Introduction to Nondynamical Correlation

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Two Types of Electron Correlation

Basis Set Correlation for H_2O with a DZ Basis

Geometry	E_{corr} (hartree)[a]
R_e	-0.148028
1.5 R_e	-0.210992
2.0 R_e	-0.310067

[a] R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.* **95**, 386 (1983)

"Dynamical" correlation, electrons instantaneously avoiding each other, should become *less important* at stretched geometries, since the electrons are further apart. However, the correlation energy *increases* with stretching! There must be a "nondynamical" (also called "static") correlation.

What Causes the Nondynamical Correlation?

- Correlation energy is the difference between Full CI and Hartree-Fock energies
- Hartree-Fock neglects instantaneous electron-electron repulsions ("dynamical correlation")
- What else is it missing? *It does not account for nearly degenerate electron configurations*

Simplest Example of Degeneracy: Stretched H_2

For minimal basis H_2, only two 1s functions, one on each H atom: ϕ_A, ϕ_B. Restricted Hartree-Fock orbitals determined completely by symmetry. Let overbars denote β spin.

$$\begin{aligned}
\phi_\sigma &= \frac{1}{\sqrt{2(1+S_{12})}}\left(\phi_A + \phi_B\right) \\
\phi_{\sigma^*} &= \frac{1}{\sqrt{2(1-S_{12})}}\left(\phi_A - \phi_B\right) \\
|\phi_\sigma \overline{\phi}_\sigma\rangle &= \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_\sigma(1) & \overline{\phi}_\sigma(1) \\ \phi_\sigma(2) & \overline{\phi}_\sigma(2) \end{vmatrix}
\end{aligned}$$

Expansion of the Determinant

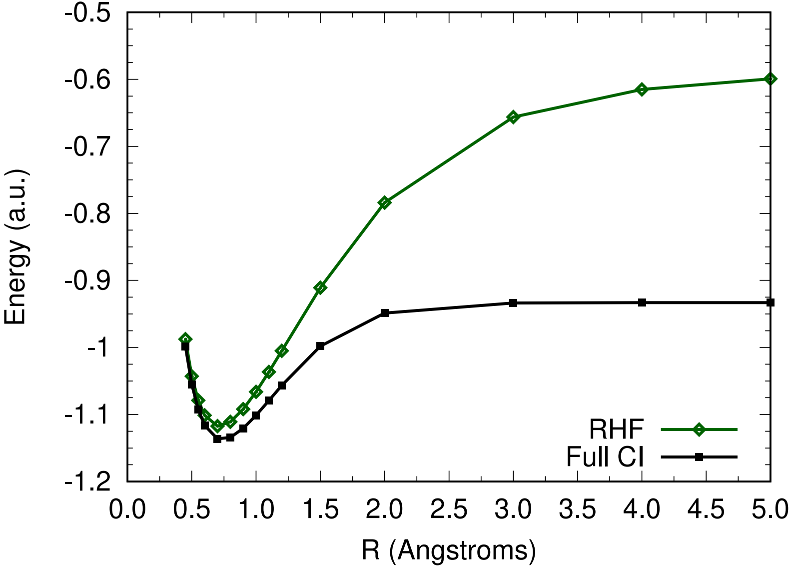
$$\begin{aligned}
|\phi_\sigma\overline{\phi}_\sigma\rangle &= \frac{1}{\sqrt{2}}\left[\phi_\sigma(1)\overline{\phi}_\sigma(2) - \phi_\sigma(2)\overline{\phi}_\sigma(1)\right] \\
&= \frac{1}{2\sqrt{2}(1+S_{12})}\big[(\phi_A(1)+\phi_B(1))(\overline{\phi}_A(2)+\overline{\phi}_B(2)) \\
&\quad -(\phi_A(2)+\phi_B(2))(\overline{\phi}_A(1)+\overline{\phi}_B(1))\big] \\
&= \frac{1}{2\sqrt{2}(1+S_{12})}\big[\phi_A(1)\overline{\phi}_A(2)+\phi_A(1)\overline{\phi}_B(2) \\
&\quad +\phi_B(1)\overline{\phi}_A(2)+\phi_B(1)\overline{\phi}_B(2)-\phi_A(2)\overline{\phi}_A(1)-\phi_A(2)\overline{\phi}_B(1) \\
&\quad -\phi_B(2)\overline{\phi}_A(1)-\phi_B(2)\overline{\phi}_B(1)\big]
\end{aligned}$$

Simplified Notation for Expanded Determinant

The expanded determinant looks like the sum of four determinants made of *atomic spin orbitals*:

$$|\phi_\sigma \overline{\phi}_\sigma\rangle = \frac{1}{2(1+S_{12})}\left[|\phi_A \overline{\phi}_A\rangle + |\phi_A \overline{\phi}_B\rangle + |\phi_B \overline{\phi}_A\rangle + |\phi_B \overline{\phi}_B\rangle\right]$$

So...what's the problem? The first and last terms are *ionic* valence bond structures and *should not contribute* to the wavefunction (they place *both* electrons on *one* of the hydrogens) as $R_{AB} \rightarrow \infty$. However, they are required by RHF. Thus, *RHF does not work for bond-breaking processes in general*.


-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
Energy (a.u.)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
R (Angstroms)
RHF
Full CI

RHF Energy Much Too High for Bond-Breaking

- The RHF energy associated with determinant $|\phi_\sigma \overline{\phi}_\sigma\rangle$ is $E(\mathrm{RHF}) = 2h_{\sigma\sigma} + \mathrm{J}_{\sigma\sigma}$.
- However, as $R_{AB} \rightarrow \infty$, we should have E(RHF) $\rightarrow 2E$(H atom) as $R_{AB} = \infty$. This is just $h_{AA} + h_{BB}$, which at infinity is also just $2h_{\sigma\sigma} = (h_{AA} + h_{AB} + h_{BA} + h_{BB}) = h_{AA} + h_{BB}$.
- Energy is overestimated by spurious term $J_{\sigma\sigma}$ at long distances.

Thinking about Degeneracy

- Another way to view the problem of RHF with dissociation is to realize we have a degeneracy problem as $R_{AB} \to \infty$
- Recall Hartree-Fock assumes only one electron configuration is dominant
- RHF energies of the σ^2 and $(\sigma^*)^2$ configurations are *both* equal to $2h_{\sigma\sigma} + J_{\sigma\sigma}$ at $R_{AB} = \infty$. They are completely degenerate!
- Solution: need to mix in the other determinant by configuration interaction

Two-Determinant CI Fixes Minimal Basis H_2 Dissociation

$$|\Phi_{CI}\rangle = c_1|\phi_\sigma\overline{\phi}_\sigma\rangle + c_2|\phi_{\sigma^*}\overline{\phi}_{\sigma^*}\rangle$$

$$\begin{aligned}
E_{CI} &= \langle\Phi_{CI}|\hat{H}|\Phi_{CI}\rangle \\
&= \begin{bmatrix} c_1 & c_2 \end{bmatrix} \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \\
&= c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}
\end{aligned}$$

Evaluating the CI Energy

We can use Slater's Rules (see Intro to Electron Correlation) to evaluate the matrix elements H_{IJ}. We obtain

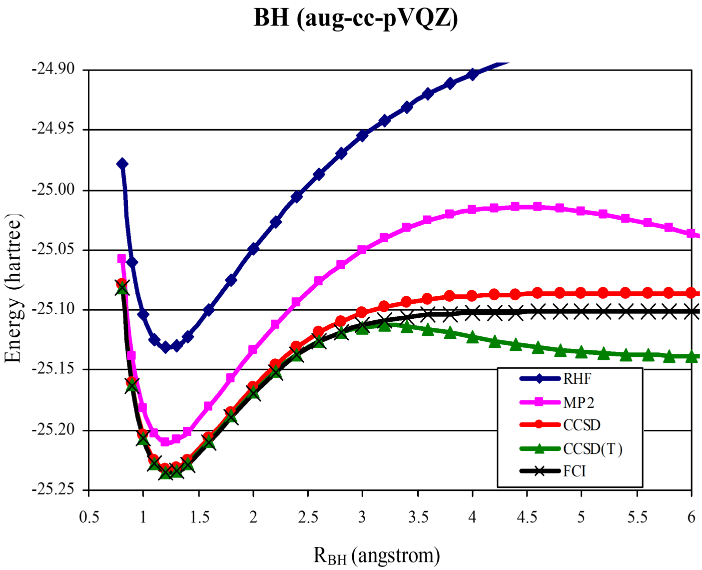
$$\begin{aligned} H_{11} &= \langle \phi_\sigma \overline{\phi}_\sigma | \hat{H} | \phi_\sigma \overline{\phi}_\sigma \rangle = 2h_{\sigma\sigma} + J_{\sigma\sigma} \\ H_{12} &= \langle \phi_\sigma \overline{\phi}_\sigma | \hat{H} | \phi_{\sigma^*} \overline{\phi}_{\sigma^*} \rangle = (\sigma\sigma^* | \sigma\sigma^*) \\ H_{21} &= \langle \phi_{\sigma^*} \overline{\phi}_{\sigma^*} | \hat{H} | \phi_\sigma \overline{\phi}_\sigma \rangle = (\sigma^*\sigma | \sigma^*\sigma) \\ H_{22} &= \langle \phi_{\sigma^*} \overline{\phi}_{\sigma^*} | \hat{H} | \phi_{\sigma^*} \overline{\phi}_{\sigma^*} \rangle = 2h_{\sigma^*\sigma^*} + J_{\sigma^*\sigma^*} \end{aligned}$$

$$E_{CI} = c_1^2 \left(2h_{\sigma\sigma} + J_{\sigma\sigma}\right) + c_2^2 \left(2h_{\sigma^*\sigma^*} + J_{\sigma^*\sigma^*}\right) + 2c_1 c_2 (\sigma\sigma^* | \sigma\sigma^*).$$

One can plug in for ϕ_σ and ϕ_{σ^*} (realizing integrals mixing A & B vanish as $R_{AB} \to \infty$) to show $E_{CI} = h_{AA} + h_{BB}$ if $c_1 = -c_2 = 1/\sqrt{2}$. At dissociation, 50/50 mix of σ^2 and $(\sigma^*)^2$!

Dynamical Correlation Does Not Fix Things In General

- Although doing CI works for minimal basis H_2, it does not work in general
- The orbitals need to be determined not for the one determinant ($|\phi_\sigma \overline{\phi}_\sigma\rangle$), but for both determinants at the same time!
- With regular RHF orbitals, even correlated methods (MP2, CISD, CCSD, CCSD(T)) can fail


BH (aug-cc-pVQZ)
Energy (hartree)
-24.90
-24.95
-25.00
-25.05
-25.10
-25.15
-25.20
-25.25
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
R_{BH} (angstrom)
RHF
MP2
CCSD
CCSD(T)
FCI

Near-Degeneracies Invalidate Perturbative Treatments

The σ and σ^* orbitals become degenerate at large distances; this is bad for energy denominators in perturbation theory.

$$\Delta E(\mathrm{MP2}) = -\sum_{a<b,r<s} \frac{|\langle ij||ab\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

The $(\sigma^*)^2$ configuration needs to be treated on an equal footing with $(\sigma)^2$, not as a perturbation.

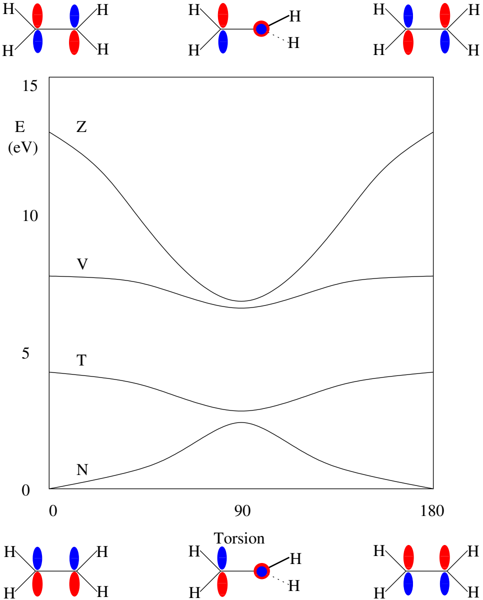


Figure 2: Krylov, Sherrill, Byrd, and Head-Gordon, *J. Chem. Phys.* **109**, 10669 (1998).

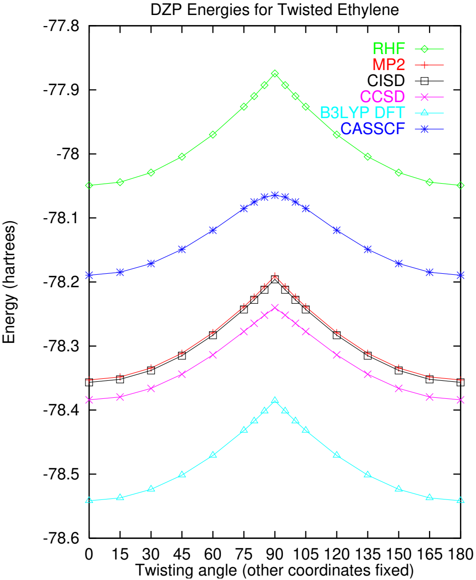
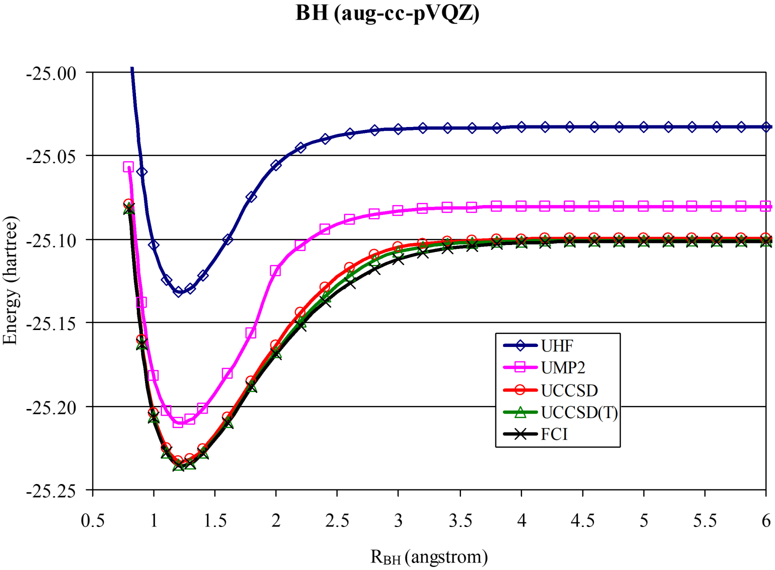
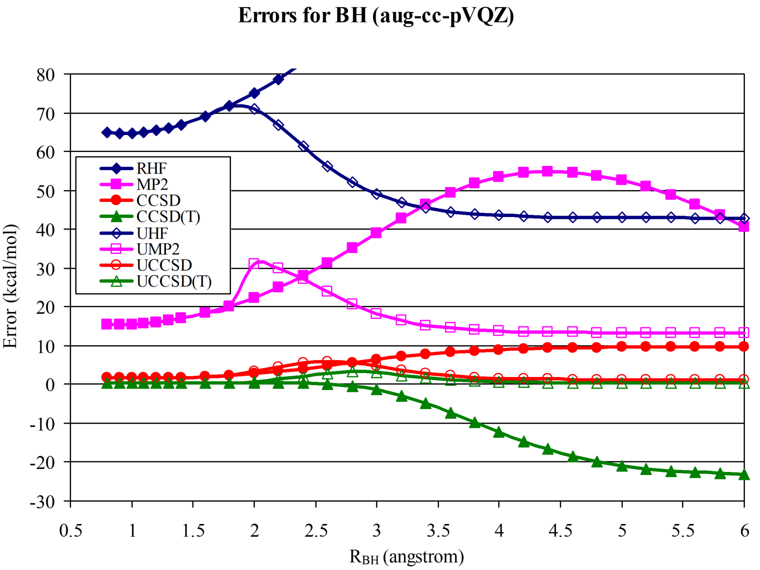


Figure 3: Krylov, Sherrill, Byrd, and Head-Gordon, *J. Chem. Phys.* **109**, 10669 (1998).

A Simple (“Cheat”) Solution

- Sometimes, we can get good energies using *unrestricted Hartree-Fock references*, especially when dynamical correlation is treated subsequently
- This has the major disadvantage that any spin-dependent properties are completely wrong; the wavefunction becomes a 50/50 mixture of singlet and triplet at dissociation
- Hard to find a UHF solution for a singlet which breaks spin symmetry; need to use `GUESS_MIX` option and have good luck!
- The energies may still exhibit problems
- Sometimes denote methods based on UHF reference with a ‘U’ prefix: UMP2, UCCSD, etc.


BH (aug-cc-pVQZ)
-25.00
-25.05
-25.10
-25.15
-25.20
-25.25
Energy (hartree)
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
R_BH (angstrom)
UHF
UMP2
UCCSD
UCCSD(T)
FCI


Errors for BH (aug-cc-pVQZ)
Error (kcal/mol)
80
70
60
50
40
30
20
10
0
-10
-20
-30
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
R_{BH} (angstrom)
RHF
MP2
CCSD
CCSD(T)
UHF
UMP2
UCCSD
UCCSD(T)

Non-Parallelity Error in Curves

Non-Parallelity Error (NPE): Difference between Min and Max error along curve; lower is better

Method	**BH**	**HF**	**CH_4**	**C_2**
CCSD	8.1	13.0	10.3	24.4
UMP2	17.9	25.9	17.1	40.7
UCCSD	4.7	6.0	5.1	25.4
UCCSD(T)	3.1	3.7	3.2	20.7
UB3LYP	-	5.9	11.4	-

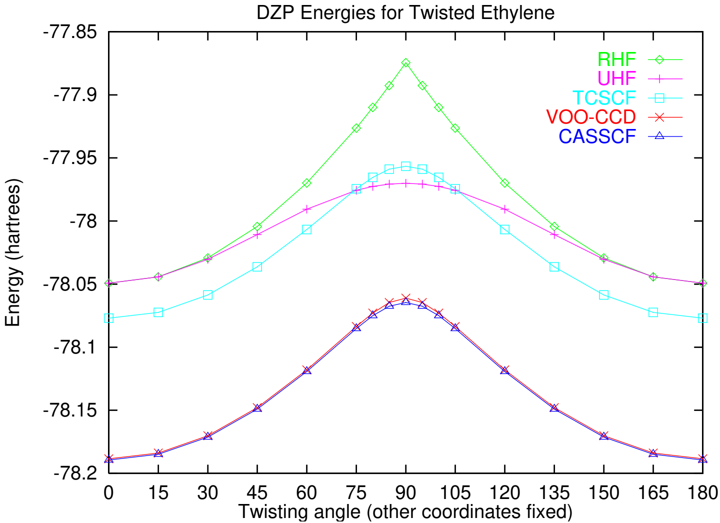


Figure 7: Krylov, Sherrill, Byrd, and Head-Gordon, *J. Chem. Phys.* **109**, 10669 (1998). UHF curve is qualitatively correct compared to higher-level curves (e.g., CASSCF), but is too shallow. TCSCF is better, this is an SCF based on two configurations (determinants).

Nondynamical Correlation Accounts for Near-Degeneracies

- We need to include *all nearly degenerate* electron configurations (or determinants) in our starting (“reference”) wavefunction
- Need to find orbitals which minimize the energy of *the mixture* of near-degenerate determinants: this is multi-configurational self-consistent-field (MCSCF)
- A special case of MCSCF which takes all possible determinants (full CI) in a given “active” orbital space is complete-active-space self-consistent-field (CASSCF)
- Need to use multi-configurational references for subsequent treatment of dynamical correlation: multi-reference CI (MRCI), multi-reference PT (e.g., CASPT2, NEVPT2), multi-reference CC, etc.

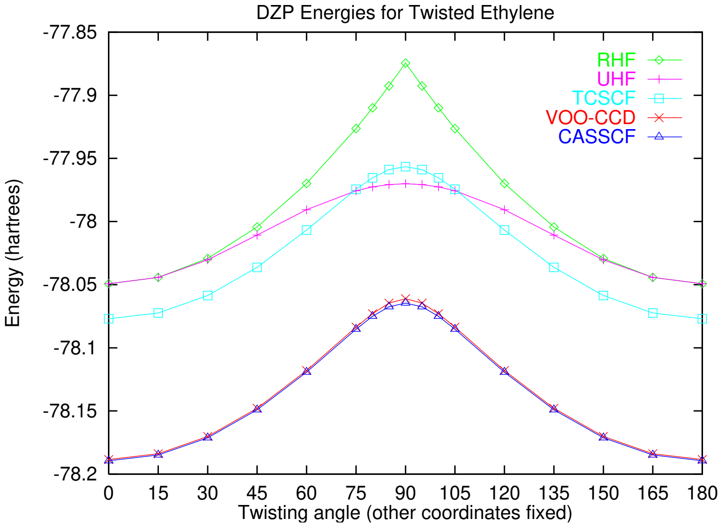
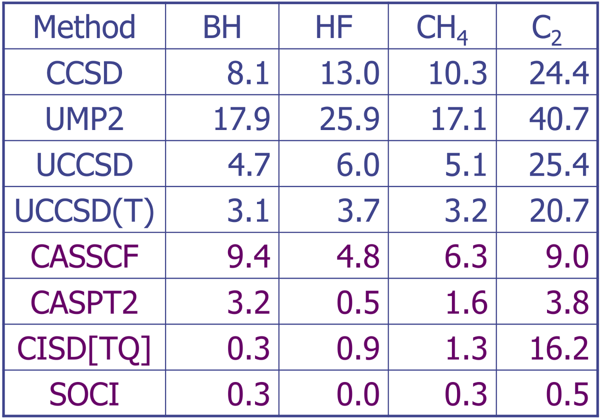


Figure 8: Krylov, Sherrill, Byrd, and Head-Gordon, *J. Chem. Phys.* **109**, 10669 (1998). CASSCF curve looks good. VOO-CCD, an analog of CASSCF based on coupled-cluster doubles, also works well.

Superiority of Multireference Methods



Method	BH	HF	CH_4	C_2
CCSD	8.1	13.0	10.3	24.4
UMP2	17.9	25.9	17.1	40.7
UCCSD	4.7	6.0	5.1	25.4
UCCSD(T)	3.1	3.7	3.2	20.7
CASSCF	9.4	4.8	6.3	9.0
CASPT2	3.2	0.5	1.6	3.8
CISD[TQ]	0.3	0.9	1.3	16.2
SOCI	0.3	0.0	0.3	0.5

Figure 9: J. S. Sears and C. D. Sherrill *Mol. Phys.* **103**, 803 (2005). SOCI is a "second-order CI" that includes all single & double excitations out of all determinants in the CASSCF (i.e., CASSCF-MRCISD). CISD[TQ] is approximation to SOCI that deletes determinants that excite more than 4 electrons compared to the RHF determinant.

The Active Space

- Methods like CASSCF are based on the selection of an active orbital space instead of a selection of individual determinants; easier for the user
- But now we still have to choose an active space!
- The *active space* is a subset of molecular orbitals whose occupations *change* when we examine all the *most important* determinants
- But ... we don't necessarily know which orbitals ahead of time!

Schemes for Picking an Active Space

- It is easier for the user if they select some pre-determined scheme for picking the active orbitals
- Unfortunately, there is not necessarily a scheme that always wins
- Some competing approaches have been presented in the literature
- Prior experience is helpful

Some Possible Active Space Strategies

1:1
One active virtual orbital per active occupied orbital

valence
All valence orbitals

minimal
Only relevant bonding/antibonding pairs

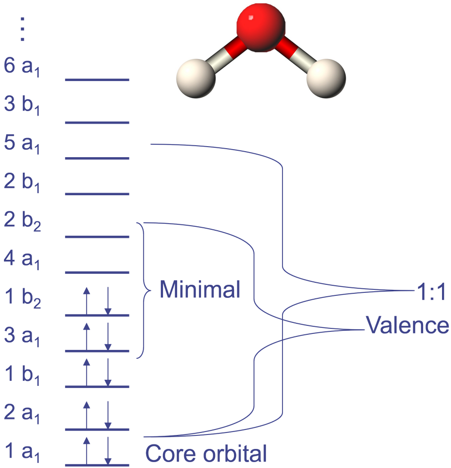


Figure 10: J. S. Sears and C. D. Sherrill *Mol. Phys.* **103**, 803 (2005).

H_2O Double Dissociation

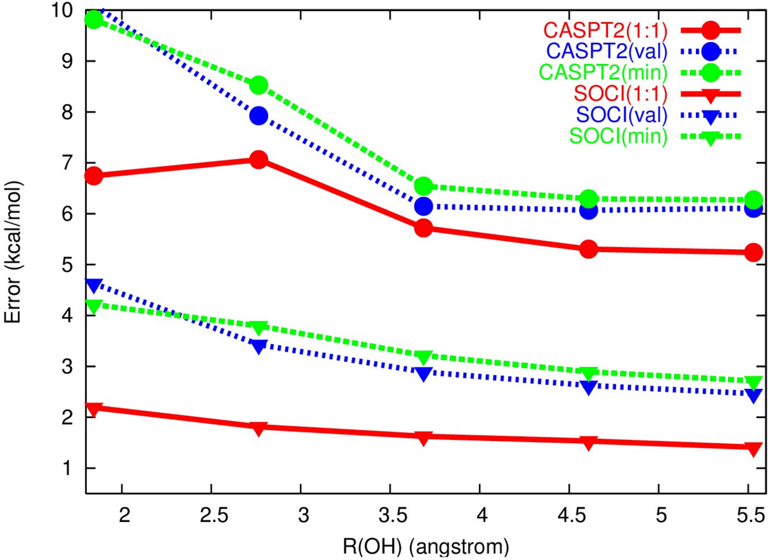


Figure 11: J. S. Sears and C. D. Sherrill *Mol. Phys.* **103**, 803 (2005).

Active Space Strategy Comparison

		HF	CH_4	H_2O	N_2
		6-31G**	6-31G*	cc-pVDZ	cc-pVDZ
CASSCF	1:1	4.83	6.33	0.65	22.93
	Val	17.96		24.78	15.03
	Min	18.66	9.25	25.87	14.59
CASPT2	1:1	0.49	1.57	1.83	1.88
	Val	2.78		4.03	3.56
	Min	0.47	1.22	3.55	5.20
SOCI	1:1	0.04	0.31	0.78	0.75
	Val	3.20		2.16	0.72
	Min	0.98	0.60	1.50	0.86

Figure 12: J. S. Sears and C. D. Sherrill *Mol. Phys.* **103**, 803 (2005).

Summary

- Bond-breaking and bond-making reactions are hard to study accurately with quantum chemical methods, particularly at the dissociation limit
- Transition states may or may not require multiconfigurational treatment, depending on the degree of degeneracy
- When electron configurations become exactly or very nearly degenerate, a multi-configurational/multi-reference treatment may be necessary
- Sometimes spin-broken UHF references will work for energies but not necessarily for properties
- This is an active area of current research