Coupled Cluster Theory

Joshua Wagner, University of Chicago

"It is the need to remove the 'unlinked clusters' and the introduction of Feynman diagrams which make MBPT [and CC theory] appear unfamiliar to quantum chemists." – K.F. Freed

Abstract

Hartree Fock does not account for electron correlation, so many post-Hartree-Fock methods have been developed including coupled cluster theory which excels at treating smaller molecules. In the worksheet, we present the definitions and ideas behind coupled cluster theory. Comparisons will be made between coupled cluster and the configuration interaction method including comments on computational complexity. This worksheet uses the Maple Quantum Chemistry Toolbox.

Introduction

The Hartree-Fock method, initiated by Daniel Hartree and antisymmetrized by Vladimir Fock, uses a mean-field approximation to account for electron interactions. Using a mean-field approximation allowed the system's wave function to be expressed as a Slater determinant or the more beautifully succinct formulation as a Grassman wedge product:

$$\psi_{HF}(1,2,3,..,N) = \varphi_i(1) \wedge \varphi_j(2) \wedge \varphi_k(3) \wedge ... \wedge \varphi_n(N).$$

Importantly, both the Slater determinant and Grassman wedge products provide an antisymmetrized wave function. The orbitals then can be optimized variationally to minimize the energy of the system, and the resulting orbitals are called the Hartree-Fock orbitals. While the mean-field approximation allows for easier calculations, it fails to capture electron-electron correlation.

Post Hartree-Fock methods have been developed to capture electron-electron correlation. A notable method is configuration interaction which provides an exact model for non-relativistic electron structure. This causes configuration interaction to be an approach that works well for excited states, non-equilibrium geometries, and open-shell systems. However, completing a full configuration interaction calculation is computationally demanding. Truncating the calculation leads to the loss of the method's size-extensivity and size-consistency.

Introduced in the 1960s by Cizek and Paldus, coupled cluster theory models electron-electron interactions by using an exponentiated excitation operator [1]. Truncations including CCSD derived by Purvis and Bartlett in 1982 offer less computationally complex methods. Untruncated coupled cluster is variational like the configuration interaction method, but its truncated forms are not variational but maintain their size-extensivity and size consistency.

Theory/Methodology

In CC Theory, the *exponential ansatz* is used in representing the wave equation [2]:

$$|\Psi_{CC}\rangle = (1+\hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + ...)|\Psi_{HF}\rangle = \sum_{k=0}^{\infty} \left(\frac{1}{k!} \hat{T}^k \right) = e^{\hat{T}} |\Psi_{HF}\rangle,$$

where $\hat{T}$ is our excitation operator that annihilates and creates molecular orbitals:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...$$

Each term in $\hat{T}$ can be expressed as a collection of individual annihilation and creation operators. We often refer to the weights c as amplitudes in CC theory.

$$\hat{T}_1 = \sum_c \sum_t c_c^t \, \hat{a}_t^\dagger \hat{a}_c$$

$$\hat{T}_2 = \sum_{c<d} \sum_{t<u} c_{cd}^{tu} \, \hat{a}_t^\dagger \hat{a}_u^\dagger \hat{a}_d \hat{a}_c$$

$$\hat{T}_3 = \sum_{c<d<e,} \sum_{t<u<v} c_{cde}^{tuv} \, \hat{a}_t^\dagger \hat{a}_u^\dagger \hat{a}_v^\dagger \hat{a}_e \hat{a}_d \hat{a}_c$$

...

$$\hat{T}_N = \sum_{b_1<b_2<b_3<...<b_N} \sum_{s_1<s_2<s_3<...<s_N} c_{b_1 b_2 ...b_N}^{s_1 s_2 s_3 ...s_N} \, \hat{a}_{s_1}^\dagger \hat{a}_{s_2}^\dagger \hat{a}_{s_3}^\dagger ..... \hat{a}_{s_N}^\dagger \hat{a}_{b_N} \hat{a}_{b_{N-1}} \hat{a}_{b_{N-2}} ...\hat{a}_{b_1}$$

We then see that our operator can be further expanded [3]:

$$e^{\hat{T}} = (1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + ...)$$

$$e^{\hat{T}} = 1 +$$

$$\hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3 \right) + \left(\hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24}\hat{T}_1^4 \right)$$
$$+...$$

Expressing $e^{\hat{T}}$ in this way allows us to group terms in a logical manner. The first term just generates our Hartree-Fock wave function, the second term gives all singly excited states. The third term gives all doubly excited states. Here we differentiate between connected excited states $\hat{T}_2$ and two unconnected singly excited states $\hat{T}_1^2$. Similarly, we represent triply excited states in our fourth term—and quadruply excited states in the fifth term. We can note the difference between an excited state with four interacting electrons $\hat{T}_4$ and two disconnected sets of interacting electrons $\hat{T}_2^2$. Each level of excitation thus has terms that evolve from lower levels of excitations, unlike in CI theory.

To show this explicitly, we can consider the truncated CC method CCSD which includes single and double connected excited states. Thus, single and double excitations introduce excitations of higher magnitude so that every level of excitation is included in the truncation.

$$e^{\hat{T}_1 + \hat{T}_2} = 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \right) + \left(\hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3 \right) + \left(\frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24}\hat{T}_1^4 \right) + ...$$

If we were to generate Goldstone Representatives, we can have a pictorial representation of the correlation energy captured by CCSD:

singly excited   connected doubly excited   two unconnected singly excited
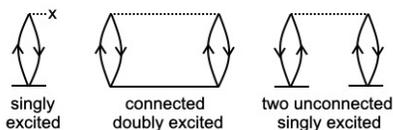
We could solve for the energy of the system in the same manner as done in a full CI calculation, variationally finding the amplitudes c. However we find that we get a series of terms that do not cancel out, leaving us with a problem of an order equal to the number of electrons in the system.

$$E = \frac{\langle \Psi_{CC}|H|\Psi_{CC}\rangle}{\langle \Psi_{CC}|\Psi_{CC}\rangle}$$

$$= \frac{\left\langle \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^N}{N!}\right)\Psi_{HF}\middle|H\middle|\left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^N}{N!}\right)\Psi_{HF}\right\rangle}{\left\langle \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^N}{N!}\right)\Psi_{HF}\middle|\left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^N}{N!}\right)\Psi_{HF}\right\rangle}$$

This makes untruncated CC unmanageable for most systems. Truncations common for CC calculations (Table 1) include CCS, CCSD, CCSD(T), and CCSDT. CCSD recovers significant electron correlation, but CCSD(T) is sometimes referred to as the "gold standard."

Table 1. Coupled Cluster Truncations

Truncation	$\hat{T}$ $\left(\text{where } \Psi_{CC} = e^{\hat{T}}\Psi_{HF}\right)$	Scaling
CCS	$\hat{T}_1$	N^4
CCSD	$\hat{T}_1 + \hat{T}_2$	N^6
CCSD(T)	$\hat{T}_1 + \hat{T}_2$ (and MP4 for triple excitations)	N^7
CCSDT	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3$	N^8
CCSDTQ	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$	N^{10}
Full CC	$\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... + \hat{T}_N$	N^{2N+2}

HF scales as N^4, and CISD scales as N^6.

We find the amplitudes c using the Schrodinger equation:

$$He^{\hat{T}}\left|\Psi_{HF}\right\rangle = E\, e^{\hat{T}}\left|\Psi_{HF}\right\rangle$$

$$E = \left\langle \Psi_{HF}\middle|e^{-\hat{T}}He^{\hat{T}}\middle|\Psi_{HF}\right\rangle = \left\langle \Psi_{HF}|\bar{H}|\Psi_{HF}\right\rangle$$

The Hausdorff expansion for $e^{-\hat{T}}He^{\hat{T}}$ can be written in only five terms when H has only two-electron operators:

$$\bar{H} = H + [H, T] + \frac{1}{2}[[H, T]T] + \frac{1}{3!}[[[H, T]T]T] + \frac{1}{4!}[[[[H, T]T]T]T]$$

The Hausdorff expansion shows that there will be a finite number of terms in the CC equations despite having an exponentiated operator. The commutators eliminate elements that are not shared by H and T that do not share indices, and this causes the equations for energy and amplitudes to be linked [4]. This results in the energy being size extensive [5]!

The excitation operator appearing as an exponent is a leading characteristic of CC theory, especially in comparison to configuration interaction (CI) theory which operates on the reference wave function just as a sum of excitation operators:

$$|\Psi_{CI}\rangle = \hat{T}'\Big|\Psi_0\rangle = \left(1 + \sum_i c_i \tau_i\right)\Big|\Psi_{HF}\rangle$$

A downfall of CI is the computational intensity of performing calculations and its inability to be truncated without losing size consistency.

Below, we show a brief sketch demonstrating that CC maintains size consistency even with truncation [7]. We consider two non-interacting systems A and B which have an energy E_{AB} and excitation operators $\hat{T}_A$ and $\hat{T}_B$ that operate on A and B respectively. Since $\hat{T}_A$ and $\hat{T}_B$ only operate on A and B respectively, we can state that they commute: $[\hat{T}_A, \hat{T}_B] = 0$. We can show that CC provides size-consistent results through some simple algebraic manipulations:

$$E_{AB} e^{\hat{T}_{AB}}\Big|\Psi_0\rangle = \hat{H}_{AB} e^{\hat{T}_{AB}}\Big|\Psi_0\rangle$$

$$= \left(\hat{H}_A + \hat{H}_B\right) e^{\hat{T}_{AB}}\Big|\Psi_0\rangle$$

$$= \hat{H}_A e^{\hat{T}_{AB}}\Big|\Psi_0\rangle + \hat{H}_B e^{\hat{T}_{AB}}\Big|\Psi_0\rangle$$

$$= \hat{H}_A e^{\hat{T}_A + \hat{T}_B}\Big|\Psi_0\rangle + \hat{H}_B e^{\hat{T}_A + \hat{T}_B}\Big|\Psi_0\rangle$$

$$= \hat{H}_A e^{\hat{T}_A} e^{\hat{T}_B}\Big|\Psi_0\rangle + \hat{H}_B e^{\hat{T}_A} e^{\hat{T}_B}\Big|\Psi_0\rangle$$

$$= e^{\hat{T}_B} \hat{H}_A e^{\hat{T}_A}\Big|\Psi_0\rangle + e^{\hat{T}_A} \hat{H}_B e^{\hat{T}_B}\Big|\Psi_0\rangle$$

$$= e^{\hat{T}_B} E_A e^{\hat{T}_A}\Big|\Psi_0\rangle + e^{\hat{T}_A} E_B e^{\hat{T}_B}\Big|\Psi_0\rangle$$

$$= \left(E_A + E_B\right) e^{\hat{T}_{AB}}\Big|\Psi_0\rangle$$

Thus we have demonstrated how CC theory provides size-consistent energies.

Applications/Results
We first load the Quantum Chemistry package.

```
> with(QuantumChemistry):
```

Carbon Monoxide — Dipole Analysis

First we define a carbon monoxide (CO) molecule. We then find the dipole moment of CO using both Hartree Fock and coupled cluster. By default, the Maple command CoupledCluster uses the CCSD truncation, but can optionally use CCSD(T).

```
> CO_mol := [["C", 0, 0, 0], ["O", 0, 0, 1.11014349622376]];
```

$$CO\_mol := [["C", 0, 0, 0], ["O", 0, 0, 1.11014350]] \qquad \textbf{(4.1.1)}$$

```
> HF_CO := HartreeFock(CO_mol, basis = "cc-pVTZ", symmetry = true):
> CC_CO := CoupledCluster(CO_mol, basis = "cc-pVTZ", symmetry =
  true):

> HF_CO[dipole];
```

$$\begin{bmatrix} -2.18953837 \ 10^{-7} \\ -2.18953837 \ 10^{-7} \\ -0.15832888 \end{bmatrix} \qquad \textbf{(4.1.2)}$$

```
> CC_CO[dipole];
```

$$\begin{bmatrix} 3.25735638 \ 10^{-7} \\ 3.25735638 \ 10^{-7} \\ 0.23554444 \end{bmatrix} \qquad \textbf{(4.1.3)}$$

Recovered Electron Correlation

Now we will consider the correlation energy calculated using coupled cluster. We use the cc-pVDZ basis set and compare to the full CI correlation energy.

Calculations

```
> Neon := [["Ne", 0, 0, 0]]:
> data_Ne_CC := CoupledCluster(Neon, basis = "cc-pVDZ", symmetry =
  true):
> data_Ne_HF := HartreeFock(Neon, basis = "cc-pVDZ", symmetry =
  true):
> data_Ne_FCI := FullCI(Neon, basis = "cc-pVDZ", symmetry = true):

> Fluorine := [["F", 0, 0, 0]]:
> data_F_CC := CoupledCluster(Fluorine, basis = "cc-pVDZ", symmetry
  = true):
> data_F_HF := HartreeFock(Fluorine, basis = "cc-pVDZ", symmetry =
  true):
> data_F_FCI := FullCI(Fluorine, basis = "cc-pVDZ", symmetry = true)
  :

> Oxygen := [["O", 0, 0, 0]]:
> data_O_CC := CoupledCluster(Oxygen, basis = "cc-pVDZ", symmetry =
  true):
> data_O_HF := HartreeFock(Oxygen, basis = "cc-pVDZ", symmetry =
```

```
   true):
```
Warning, The Hartree-Fock calculation did not fully converge.
```
> data_O_FCI := FullCI(Oxygen, basis = "cc-pVDZ", symmetry = true):
> data_O_CC_ccsdt := CoupledCluster(Oxygen, basis = "cc-pVDZ",
  symmetry = true, ccsdt = true):

> Nitrogen := [["N", 0, 0, 0]]:
> data_N_CC := CoupledCluster(Nitrogen, basis = "cc-pVDZ", symmetry
  = true):
> data_N_HF := HartreeFock(Nitrogen, basis = "cc-pVDZ", symmetry =
  true):
```
Warning, The Hartree-Fock calculation did not fully converge.
```
> data_N_FCI := FullCI(Nitrogen, basis = "cc-pVDZ", symmetry = true)
  :

> data_O_CC_ccsdt[mo_occ], data_O_CC[mo_occ], data_O_FCI[mo_occ],
  data_O_HF[mo_occ]:

> Carbon := [["C", 0, 0, 0]]:
> data_C_CC := CoupledCluster(Carbon, basis = "cc-pVDZ", symmetry =
  true):
> data_C_HF := HartreeFock(Carbon, basis = "cc-pVDZ", symmetry =
  true):
> data_C_FCI := FullCI(Carbon, basis = "cc-pVDZ", symmetry = true):

> Boron := [["B", 0, 0, 0]]:
> data_B_CC := CoupledCluster(Boron, basis = "cc-pVDZ", symmetry =
  true):
> data_B_HF := HartreeFock(Boron, basis = "cc-pVDZ", symmetry =
  true):
> data_B_FCI := FullCI(Boron, basis = "cc-pVDZ", symmetry = true):

> Ber := [["Be", 0, 0, 0]]:
> data_Be_CC := CoupledCluster(Ber, basis = "cc-pVDZ", symmetry =
  true):
> data_Be_HF := HartreeFock(Ber, basis = "cc-pVDZ", symmetry = true)
  :
> data_Be_FCI := FullCI(Ber, basis = "cc-pVDZ", symmetry = true):

> Lithium := [["Li", 0, 0, 0]]:
> data_Li_CC := CoupledCluster(Lithium, basis = "cc-pVDZ", symmetry
  = true):
> data_Li_HF := HartreeFock(Lithium, basis = "cc-pVDZ", symmetry =
  true):
> data_Li_FCI := FullCI(Lithium, basis = "cc-pVDZ", symmetry = true)
  :

> Helium := [["He", 0, 0, 0]]:
> data_He_CC := CoupledCluster(Helium, basis = "cc-pVDZ", symmetry =
  true):
> data_He_HF := HartreeFock(Helium, basis = "cc-pVDZ", symmetry =
  true):
```

```
> data_He_FCI := FullCI(Helium, basis = "cc-pVDZ", symmetry = true)
  :
```

```
> m2 := Matrix([[Method, He, Li, Be, B, C, N, O, F, Ne], [HF,
  data_He_HF[e_tot], data_Li_HF[e_tot], data_Be_HF[e_tot], data_B_HF
  [e_tot], data_C_HF[e_tot], data_N_HF[e_tot], data_O_HF[e_tot],
  data_F_HF[e_tot], data_Ne_HF[e_tot]],[CC, data_He_CC[e_tot],
  data_Li_CC[e_tot], data_Be_CC[e_tot], data_B_CC[e_tot], data_C_CC
  [e_tot], data_N_CC[e_tot], data_O_CC[e_tot], data_F_CC[e_tot],
  data_Ne_CC[e_tot]], [FCI, data_He_FCI[e_tot], data_Li_FCI[e_tot],
  data_Be_FCI[e_tot], data_B_FCI[e_tot], data_C_FCI[e_tot],
  data_N_FCI[e_tot], data_O_FCI[e_tot], data_F_FCI[e_tot],
  data_Ne_FCI[e_tot]]]);
```

$$
m2 := \begin{bmatrix}
Method & He & Li & Be & B & C & \dots \\
HF & -2.85516048 & -7.43241988 & -14.57233763 & -24.52659091 & -37.59598443 & \dots \\
CC & -2.88759484 & -7.43263729 & -14.61736901 & -24.58934794 & -37.69937564 & \dots \\
FCI & -2.88759483 & -7.43263751 & -14.61740951 & -24.59062960 & -37.70729527 & \dots
\end{bmatrix}
$$
(4.2.

$$4 \times 10 \text{ Matrix}$$

```
> m3 := Matrix([[Method, He, Li, Be, B, C, N, O, F, Ne], [CC,
  data_He_CC[e_corr], data_Li_CC[e_corr], data_Be_CC[e_corr],
  data_B_CC[e_corr], data_C_CC[e_corr], data_N_CC[e_corr], data_O_CC
  [e_corr], data_F_CC[e_corr], data_Ne_CC[e_corr]], [FCI,
  data_He_FCI[e_corr], data_Li_FCI[e_corr], data_Be_FCI[e_corr],
  data_B_FCI[e_corr], data_C_FCI[e_corr], data_N_FCI[e_corr],
  data_O_FCI[e_corr], data_F_FCI[e_corr], data_Ne_FCI[e_corr]]])
```

$$
m3 := \begin{bmatrix}
Method & He & Li & Be & B & C & \dots \\
CC & -0.03243436 & -0.00021741 & -0.04503138 & -0.06275703 & -0.10339121 & \dots \\
FCI & -0.03243435 & -0.00021764 & -0.04507188 & -0.06403869 & -0.11131084 & \dots
\end{bmatrix}
$$
(4.2.1.2

$$3 \times 10 \text{ Matrix}$$

```
> m3 := Matrix([[Element, He, Li, Be, B, C, N, O, F, Ne],
  [Recovered, data_He_CC[e_corr]/data_He_FCI[e_corr], data_Li_CC
  [e_corr]/data_Li_FCI[e_corr], data_Be_CC[e_corr]/data_Be_FCI
  [e_corr], data_B_CC[e_corr]/data_B_FCI[e_corr], data_C_CC[e_corr]
  /data_C_FCI[e_corr], data_N_CC[e_corr]/data_N_FCI[e_corr],
  data_O_CC[e_corr]/data_O_FCI[e_corr], data_F_CC[e_corr]/data_F_FCI
  [e_corr], data_Ne_CC[e_corr]/data_Ne_FCI[e_corr]]]);
```
$$m3 :=$$ (4.2.1.3)

$$
\begin{bmatrix}
Element & He & Li & Be & B & C & \dots \\
Recovered & 1.00000014 & 0.99898097 & 0.99910151 & 0.97998624 & 0.92885120 & \dots
\end{bmatrix}
$$

$$2 \times 10 \text{ Matrix}$$

```
> data_O_CC_ccsdt[e_corr];
```
$$-0.15552905$$ (4.2.1.4)

```
> data_O_CC[e_corr];
```
(4.2.1.5)

$$-0.15552905 \tag{4.2.1.5}$$

```
> m4 := Matrix([[2, 3, 4, 5, 6, 7, 8, 9, 10], [data_He_CC[e_corr]
  /data_He_FCI[e_corr], data_Li_CC[e_corr]/data_Li_FCI[e_corr],
  data_Be_CC[e_corr]/data_Be_FCI[e_corr], data_B_CC[e_corr]
  /data_B_FCI[e_corr], data_C_CC[e_corr]/data_C_FCI[e_corr],
  data_N_CC[e_corr]/data_N_FCI[e_corr], data_O_CC[e_corr]/data_O_FCI
  [e_corr], data_F_CC[e_corr]/data_F_FCI[e_corr], data_Ne_CC[e_corr]
  /data_Ne_FCI[e_corr]]]);
```

$$m4 := \tag{4.2.1.6}$$

$$\begin{bmatrix} 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ 1.00000014 & 0.99898097 & 0.99910151 & 0.97998624 & 0.92885120 & 0.89775836 & \dots \end{bmatrix}$$

$$2 \times 9 \text{ Matrix}$$

```
> with(plots):
> with(LinearAlgebra):

> plot([2, 3, 4, 5, 6, 7, 8, 9, 10], [data_He_CC[e_corr]/data_He_FCI
  [e_corr], data_Li_CC[e_corr]/data_Li_FCI[e_corr], data_Be_CC
  [e_corr]/data_Be_FCI[e_corr], data_B_CC[e_corr]/data_B_FCI
  [e_corr], data_C_CC[e_corr]/data_C_FCI[e_corr], data_N_CC[e_corr]
  /data_N_FCI[e_corr], data_O_CC[e_corr]/data_O_FCI[e_corr],
  data_F_CC[e_corr]/data_F_FCI[e_corr], data_Ne_CC[e_corr]
  /data_Ne_FCI[e_corr]], style=line,symbol=asterisk,color="blue",
  thickness = 3, axes = boxed);
```
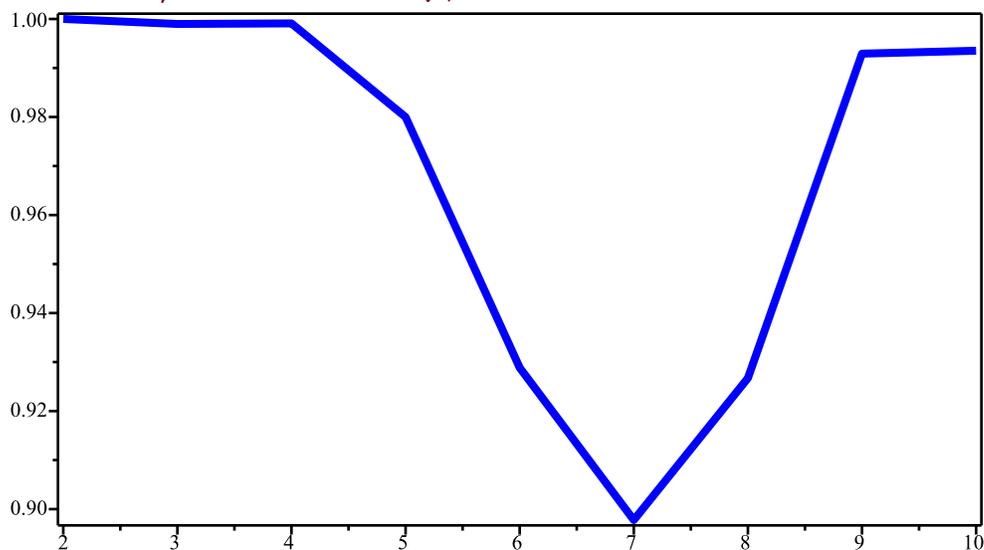

Figure 1. Electron correlation energy of elements He through Neon was calculated using both Full CI and CCSD with

[Figure 1. Electron correlation energy of elements He through Neon was calculated using both Full CI and CCSD with a cc-pVDZ basis set. Here we plot the fraction of electron correlation covered using CCSD in reference to that recovered using full CI. We note that open-shell systems pose a challenge to CCSD.]
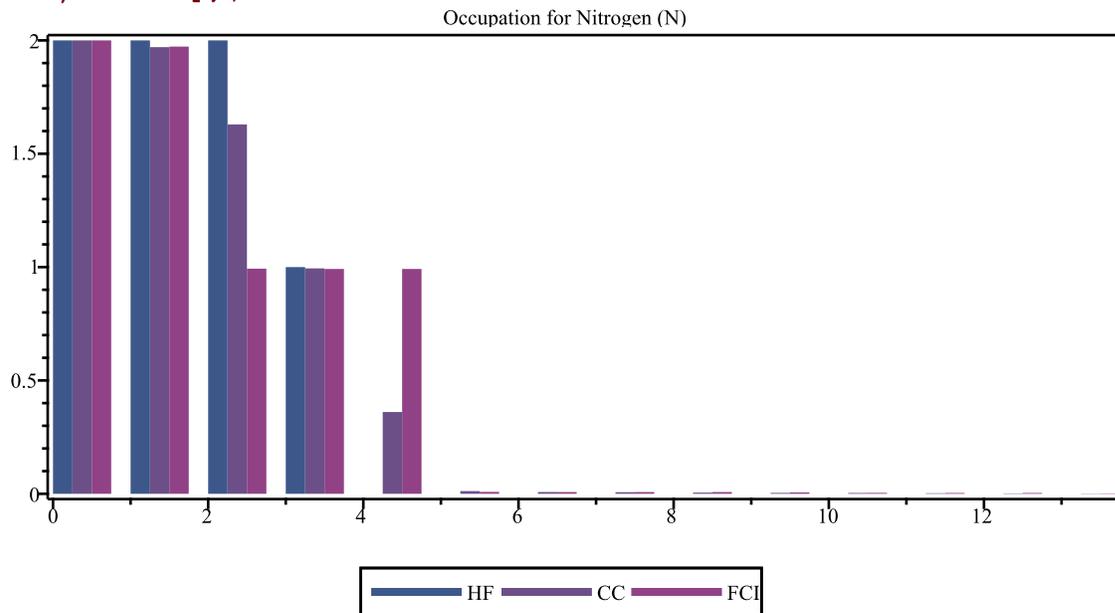
```
> with(Statistics):
> ColumnGraph( [data_O_HF[mo_occ], data_O_CC[mo_occ], data_O_FCI
  [mo_occ]] , title = "MO Occupation for Oxygen", legend = ["HF",
  "CC", "FCI"]);
```

Occupation for Oxygen (O)
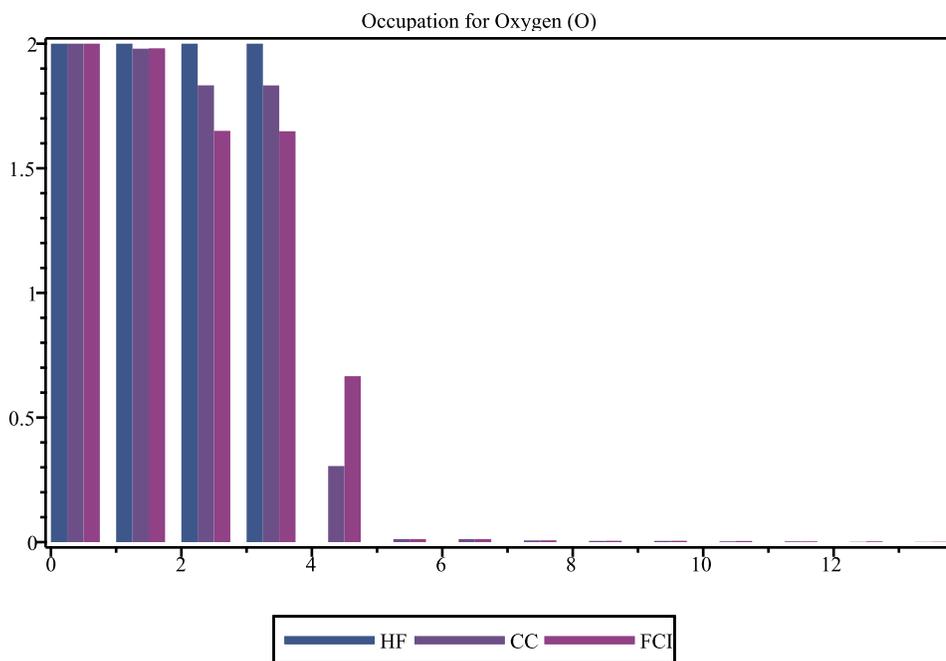
```
> with(Statistics):
> ColumnGraph( [data_N_HF[mo_occ], data_N_CC[mo_occ], data_N_FCI
  [mo_occ]] , title = "MO Occupation for Nitrogen", legend = ["HF",
  "CC", "FCI"]);
```


Occupation for Nitrogen (N)

Pulling Apart N$_2$

Calculations

```
> NN05 := [["N", 0, 0, 0], ["N", 0, 0, 0.5]]:
> dNN05 := CoupledCluster(NN05, basis = "STO-3G", symmetry = true):

> NN06 := [["N", 0, 0, 0], ["N", 0, 0, 0.6]]:
```

```
> dNN06 := CoupledCluster(NN06, basis = "STO-3G", symmetry = true):

> NN07 := [["N", 0, 0, 0], ["N", 0, 0, 0.7]]:
> dNN07 := CoupledCluster(NN07, basis = "STO-3G", symmetry = true):

> NN08 := [["N", 0, 0, 0], ["N", 0, 0, 0.8]]:
> dNN08 := CoupledCluster(NN08, basis = "STO-3G", symmetry = true):

> NN09 := [["N", 0, 0, 0], ["N", 0, 0, 0.9]]:
> dNN09 := CoupledCluster(NN09, basis = "STO-3G", symmetry = true):

> NN10 := [["N", 0, 0, 0], ["N", 0, 0, 1]]:
> dNN10 := CoupledCluster(NN10, basis = "STO-3G", symmetry = true):

> NN11 := [["N", 0, 0, 0], ["N", 0, 0, 1.1]]:
> dNN11 := CoupledCluster(NN11, basis = "STO-3G", symmetry = true):

> NN12 := [["N", 0, 0, 0], ["N", 0, 0, 1.2]]:
> dNN12 := CoupledCluster(NN12, basis = "STO-3G", symmetry = true):

> NN13 := [["N", 0, 0, 0], ["N", 0, 0, 1.3]]:
> dNN13 := CoupledCluster(NN13, basis = "STO-3G", symmetry = true):

> NN14 := [["N", 0, 0, 0], ["N", 0, 0, 1.4]]:
> dNN14 := CoupledCluster(NN14, basis = "STO-3G", symmetry = true):

> NN15 := [["N", 0, 0, 0], ["N", 0, 0, 1.5]]:
> dNN15 := CoupledCluster(NN15, basis = "STO-3G", symmetry = true):

> NN16 := [["N", 0, 0, 0], ["N", 0, 0, 1.6]]:
> dNN16 := CoupledCluster(NN16, basis = "STO-3G", symmetry = true):

> NN17 := [["N", 0, 0, 0], ["N", 0, 0, 1.7]]:
> dNN17 := CoupledCluster(NN17, basis = "STO-3G", symmetry = true):

> NN18 := [["N", 0, 0, 0], ["N", 0, 0, 1.8]]:
> dNN18 := CoupledCluster(NN18, basis = "STO-3G", symmetry = true):

> NN19 := [["N", 0, 0, 0], ["N", 0, 0, 1.9]]:
> dNN19 := CoupledCluster(NN19, basis = "STO-3G", symmetry = true):

> NN20 := [["N", 0, 0, 0], ["N", 0, 0, 2.0]]:
> dNN20 := CoupledCluster(NN20, basis = "STO-3G", symmetry = true):

> NN21 := [["N", 0, 0, 0], ["N", 0, 0, 2.1]]:
> dNN21 := CoupledCluster(NN21, basis = "STO-3G", symmetry = true):

> NN22 := [["N", 0, 0, 0], ["N", 0, 0, 2.2]]:
> dNN22 := CoupledCluster(NN22, basis = "321g", symmetry = true):
```

```
> dNN05f := FullCI(NN05, basis = "STO-3G", symmetry = true):
> dNN06f := FullCI(NN06, basis = "STO-3G", symmetry = true):
> dNN07f := FullCI(NN07, basis = "STO-3G", symmetry = true):
> dNN08f := FullCI(NN08, basis = "STO-3G", symmetry = true):
> dNN09f := FullCI(NN09, basis = "STO-3G", symmetry = true):
> dNN10f := FullCI(NN10, basis = "STO-3G", symmetry = true):
> dNN11f := FullCI(NN11, basis = "STO-3G", symmetry = true):
> dNN12f := FullCI(NN12, basis = "STO-3G", symmetry = true):
> dNN13f := FullCI(NN13, basis = "STO-3G", symmetry = true):
> dNN14f := FullCI(NN14, basis = "STO-3G", symmetry = true):
> dNN15f := FullCI(NN15, basis = "STO-3G", symmetry = true):
> dNN16f := FullCI(NN16, basis = "STO-3G", symmetry = true):
> dNN17f := FullCI(NN17, basis = "STO-3G", symmetry = true):
> dNN18f := FullCI(NN18, basis = "STO-3G", symmetry = true):
> dNN19f := FullCI(NN19, basis = "STO-3G", symmetry = true):
> dNN20f := FullCI(NN20, basis = "STO-3G", symmetry = true):
> dNN21f := FullCI(NN21, basis = "STO-3G", symmetry = true):
> dNN22f := FullCI(NN22, basis = "STO-3G", symmetry = true):

> with(plots):

> CC := plot([0.5, .6, 0.7, .9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6,
  1.7, 1.8, 1.9, 2.0, 2.1, 2.2], [dNN05[e_tot], dNN06[e_tot],  dNN07
  [e_tot],dNN08[e_tot], dNN09[e_tot],dNN10[e_tot], dNN11[e_tot],
  dNN12[e_tot], dNN13[e_tot], dNN14[e_tot], dNN15[e_tot], dNN16
  [e_tot], dNN17[e_tot], dNN18[e_tot], dNN19[e_tot], dNN20[e_tot],
  dNN21[e_tot], dNN22[e_tot]], style=line, linestyle = dash ,symbol=
  diamond, color="blue", thickness = 3, axes = boxed, legend = "CC")
  ;
```
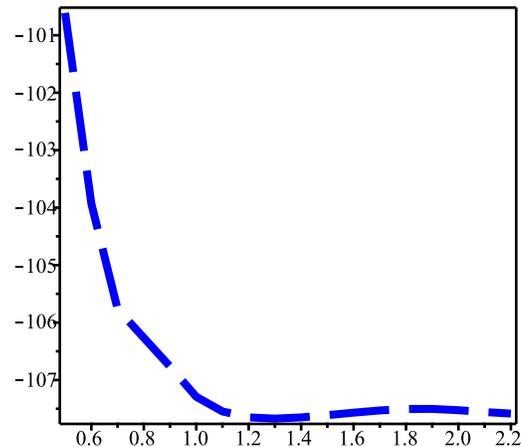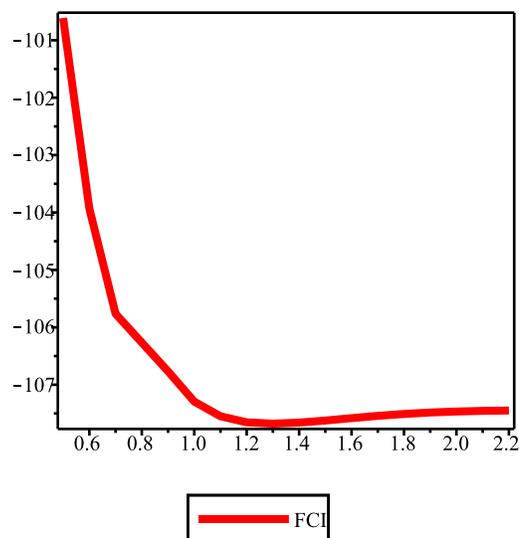


```
> FCI := plot([0.5, .6, 0.7, .9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6,
  1.7, 1.8, 1.9, 2.0, 2.1, 2.2],  [dNN05f[e_tot], dNN06f[e_tot],
  dNN07f[e_tot],dNN08f[e_tot], dNN09f[e_tot],dNN10f[e_tot], dNN11f
  [e_tot], dNN12f[e_tot], dNN13f[e_tot], dNN14f[e_tot], dNN15f
  [e_tot], dNN16f[e_tot], dNN17f[e_tot], dNN18f[e_tot], dNN19f
  [e_tot], dNN20f[e_tot], dNN21f[e_tot], dNN22f[e_tot]], style=line,
  symbol=asterisk,color="red", thickness = 3, axes = boxed, legend =
```

```
"FCI");
```



```
> display(FCI, CC, legend = ["FCI","CCSD"]);
```
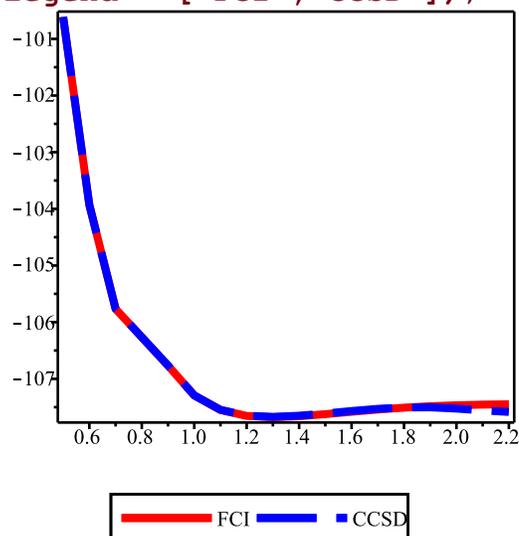

The figure above shows the energy of N_2 as a function of bond distance calculated using both full CI and CCSD.

Size Consistent

Size-consistency is useful when modeling chemical reactions, since correlations between reactants and products are often undesirable for a model. Size-consistency is one key advantage of CC theory over CI theory, since standard CI methods truncate higher order excitations which leads to the loss of size-consistency. However, in CC theory higher order excitations are represented as products of lower excitations. Here we demonstrate size-consistency of CCSD by separating two Helium atoms using the CoupledCluster command.

Calculations

```
> HeHe_mol_0_5 := [["He", 0, 0, 0], ["He", 0, 0, 0.5]]:
> CC_HeHe_0_5 := CoupledCluster(HeHe_mol_0_5, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol_1 := [["He", 0, 0, 0], ["He", 0, 0, 1]]:
```

```
> CC_HeHe_1 := CoupledCluster(HeHe_mol_1, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol := [["He", 0, 0, 0], ["He", 0, 0, 2]]:
> CC_HeHe := CoupledCluster(HeHe_mol, basis = "cc-pVTZ", symmetry =
  true):

> HeHe_mol_3 := [["He", 0, 0, 0], ["He", 0, 0, 3]]:
> CC_HeHe_3 := CoupledCluster(HeHe_mol_3, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol_4 := [["He", 0, 0, 0], ["He", 0, 0, 4]]:
> CC_HeHe_4 := CoupledCluster(HeHe_mol_4, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol_5 := [["He", 0, 0, 0], ["He", 0, 0, 5]]:
> CC_HeHe_5 := CoupledCluster(HeHe_mol_5, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol_6 := [["He", 0, 0, 0], ["He", 0, 0, 6]]:
> CC_HeHe_6 := CoupledCluster(HeHe_mol_6, basis = "cc-pVTZ",
  symmetry = true):

> HeHe_mol_7 := [["He", 0, 0, 0], ["He", 0, 0, 7]]:
> CC_HeHe_7 := CoupledCluster(HeHe_mol_7, basis = "cc-pVTZ",
  symmetry = true):

> plot([0.5, 1, 2, 3, 4, 5, 6, 7], [CC_HeHe_0_5[e_tot], CC_HeHe_1
  [e_tot],  CC_HeHe[e_tot], CC_HeHe[e_tot], CC_HeHe_3[e_tot],
  CC_HeHe_3[e_tot], CC_HeHe_4[e_tot], CC_HeHe_5[e_tot], CC_HeHe_6
  [e_tot], CC_HeHe_7[e_tot]], style=line ,symbol=asterisk,color=
  "blue", thickness = 3, axes = boxed);
```
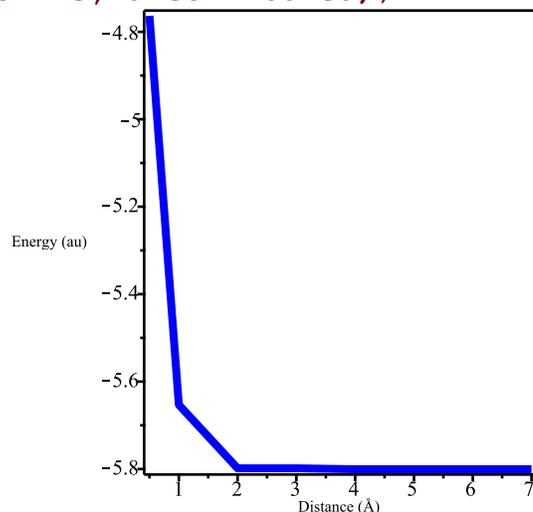
Figure 2. The total electron energy of two helium atoms was de

Size Extensive

Calculations

```
> He1_mol := [["He", 0, 0, 0]]:
> He2_mol := [["He", 0, 0, 0], ["He", 0, 0, 3]]:
> He3_mol := [["He", 0, 0, 0], ["He", 0, 0, 3], ["He", 0, 0, 6]]:
> He4_mol := [["He", 0, 0, 0], ["He", 0, 0, 3], ["He", 0, 0, 6],
  ["He", 0, 0, 9]]:
> He5_mol := [["He", 0, 0, 0], ["He", 0, 0, 3], ["He", 0, 0, 6],
  ["He", 0, 0, 9], ["He", 0, 0, 12]]:
> CC_He1 := CoupledCluster(He1_mol, basis = "cc-pVTZ", symmetry =
  true):
> CC_He2 := CoupledCluster(He2_mol, basis = "cc-pVTZ", symmetry =
  true):
> CC_He3 := CoupledCluster(He3_mol, basis = "cc-pVTZ", symmetry =
  true):
> CC_He4 := CoupledCluster(He4_mol, basis = "cc-pVTZ", symmetry =
  true):
> CC_He5 := CoupledCluster(He5_mol, basis = "cc-pVTZ", symmetry =
  true):

> He10_mol := [["He", 0, 0, 0], ["He", 0, 0, 3], ["He", 0, 0, 6],
  ["He", 0, 0, 9], ["He", 0, 0, 12], ["He", 0, 0, 15], ["He", 0, 0,
  18], ["He", 0, 0, 21], ["He", 0, 0, 24], ["He", 0, 0, 27]]:
> CC_He10 := CoupledCluster(He10_mol, basis = "cc-pVTZ", symmetry =
  true):
```
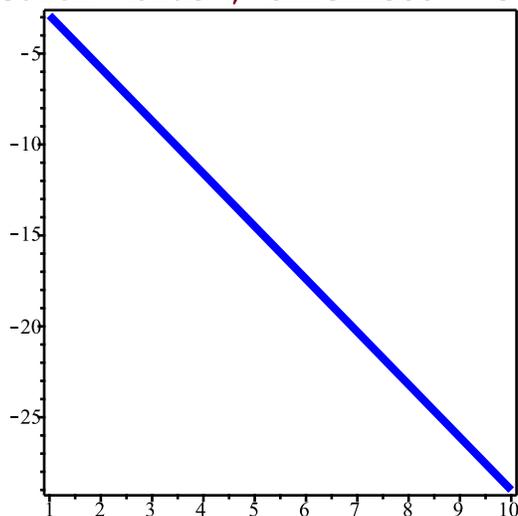
We can plot the energy of systems containing multiple helium atoms. We notice that the energy scales linearly with the number of helium atoms using CCSD calculations.

```
> plot([1, 2, 3, 4, 5, 10], [CC_He1[e_tot], CC_He2[e_tot],  CC_He3
  [e_tot], CC_He4[e_tot], CC_He5[e_tot], CC_He10[e_tot]], style=line
  ,symbol=asterisk,color="blue", thickness = 3, axes = boxed);
```


Discussion/Conclusions

In analyzing the dipole moment of carbon monoxide, we observed that Hartree Fock predicted the wrong direction of the dipole moment. Implementing the coupled cluster method however illustrated that including electron correlation not only provides lower energies, but also improves calculations for other physical properties. Using the singles/doubles truncation of coupled cluster, the dipole was

calculated to be 0.2355 Debye. This compares better to the experimental value (0.1222 Debye).

Calculations used in the CCSD method do not involve connected excited states greater than second order. In systems with highly correlated electrons, such as open shell systems this leads to less electron correlation energy being recovered. Just looking at atomic systems, this is particularly relevant for carbon, nitrogen, and oxygen which have a partially filled 2p sub-shell. Comparing CCSD to full CI, less than 90% of the electron correlation energy was recovered when computing the energy of a ground state nitrogen atom using a cc-pVDZ basis set. The wave functions generated by full CI and CCSD also provide a different orbital occupations. Graphing the orbital occupation generated by both full CI and CCSD for nitrogen this was apparent. We observe that the three 2p orbitals are each occupied by one electron using full CI, and CCSD showed an uneven filling of the three orbitals.

Untruncated CC is variational, but scales similarly to full CI. Truncations like CCSD are computationally easier, but are not variational. This can lead to instances where full CI provides a higher energy than CCSD. This was observed while dissociating a nitrogen molecule and can be clearly observed by comparing plots of energy as a function of bond distance. However, one should note that the energies are similar until the two nitrogen atoms were sufficiently distanced apart (~1.8 Å).

A simple demonstration that CCSD is size consistent was made by separating two helium atoms and finding that the energy remained constant as the atoms moved apart. Size extensivity can also be demonstrated by calculating the energy of various numbers of helium atoms using CCSD and then observing that energy scales linearly with the number of atoms.

References

[1] T. Crawford, H. Schaefer 33-136 (2000). An Introduction to Coupled Cluster Theory for Computational Chemists
[2] E. Lewars, Kluwer Academic Publishers 248-250 (2003). Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics
[3] F. Jensen 169-178 (2007). Introduction to Computational Chemistry
[4] R. Bartlett, M. Musia, Rev. Modern Phys. 79, 291-352 (2007). Coupled-Cluster Theory in Quantum Chemistry
[5] G. Purvis, R. Barlett, J. Chem. Phys. 76, 1910 (1982). A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples
[6] D. Lyakh, M. Musiaz, V. Lotrich, R. Bartlett, Chem. Rev. 112, 182–243 (2012). Multireference Nature of Chemistry: The Coupled-Cluster View
[7] R. Bartlett, G. Purvis, Int J. Quantum Chemistry 14, 561-581 (1978). Many-Body Perturbation Theory, Coupled-Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem
>