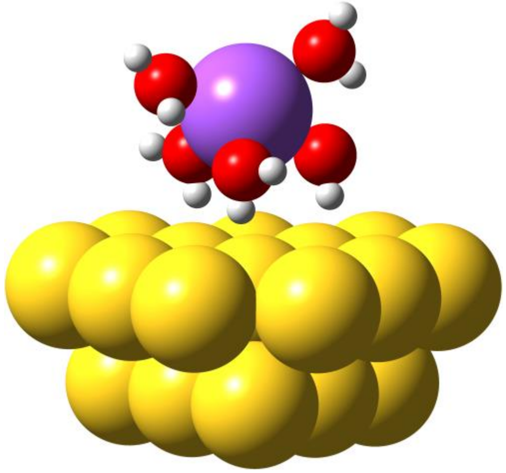
Carbon fullerene (0D)

Finite models of periodic systems

- 3D -> 0D: Cut molecules from 3D molecular crystals (mind the possible intermolecular interactions / packing effects)
- 2D -> 0D: Cluster models for modelling surface reactions (be very careful with surface termination, definitely avoid for metals)
- 1D -> 0D: Finite segments of polymers (nanotubes/-wires/-rods, etc.)

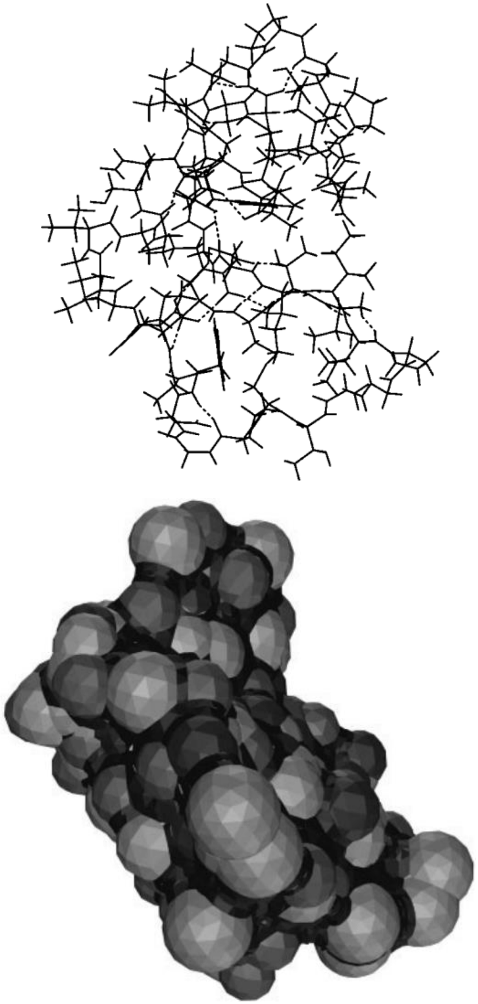


CSD: BEDJIE



Liquid state: Implicit solvation

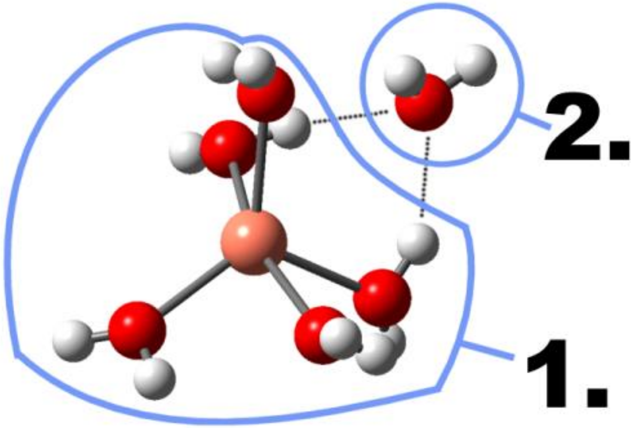
- The most simple way of introducing solvent effects into molecular models are **implicit** solvation models
  - Polarizable Continuum Model (PCM)
  - Conductor-like Screening Model (COSMO)
- COSMO in brief (from TURBOMOLE manual):
  - Solute molecule forms a **cavity** within the dielectric **continuum** of permittivity *ε* (representing the solvent)
  - The charge distribution of the solute polarizes the dielectric medium
  - The response of the medium is described by the generation of screening charges on the cavity surface
- Literature: *Chem. Rev.* **2005**, *105*, 2999−3093



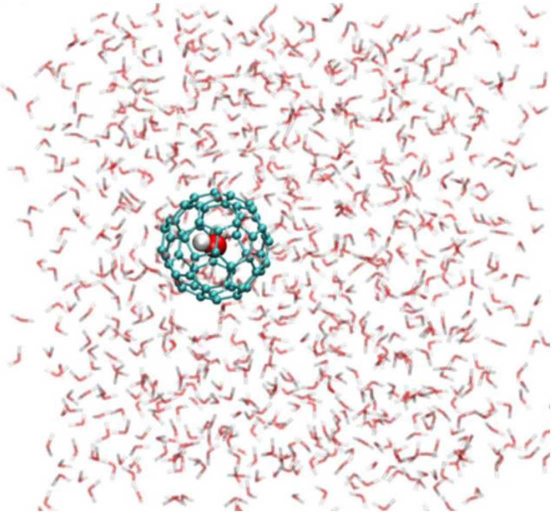
Crambin protein and its solute cavity
(Cossi et al. *J. Comput. Chem.* **2003**, *24*, 669).

Liquid state: Explicit solvation

- Often, the solvent molecules need to be explicitly introduced into the models
- The first solvation shell is the most important, but sometimes the second solvation shell cannot be neglected
- The most sophisticated way to consider solvation is via **molecular dynamics simulation** of the solute + solvent (computationally very demanding)



Cu^+ ion with 5 water molecules in the first solvation shell and one in the second solvation shell



C_{60} fullerene solvated inside a 3D box of 868 water molecules *Chem. Phys. Lett.* **2012**, *534*, 38–42.

A note about symmetry

- For **small molecules in gas phase**, especially inorganic/organometallic ones, one should always pay attention to possible point group symmetry
  - Often very relevant for the chemical problem at the hand (e.g. spectroscopic properties)
  - Speeds up computational work (up to a factor of **120** with some programs)
  - But keep in mind that utilizing point group symmetry is a also **constraint** that may limit the flexibility and applicability of the model!
- For **solid-state systems**, one should always pay close attention to the space group symmetry (translational + point group symmetry)
  - Highly relevant for understanding the structural characteristics, electronic properties and chemical behavior of the system!
  - Also, the computational speed-up can be even more significant than for molecules due to the dense-packed nature of solid-state systems
- For **liquid systems**, symmetry is normally irrelevant
- For **biomolecules**, symmetry is normally irrelevant

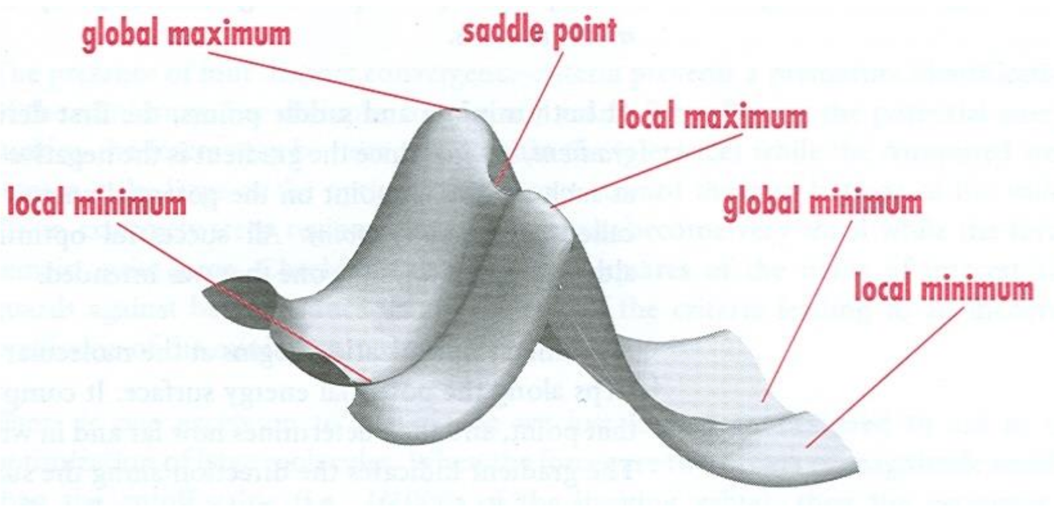
Accounting for the relativity

- When dealing with light elements (up to Ar), the relativistic effects can be neglected in all but the most accurate benchmark calculations
- For K-Kr, one can consider incorporating the scalar relativistic effects via ***effective core potentials*** (ECP, the inner core electrons are replaced with a potential)
- From Rb on, the scalar relativistic effects ***must*** be taken into account
- For the heaviest elements (for example, Au, Hg, Pb, Bi), the ***spin-orbit*** coupling becomes significant and can sometimes affect the chemical interpretation
- Spin-orbit effects can be taken into account by including relativity in the Hamiltonian operator (e.g. two-component or four-component DFT)
  - Nowadays many codes can treat spin-orbit effects (like TURBOMOLE)
- The ***take-home message***: Keep in mind that the relativistic effects ***must*** be taken into account for the heavier elements starting from ~Rb)
- Normally it’s enough to take a basis set which includes ECP for such elements
  - The Karlsruhe def2-basis sets include ECP for Rb-Rn

Some typical steps in quantum chemistry studies

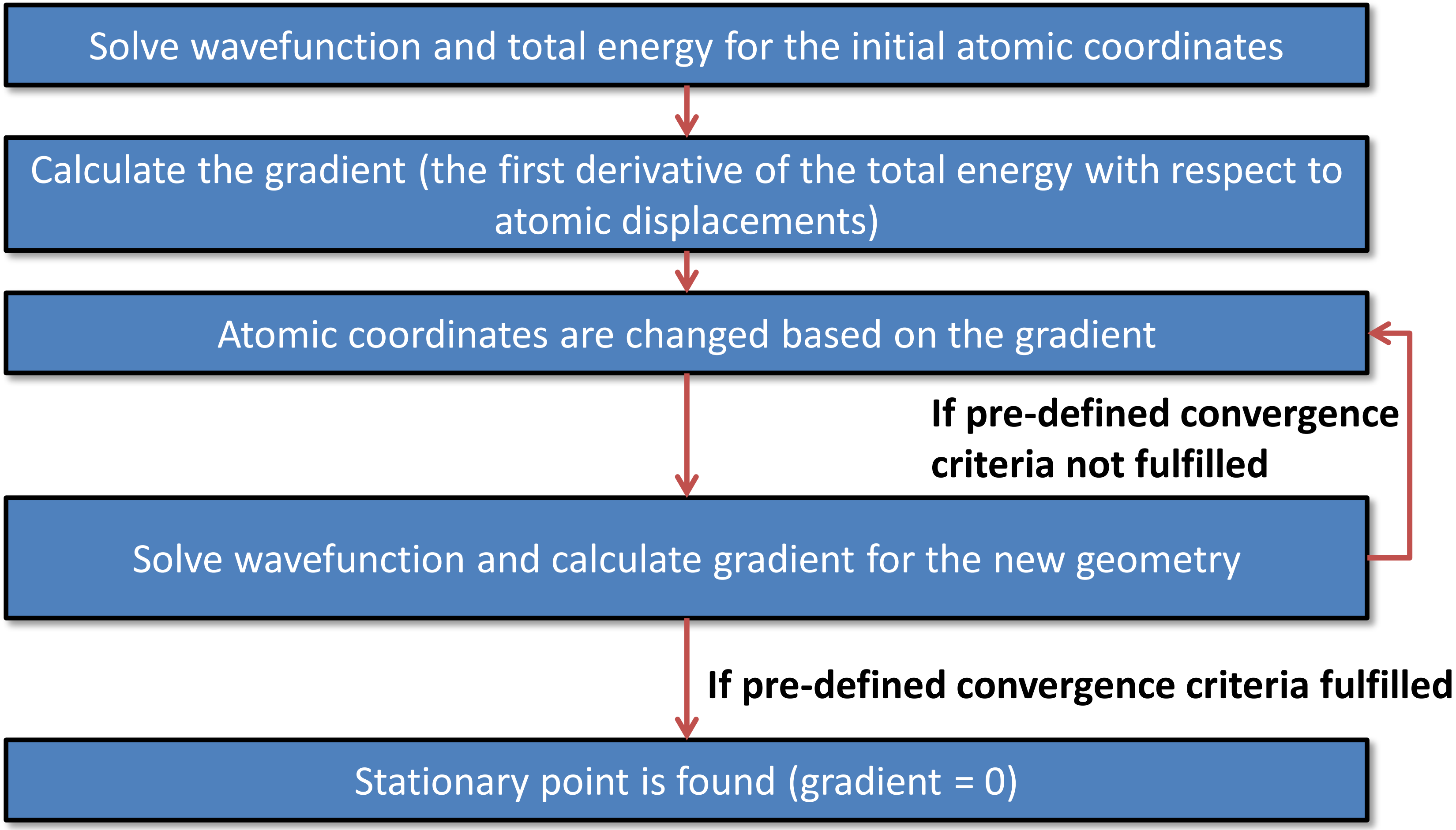
Geometry optimization

- One of the most fundamental tasks in quantum chemical calculations is ***geometry optimization***.
- The purpose of a geometry optimization is to find a stationary point on the potential energy surface (PES) of the studied system (usually a minimum, but a ***saddle point*** for transition states)
  - Total energy comparisons or any property calculations typically only make sense when the molecule is at a stationary point.
- A minimum can be **local** or **global**. A local minimum can be found with a normal geometry optimization, but finding a global minimum requires more complicated approaches (conformation analysis, genetic algorithms, etc.)



Geometry optimization in practice

- Similar to SCF method, the geometry optimization is an iterative process



Solve wavefunction and total energy for the initial atomic coordinates

Calculate the gradient (the first derivative of the total energy with respect to atomic displacements)

Atomic coordinates are changed based on the gradient

If pre-defined convergence criteria not fulfilled

Solve wavefunction and calculate gradient for the new geometry

If pre-defined convergence criteria fulfilled

Stationary point is found (gradient = 0)

Harmonic frequencies

- What can be determined based on the harmonic frequencies of a system?
  - Molecular vibrations (-> infrared and Raman wavenumbers)
  - Nature of the stationary point on the PES (minimum/transition state)
  - Zero point energy (ZPE) and various thermodynamic quantities (enthalpy, entropy, **Gibbs free energy**, etc.)
- Harmonic frequencies need to be determined for an optimized geometry using the **same level of theory** as in the geometry optimization
- The nature of the stationary point on the PES can be deduced from the number of "imaginary" frequencies (frequencies with negative wavenumbers in Gaussian) :

Number of img. freq.	Nature of the stationary point
0	Local or global minimum
1	Transition state (local maximum). Always **visualize the normal mode** ("vibration")
> 1	Higher order saddle point (maximum)

Computational cost

Computational cost

- The computational cost of different quantum chemical methods is usually described in terms of their ***computational scaling N^X***
- N = the number of basis functions
- Example: If $X = 2$ and the size of the system is doubled, the cost is quadrupled
- **Density functional theory**
  - The computational cost formally scales as N^3 (N^4 for hybrids due to HF_X!)
  - Nowadays even linear-scaling implementations exist
  - Currently the most feasible approach for large molecules and solids
- ***Ab initio* Molecular Orbital theory**
  - For Hartree-Fock, the computational cost formally scales as N^4
  - The true scaling is lower (even less than 2.5 for large molecules)
  - The very accurate methods are also very costly
  - MP2: N^5; CCSD: N^6; CCSD(T): N^7; CCSDTQ: N^{10}
  - Various techniques and approximations to reduce the computational cost exist

Reducing computation times (1)

- The computational cost can be significantly reduced with numerical approximations and techniques that do not significantly change the results in comparison to non-approximated methods
- What is a ***significant change*** for the chemical interpretation?
- If the absolute energy changes due to a numerical approximation, this is usually not a problem at all
- In chemistry we are interested in quantities like **relative** energies and geometries, and the numerical errors are canceled out when comparing the absolute energies
- Three examples of common speed-up techniques:
  - Resolution of identity (also known as Density fitting). Speed ups of factor 10 typical for DFT and MP2. Available in many modern codes.
  - Fast Multipole Method (FMM). Significant speed ups for large systems. Available in many modern codes.
  - Seminumerical exchange for HF and hybrids (Orca, TURBOMOLE)

Reducing computation times (2)

- An example from the Orca program: ***RIJCOSX-DLPNO-CCSD***[1]
    - RIJ: ”Resolution of Identity” approximation for the Coulomb term (**J**)
    - COSX: ”**C**hain **O**f **S**pheres” approximation for the e**X**change term
    - **D**omain **B**ased **L**ocal **P**air **N**atural **O**rbitals
    - Massive speed-ups in comparison to normal CCSD (> 1000-fold)
    - No significant errors in relative energies (with proper cut-offs).
- Keep an eye on the program manuals and literature to stay informed!

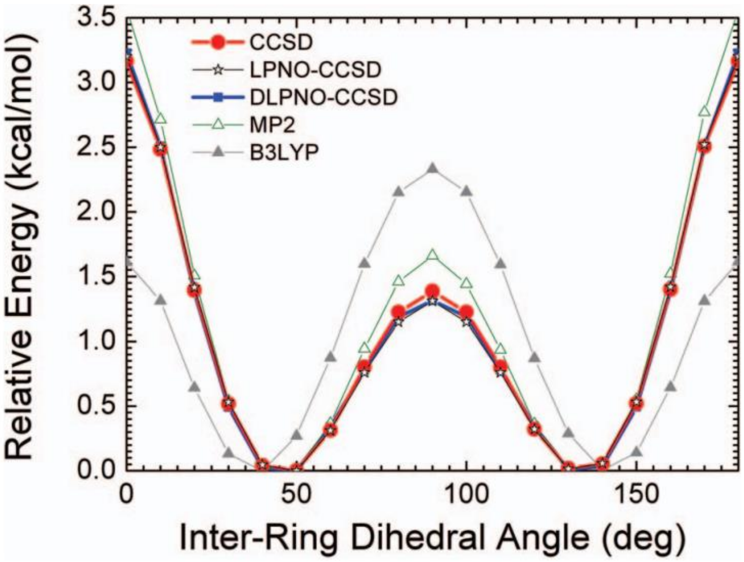


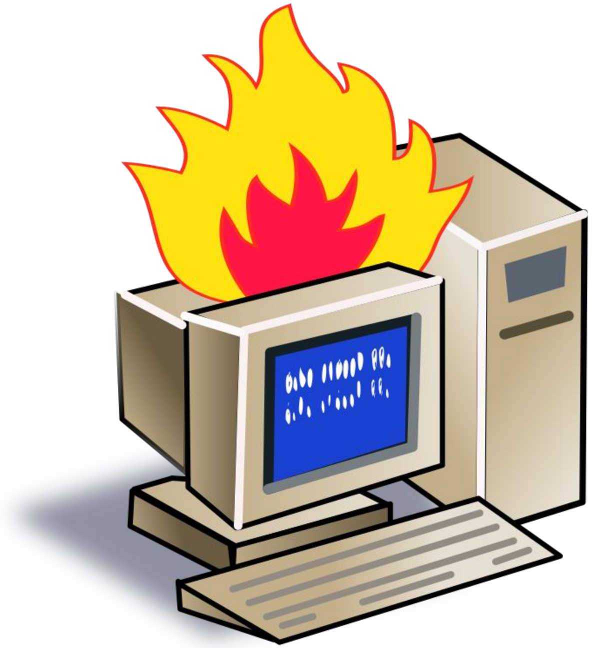
FIG. 8. Rotational barrier of biphenyl. The structures come from a relaxed

[1] C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106

Software and practical suggestions

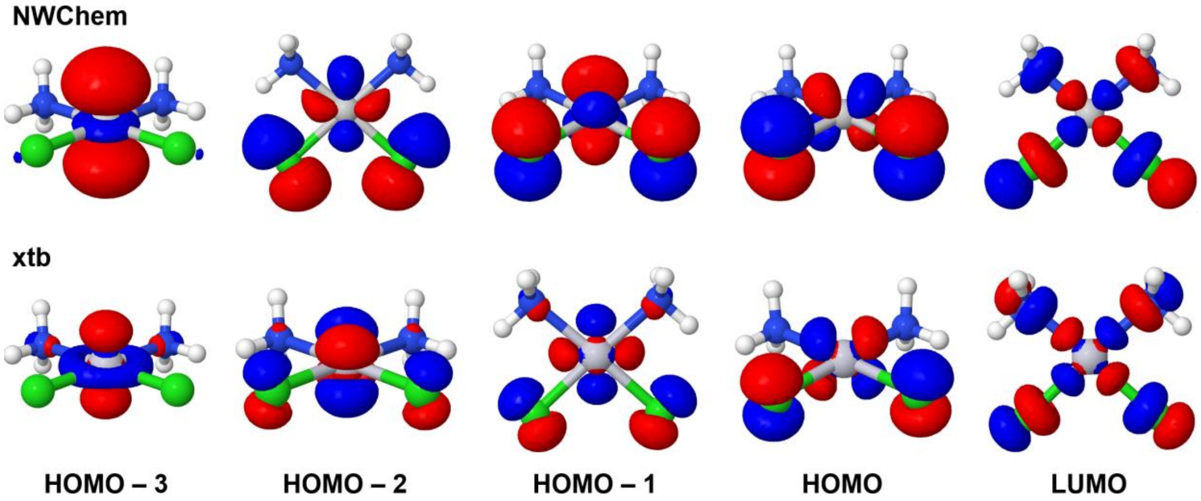
Free and open source quantum chemistry codes (1)

- In our recent paper on **Free and open source software for computational chemistry education**, we give practical examples and guidelines
  - Susi Lehtola and Antti J. Karttunen https://doi.org/10.1002/wcms.1610 (Open Access)
- Step-by-step tutorials are available at https://github.com/susilehtola/fosschemistry
- It can also be run on Windows computers with Windows Subsystem for Linux

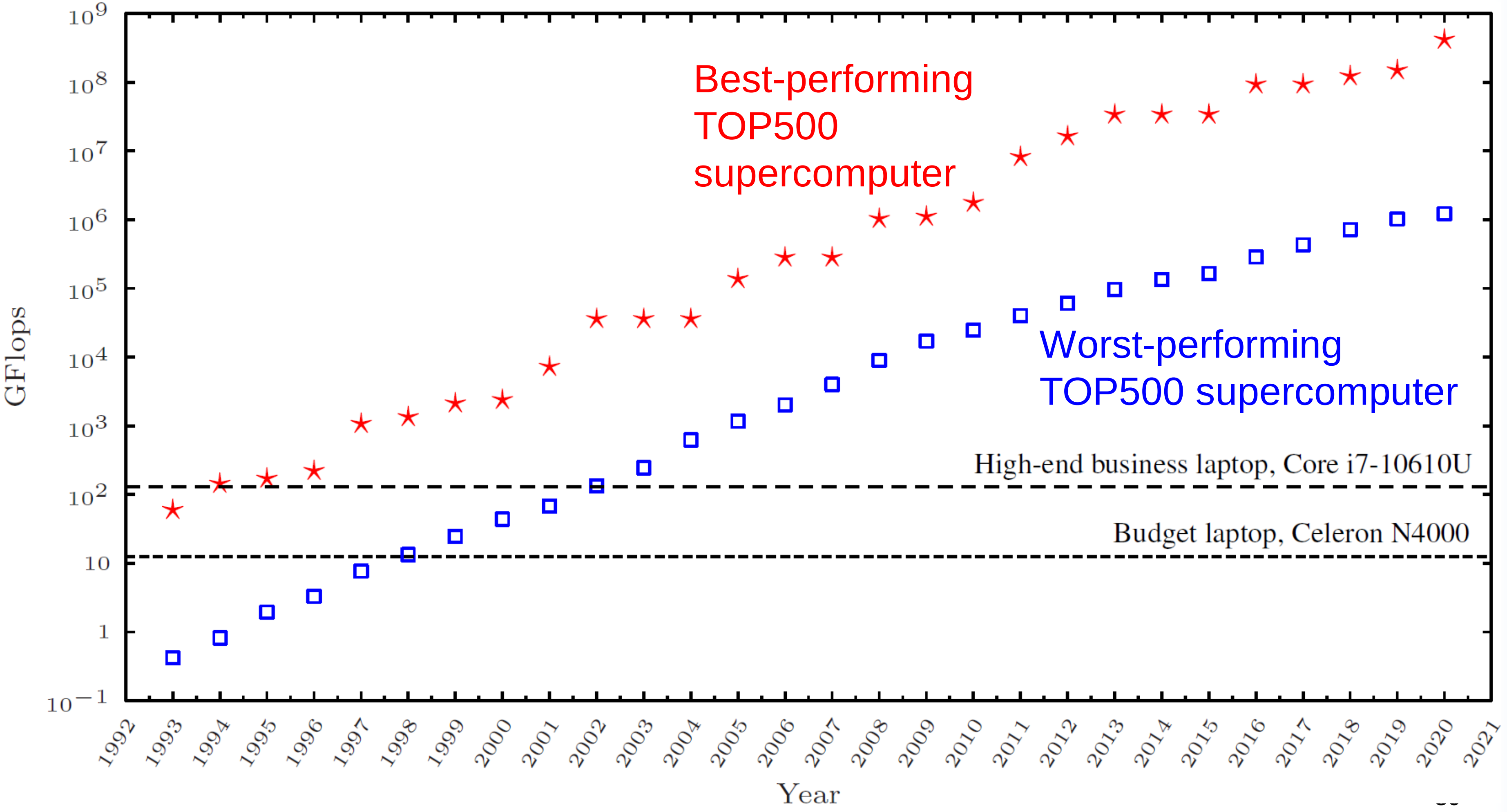


Free and open source quantum chemistry codes (2)

- “We point out the existence of software offering a wide range of functionality, all the way from approximate semiempirical calculations with tight-binding density functional theory to sophisticated ab initio wave function methods such as coupled-cluster theory, covering both molecular and solid-state systems.”
  - Practical tutorials available for **xtb**, **NWChem**, **Psi4**, **Quantum Espresso**
- “We exemplify what kinds of calculations are feasible with four FOSS electronic structure programs, assuming only extremely modest computational resources, to illustrate how FOSS packages enable decentralized approaches to computational chemistry education within the BYOD scheme.”



Quantum chemistry on a personal computer



Software: *Ab initio* / first principles

- Commercial or available for a moderate fee
  - TURBOMOLE (a very efficient program package)
  - Gaussian (one of the oldest, still used a lot)
  - ADF, Q-Chem, MOLPRO, MOLCAS, JAGUAR, etc. (molecular systems)
  - Crystal (periodic systems with GTOs)
  - VASP, WIEN2K, CASTEP, etc. (periodic systems with PWs/PAWs)
- Freely available for academic use
  - Orca (modern and efficient program package with lots of features)
  - CFOUR (efficient high-level *ab initio* tehcniques)
  - NWChem (both molecular and periodic systems)
  - Dalton, PSI4, DIRAC, etc. (molecular systems)
  - Quantum Espresso, CP2k, ABINIT, GPAW, … (periodic systems with PWs/PAWs)

Practical suggestions (1)

- After a broad overview of *ab initio* wavefunction and DFT methods, some practical suggestions for different-sized systems follow
  - Suggestions are for gas-phase, implicit solvation usually adds little computational cost, but might not be available for the higher-level methods
- Not all the suggested methods are available in all programs

- For molecular quantum chemistry, I would currently recommend TURBOMOLE or Orca:
  - Versatile and in active development
  - Fast
  - Work with practically all builder applications (accept XYZ coordinates)
  - More advanced interfaces are appearing, too

Practical suggestions (2)

- Always start the work on a new molecule by optimizing the structure
  - Otherwise there’s no point in investigating the energetics or properties
  - Remember to check if ***symmetry*** plays a role in your case
  - If the optimization yields ”strange” results (too long bond lenghts, etc.), this might indicate that the chosen ***method*** or even the ***model*** is not suitable
  - -> benchmark few other methods / consider adding implicit solvation /...
- If possible, calculate the harmonic frequencies for the optimized structure to see whether it is a ***true local minimum*** (no imaginary / negative frequencies)
  - Remember that proving some structure to be a global minimum is usually a much more complicated task and might not be worth the trouble (see crest from Grimme group for conformational analysis)
  - Frequency calculation also yields thermochemistry via partition functions
  - Comparing Gibbs free energies instead of electronic total energies is very important for reactions involving small gaseous species (e.g. CH_4)
- Tip: ***Always*** operate with energies using atomic units and convert only the very final relative energies to kJ/mol (with conversion factor 1 a.u. = 2625.5 kJ/mol)

Suggestions: Small systems

- Small system in the year 2023: ~**10-50** non-hydrogen atoms
- DFT/TZVP geometry optimization and frequency calculations practically ”free” and always doable
  - PBE0 is a good all-around functional. Be careful with weak interactions and consider PBE0-D3 or PBE0-D4.
- Geometry optimization at the MP2/TZVPP level feasible with the right programs
  - MP2 with ***RI***/***density fitting***
- Single point energies with CCSD or even CCSD(T) feasible with the right programs
  - Always use basis sets of at least def2-TZVPP/cc-pVTZ quality!
  - The most difficult cases may require even def2-QZVPP or cc-pVQZ level
- Keep in mind that some systems (like radicals) might have ***multireference*** character, where simple HF single determinant reference is not enough!

Suggestions: Medium systems

- Medium-sized systems: < **200** non-hydrogen atoms
- DFT/TZVP geometry optimization is still cheap (with programs having RI-approximation)
- Consider mixed basis sets with TZVP for critical atoms and SVP for hydrogen, for example.
- RI-MP2/TZVPP single-point energies should be doable
- Higher-level electron-correlated methods only with some advanced techniques / approximations
  - For example the previously mentioned ***DLPNO-CCSD*** implemented in Orca

Suggestions: Large systems

- Large systems: > **200** non-hydrogen atoms
- For large systems, always consider applying modern numerical techniques such as ***RI***/***density fitting*** and seminumerical exchange (unless you really have lots of resources to waste)
- Consider mixed basis sets with TZVP for critical atoms and SVP for hydrogen, for example.
- RI-MP2/TZVP or TZVPP single-point energies might be doable.
- MP2 might not be that great for transition metals, consider ***double-hybrid*** DFT
- Always read the program manuals and literature
- Check out what methods others have used on similar molecules
- But keep in mind that calculations that were considered “heavy” 10 years ago may be ridiculously cheap nowadays

Extra slides on Post-HF methods

Electron-correlated MO-methods

- **Post-HF** methods aim to account for the missing **electron correlation**
  - $E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}}$
- ***Dynamical correlation*** arises because HF is a mean-field approximation (each electron moves in an average potential created by the other electrons)
  - Dynamical electron correlation is dominated by electrons with ***opposite spins***
  - Exchange interaction between ***parallel spins*** is described exactly in HF
- Three classes of methods describing dynamical correlation will be discussed:
  - Configuration interaction (CI)
  - Møller–Plesset perturbation theory (MP)
  - Coupled cluster (CC)
- ***Non-dynamical or static correlation*** arises because the HF wavefunction is described by only one Slater determinant
  - For electronically complex systems, single Slater determinant is not enough to describe the ground state
  - **Multiconfigurational** / **multi-reference** methods account for this

Dynamical vs. Non-dynamical

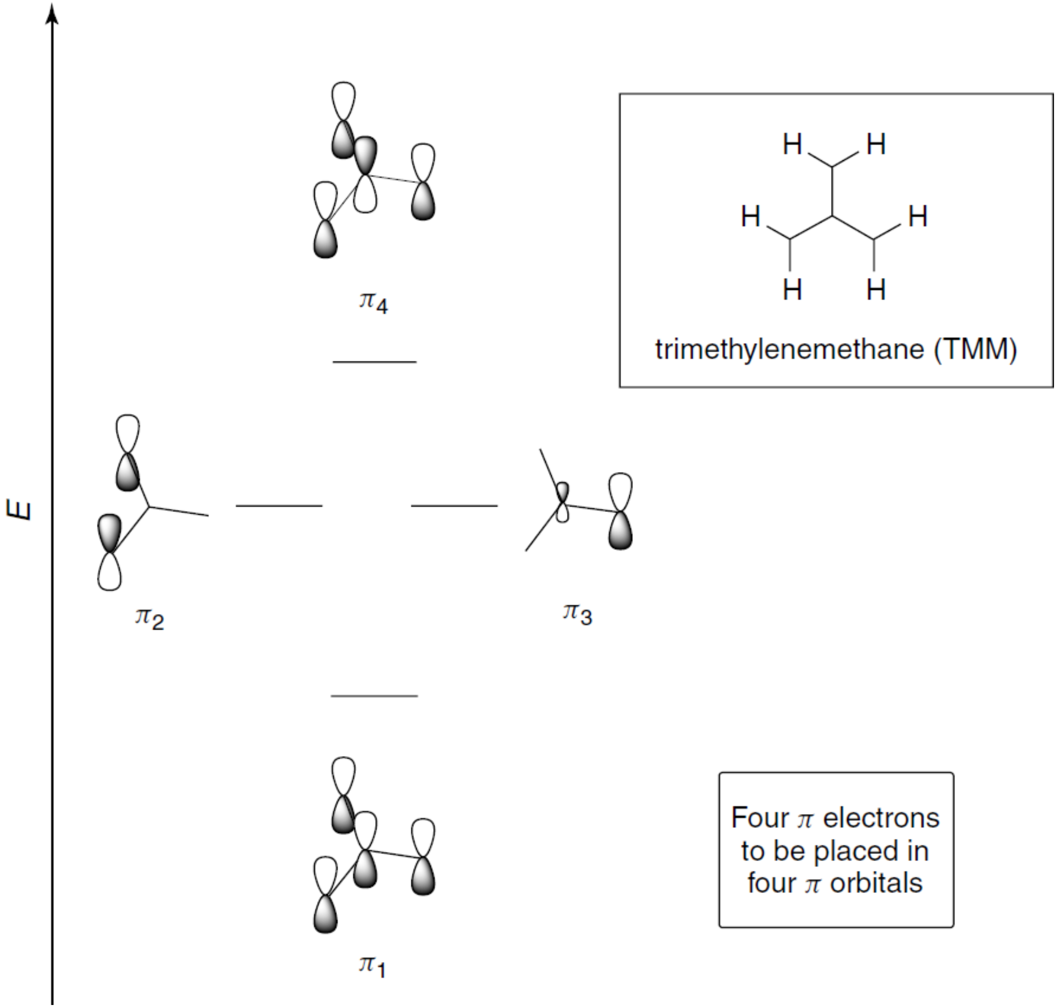
- The single-determinant HF wave function can be improved by constructing the wave function as a linear combination of multiple determinants

$$\Psi = c_0 \Psi_{\mathrm{HF}} + c_1 \Psi_1 + c_2 \Psi_2 + \cdots$$

- The coefficients *c* reflect the weight of each determinant in the expansion
- For most chemical species, Ψ_{HF} dominates the total wave function and the missing electron correlation is of ***dynamical*** nature (we are missing the ***dynamical character*** of electron-electron interactions)
- The contributions from the other determinants might be individually small, but the correlation energy resulting from their sum can be significant
- However, sometimes the other determinants can have a significant weight
- In this case, we are dealing with ***non-dynamical*** (static) electron correlation, which is not due to the mean-field nature of HF
- Let's use trimethylenemethane as an example

Non-dynamical correlation (1)

- Trimethylenemethane (TMM)
- The ground state is a triplet $\Psi_T = |\ldots \pi_1^2\, \pi_2^1\, \pi_3^1 >$
- But the closed-shell singlet state is ***degenerate***
- $\Psi_{S1} = |\ldots \pi_1^2\, \pi_2^2\, \pi_3^0 >$
- $\Psi_{S2} = |\ldots \pi_1^2\, \pi_2^0\, \pi_3^2 >$
- Ψ_{S1} and Ψ_{S2} must have equal weights in the total wavefunction of the singlet state!



---

[1] C. J. Cramer, *Essentials of Computational Chemistry*

Non-dynamical correlation (2)

- To correctly describe degenerate systems like TMM, we also need to optimize the orbitals for each configuration
- In Multiconfiguration self-consistent-field (MCSCF), both the orbitals and the weights are optimized simultaneously:

$$\Psi_{\mathrm{MCSCF}} = a_1|\cdots\pi_1^2\pi_2^2\rangle + a_2|\cdots\pi_1^2\pi_3^2\rangle$$

- For TMM, MCSCF includes only two orbitals, but often many more are required
  - All π orbitals, if a π-conjugated system is being considered
  - All or several *d* orbitals, if a transition metal system is being considered
- The choice of the ***active space*** for MCSCF can be a very complicated task
- Furthermore, actual ***Complete Active Space*** (***CASSCF***) calculations quickly become very demanding when the active space (# of orbitals) becomes larger
- There are schemes such as Restricted Active Space (RASSCF), which decrease the computational cost, but they do not simplify the choice of the active space

Configuration interaction (CI)

- Let's see how the ***dynamical correction*** can be included by constructing the wave function as a linear combination of multiple determinants
- The previous expansion of the wave function in a more descriptive form is

$$\Psi = a_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\text{occ.}} \sum_{r}^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i<j}^{\text{occ.}} \sum_{r<s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$$

- Now, *i* and *j* are occupied orbitals, *r* and *s* virtual orbitals. a_n are the weights.
- a_i^r / Ψ_i^r -> single electron excitations from occupied orbital *i* to virtual orbital *r*
- a_{ij}^{rs} / Ψ_{ij}^{rs} -> double excitations from occupied orbitals *i,j* to virtual orbitals *r,s*
- The HF orbitals are ***not reoptimized*** for the excitations
- The higher terms become increasingly costly to evaluate -> truncation of the series
  - CIS does not improve the HF energy, CID and ***CISD*** are the first ones to do so
- CI methods can further be combined with MCSCF wave functions, resulting in multireference configuration interaction (MRCI) methods

Truncated CI is not size-consistent

- CI is a variational approach
  - The energy approaches the exact energy from above
  - Beneficial for improving the accuracy systematically
- However, truncated CI is not a ***size-consistent*** method
  - Size-consistency is also known as ***strict separability***
  - The energy of a molecular system should behave consistently when the interaction is nullified by taking the constituent fragments very far apart
- Consider two interacting H_2 molecules A and B described by CISD
  - If A and B are very far apart (e.g. 50 Å), there is no interaction between them
  - If we calculate E(A) or E(B) separately, both will include double excitations
  - If we calculate E(A+B) ”supermolecule”, simultaneous double excitations in A and B would correspond to quadruple excitations, which CISD won’t include!
  - In this case, E(A+B) should be E(A) + E(B), but for CISD it is not
  - The situation can be corrected by including quadruple excitations (QCISD), but the lack of size-consistency is a major drawback in truncated CI

Full configuration interaction

- What if we don't truncate the CI series?

$$\Psi = a_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\mathrm{occ.}} \sum_{r}^{\mathrm{vir.}} a_i^r \Psi_i^r + \sum_{i<j}^{\mathrm{occ.}} \sum_{r<s}^{\mathrm{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$$

- The resulting method is called Full Configuration Interaction (FCI or Full-CI)
- In short it corresponds to a complete active space calculation for all electrons including all orbitals in the active space
- The reoptimization of HF orbitals is not required, since all possible configurations are included
- The resulting wavefunction is the best possible for the chosen basis set
- With infinite basis set, Full-CI would correspond to ***exact solution*** of the Schrödinger equation (non-relativistic, Born-Oppenheimer, time-independent SE)
- Only possible for the smallest molecules due to extreme computational cost

MPn methods (1)

- The idea of the Møller–Plesset perturbation theory was published already in 1934 (based on the Rayleigh–Schrödinger perturbation theory)
- A small external perturbation ***V*** is added to the operator ***A***$^{(0)}$ (for example, ***H***):

$$\mathbf{A} = \mathbf{A}^{(0)} + \lambda \mathbf{V}$$

- Dimensionless parameter λ varies from 0 to 1. Now, expanding ground state eigenfunctions Ψ_0 and eigenvalues a_0 as Taylor series in λ:

$$\Psi_0 = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \cdots$$

$$a_0 = a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \cdots$$

- By truncating the series, the eigenvalue corrections $a_0^{(n)}$ can be solved

$$(\mathbf{A}^{(0)} + \lambda \mathbf{V})|\Psi_0\rangle = a|\Psi_0\rangle$$

$$(\mathbf{A}^{(0)} + \lambda \mathbf{V})|\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \cdots\rangle =$$

$$(a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \cdots)|\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \cdots\rangle$$

- The resulting methods are called ***MPn*** (MP2, MP3, MP4), depending on truncation

MPn methods (2)

Two-electron integrals in MO basis

- MP2 energy expression: $$a^{(2)} = \sum_{i}^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \sum_{a}^{\text{vir.}} \sum_{b>a}^{\text{vir.}} \frac{[(ij|ab) - (ia|jb)]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$
- MP*n* methods are not variational
  - E(MP*n*) might be lower than the exact energy
- Most importantly, MP*n* methods are ***size-consistent***
  - Very practical class of methods for investigating e.g. dispersion effects
- MP2 can be considered as the simplest approach to electron correlation
  - Retrieves a large part of the correlation energy
  - Can fail miserably for complicated systems
- Very fast implementations of the MP2 method are nowadays available
  - Semi-empirical spin-component-scaled (SCS-MP2) variants available (Grimme)
  - Has been coupled with DFT to create double hybrid functionals (Grimme)
- The higher-order MP*n* methods have been largely superceded by Coupled Cluster
- Multireference MP2 methods exist, as well (CASPT2)

Coupled cluster methods (1)

- In coupled cluster (CC) theory, the exact wavefunction is described as

$$\Psi = e^{\mathbf{T}} \Psi_{\mathrm{HF}}$$

- The cluster operator ***T*** is defined as

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \cdots + \mathbf{T}_n$$

- n is the total number of electrons and the various $\boldsymbol{T}_i$ operators generate all possible determinants having i excitations. For example, truncating at second order:

$$\mathbf{T}_2 = \sum_{i<j}^{\text{occ.}} \sum_{a<b}^{\text{vir.}} t_{ij}^{ab} \Psi_{ij}^{ab}$$

- The terms t_{ij}^{ab} are called the ***amplitudes*** (they are determined in CC calculation)
- For second order CCD, the Taylor expansion of the original CC expression becomes

$$\begin{aligned}\Psi_{\mathrm{CCD}} &= e^{\mathbf{T}} \Psi_{\mathrm{HF}} \\ &= \left(1 + \mathbf{T}_2 + \frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \cdots\right) \Psi_{\mathrm{HF}}\end{aligned}$$

- Now, $\boldsymbol{T}_2^2$ generates quadruple excitations, which were missing in truncated CI!

Coupled cluster methods (2)

- Like MP*n* methods, CC methods are not variational
  - E(CC) might be lower than the exact energy
- Most importantly, CC methods are ***size-consistent***
  - Using the exponential of the cluster operator ***T*** ensures size-consistency
  - Very practical and robust class of methods for highly accurate studies
- CCS does not improve HF energy, CCD and ***CCSD*** are the first to do so
- Triple and quadruple excitations are also available (CCSDT, CCSDTQ), but expensive
- A very important step was the discovery that including triples in a perturbative manner results in a very good performance -> ***CCSD(T)***
- CCSD(T) is considered as the current ***gold standard*** of post-HF methods
- Multireference-CC methods (MRCC) do exist, but are not used very commonly

Basis sets for post-HF methods (1)

- The excited determinants of the post-HF methods include occupation of orbitals that are virtual in the HF determinant
- However, the HF determinant already “uses up” the best combinations of basis functions for the occupied orbitals
- Therefore, post-HF methods are more dependent on the ***basis set completeness***
- In practice, post-HF methods equire larger and more flexible basis sets in comparison to HF
  - Multiple-zeta-valence (for HF/DFT, split-valence is often enough)
  - High angular momentum polarization functions (f, g, h, ...)
  - Even diffuse functions might be required for very weak interactions
- Another important point is that in post-HF calculations, the core electrons are normally ***frozen***, that is, their contribution to E_{corr} is neglected
  - Greatly reduces the computational cost for the heavier elements
  - Accurate electron correlation for the core orbitals requires special basis sets with proper core-valence balance (normally the basis sets focus on valence)

Basis sets for post-HF methods (2)

- Post-HF methods should always be combined with ***at least triple-zeta-valence*** level basis sets! (for example, 6-311G(3df,2p) in Pople notation)
- However, the Pople basis sets are obsolete and should not be used for electron-correlated calculations
- The Correlation Consistent basis set family of Dunning and Petersen was developed in particular for electron-correlated calculations
  - cc-pV**D**Z, cc-pV**T**Z, cc-pV**Q**Z, ...
  - Very consistent improvement with increasing **zeta**
  - Diffuse functions can be included with **aug**-prefix (aug-cc-pVTZ)
  - The higher-zeta basis sets are computationally rather demanding
- The Karlsruhe basis sets are another good option
  - Def2-SVP, def2-TZVP, def2-TZVPP, def2-QZVP, def2-QZVPP
  - Diffuse functions can be included with **D** (def2-TZVPP**D**)
  - Computationally cheaper than the Correlation Consistent basis sets for codes like TURBOMOLE (depends on the details of the integral engine)

Basis set convergence

- Comparison between the basis set convergence for HF and Full-CI
- CO molecule for HF, O atom for Full-CI

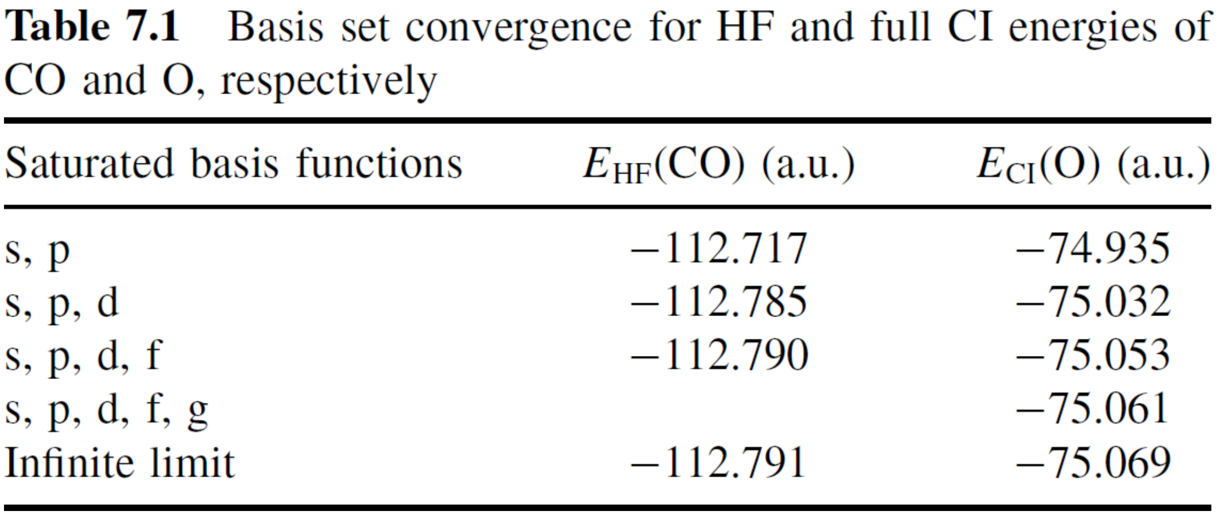


Table 7.1 Basis set convergence for HF and full CI energies of CO and O, respectively

Saturated basis functions	E_{HF}(CO) (a.u.)	E_{CI}(O) (a.u.)
s, p	−112.717	−74.935
s, p, d	−112.785	−75.032
s, p, d, f	−112.790	−75.053
s, p, d, f, g		−75.061
Infinite limit	−112.791	−75.069

- Note that ***relative*** energies and some molecular properties (such as vibrational frequencies) might converge much faster than the absolute energy!

[1] C. J. Cramer, *Essentials of Computational Chemistry*

Accuracy of post-HF methods (1)

- A rough quality ordering (BD = Brueckner Doubles = CC with modified orbitals):

$$\begin{aligned}
&\mathrm{HF} < \mathrm{MP2} \sim \mathrm{MP3} \sim \mathrm{CCD} < \mathrm{CISD} \\
&< \mathrm{MP4SDQ} \sim \mathrm{QCISD} \sim \mathrm{CCSD} < \mathrm{MP4} \\
&< \mathrm{QCISD(T)} \sim \mathrm{CCSD(T)} \sim \mathrm{BD(T)}
\end{aligned}$$

- The inclusion of triple excitations is very important to achieve high accuracy
- In the above scheme, hybrid DFT methods are located around MP2 ~ MP3 (but they are not capable of describing weak dispersion interactions)

Accuracy of post-HF methods (2)

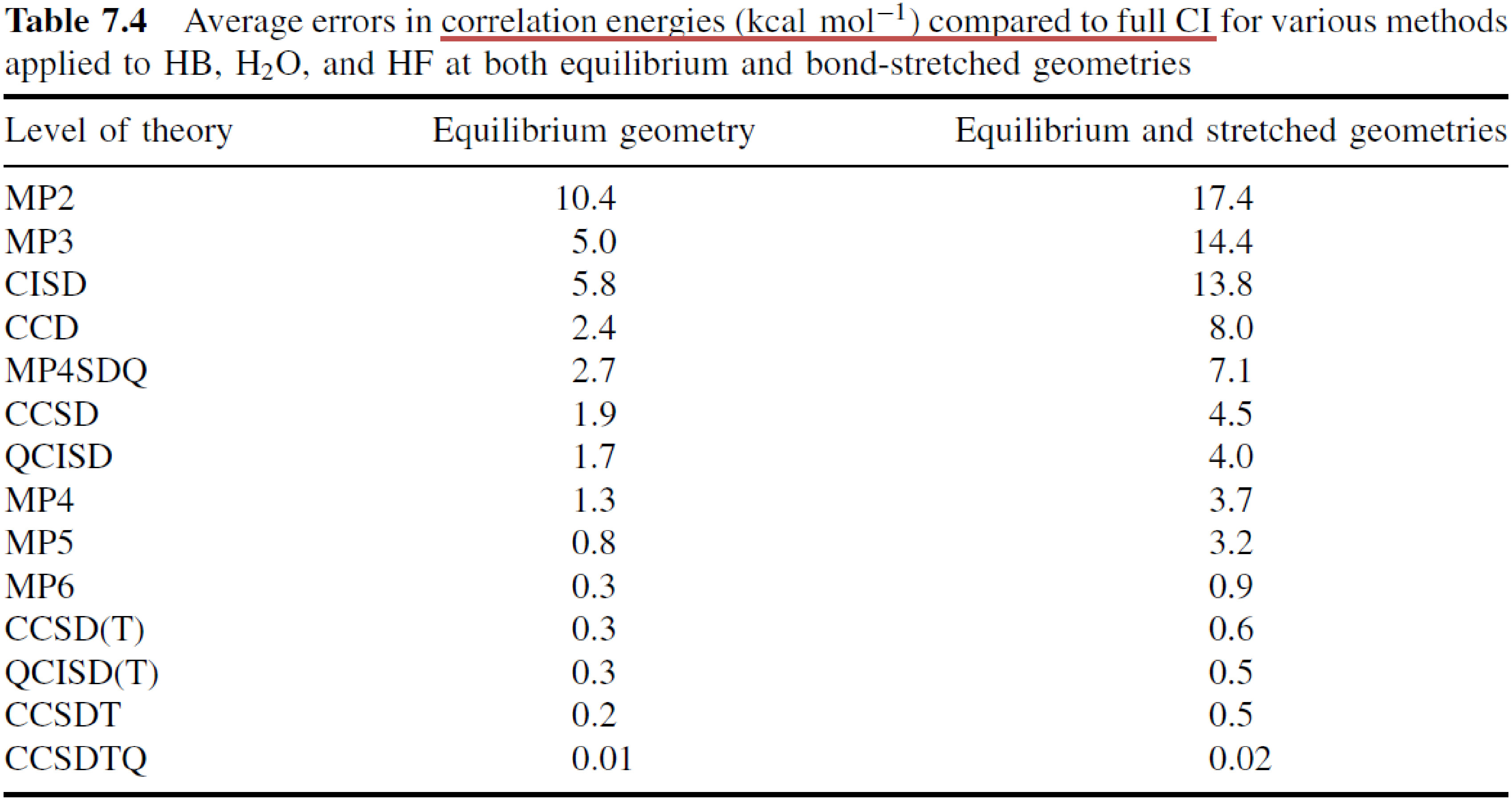


Table 7.4 Average errors in correlation energies (kcal mol^{-1}) compared to full CI for various methods applied to HB, H_2O, and HF at both equilibrium and bond-stretched geometries

Level of theory	Equilibrium geometry	Equilibrium and stretched geometries
MP2	10.4	17.4
MP3	5.0	14.4
CISD	5.8	13.8
CCD	2.4	8.0
MP4SDQ	2.7	7.1
CCSD	1.9	4.5
QCISD	1.7	4.0
MP4	1.3	3.7
MP5	0.8	3.2
MP6	0.3	0.9
CCSD(T)	0.3	0.6
QCISD(T)	0.3	0.5
CCSDT	0.2	0.5
CCSDTQ	0.01	0.02