

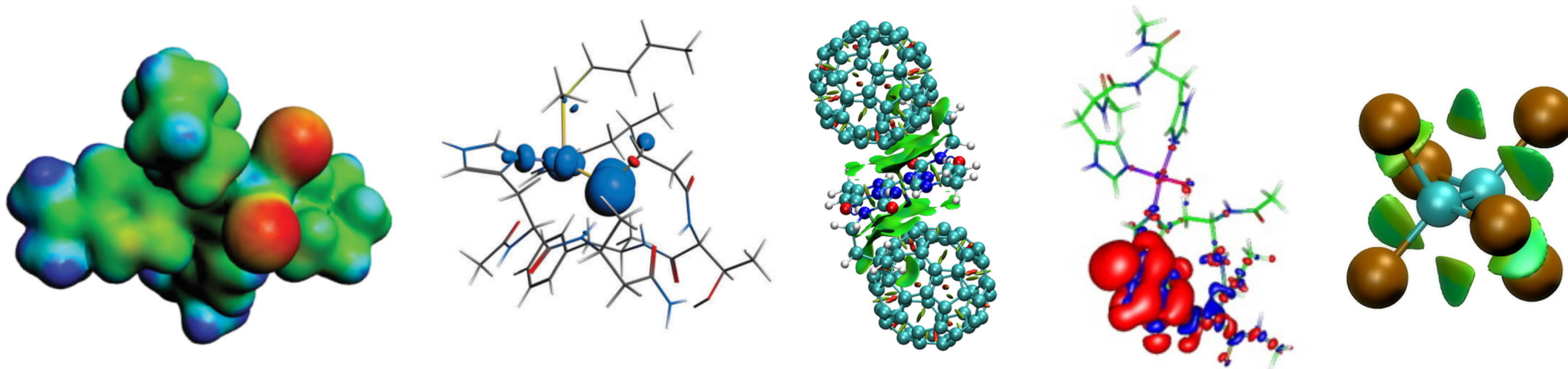
CSC/PRACE Spring School in Computational Chemistry 2019

## Introduction to Electronic Structure Theory

Mikael Johansson

<http://iki.fi/mpjohans>

**Objective:** To get familiarised with the, subjectively chosen, most important concepts of electronic structure theory from a computational chemistry viewpoint. After these lectures, the student will hopefully go for lunch with at least a rudimentary exposure to different approximations to the molecular Schrödinger equation, and the alternative theory of density functionals



# Part I: Wave-function based *ab initio* computational chemistry

## What is quantum chemistry?

- “Simply”, the application of quantum mechanics in chemistry

- Based largely on solving **the Schrödinger equation** (1926):

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left( E + \frac{e^2}{r} \right) \psi = 0$$

- Or even more condensed:

$$\hat{H}\Psi(\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N, \mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = E\Psi(\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N, \mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n)$$

- $\hat{H}$  is the *Hamiltonian operator*,  $\Psi$  is the *wave function*,  $E$  is the energy of the system,  $\mathbf{R}$  are the coordinates of the nuclei, and  $\mathbf{r}$  the coordinates of the electrons

- The central creature is the **wave function  $\Psi$**
- The Schrödinger wave function  $\Psi$  implies that small, light particles can *and should* be described as waves



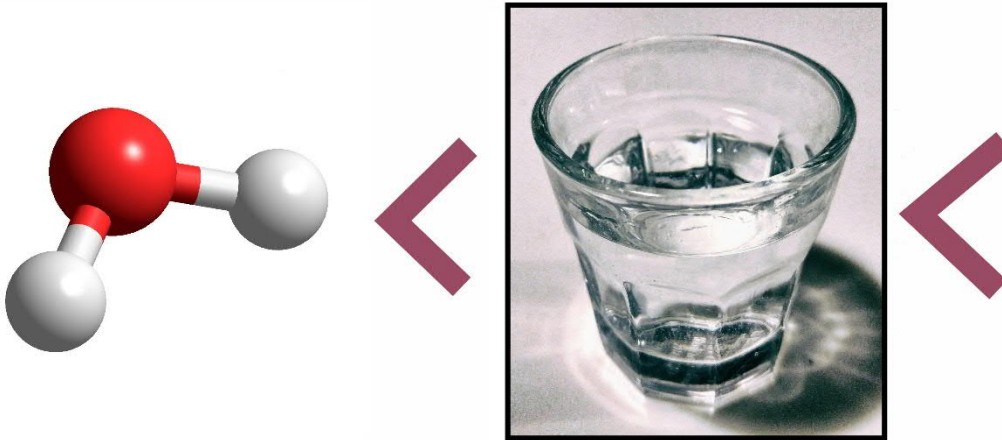
## Quantum chemistry is for small systems

- Molecules *are* small, electrons even smaller (or at least lighter!)
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## The Schrödinger equation

- For one-electron systems, the Schrödinger equation is simple to solve
- The resulting wave-functions  $\Psi$  are the hydrogen-like atomic orbitals:

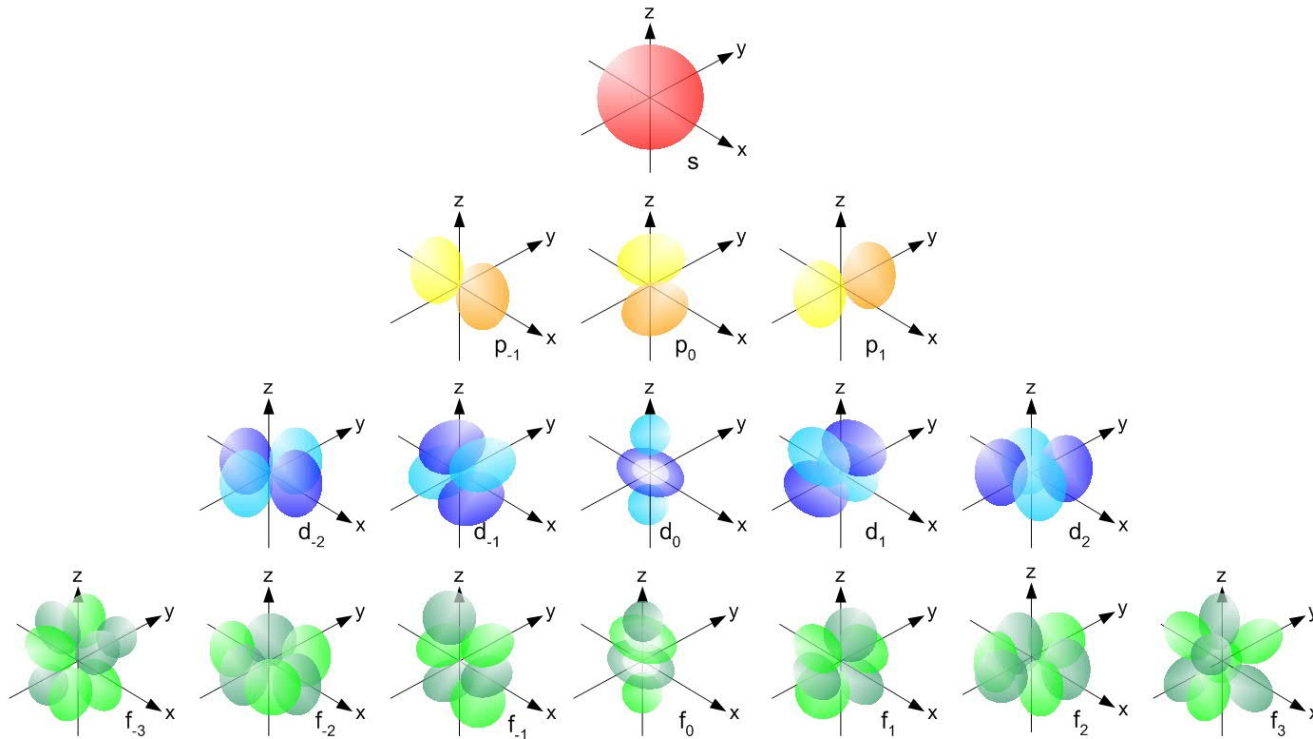
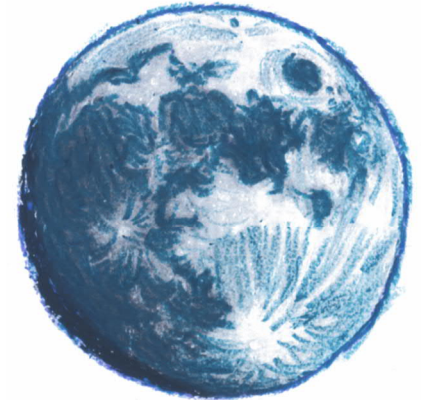
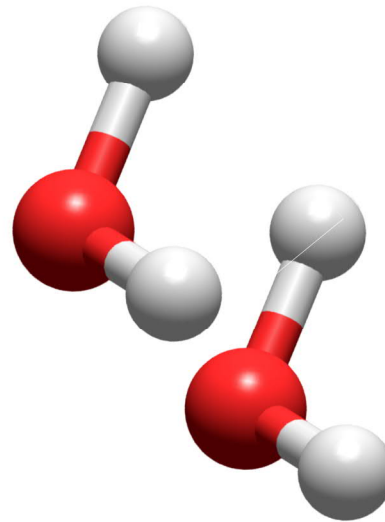
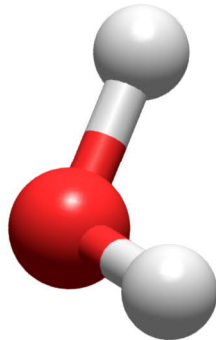
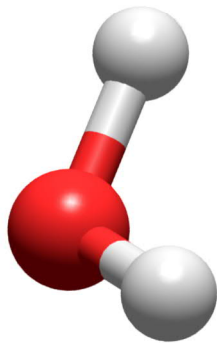
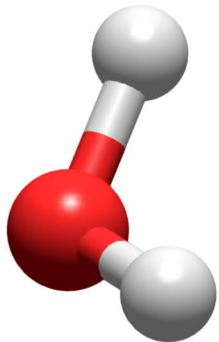


Image from  
[chem.libretexts.org](http://chem.libretexts.org)

- For more than two particles, the SE *cannot be solved analytically*

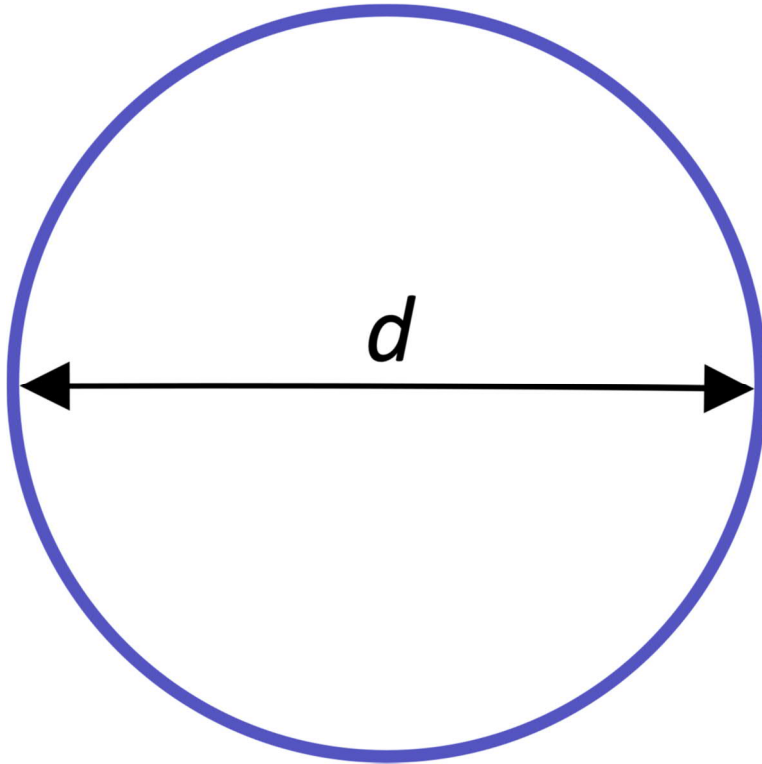
## Computational quantum chemistry

- In a world where everything seems instant, it may be difficult to grasp that **computers can actually be slow**
  - A microwave is more powerful than the Apollo Guidance Computer...
- **Even supercomputers are too slow for solving the Schrödinger equation perfectly!**
- CCSD(T), the “gold standard” of QC
  - Scales as  $\sim N^7$  with system size  $N$
  - 1 water molecule: 1 second
  - 10 water molecules: 100 days
  - 100 water molecules: **3 million years**



## What is quantum chemistry?

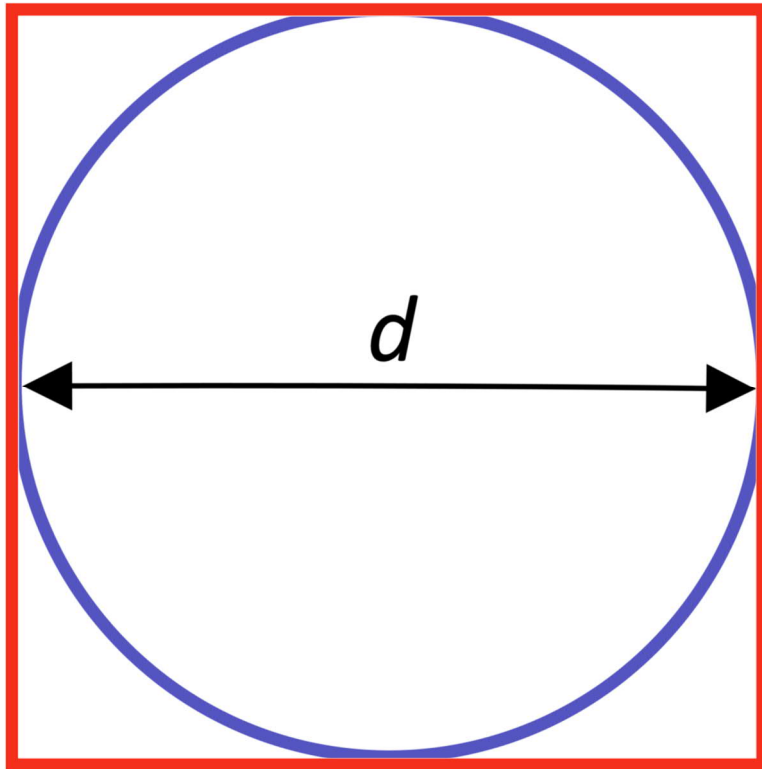
- Designing and solving *approximations* to the Schrödinger equation



$$A = \pi r^2$$

## What is quantum chemistry?

- Designing and solving *approximations* to the Schrödinger equation

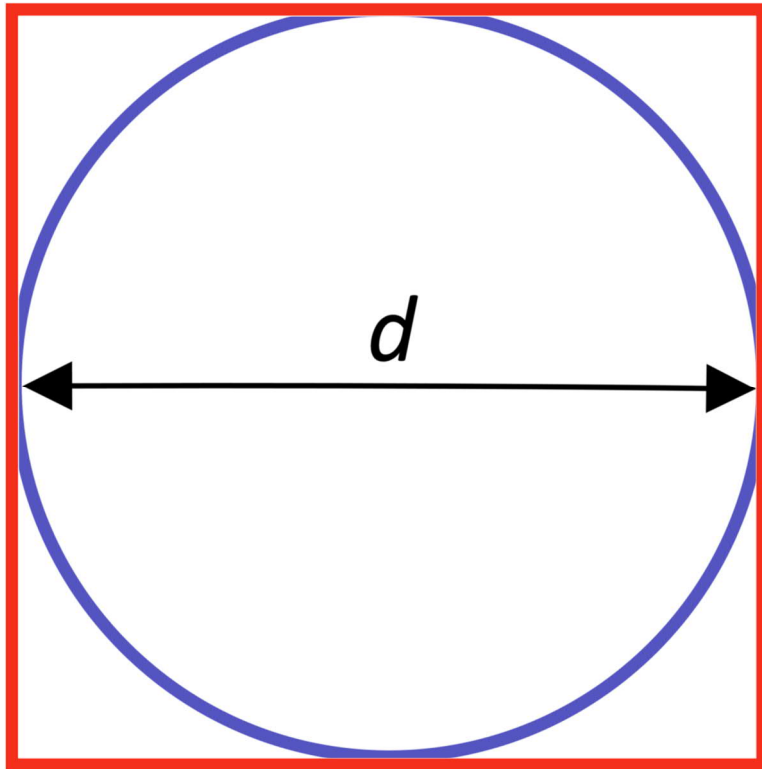


$$A = \pi r^2$$

$$A \approx d^2 = 4r^2 \quad \text{27\% error}$$

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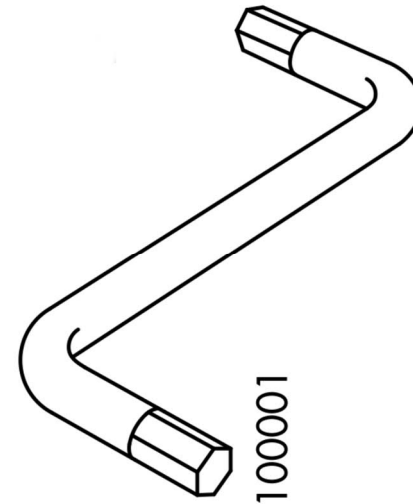
$$A = \pi r^2$$

$$A \approx d^2 = 4r^2 \quad \text{27\% error}$$

$$\text{or } \pi \approx 3 \rightarrow \quad \text{5\% error}$$

## What is quantum chemistry?

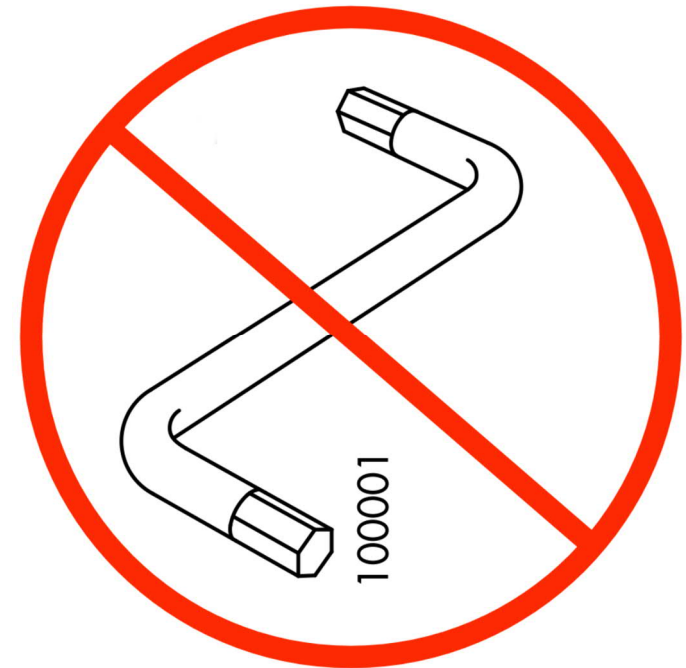
- Designing and solving *approximations* to the Schrödinger equation
- The number of different approximations is humongous
  - Hartree–Fock, MP2, Full CI, B3LYP, ...
- The challenge is to find the *right tool for the right purpose*



## What is quantum chemistry?

- Designing and solving **approximations** to the Schrödinger equation
- The number of different approximations is humongous
  - RASPT2, quantum Monte Carlo, revTPSS-D3, DLPNO-CCSD(T)-F12, ...
- The challenge is to find the **right tool for the right purpose**
- There is no single tool that works for everything!

- Before looking at various theories of how to approximate the SE, we need to be aware that what we will be doing is *approximating an approximation itself!*



## Initial approximations

The following **approximations of nature** are invoked already before the computational approximations; nothing we learn today is even in principle rigorously true

1. The Schrödinger equation is **non-relativistic**
  - To account for relativity, the Dirac equation should be used
  - In effect an assumption that the speed of light is infinite
2. The nuclei are considered to be **point-like**
  - In reality, nuclei naturally have a volume
3. The time-independent SE is, well, **time-independent**
  - Time doesn't actually stand still
4. We will employ the **Born-Oppenheimer approximation**
  - Due to the large mass-difference between nuclei and electrons, their motion can be considered separately
  - In effect an assumption that the masses of nuclei are infinite

## Initial approximations

In addition, we **approximate the true environment** of our systems

1. The molecules are considered **independent entities** experiencing no outside interaction
  - Even in gas-phase, this is not really true, our universe consists of more than one molecule
  - Often real-world chemistry takes place in solution, where the interaction between the molecule under study and its environment is of major importance
    - This will be addressed later on during the School
2. We will work at **zero Kelvin**
  - Doesn't exist; temperature effects can be *very* important
    - Also this aspect will be addressed later on

## Approximate lecturing

Next, we will go through a few central concepts of electronic structure theory, concentrating on the implications and practical consequences

- Most of the mathematics and proofs will be skipped
- See the *Further reading* section for good literature that includes essential derivations and maths

## The variational principle

- First thing to note, there are *several* (infinite) solutions to the Schrödinger equation, corresponding to different wave functions and their corresponding energies:

$$\hat{H}\Psi_i = E_i\Psi_i, i = 0, 1, 2, 3, \dots, \infty$$

- By convention, we assume the solutions are energy ordered, so that  $\Psi_0$  corresponds to the lowest energy solution with  $E_0$ . As a side note, quantum mechanics makes  $E_0$  have a *finite value* above  $-\infty$
- Further, the solutions are orthogonal and normalised (orthonormal):

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

- The solutions to the SE form a complete set, basis, so any approximate wave function  $\Phi$  can be expressed, expanded, in the exact solutions, and have a defined energy  $W$ :

$$\Phi = \sum_{i=0}^{\infty} a_i \Psi_i$$

$$W = \frac{\langle \Phi | \mathbf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

- The **variational principle** states that **the energy  $W$  of an approximate wave function is always higher or equal to the lowest energy state  $E_0$** ; if equal, then  $\Phi$  is actually the ground state wave function  $\Psi_0$
- The principle makes it possible to look for the ground state solution mathematically: Almost any function can approximate the wave function we are looking for, and an initial guess can be refined by distorting the *trial wave function* by looking for minima for the energy expression!

## Size-consistency

- A given electronic structure method is **size consistent** if the computed energy of  $N$  “infinitely” separated, and thus non-interacting monomers is  $N$  times that of the individual monomers
  - Non-size consistency leads to poor description of dissociation energies
  - Problem increases with system size; with large systems, the correlation energy of subsystems decreases towards zero

## The Born–Oppenheimer approximation

- The BO approximation is based on the *usually good approximation* that the motion of electrons is *instant* upon rearrangement of the atomic centres in our molecule due to the large **mass difference**
  - In other words, the nuclear **velocities** are much smaller than the electron velocities; *no coupling* between the velocities of the two
  - The electronic wave function depends only **parametrically** on the atomic coordinates

## The Born–Oppenheimer approximation

- This allows us to separate the Schrödinger equation into a *nuclear wave function*  $\Phi$  and an *electronic wave function*  $\psi$ :

$$\Psi(\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N, \mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = \Phi(\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N) \psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n)$$

- The BO approximation also gives us the concept of **molecular structure**; without it, definite bond lengths and such would have little meaning
- After the BO approximation, **our Hamiltonian today** takes the following form (in atomic units):

$$\hat{H} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}} + \sum_{i < j}^n \frac{1}{r_{ij}} + V^{\text{nuc}}$$

$\hat{T}_e$ , **electronic** kinetic energy       $\hat{V}_{ee}$ , **electron-electron** repulsion  
 $\hat{V}_{ne}$ , **electron-nucleus** attraction       $\hat{V}_{nn}$ , **nucleus-nucleus** repulsion

## The Hartree equations

- Soon after the introduction of the Schrödinger equation, Hartree proposed that the electronic wave function could be approximated by assuming that, in addition to the nuclei, the individual electrons could be separated as well
- Thus, the many-electron wave function would be a **product of one-electron wave functions**  $\phi$ :

$$\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \dots \phi_n(\mathbf{r}_n)$$

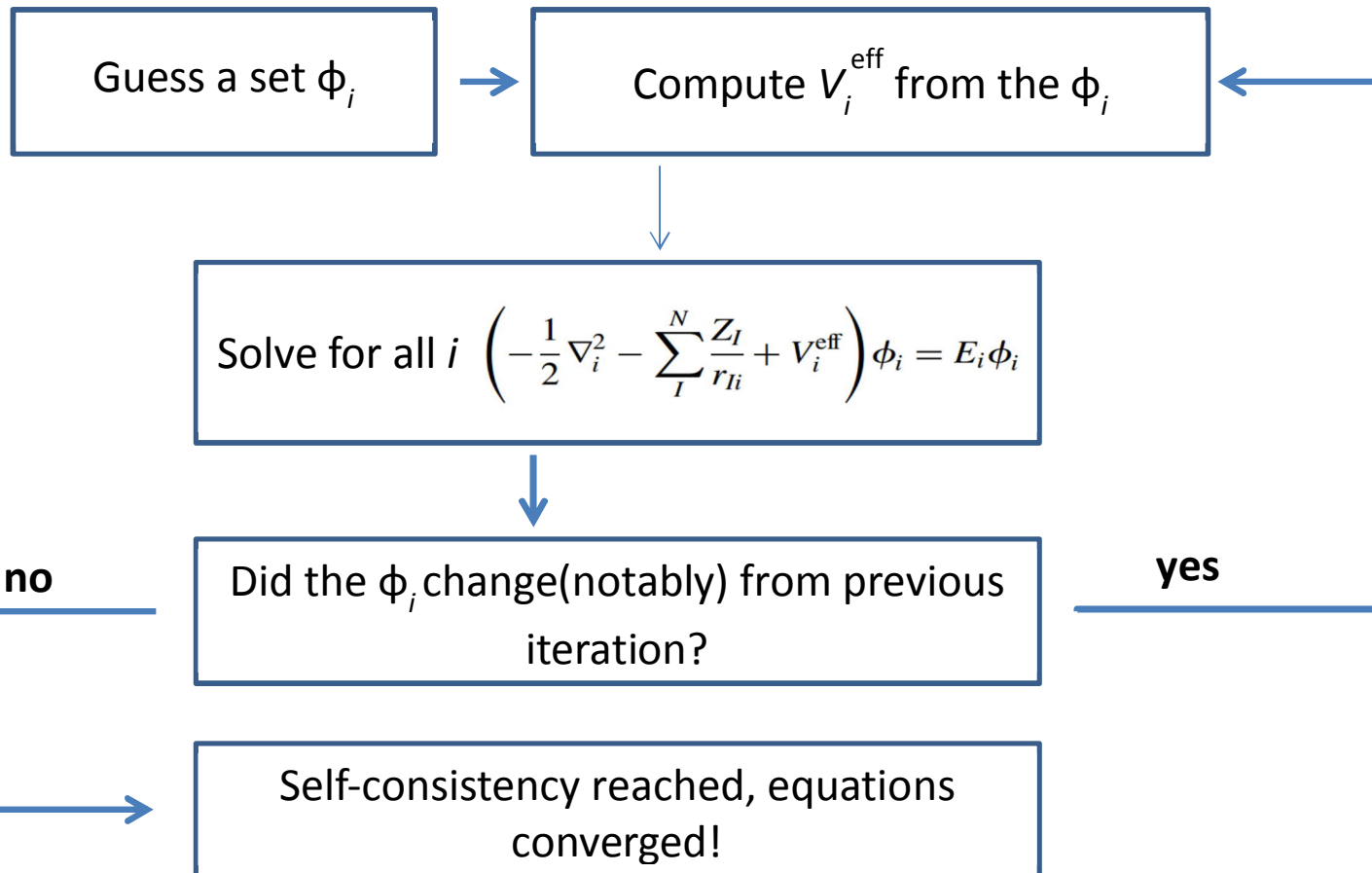
- This wave-function completely ignores the **electron-electron repulsion**
- To account for this, the **Hartree equations** assume that the repulsion between electron  $i$  and all the other electrons can be accounted for by only considering the average positions of all other electrons in the molecule; an individual electron moves in a **mean field**  $V_i^{\text{eff}}$  of all other electrons:

$$\left( -\frac{1}{2} \nabla_i^2 - \sum_I^N \frac{Z_I}{r_{Ii}} + V_i^{\text{eff}} \right) \phi_i = E_i \phi_i$$

- The solutions of the individual Hartree equations depend on the solutions of all the other equations *via*  $V_i^{\text{eff}}$ . Thus, they have to be solved *iteratively*

## The Self-Consistent Field (SCF) method

- First, an initial guess for the individual one-electron wave functions is needed
- After this, iterate until all  $\phi_i$  stay the same, that is, a **self-consistent field** has been achieved:



Loosely based on D.R. Hartree, "The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion", *Math. Proc. Cambridge Philos. Soc.* **24** (1928) 111.

<http://dx.doi.org/10.1017/S0305004100011920>

## The Hartree–Fock method

- The Hartree product wave-function violates the Pauli principle, it is not **antisymmetric**, that is, the wave function doesn't change sign upon swapping two electrons (which it should)
- Fock noticed and fixed this by expressing the wave function as a **Slater Determinant** (SD)

$$\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(e_1) & \phi_2(e_1) & \dots & \phi_n(e_1) \\ \phi_1(e_2) & \phi_2(e_2) & \dots & \phi_n(e_2) \\ \dots & \dots & \dots & \dots \\ \phi_1(e_n) & \phi_2(e_n) & \dots & \phi_n(e_n) \end{vmatrix}$$

- The Hartree–Fock energy of an SD can be obtained from

$$E = \sum_{i=1}^{N_{\text{elec}}} h_i + \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{\text{nn}}$$

- Without further details, let's just point out two of the terms
  - **$J_{ij}$  is obtained by the Coulomb operator** and is composed of two-electron terms, integrals, arising from the Coulomb repulsion between electrons
  - **$K_{ij}$  is obtained by the exchange operator** and is composed of two-electron terms having no classical counterpart. Among other things,  $K$  ensures antisymmetry and removes the self-interaction arising from the  $J_{ij}$  integrals.

## Linear Combination of Atomic Orbitals (LCAO)

- What are the one-electron wave-functions  $\phi_i$  on the preceding slides?
- Considering the simplest case, one-electron, hydrogen-like atoms, it is easy to be convinced that the solutions are **atomic orbitals** (AOs)

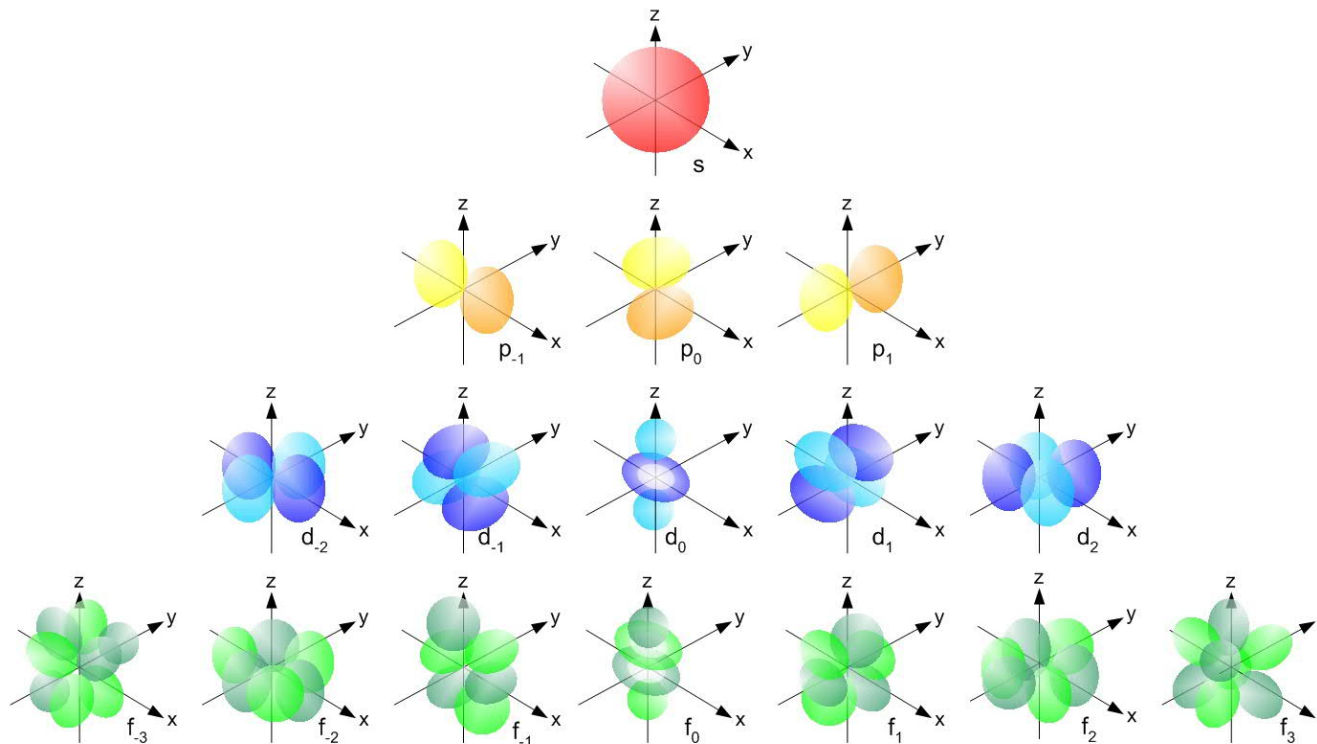
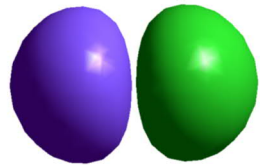


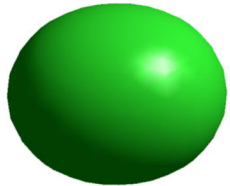
Image from *chem.libretexts.org*

## Linear Combination of Atomic Orbitals (LCAO)

- For more complex cases, with more atoms and electrons, it is reasonable to expect *some similarity* to atomic orbitals to be transferred
- In fact, the solutions to the HF equations gives **molecular orbitals**
- A simple first guess is then to construct the MOs  $\phi_i$  from the AOs  $\chi_\mu$  as 
$$\phi_i = \sum_{\mu}^k c_{i\mu} \chi_{\mu}$$
  - The sum over  $\mu$  runs over all  $k$  atomic orbitals of the atoms
  - The **coefficients**  $c_i$  are optimised to minimise the total energy
  - For  $H_2$ , this simple **minimal basis set** leads to two HF orbital solutions based on the 1s AOs:

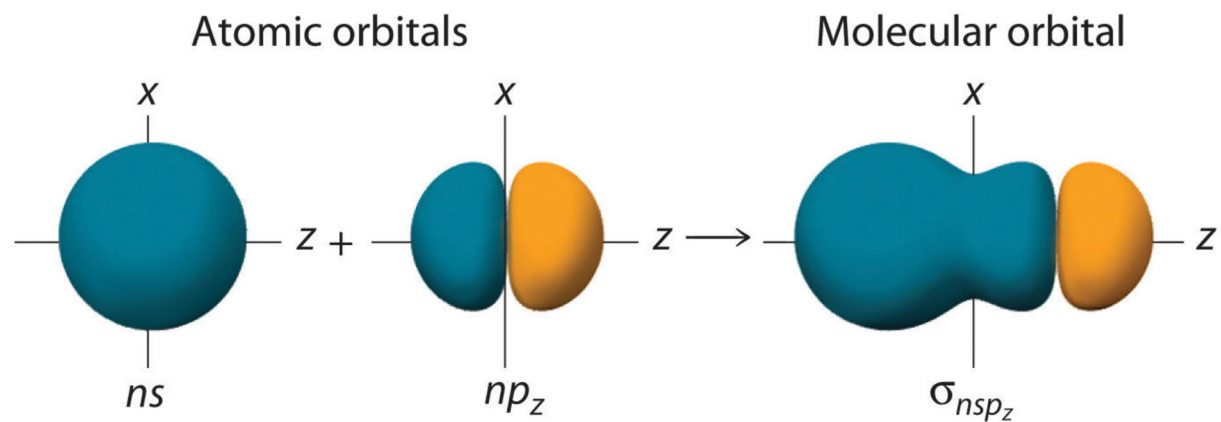


$$\psi_2 = \sigma^* = \frac{1}{\sqrt{2}} (\chi_{1s}^A - \chi_{1s}^B) \quad \text{antibonding orbital (virtual)}$$

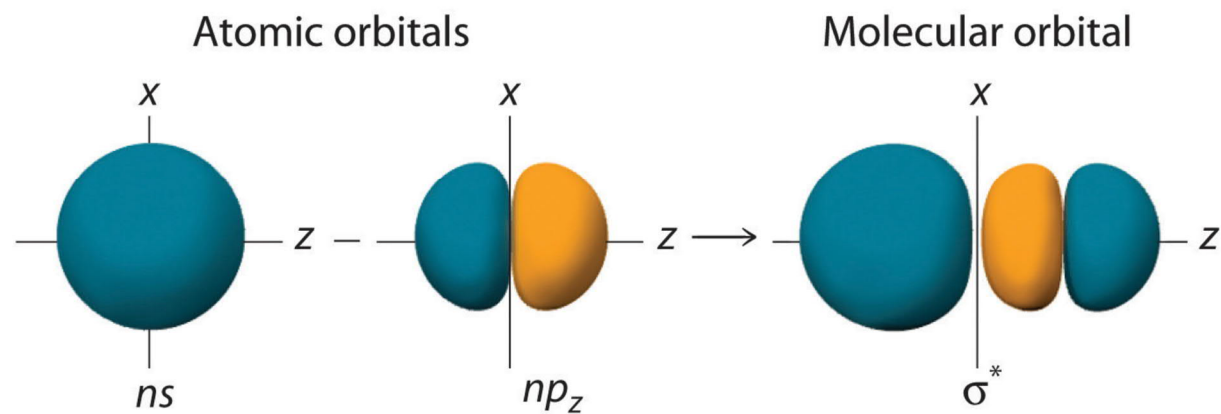


$$\psi_1 = \sigma = \frac{1}{\sqrt{2}} (\chi_{1s}^A + \chi_{1s}^B) \quad \text{bonding orbital (occupied)}$$

## Linear Combination of Atomic Orbitals (LCAO)



**(a) Bonding**

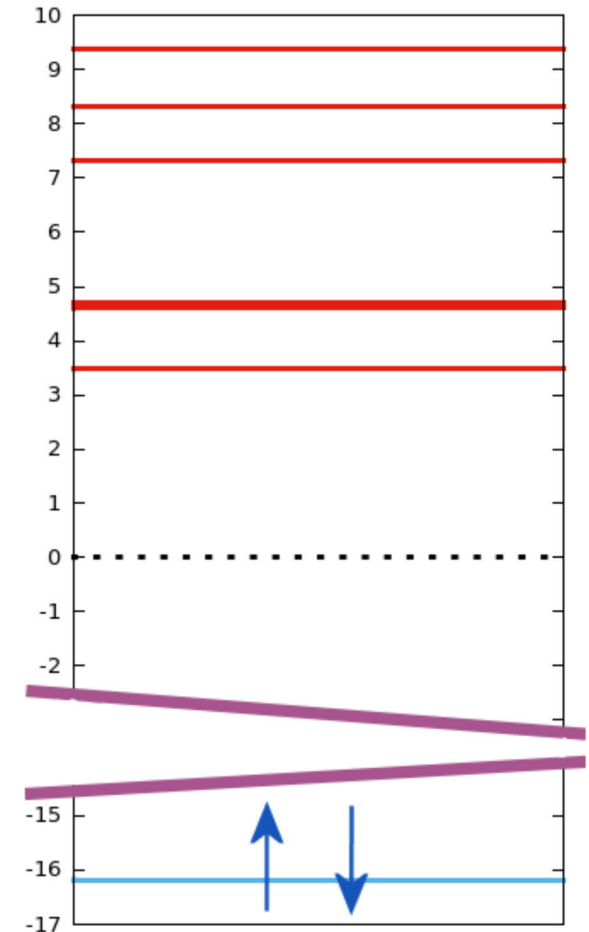


**(b) Antibonding**

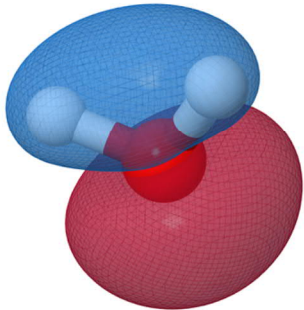
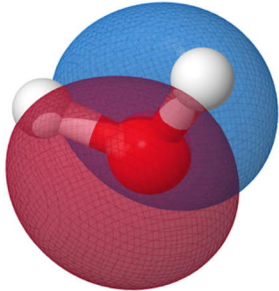
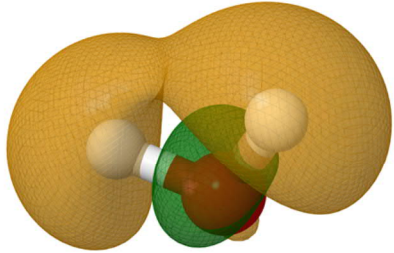
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## Hartree–Fock orbitals

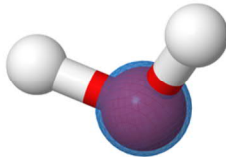
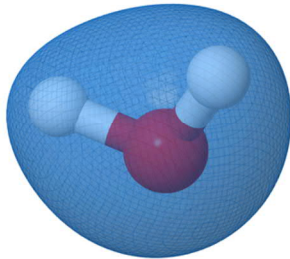
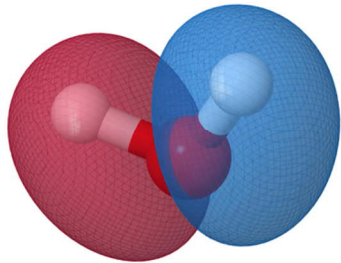
- In effect, what the HF SCF procedure produces is, in addition to the energy, a set of molecular orbitals
- The number of orbitals depends on the number of **basis functions**
  - The minimal basis consists of only the atomic orbitals of the constituent atoms, very crude
  - For the exact solution of the HF equations, that is, the lowest HF energy possible, in principle an *infinite* amount of basis functions is needed
  - In practice, a balance has to be struck → basis sets of varying size and quality: double-zeta (DZ), triple-zeta (TZ), *etc.*
- The lowest energy HF solution is then obtained by the **aufbau principle**, by inserting the electrons into the lowest energy orbitals (one of each spin per orbital)
  - Orbital diagram for a reasonably large basis set for H<sub>2</sub>:



# SCF of water: iteration 1

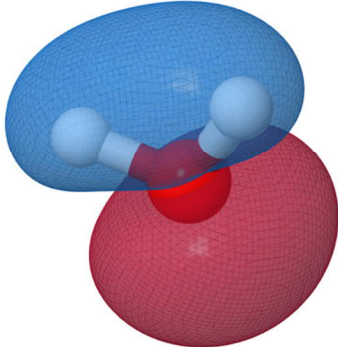
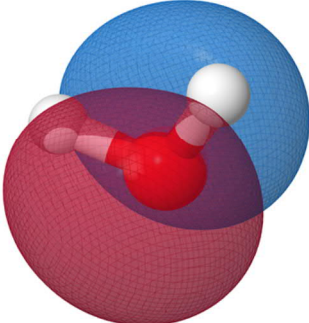
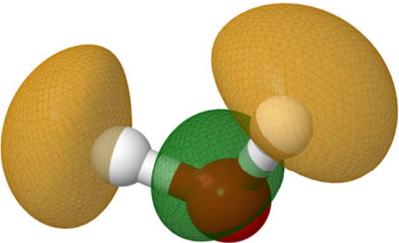


-60.970241 H \_\_\_\_\_

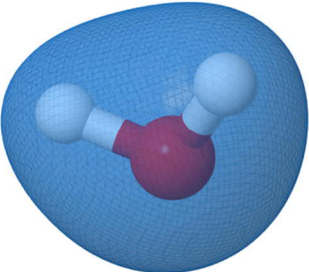
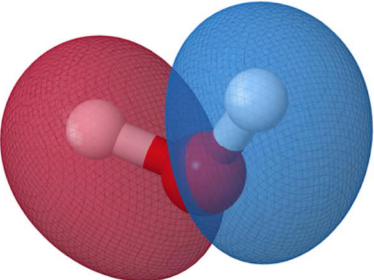


-37.447 eV \_\_\_\_\_  
-55.573 eV \_\_\_\_\_

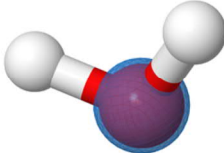
SCF of water: iteration 2



-76.126684 H \_\_\_\_\_

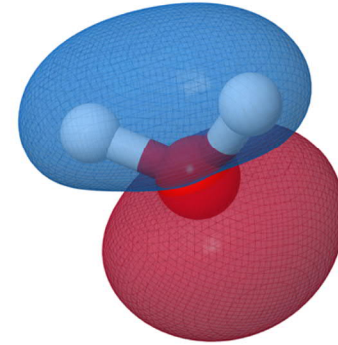
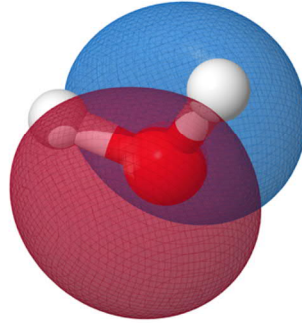
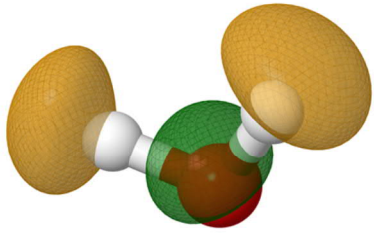


-9.316 eV \_\_\_\_\_



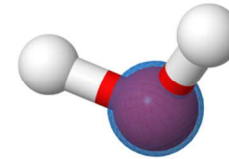
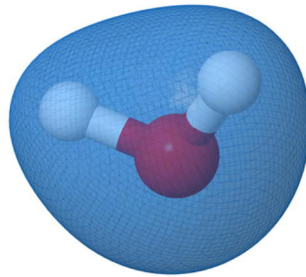
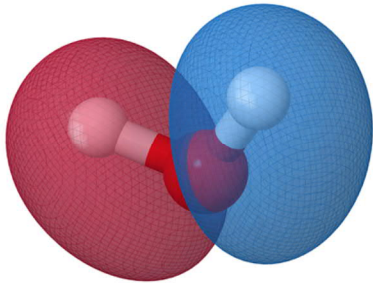
-18.463 eV \_\_\_\_\_

# SCF of water: iteration 3



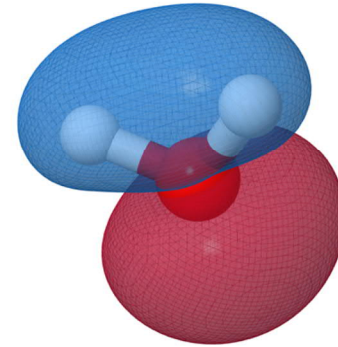
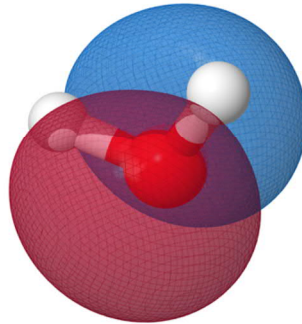
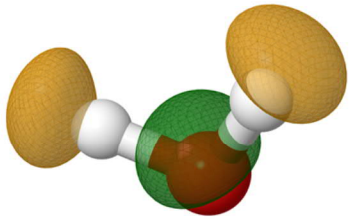
-76.398064 H \_\_\_\_\_

-3.526 eV \_\_\_\_\_



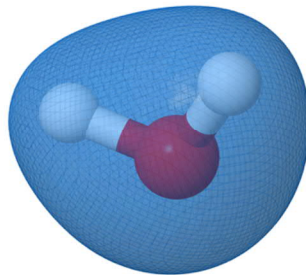
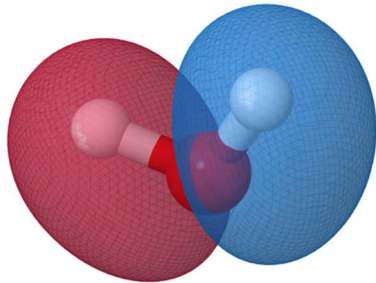
-13.014 eV \_\_\_\_\_

# SCF of water: iteration 4

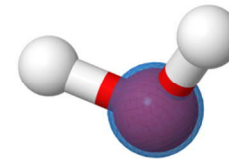


-1.202 eV \_\_\_\_\_

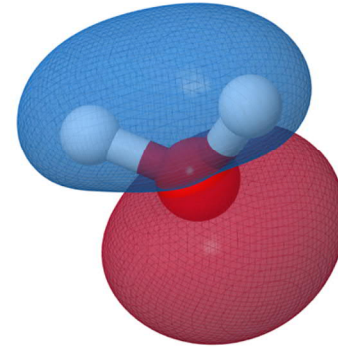
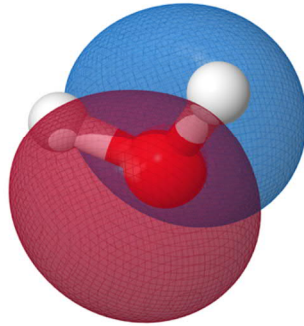
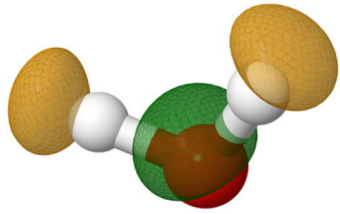
-76.461504 H \_\_\_\_\_



-9.852 eV \_\_\_\_\_



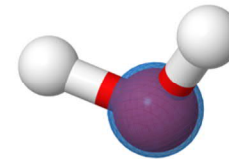
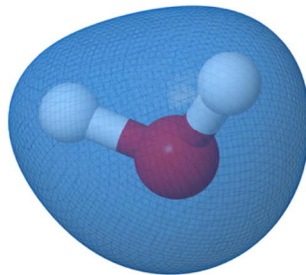
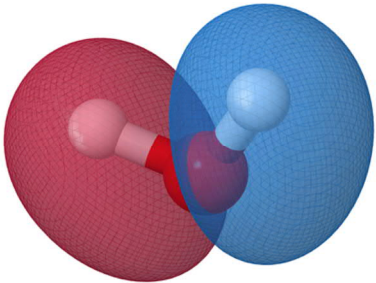
# SCF of water: iteration 5



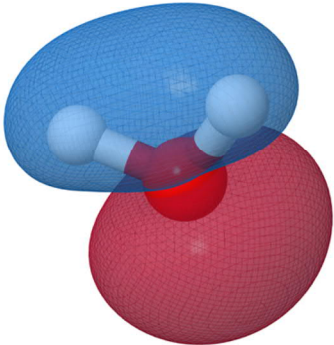
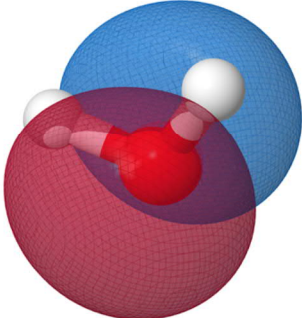
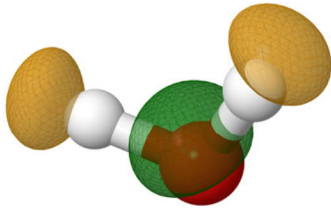
-0.334 eV \_\_\_\_\_

-76.463901 H \_\_\_\_\_

-8.695 eV \_\_\_\_\_

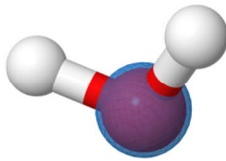
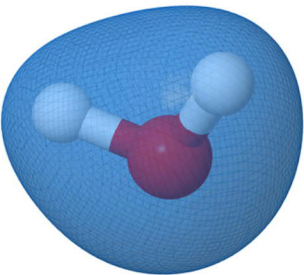
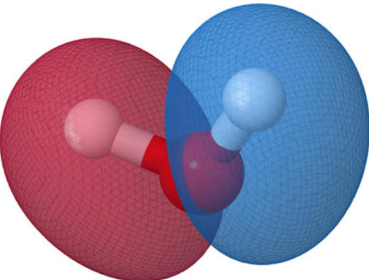


SCF of water: iteration 6

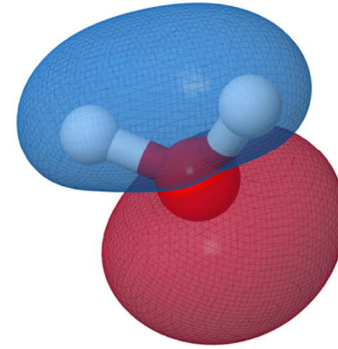
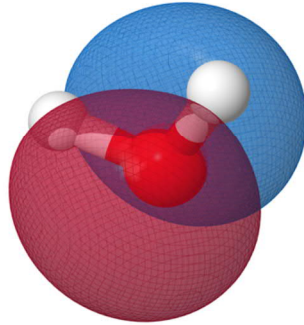
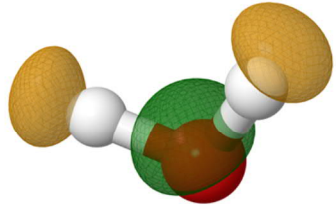


+0.028 eV \_\_\_\_\_

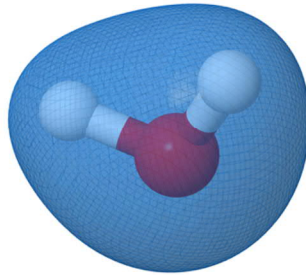
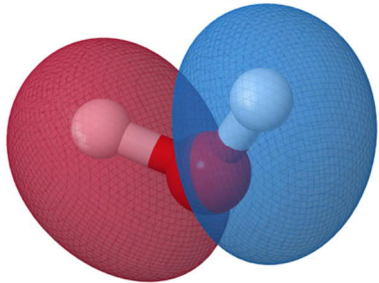
-76.464217 H \_\_\_\_\_  
-8.225 eV \_\_\_\_\_



# SCF of water: iteration 7

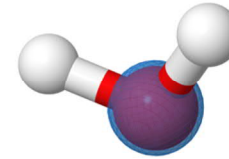


+0.159 eV \_\_\_\_\_

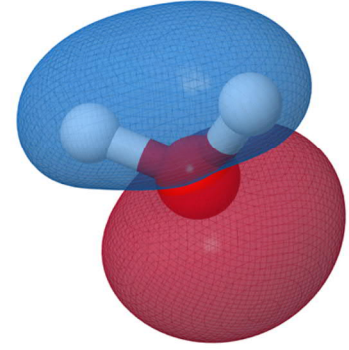
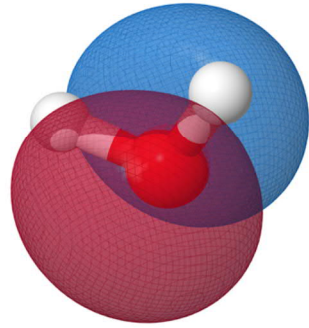
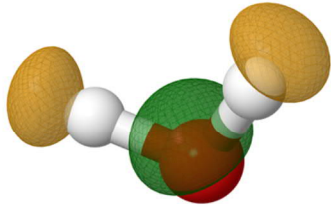


-8.063 eV \_\_\_\_\_

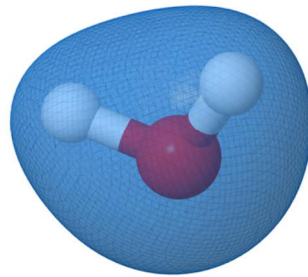
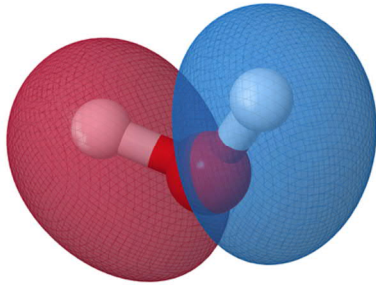
-76.464262 H \_\_\_\_\_



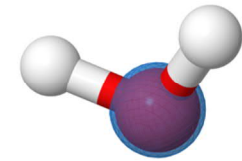
# SCF of water: iteration 8



+0.193 eV \_\_\_\_\_

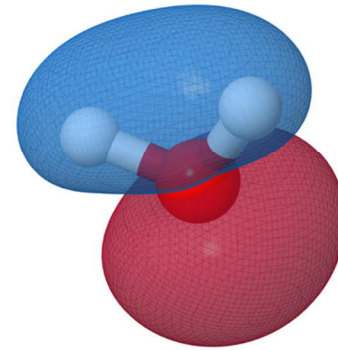
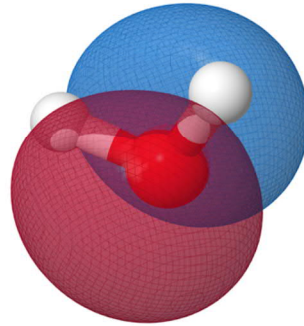
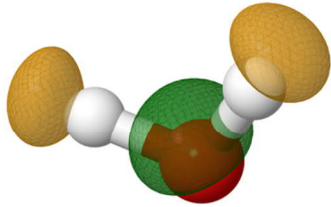


-8.014 eV \_\_\_\_\_



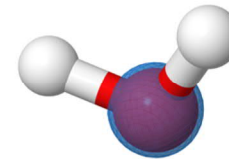
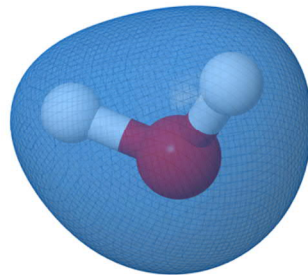
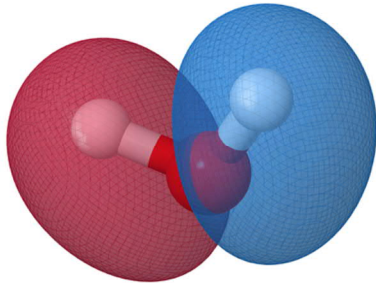
-76.464267 H \_\_\_\_\_

# SCF of water: iteration 9



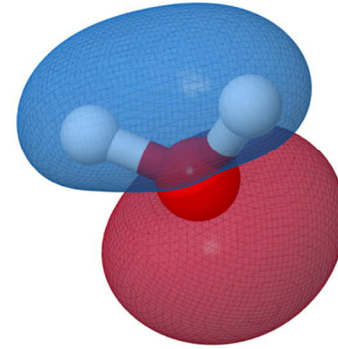
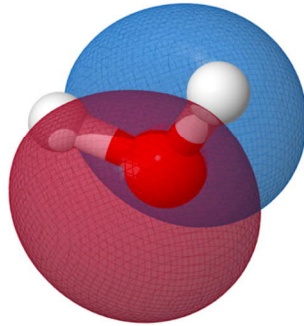
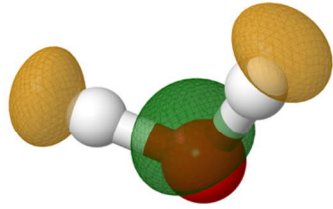
+0.201 eV \_\_\_\_\_

-8.004 eV \_\_\_\_\_



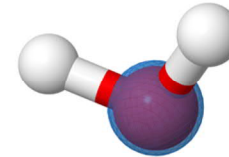
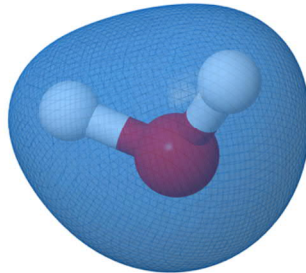
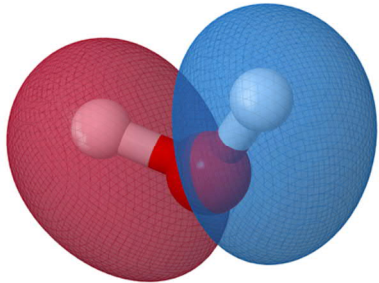
-76.464268 H \_\_\_\_\_

# SCF of water: iteration 10



+0.205 eV \_\_\_\_\_

-7.999 eV \_\_\_\_\_



-76.464268 H \_\_\_\_\_

## Usefulness of Hartree–Fock

- The Hartree–Fock wave function is rather well behaved, but just an approximation!
  - It is **variational and size consistent**
- The HF energy usually corresponds to around 99% of the true total energy of the system
  - Due to the variational principle, the HF wave function is too high in energy
- The main approximation of HF is that the electrons only see a *mean field* of the  $N-1$  other electrons
- *In reality*, the motions of the electrons are *correlated*, instantly avoiding each other
  - This means that the electrons actually are further apart from each other than what the HF orbitals describe
  - Being further apart decreases the electron–electron repulsion
  - Thus, **electron correlation effects lower the energy**
- Although only ~1% of the total true energy, **the correlation energy is very important for chemistry**
  - The total energy is a *very large number*, so 1% is chemically a significant energy
  - Example: the helium atom; just two electrons and one nucleus
    - HF energy: -7513 kJ/mol
    - exact E: -7624 kJ/mol, **HF error 110 kJ/mol!**
- → **Hartree–Fock is not that useful for chemical applications!**

## Usefulness of Hartree–Fock

- **Hartree–Fock is not that useful for chemical applications**
- It does provide reasonable chemical structures, but thermochemistry is bad
  - Sometimes error cancellation helps, a bit
- Today, HF is mainly used as a starting point for **correlated wave-function methods**
  - Also, as an *ingredient* in Density Functional Theory (DFT) discussed in Part II
- A recently presented HF-based method might turn out to be an exception:

## HF-3c

- R. Sure, S. Grimme, “Corrected small basis set Hartree-Fock method for large systems”, *J. Comput. Chem.* **34** (2013) 1672. <http://dx.doi.org/10.1002/jcc.23317>
- Parameterised scheme based on minimal HF calculations including three main corrections:
  - Basis set superposition correction
  - Dispersion interactions
  - short-ranged basis set incompleteness effects
- Intended for “*the computation of structures, **vibrational frequencies**, and noncovalent interaction energies in huge molecular systems*”
- For a “correlated version” (next section), look up **PBEh-3c**: <http://dx.doi.org/10.1063/1.4927476>

## Electron correlation

- The Hartree–Fock wave function is usually considered to contain no electron correlation effects
  - **Pauli correlation** is already imposed by the exchange operator
- The missing (negative) energy is thus *defined* to be the **correlation energy**  $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$
- Correlation arises from the instantaneous interaction between electrons
- correlation is often divided into two main flavours; the division is all but rigorous and still discussed
  - Not that surprising as only the **total energy** is an observable; even the division between HF and correlation energy is more or less a mathematical construct as opposed to real physics

### 1. Dynamic correlation

- Usually considered to be short-range, for example between electrons in the same orbital
  - Example:  $E_{\text{corr}}$  of the helium atom almost purely dynamical
- Characterised by the HF wave function being qualitatively, if not quantitatively right
- Most efficiently recovered by **single-reference correlation methods**

### 2. Static Correlation, aka non-dynamic correlation, left-right correlation

- Usually considered to be long-range
  - Example:  $E_{\text{corr}}$  of stretched  $\text{H}_2$  almost purely static
- Characterised by near-degenerate states and the HF solution being even qualitatively wrong
- Most efficiently recovered by **multi-reference correlation methods**

## Second order Møller–Plesset perturbation theory (MP2)

- The simplest commonly used method for introducing electron correlation
- Based on Many-Body Perturbation Theory (MBPT), which, in short, requires that a good zeroth-order (reference) solution to an eigenvalue problem is known, and that the exact solution is only a small perturbation upon that:  $\hat{H} = \hat{H}_0 + \lambda\hat{H}'$
- In MP2, the zeroth order reference solution is the Hartree–Fock wave function
  - **If HF is very wrong, MP2 will be very wrong as well.** Example: transition metals
- The MP2 correlation energy depends on the HF orbitals  $\phi_i$  and their corresponding eigenvalues, orbital energies  $\epsilon_i$ . Note that **both occupied and virtual orbitals are included**

$$E(MP2) = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{(\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- The denominator contains the energy difference between occupied and virtual orbitals
  - **In systems with a small or vanishing HOMO-LUMO gap, problems!**

## Second order Møller–Plesset perturbation theory (MP2)

- With modern software, computing the MP2 correction is usually *faster* than obtaining the HF reference solution
- Even for systems that are “well-behaved”, the MP2 correlation energy is not that good, though
  - It is **size-consistent**
  - It is **not variational**

## SCS-MP2

- Instead of using standard MP2, I recommend using the semi-empirical, Spin Component Scaled version, **SCS-MP2**
  - S. Grimme, “Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies”, *J. Chem. Phys.* **118** (2003) 9095.  
<http://dx.doi.org/10.1063/1.1569242>
- Based on the observation that low-level correlation methods are biased towards parallel electrons, accompanied by an underestimation of  $E_{\text{corr}}$  between anti-parallel electrons
- “Fixed” by scaling the anti-parallel (opposite-spin) contribution by something  $> 1$  and the parallel (same-spin) contribution by something  $< 1$ . Standard values:
  - $p_S = 6/5$ ,  $p_T = 1/3$
- **Works notably better than standard MP2 at identical computational cost!**

## Higher order MP

- While formulated, *higher order Møller–Plesset is seldom used anymore*
  - MP3 usually *worse* than MP2
  - MP4 already very expensive
  - The MP $n$ -series often diverges:
  - Olsen *et al*, *JCP* **112** (2000) 9736.

<http://dx.doi.org/10.1063/1.481611>

*“Even though the inherent divergence of the MP series does not invalidate the use of the highly successful MP2 level of theory, higher-order corrections should always be treated with caution.”*

J. Chem. Phys., Vol. 112, No. 22, 8 June 2000

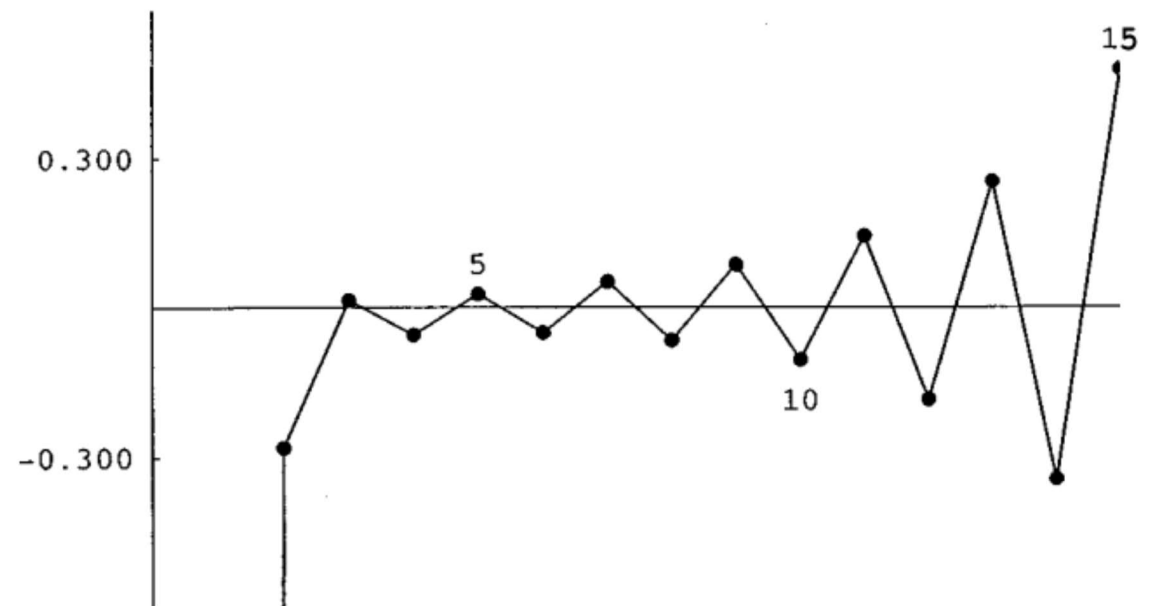


FIG. 14. The energy corrections for HF at stretched geometry in the aug'-cc-pVDZ basis.

## Configuration Interaction (CI)

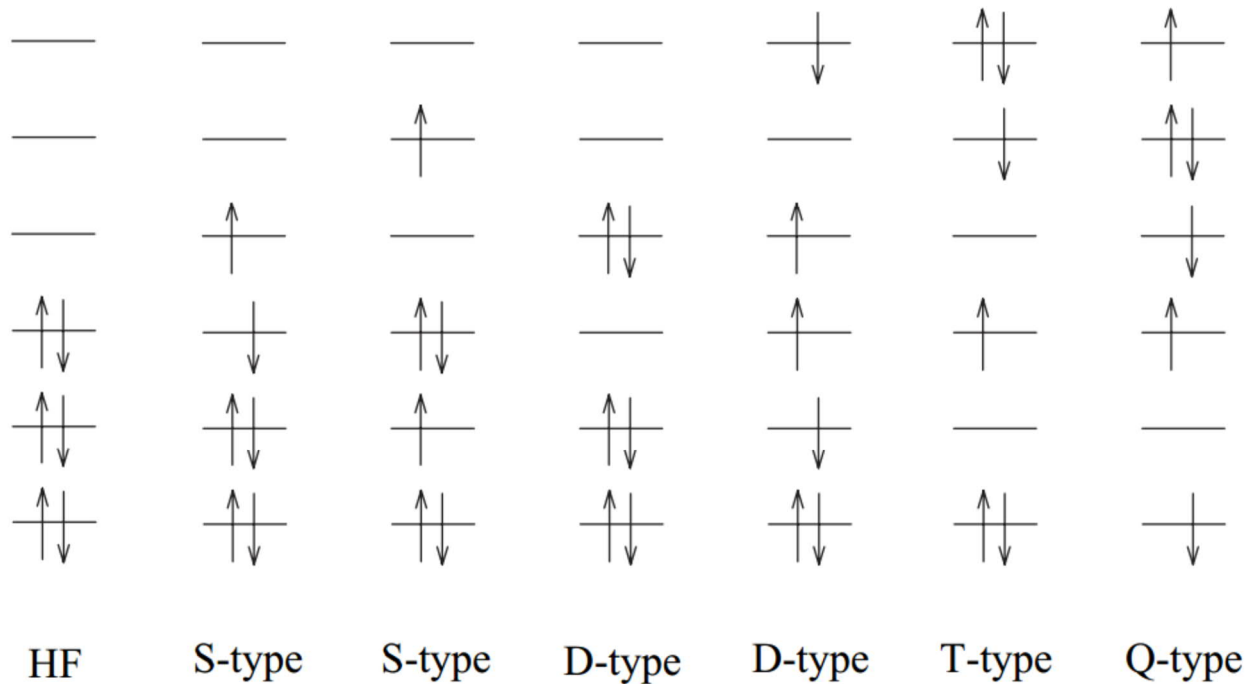
- Of the correlated methods, the **configuration interaction** (CI) treatment is the conceptually simplest
- We again start from the HF solution, configuration, so like MPn, it's a **single-reference method**
- The HF SCF equations give us *a set of M HF (spin) orbitals*, with M dependent on the **basis set size**
  - Of these, the N lowest are occupied, with N = the number of electrons
  - The remaining M-N orbitals are unoccupied, virtual
- In CI, we improve upon the wave function by making a **superposition** of the ground state HF configuration, and configurations constructed by “exciting” electrons from the GS, that is, **moving electrons from the occupied (i, j, ...) to the virtual (a, b, ...) orbitals**

$$\Psi_{\text{CI}} = c_0 \psi_{\text{HF}} + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a \psi_i^a + \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{vir}} c_{ij}^{ab} \psi_{ij}^{ab} \\ + \sum_{i,j,k}^{\text{occ}} \sum_{a,b,c}^{\text{vir}} c_{ijk}^{abc} \psi_{ijk}^{abc} + \sum_{i,j,k,l}^{\text{occ}} \sum_{a,b,c,d}^{\text{vir}} c_{ijkl}^{abcd} \psi_{ijkl}^{abcd} + \dots = \sum_i c_i \psi_i$$

- The coefficients c are optimised with the orthonormality constraint of the CI wave function
- The orbitals that make up the individual  $\psi$  stay the same as in the HF reference

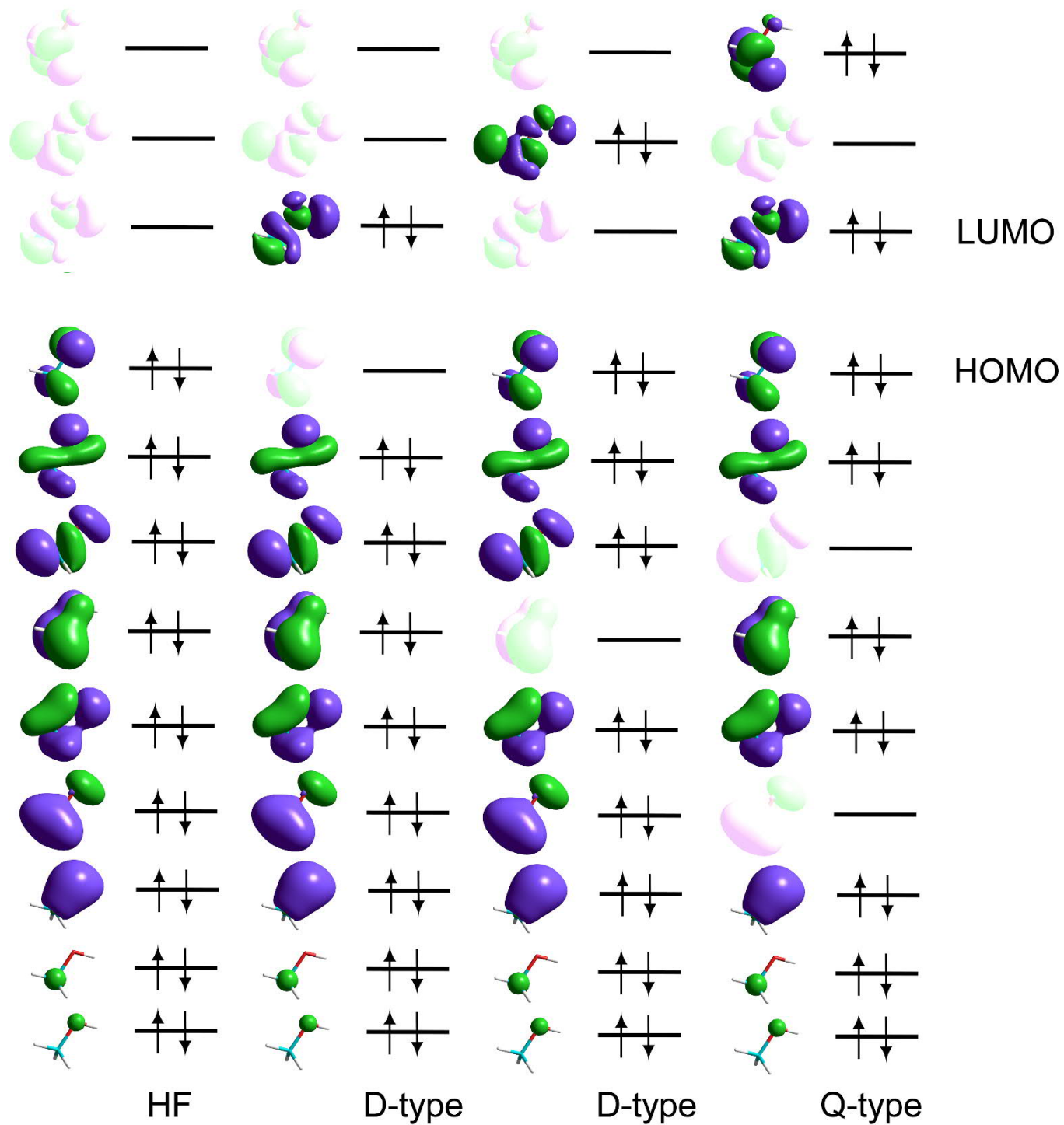
## Configuration Interaction (CI)

- Depending on how many electrons are “excited” out of the HF configuration at a time, we have single (S), double (D), triple (T), ... excitations in the CI description, giving CIS, CID, CISD, *etc.* levels of theory
- If **all possible excitations** are considered, the method is called **Full CI** (FCI) which, within a given basis set, is the most complete solution to the Schrödinger equation obtainable
  - With a hypothetical *infinite* basis set (of properly chosen basis functions) we would have **Complete CI**, which would be the exact solution to the Schrödinger equation



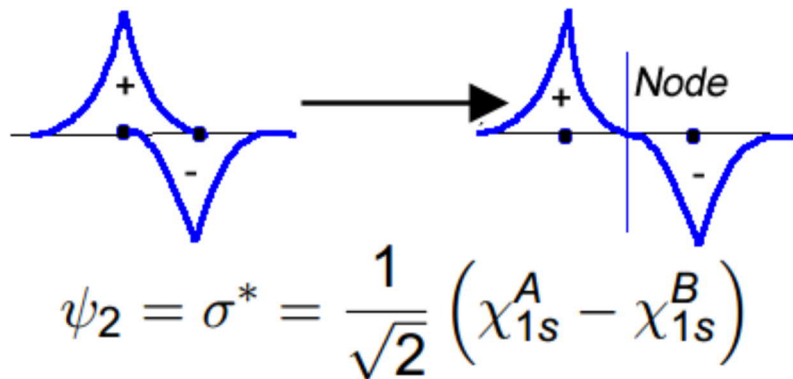
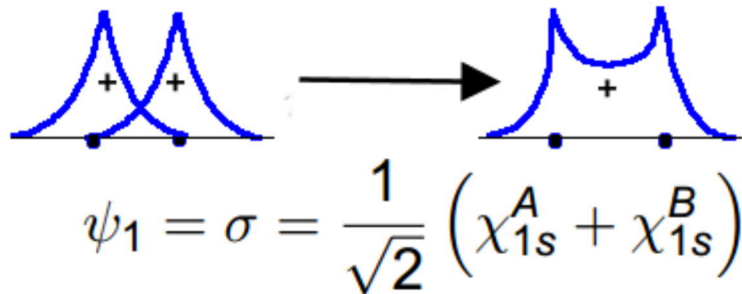
# Configuration Interaction (CI)

4 different configurations of methanol (18 electrons):



## Configuration Interaction (CI)

- The classic example of how electron correlation lowers the energy, **H<sub>2</sub> in a minimal basis**:



- The Hartree–Fock configuration has both electrons in the **bonding σ orbital**
- The **anti-bonding σ\* orbital** is virtual
- When doing CI, we get a **mixture** of the two configurations
- The σ\* orbital has a nodal plane between the two hydrogens; thus, with the total wave function containing parts of this configuration, *the electrons are on average further apart* compared to the HF configuration → **lower energy, better WF**

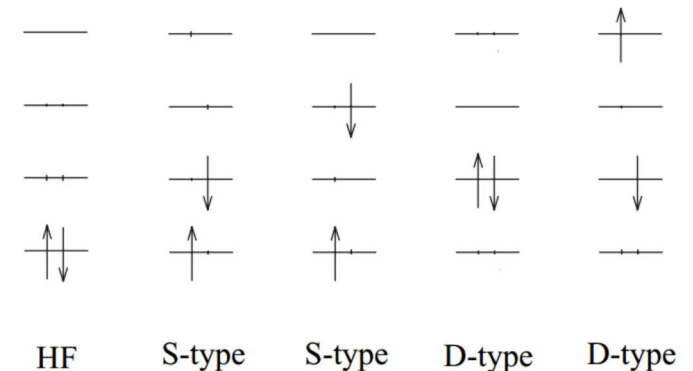
## Configuration Interaction (CI)

- Today, CI is not that extensively used
  - CI **is variational**
  - But **it is not size consistent** (with the exception of FCI)
- The non-size-consistency is easily demonstrated for **two non-interacting H<sub>2</sub> molecules** at CISD level
  - For *non-interacting* systems A and B, size consistency requires  $E(\mathbf{A}, \mathbf{B}) = E(\mathbf{A}) + E(\mathbf{B})$
  - When  $A=B=H_2$ , we note that CISD is equivalent to FCI; H<sub>2</sub> has two electrons, and the maximum, full excitation level is thus also two:

- With *two* H<sub>2</sub> fragments *at all separations*, we have *four* electrons: **not all configurations can be constructed!**

That would require CISDTQ

- For example, the configurations where both electrons of both fragments have been excited are completely missing



- *With increasing systems size, proportionally less and less of the correlation energy is recovered!*

## Coupled Cluster (CC)

- The coupled cluster wave function is defined as  $\Psi = e^{\hat{T}} \psi_{\text{HF}}$       $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n$
- The excitation operator  $\mathbf{T}$  constructs *all possible excitations*
  - $\mathbf{T}_1$  all single excitations,  $\mathbf{T}_2$  all double excitations, ...
- The main idea of CC is to include all corrections of a given type (S, D, T, ...) to *infinite order*

$$\mathbf{T}_1 \Phi_0 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \Phi_i^a$$

$$\mathbf{T}_2 \Phi_0 = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} t_{ij}^{ab} \Phi_{ij}^{ab}$$

- **For comparison and clarity**, the now familiar CI wave function can be expressed as

$$\Psi_{\text{CI}} = (\mathbf{1} + \mathbf{T})\Phi_0 = (\mathbf{1} + \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \mathbf{T}_4 + \dots)\Phi_0$$

- The truncated **CID** model, with just double excitations, thus takes the form:

$$\Psi_{\text{CID}} = (\mathbf{1} + \mathbf{T}_2)\Phi_0$$

- The Taylor expansion of the **exponential form of CC** gives the following for the corresponding doubles-only coupled cluster model, **CCD**:

$$\Psi_{\text{CCD}} = e^{\mathbf{T}_2} \Psi_{\text{HF}} = \left( 1 + \mathbf{T}_2 + \frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \dots \right) \Psi_{\text{HF}}$$

## Coupled Cluster (CC)

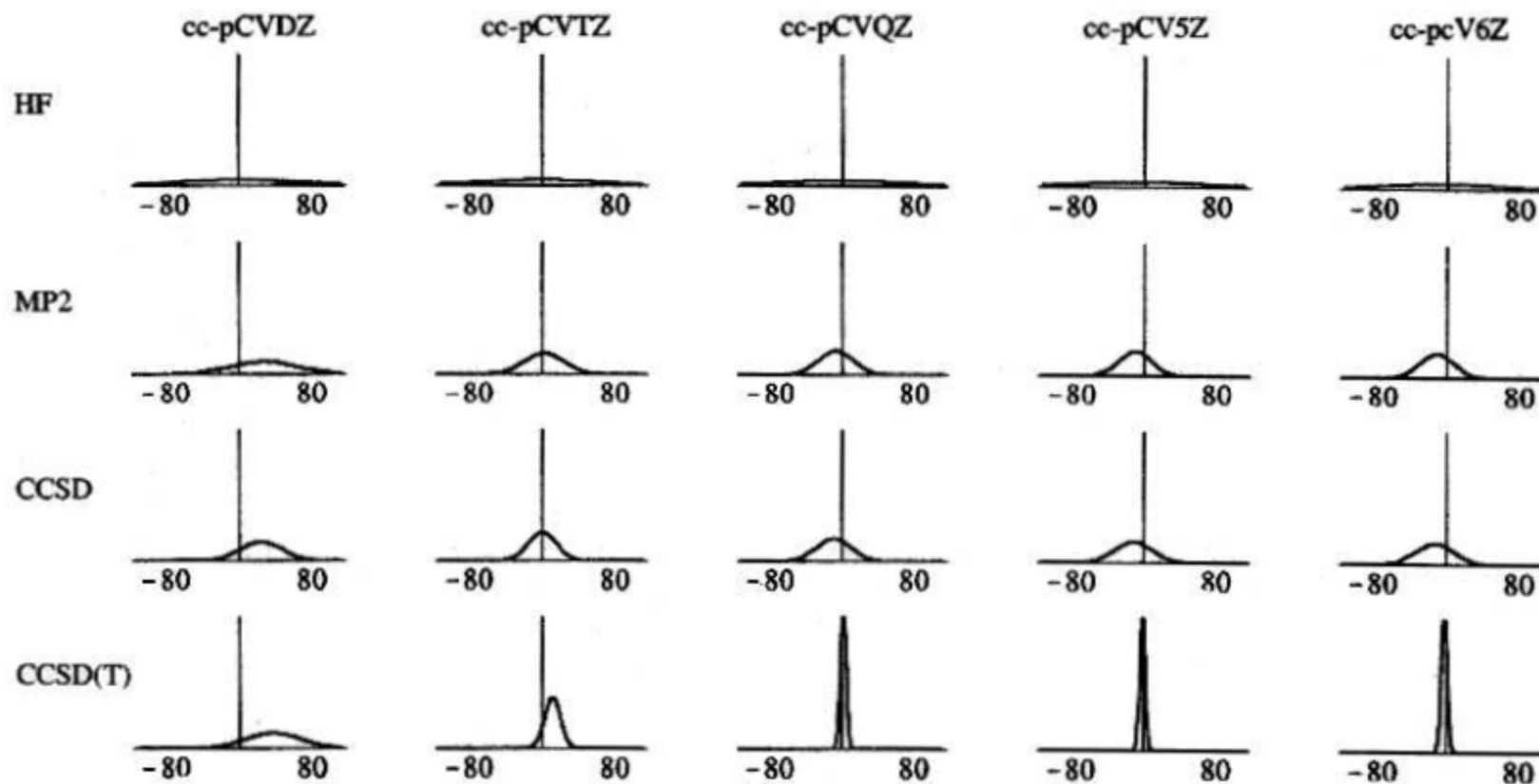
- The CCD form nicely shows the **size consistency** of coupled cluster compared to configuration interaction  $\left(1 + \mathbf{T}_2 + \frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \dots\right) \Psi_{\text{HF}}$ 
  - $\mathbf{T}_2$  itself constructs all *connected double excitations*
  - $\mathbf{T}_2^2$  generates *disconnected quadruple excitations*, in essence, the *simultaneous double excitations of two non-interacting electron pairs*
  - The absence of the  $\mathbf{T}_2^2$  term was the reason for non-size-consistency of CISD in the example of two separated  $\text{H}_2$  molecules!
- Coupled cluster is *not variational*, though

## The practical “gold standard for quantum chemistry” – CCSD(T)

- Of the truncated coupled cluster models, only CCSD can be semi-regularly employed; the scaling of the next level, CCSDT is already prohibitively steep for all but the smallest molecules
- The accuracy of CCSD is, however, not spectacular
  - Inclusion of connected triple excitations  $\mathbf{T}_3$  would be desirable, *still chemically important!*
- In the **CCSD(T)** model, the triples are added onto the CCSD solution using **perturbation theory**
  - **CCSD(T) is remarkably accurate** provided that a single-determinant reference is sufficient!
    - **Error cancellation**, the T contribution slightly overestimated, compensating for missing Q
  - **Requires sufficiently large basis sets!**

## The practical “gold standard for quantum chemistry” – CCSD(T)

- Errors for a set of reaction enthalpies (kJ/mol) for different methods and basis sets (from Helgaker, Jørgensen, Olsen, “Molecular Electronic-Structure Theory”)



## Really Quick CCSD(T): DLPNO-CCSD(T)

- Domain based Local Pair Natural Orbital coupled cluster method

THE JOURNAL OF CHEMICAL PHYSICS **139**, 134101 (2013)

## Natural triple excitations in local coupled cluster calculations with pair natural orbitals

Christoph Riplinger,<sup>a)</sup> Barbara Sandhoefer,<sup>b)</sup> Andreas Hansen,<sup>c)</sup> and Frank Neese<sup>d)</sup>

*Max Planck Institut für Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany*

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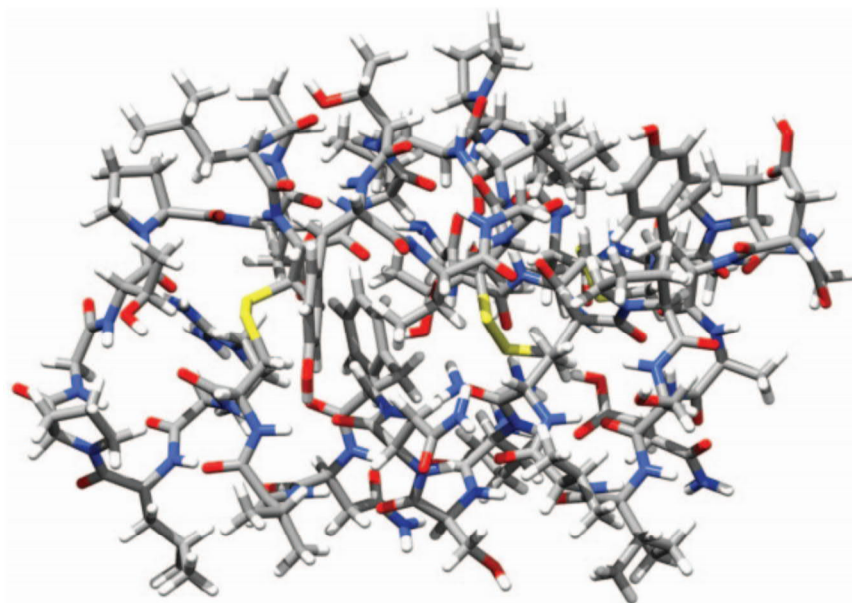


FIG. 9. Structure of Crambin (644 atoms).

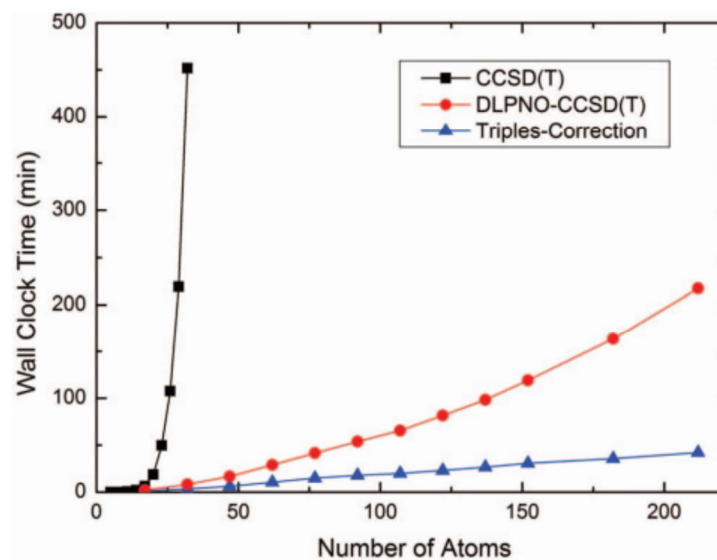


FIG. 8. Scaling behavior of the CCSD(T) and DLPNO-CCSD(T) methods. The calculations were carried out on linear hydrocarbon chains  $\text{H}_3\text{C}-(\text{CH}_2)_{n-2}-\text{CH}_3$  (in standardized geometries with all angles =  $109.4712^\circ$ ,  $\text{RCH} = 109$  pm, and  $\text{RCC} = 155$  pm) and default thresholds. All calculations were done with the def2-SVP basis set. Default thresholds were used ( $T_{\text{CutPairs}}$

## DLPNO-CCSD(T)

- Localise orbitals; Compute **pair-correlation energies**  $\epsilon_{ij}$  at MP2 level ( $\sum \epsilon_{ij} = E_{\text{corr}}$ ); only compute CC correlation energies for the most strongly correlated pairs, **estimate the rest with MP2**
- Further, consider only virtual orbitals with a **significant occupation number**, and again estimate the remaining correlation energy with MP2.

Sparta & Neese, *Chem. Soc. Rev.* **43** (2014) 5032:

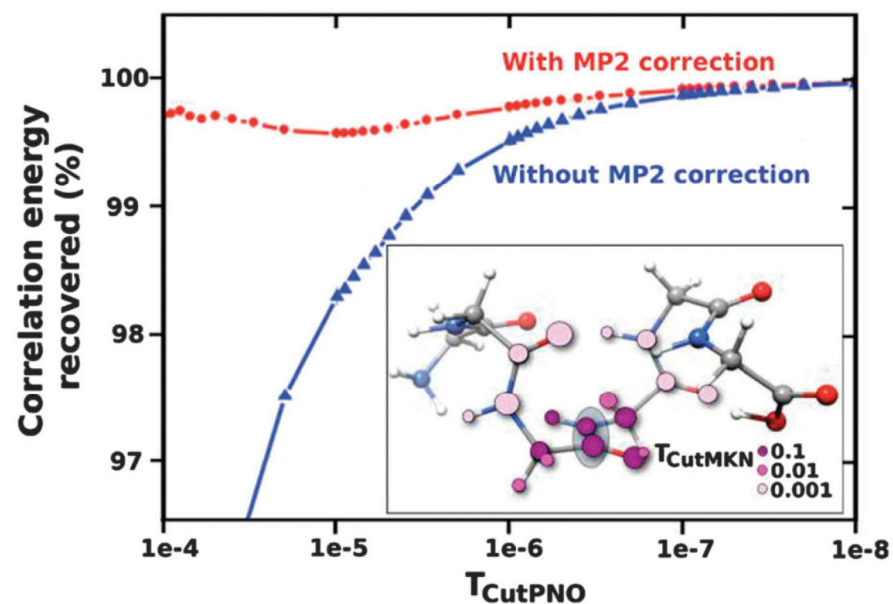
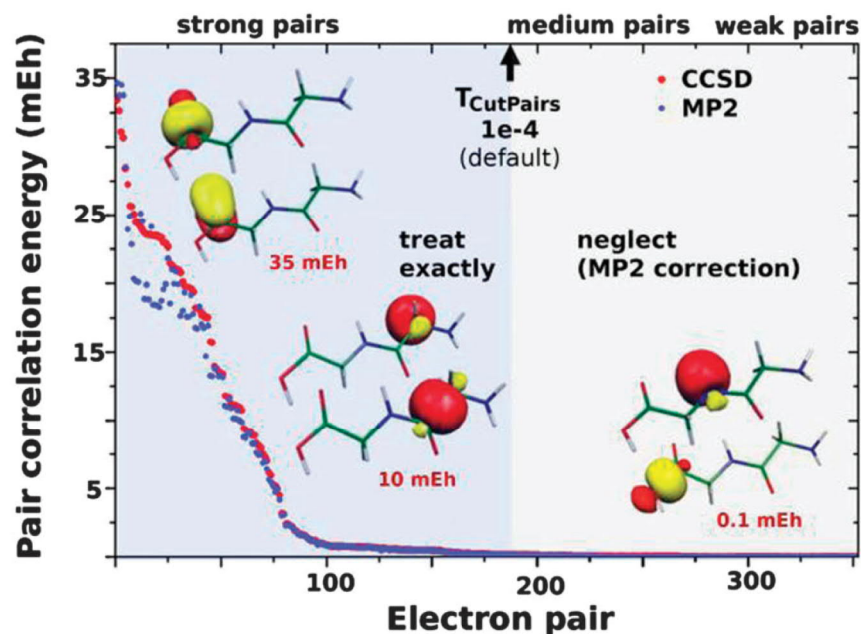


Fig. 1 Left panel: the strong pair approximations. Pairs of localized orbitals are partitioned into “strong” and “weak” based on MP2 pair correlation estimates. Strong pairs enter the coupled-cluster procedure whereas MP2 additive corrections to the total correlation energy are computed for the weak pairs. Right panel: PNO truncation of the virtual space. Percentage of the correlation energy recovered for a given electron pair as a function of the  $T_{\text{CutPNO}}$  threshold. Inset: representation of the PAOs domains as a function of the  $T_{\text{CutMKN}}$  threshold (the gray shadow highlights the position of the correlated orbitals).

## Extrapolating the CC series towards FCI

- Having computed CCSD(T) energies, it is actually possible to get even better results **for free**
- **Goodson's continued fraction** approach, CC-cf, **extrapolates correlation towards FCI**
  - *J. Chem. Phys.* **116** (2002) 6948, <http://dx.doi.org/10.1063/1.1462620>
  - Compare to extrapolating basis sets towards the complete basis set (CBS) limit

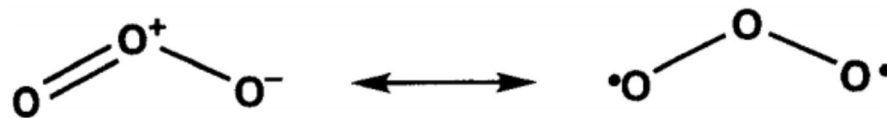
$$\delta_1 = E[\text{HF}] \quad \delta_2 = E[\text{CCSD}] - E[\text{HF}]$$
$$\delta_3 = E[\text{CCSD(T)}] - E[\text{CCSD}]$$

$$E[\text{CC-cf}] = \frac{\delta_1}{1 - \frac{\delta_2/\delta_1}{1 - \delta_3/\delta_2}}$$

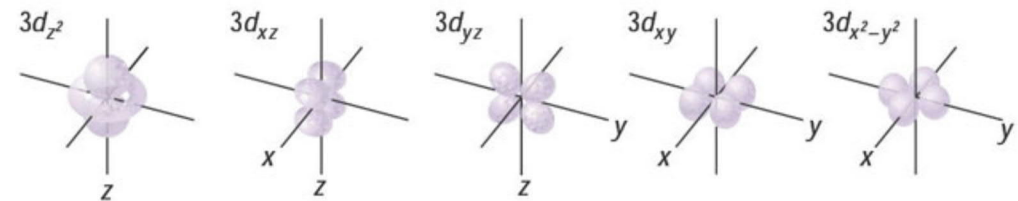
- Robust combination for squeezing out highly accurate energies (when multi-reference is a non-issue)
  - See, *e.g.*, M.P.J., J. Olsen, "Torsional Barriers and Equilibrium Angle of Biphenyl: Reconciling Theory with Experiment", *JCTC* **4** (2008) 1460, <http://dx.doi.org/10.1021/ct800182e>
- *Empirical*
- Due to non-variational nature of CC, *can* actually lead to total energies **further away** from FCI than CCSD(T).

## Multi-reference methods

- For some systems, the Hartree–Fock solution is **qualitatively wrong**
- This happens when more than one electronic configuration are close in energy, **near-degenerate**
- Then, choosing just the absolutely lowest energy configuration is a very incomplete description
- Typical examples are molecules with **different resonance structures**, like ozone:

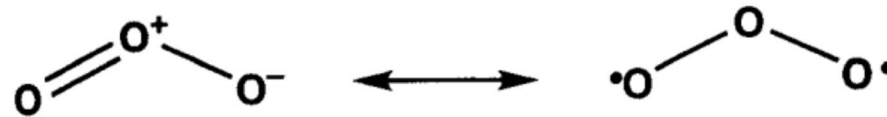


- The two structures are described by two quite different Slater determinant configurations
  - One closed shell and one **biradical**
- **Transition metals**, with many *d*-orbitals, are also problematic; **configurations with different *d*-orbital occupations can be very close in energy**
- **Stretching bonds** also leads to near-degeneracy between orbitals that are occupied and virtual
- For these **multi-reference** systems, not only the HF solution is bad, *also correlated methods based on one reference wave function suffer!*
  - At heavy cost, that is, sufficiently high orders of excitation, this can be alleviated (FCI is FCI)



## Multi-Configuration Self-Consistent Field (MCSCF)

- CI, where one optimises **both** the coefficients in front of the different configurations **and the orbitals for each determinant**
- In the ozone example, usually **two determinants** corresponding to the two resonance structures is sufficient



- For more complex cases, deciding which configurations should be included becomes the problem **and the art**

## Complete Active Space (CASSCF) and Restricted Active Space SCF (RASSCF)

- In **CASSCF**, one aims at including only the part of the orbital space where large differences between configurations occurs (for example the *d*-electron region for TMs). This is the **active space**
- Other orbitals, occupied and unoccupied, are **inactive** and kept as HF orbitals with double or zero occupancy
- **Within the active space, a Full CI is performed**
  - Sometimes called *as full a CI as possible*

## Complete Active Space (CASSCF) and Restricted Active Space SCF (RASSCF)

- Full CI is very expensive even for a small number of orbitals
- **RASSCF** is a variation on CASSCF, where the orbital space is further divided into “less active” regions

### CASPT2

- CASSCF can in practice seldom recover enough of the correlation energy
  - The active space is by necessity rather small
  - “Only” the **static correlation** part is efficiently recovered
  - If only one determinant is important, CASSCF is not much better than simple HF
- **CASPT2** combines the static-correlation recovering CASSCF with dynamic-correlation recovering 2<sup>nd</sup> order perturbation theory

### MRCI and MRCC

- Also CI and CC methods operating on a multideterminantal reference wave function have been developed

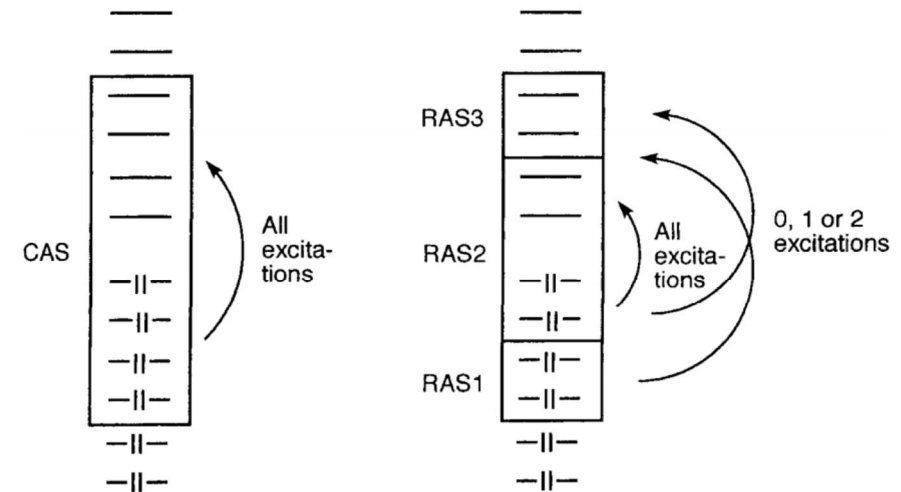


Figure 4.11 Illustrating the CAS and RAS orbital partitions