# Post-Hartree Fock Methods:

**(Methods that use Hartree-Fock as a starting point and go beyond it, i.e. that take electron correlation into account)**

## 1. Configuration Interaction (CI)

**(Script: Chapter 5)**

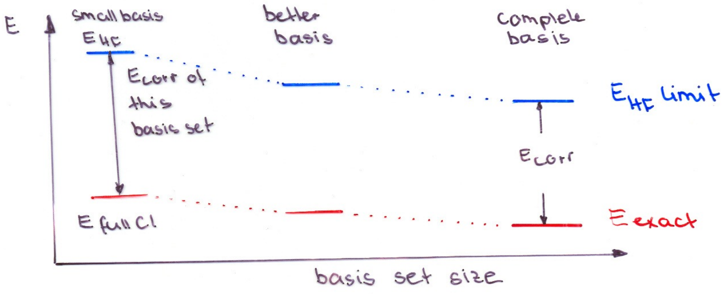
---

Per-Olov Löwdin
(1916-2000)

# Electron Correlation

## Chemist's definition of E$_{corr}$ (Lowdin):

$$E^{nonrel}_{exact} = E_{HF_{limit}} - E_{corr}$$



**→E$_{corr}$ is basis set dependent!**

## Electron Correlation: Physicist's view

Probability distribution of a system with 2 electrons is not given by the product $\rho(1)\rho(2)$ only:

$$\rho_2(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\rho(\vec{r}_1)\rho(\vec{r}_2)[1 + h(\vec{r}_1,\vec{r}_2)]$$

$h(\vec{r}_1,\vec{r}_2)$: pair correlation function

The presence of electron(1) modifies the probability distribution for electron(2):
→exchange-correlation hole

$$\rho_{xc}(\vec{r}_1,\vec{r}_2) = \rho(\vec{r}_2)h(\vec{r}_1,\vec{r}_2)$$

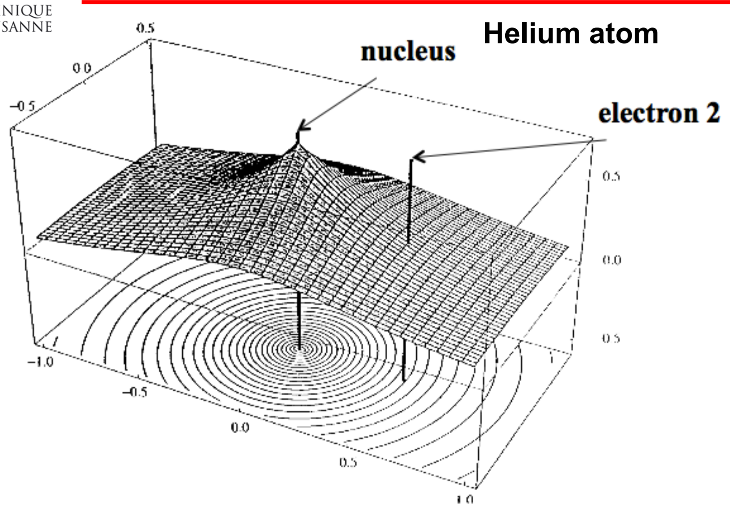
(exchange-correlation hole created by an electron at $\vec{r}_1$).

→correlated motion of electrons
(electrons 'avoid each other' → electron-electron repulsion is lowered)

→$HF_{limit}$ is higher than the true total energy of the system

---

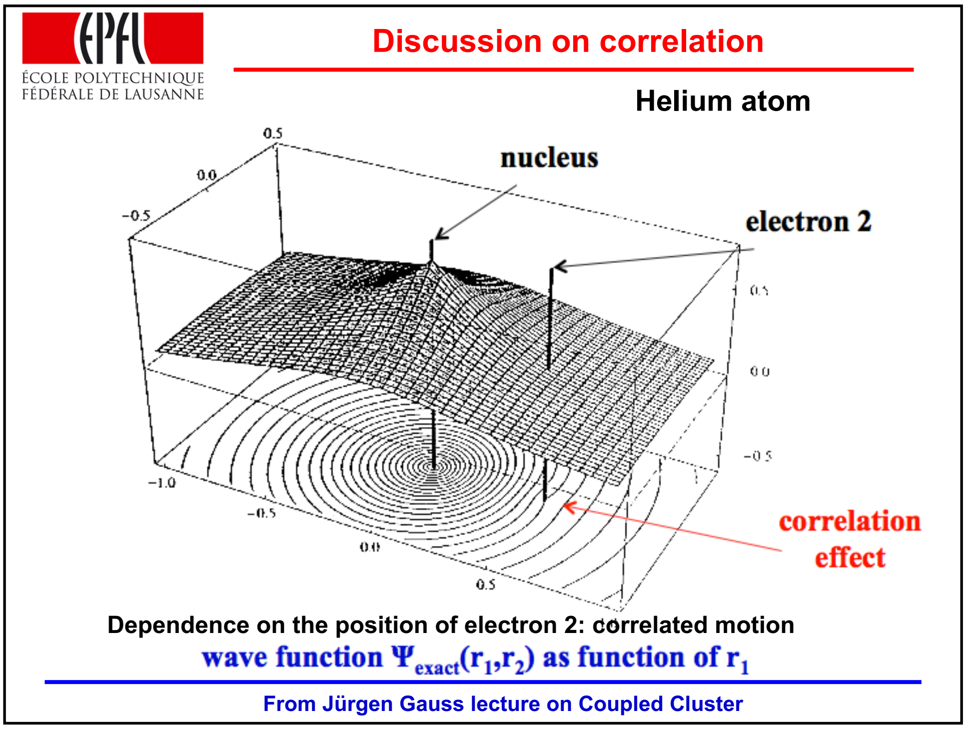
## Discussion on correlation



wave function $\Psi_{HF}(r_1,r_2)$ *as function of* $r_1$

No dependence on the instantaneous position of electron 2 -> independent motion

From Jürgen Gauss lecture on Coupled Cluster, figure from T. Helgaker, P. Jørgensen, J. Olsen „Molecular Electronic-Structure Theory"



## Discussion on correlation

**Helium atom**

**nucleus**

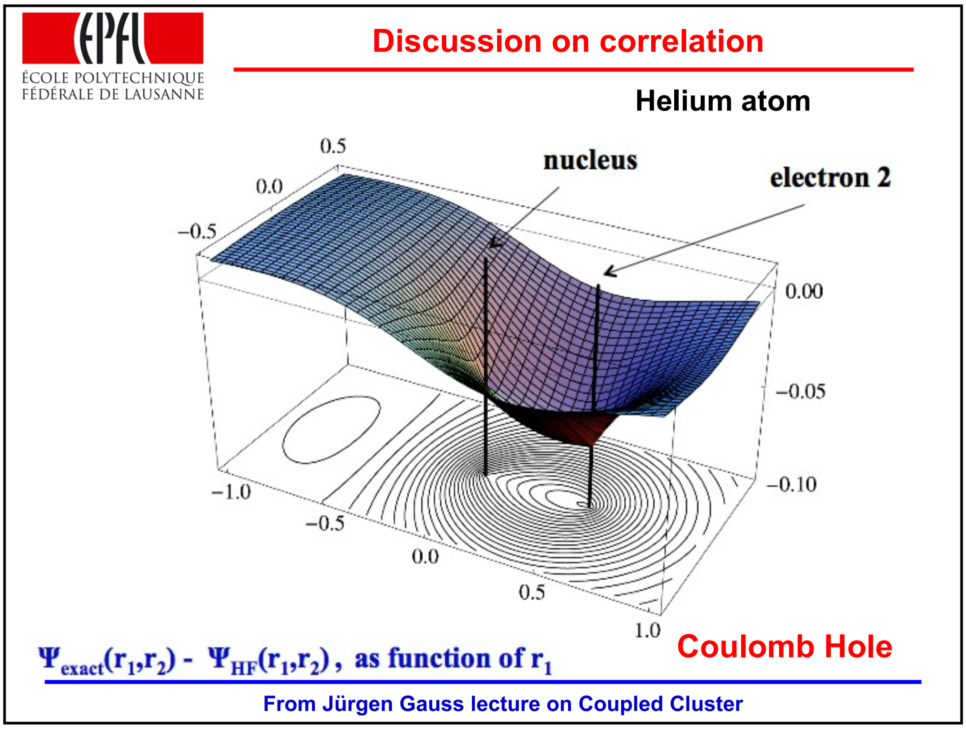
**electron 2**

**correlation effect**

**Dependence on the position of electron 2: correlated motion**

**wave function $\Psi_{exact}(r_1,r_2)$ as function of $r_1$**

**From Jürgen Gauss lecture on Coupled Cluster**



## Discussion on correlation

**Helium atom**

**nucleus**

**electron 2**

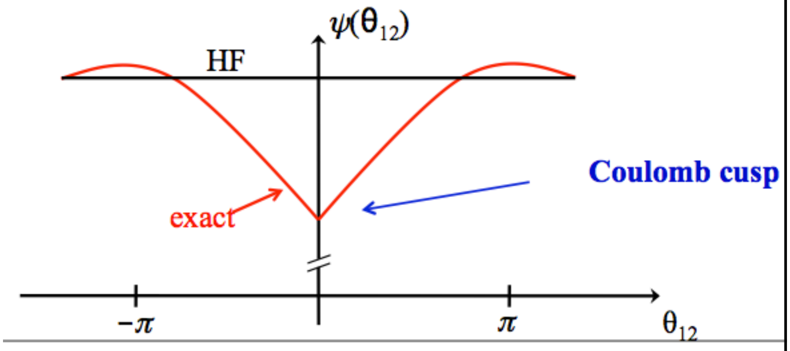
**$\Psi_{exact}(r_1,r_2)$ - $\Psi_{HF}(r_1,r_2)$, as function of $r_1$**

**Coulomb Hole**

**From Jürgen Gauss lecture on Coupled Cluster**

## Discussion on correlation

**Helium atom**



Another view : wavefunction plotted on a circle of radius 0.5 $a_0$
centered at the nucleus.
Variation of the angle between the two electron coordinate vectors.

**From Jürgen Gauss lecture on Coupled Cluster**

---

# Post-Hartree-Fock Methods

**Methods use a Hartree-Fock calculation as starting point and try to improve the HF results by taking account of electron correlation:**

- **Configuration Interaction (CI)**
- **Møller-Plesset Perturbation (MP)**
- **Coupled-Cluster (CC)**

## Quiz X: Post-Hartree Fock Methods

1) What would be a straightforward way to improve over the Hartree-Fock approximation? What better Ansatz could we use for the many-electron wavefunction?

2) Does this Ansatz lead to solutions that take account of the correlation hole?

3) Using this improved Ansatz for the many-electron wavefunction, can the electronic Schrodinger equation be solved in practise?

## How can we construct a basis of Slater determinants?

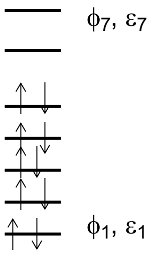
=> let's make use of what we already have: the Hartree-Fock solution:

$$\boxed{F'C' = E\,C'}$$

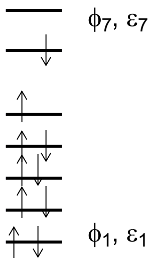
For a basis set with M basis functions, the dimensions of the Fock matrix are MxM:

Examples:

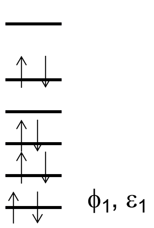
minimal basis set for $H_2O$ => 10 electrons, 7 basis functions => 7 HF orbitals and HF eigenvalues => 5 (doubly) occupied and 2 empty (virtual orbitals)



HF ground state configuration

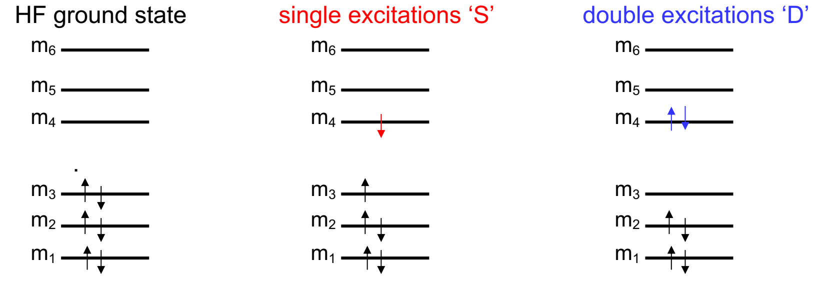


excited state configuration



excited state configuration

Each Slater determinant corresponds to a different electronic configuration (therefore the name Configuration Interaction (CI)) that is generated by creating excited state configurations from the ground state Hartree-Fock wavefunction.



HF ground state

single excitations 'S'

double excitations 'D'

$$\Phi_0 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m3}^2 \right| \qquad \Phi_1 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m3} \phi_{m4} \right| \qquad \Phi_2 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m4}^2 \right|$$

All possible singly excited configurations in this example:

$$\Phi_1 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m3} \phi_{m4} \right| \qquad \Phi_1 = \left| \phi_{m1}^2 \phi_{m2} \phi_{m3}^2 \phi_{m4} \right| \qquad \Phi_1 = \left| \phi_{m1} \phi_{m2}^2 \phi_{m3}^2 \phi_{m4} \right|$$

$$\Phi_1 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m3} \phi_{m5} \right| \qquad \Phi_1 = \left| \phi_{m1}^2 \phi_{m2} \phi_{m3}^2 \phi_{m5} \right| \qquad \Phi_1 = \left| \phi_{m1} \phi_{m2}^2 \phi_{m3}^2 \phi_{m5} \right|$$

$$\Phi_1 = \left| \phi_{m1}^2 \phi_{m2}^2 \phi_{m3} \phi_{m6} \right| \qquad \Phi_1 = \left| \phi_{m1}^2 \phi_{m2} \phi_{m3}^2 \phi_{m6} \right| \qquad \Phi_1 = \left| \phi_{m1} \phi_{m2}^2 \phi_{m3}^2 \phi_{m6} \right|$$

## Quiz XI: Configuration Interaction

1) How many occupied and virtual orbitals do you get from a HF calculation of $H_2O$ with a 6-31G* basis set?

2) How many Slater determinants can you construct out of these HF orbitals?

We often use the letters a,b,c etc.. for the occupied molecular orbitals from which we excite an electron, and the letters r,s, etc.. to label the empty (virtual) orbitals to which we excite electrons.

In this way, we can write the linear combination of Slater determinants that describe the many electron wavefunction $\Psi$ as

$$\boxed{\left|\Psi^{CI}\right\rangle = C_0\left|\Phi_0\right\rangle + \sum_a\sum_r C_a^r\left|\Phi_a^r\right\rangle + \sum_{a\neq b}\sum_b\sum_{r\neq s}\sum_s C_{ab}^{rs}\left|\Phi_{ab}^{rs}\right\rangle + \ldots}$$

If we include Slater determinants for all possible excitations, the method is called full CI and The result is exact (within a chosen basis set)!

$\left|\Phi_0\right\rangle$ Hartree-Fock ground-state determinant

$\left|\Phi_a^r\right\rangle$ singly-excited determinants

$\left|\Phi_{ab}^{rs}\right\rangle$ doubly-excited determinants

r,s: indices for virtual orbitals
a,b: indices for occupied orbitals

---

If we include all possible excited state configurations where one electron is promoted from the occupied to the unoccupied orbitals, the method is called CIS, if we include all possible single and double excitations it is CISD etc.. (CISDT, CISDTQ…). By allowing for this increased flexibility of the wavefunction, we are able to capture the modifications of the electronic distribution caused by correlation effects. If we include all possible excited state configurations, the method is called full CI and the results is exact.

So in theory we now know how to solve a many-electron Schrodinger equation exactly:

Like for Hartree-Fock, we can calculate the expectation value of the total energy of the system:

$$\boxed{E_{el} = \langle\Psi|\hat{H}_{el}|\Psi\rangle}$$

Where $\boldsymbol{\Psi}$ is a linear combination of Slater determinants generated from the Hartree-Fock orbitals

$$\boxed{\left|\Psi^{CI}\right\rangle = C_0\left|\Phi_0\right\rangle + \sum_a\sum_r C_a^r\left|\Phi_a^r\right\rangle + \sum_{a\neq b}\sum_b\sum_{r\neq s}\sum_s C_{ab}^{rs}\left|\Phi_{ab}^{rs}\right\rangle + \ldots}$$

To find $\Psi^{CI}$, we use the variational theorem that tells us that the best wavefunction is the one that minimizes the total energy $E_{el}$:
If we minimize E with respect to the coefficients C (but leave the one electron orbitals untouched, i.e. equal to the Hartree-Fock orbitals), the method is called CI (it takes account of dynamic correlation).
If we include only few determinants and minimize with respect to the coefficients $C_i$ and the one-electron MOs $\Phi_i$ ($c_{im}$) the method is called multireference (multireference methods are especially good for taking static correlation effects into account => lecture on multifreference methods!).

We get the matrix equation

$$\boxed{HC = CE}$$

with the Hamiltonian matrix elements:

$$\boxed{H_{KL} = \langle \Phi_K | H | \Phi_L \rangle}$$

All we have to do is to diagonalize this matrix and we have found the exact solution of the many-electron Schrodinger equation in a given basis!

We do not have to calculate all of the Hamiltonian matrix elements because some of them are zero. There are simple rules (Slater-Condon rules) that help us to know which ones (see script):

$$\boxed{H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle}$$

First arrange determinants with maximum coincidence:

$$\begin{aligned} |\Phi_1\rangle &= |abcd\rangle \\ |\Phi_2\rangle &= |crds\rangle \end{aligned} \quad \Longrightarrow \quad |\Phi_2\rangle = |crds\rangle = -|crsd\rangle = |srcd\rangle$$

## Slater-Condon Rules

**1. Identical Determinants:** If the determinants are identical, then

$$\langle \Phi_1 | \hat{H} | \Phi_1 \rangle = \sum_m^N \langle m | \hat{h} | m \rangle + \sum_{m>n}^N \langle mn || mn \rangle \tag{5.9}$$

**2. Determinants that Differ by One Spin Orbital:**

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mn \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pn \cdots\rangle \\ \langle \Phi_1 | \hat{H} | \Phi_2 \rangle &= \langle m | \hat{h} | p \rangle + \sum_n^N \langle mn || pn \rangle \end{aligned} \tag{5.10}$$

**3. Determinants that Differ by Two Spin Orbitals:**

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mn \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pq \cdots\rangle \\ \langle \Phi_1 | \hat{H} | \Phi_2 \rangle &= \langle mn || pq \rangle \end{aligned} \tag{5.11}$$

**4. Determinants that Differ by More than Two Spin Orbitals:**

$$\begin{aligned} |\Phi_1\rangle &= |\cdots mno \cdots\rangle \\ |\Phi_2\rangle &= |\cdots pqr \cdots\rangle \\ \langle \Phi_1 | \hat{H} | \Phi_2 \rangle &= 0 \end{aligned} \tag{5.12}$$

## Quiz XII: Slater Rules

1) Which type of configurations are contributing the most to electron correlation? Singles? Doubles? Triples?

2) How large are the Hamiltonian matrix elements of the type:

A) $\boxed{H_{0S} = \left\langle \Phi_0^{HF} \middle| H \middle| \Phi_a^r \right\rangle}$

B) $\boxed{H_{0T} = \left\langle \Phi_0^{HF} \middle| H \middle| \Phi_{abc}^{rst} \right\rangle}$

C) $\boxed{H_{0Q} = \left\langle \Phi_0^{HF} \middle| H \middle| \Phi_{abcd}^{rstu} \right\rangle}$

---

**We get the matrix equation**

$$\boxed{HC = CE}$$

**with the Hamiltonian matrix elements:**

$$\boxed{H_{KL} = \left\langle \Phi_K \middle| H \middle| \Phi_L \right\rangle}$$

**All we have to do is to diagonalize this matrix and we have found the exact solution of the many-electron Schrodinger equation in a given basis!**

**We do not have to calculate all of the Hamiltonian matrix elements because some of them are zero. There are simple rules (Slater-Condon rules) that help us to know which ones (see script):**

$$\mathbf{H} = \begin{array}{c|cccccc}
\langle \Phi_0 | & \langle \Phi_0 | H | \Phi_0 \rangle & & & & & \cdots \\
\langle S | & 0 & \langle S | H | S \rangle & & & & \cdots \\
\langle D | & \langle D | H | \Phi_0 \rangle & \langle D | H | S \rangle & \langle D | H | D \rangle & & & \cdots \\
\langle T | & 0 & \langle T | H | S \rangle & \langle T | H | D \rangle & \langle T | H | T \rangle & & \cdots \\
\langle Q | & 0 & 0 & \langle Q | H | D \rangle & \langle Q | H | T \rangle & \langle Q | H | Q \rangle & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{array}$$

**In practice: the number of determinants we have to include to do a full CI calculations is intractable in most cases!**

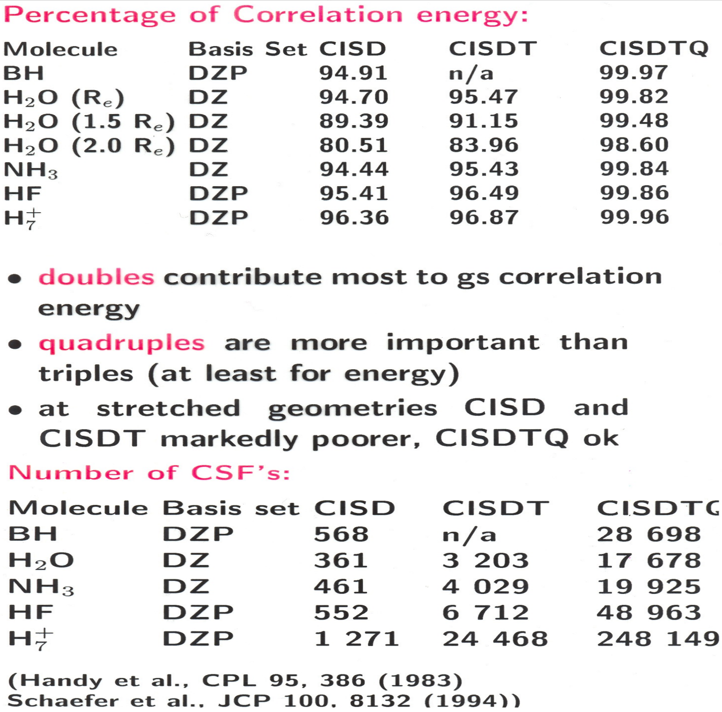
$$\binom{N_{SO}}{N_{el}} = \frac{N_{SO}!}{N_{el}!\,(N_{SO}-N_{el})!}$$

Ex.: Benzene with 6-311G** basis:

**# of determinants** $\binom{288}{42} \approx 10^{52}$

**We would have to calculate, store and diagonalize a $10^{52}$x$10^{52}$ Matrix (ca. $10^{93}$ TByte!)**

Full CI calculations have been performed as benchmarks studies for very small molecules. CIS is sometimes used for approximate excited state calculations. Otherwise CI is not used very often because it is simply too expensive and other correlated methods give results of comparable quality for a lower computational cost.



## Percentage of Correlation energy:

| Molecule | Basis Set | CISD | CISDT | CISDTQ |
|---|---|---|---|---|
| BH | DZP | 94.91 | n/a | 99.97 |
| $H_2O$ ($R_e$) | DZ | 94.70 | 95.47 | 99.82 |
| $H_2O$ (1.5 $R_e$) | DZ | 89.39 | 91.15 | 99.48 |
| $H_2O$ (2.0 $R_e$) | DZ | 80.51 | 83.96 | 98.60 |
| $NH_3$ | DZ | 94.44 | 95.43 | 99.84 |
| HF | DZP | 95.41 | 96.49 | 99.86 |
| $H_7^+$ | DZP | 96.36 | 96.87 | 99.96 |

- doubles contribute most to gs correlation energy
- quadruples are more important than triples (at least for energy)
- at stretched geometries CISD and CISDT markedly poorer, CISDTQ ok

## Number of CSF's:

| Molecule | Basis set | CISD | CISDT | CISDTQ |
|---|---|---|---|---|
| BH | DZP | 568 | n/a | 28 698 |
| $H_2O$ | DZ | 361 | 3 203 | 17 678 |
| $NH_3$ | DZ | 461 | 4 029 | 19 925 |
| HF | DZP | 552 | 6 712 | 48 963 |
| $H_7^+$ | DZP | 1 271 | 24 468 | 248 149 |

(Handy et al., CPL 95, 386 (1983)
Schaefer et al., JCP 100, 8132 (1994))