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] Data from Harrision, 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" correlation.

What Causes the Nondynamical Correlation?

- Recall the correlation energy is the difference between Full CI and Hartree-Fock.
- We know 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

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

Simplified Notation for Expanded Determinant

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

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

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.*

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 $R_{AB} \rightarrow \infty$
- 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

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

$$\begin{aligned}
E_{CI} &= \langle\Phi_{CI}|\hat{H}|\Phi_{CI}\rangle \\
&= \begin{pmatrix} c_1 & c_2 \end{pmatrix} \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\
&= c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2H_{12}
\end{aligned}$$

Evaluating the CI Energy

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

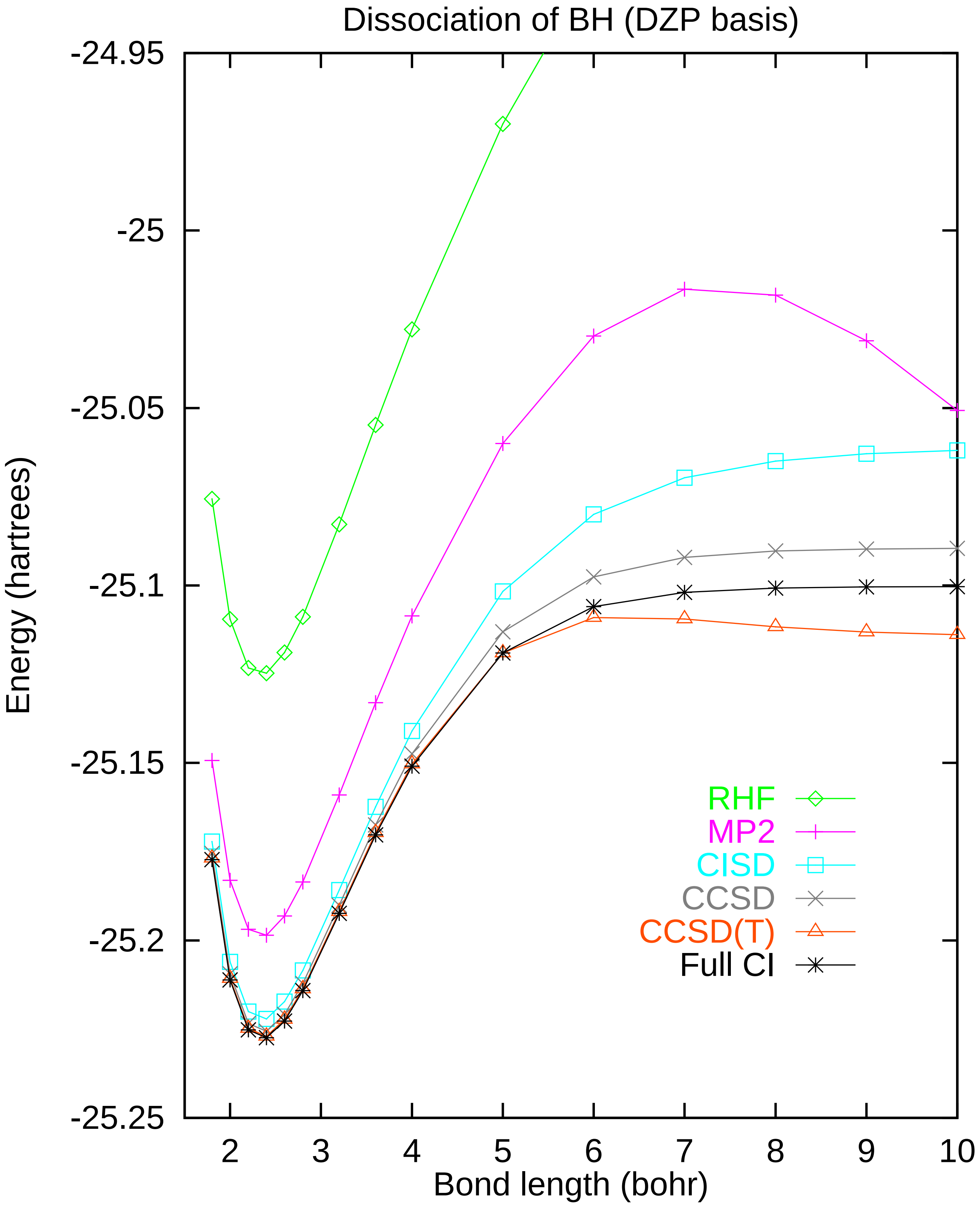
$$\begin{aligned}
H_{11} &= \langle \phi_\sigma \overline{\phi}_\sigma | \hat{H} | \phi_\sigma \overline{\phi}_\sigma \rangle = 2h_{\sigma\sigma} + J_{\sigma\sigma} \\
H_{12} &= \langle \phi_\sigma \overline{\phi}_\sigma | \hat{H} | \phi_{\sigma^*} \overline{\phi}_{\sigma^*} \rangle = (\sigma\sigma^*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

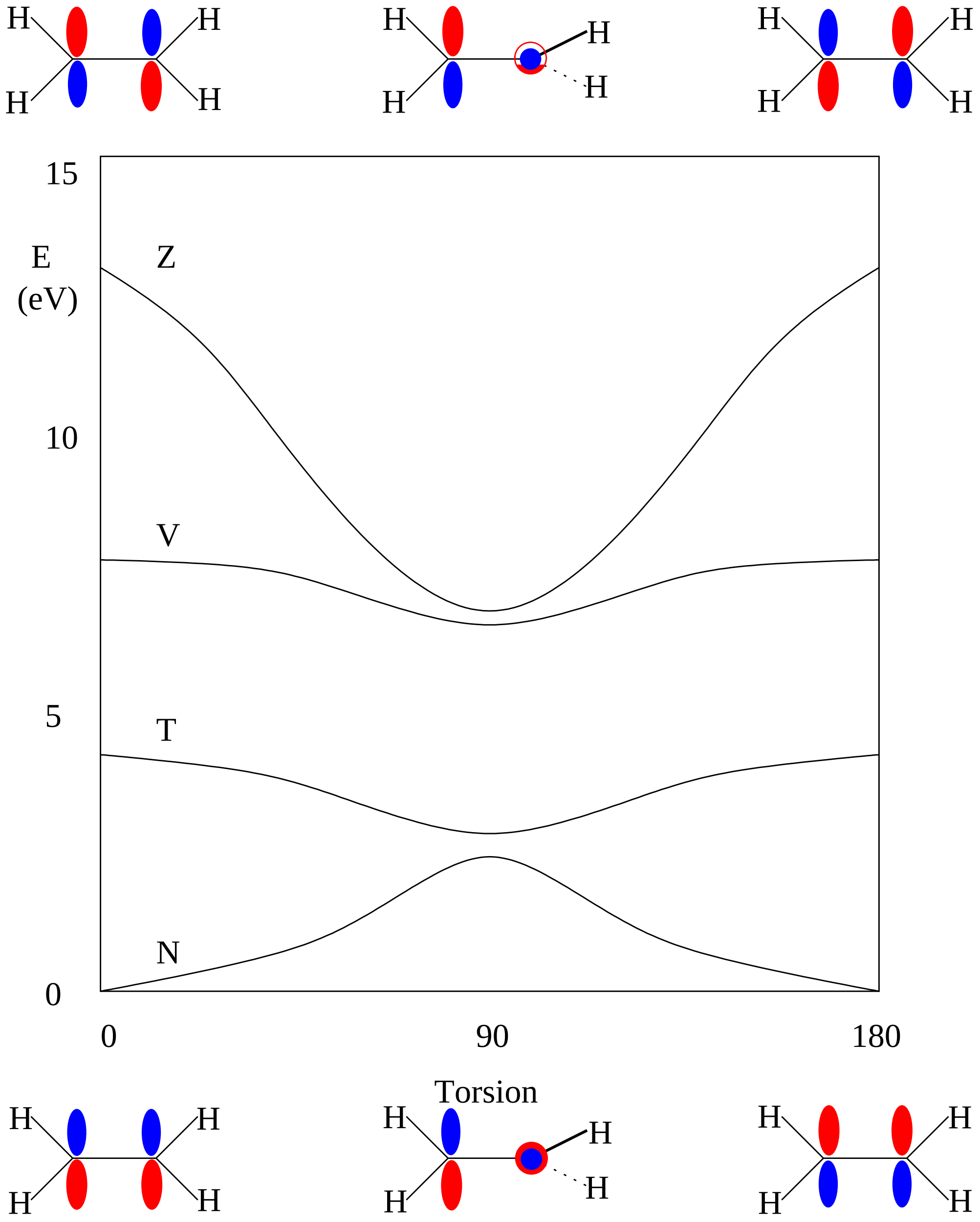
$$E_{CI} = c_1^2 \left(2h_{\sigma\sigma} + J_{\sigma\sigma}\right) + c_2^2 \left(2h_{\sigma^*\sigma^*} + J_{\sigma^*\sigma^*}\right) + 2c_1 c_2 (\sigma\sigma^* | \sigma\sigma^*).$$

One can plug in for ϕ_σ and ϕ_{σ^*} (realizing integrals mixing A & B vanish as $R_{AB} \rightarrow \infty$) 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 $(\sigma^*)^2$!

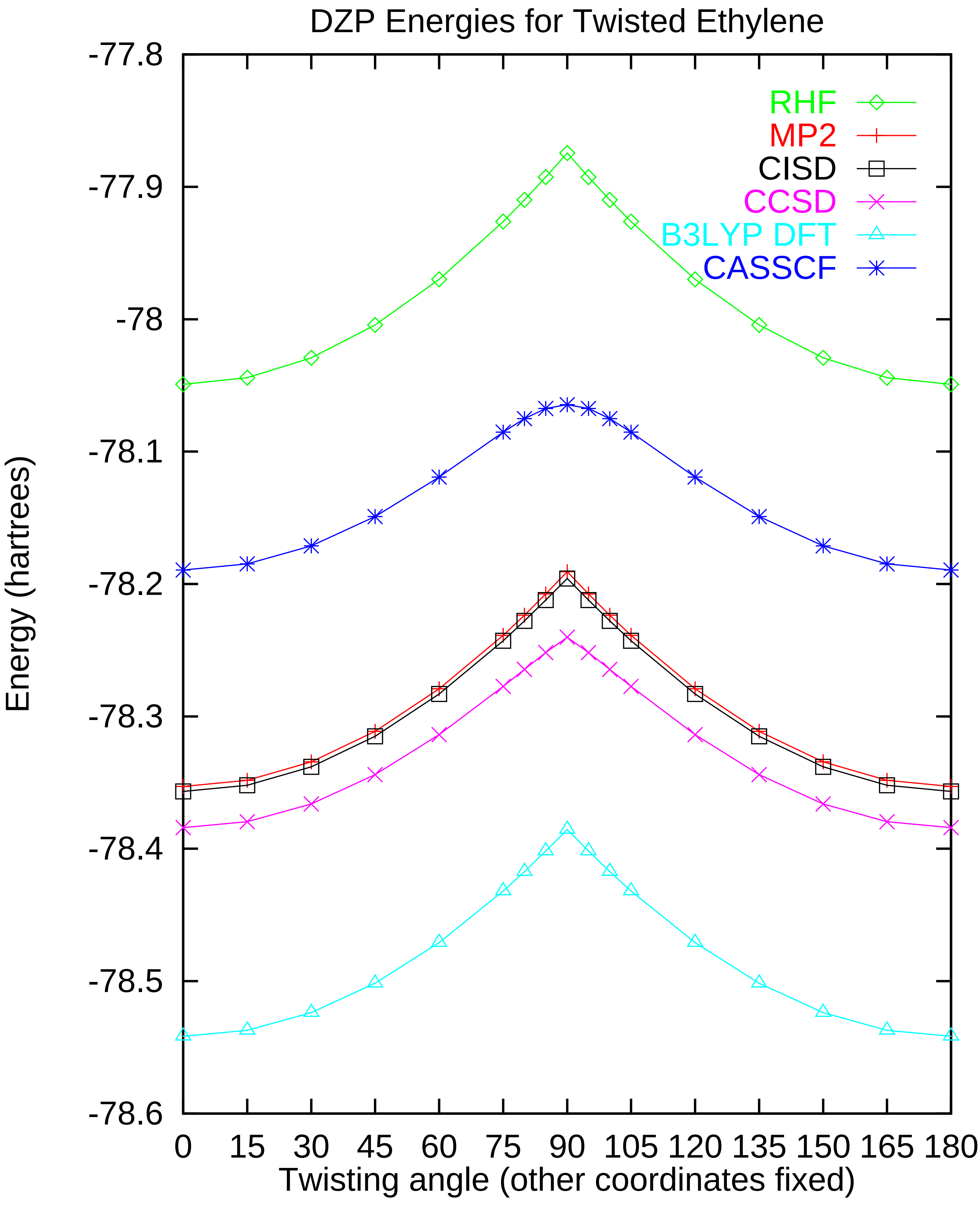
Dynamical Correlation Does Not Fix Things In General

- 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


Dissociation of BH (DZP basis)
-24.95
-25
-25.05
-25.1
-25.15
-25.2
-25.25
Energy (hartrees)
2
3
4
5
6
7
8
9
10
Bond length (bohr)
RHF
MP2
CISD
CCSD
CCSD(T)
Full CI



H
H
H
H
15
10
5
0
E
(eV)
Z
V
T
N
0
90
180
Torsion


DZP Energies for Twisted Ethylene
Energy (hartrees)
-77.8
-77.9
-78
-78.1
-78.2
-78.3
-78.4
-78.5
-78.6
0
15
30
45
60
75
90
105
120
135
150
165
180
Twisting angle (other coordinates fixed)
RHF
MP2
CISD
CCSD
B3LYP DFT
CASSCF

Near-Degeneracies Invalidate Perturbative Treatments

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

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

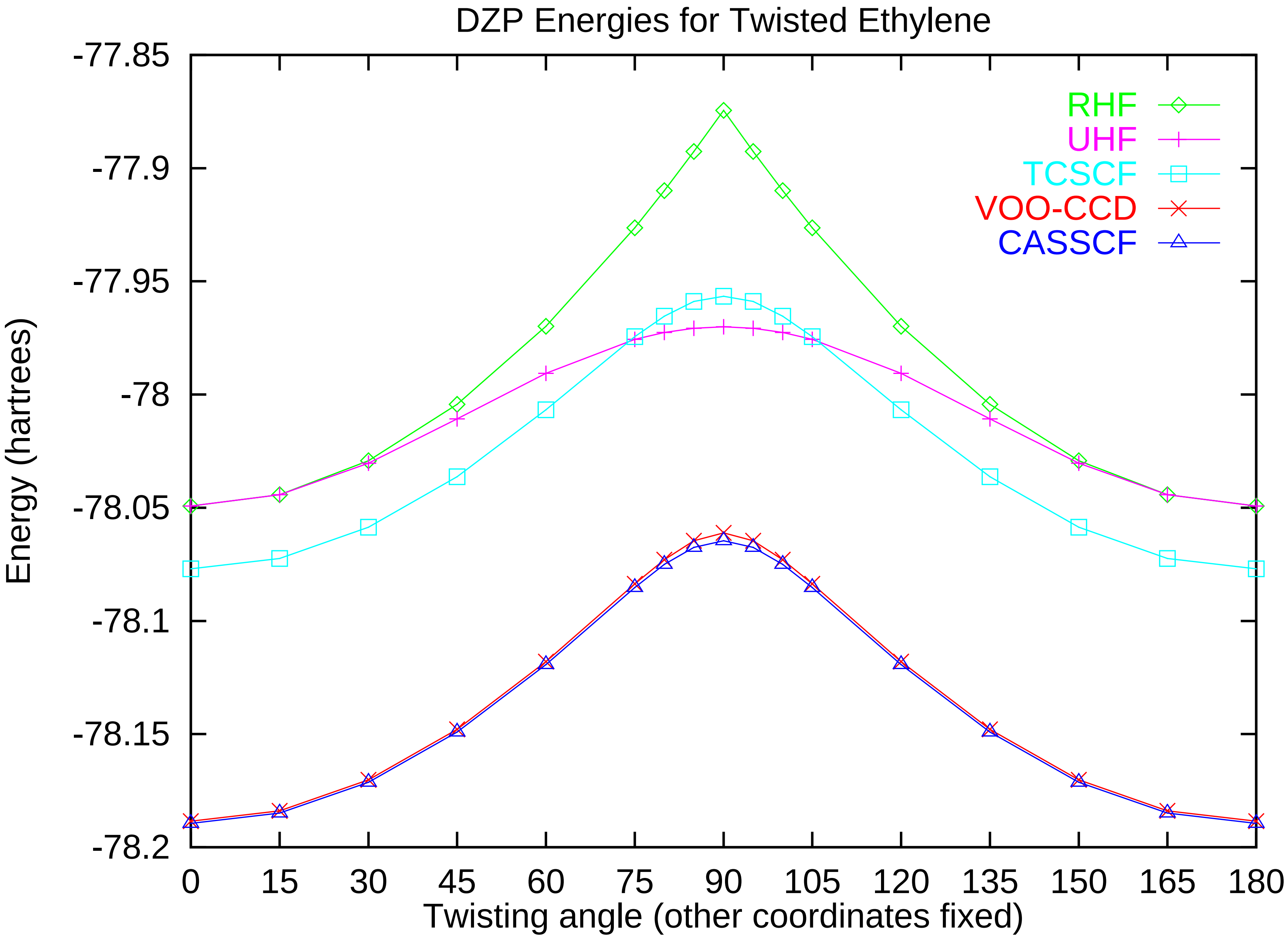
The $(\sigma^*)^2$ configuration needs to be treated on an equal footing with $(\sigma)^2$, not as a perturbation.

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, multi-reference PT, multi-reference CC, CASPT2, ...

A Simpler ("Cheat") Solution

- Multi-reference methods are extraordinarily complex to program and to use
- 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!


DZP Energies for Twisted Ethylene
-77.85
-77.9
-77.95
-78
-78.05
-78.1
-78.15
-78.2
Energy (hartrees)
0
15
30
45
60
75
90
105
120
135
150
165
180
Twisting angle (other coordinates fixed)
RHF
UHF
TCSCF
VOO-CCD
CASSCF

Summary

- Bond-breaking and bond-making reactions are hard to study accurately with quantum chemical methods, particularly at the dissociation limit
- 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 properties
- This is an active area of current research