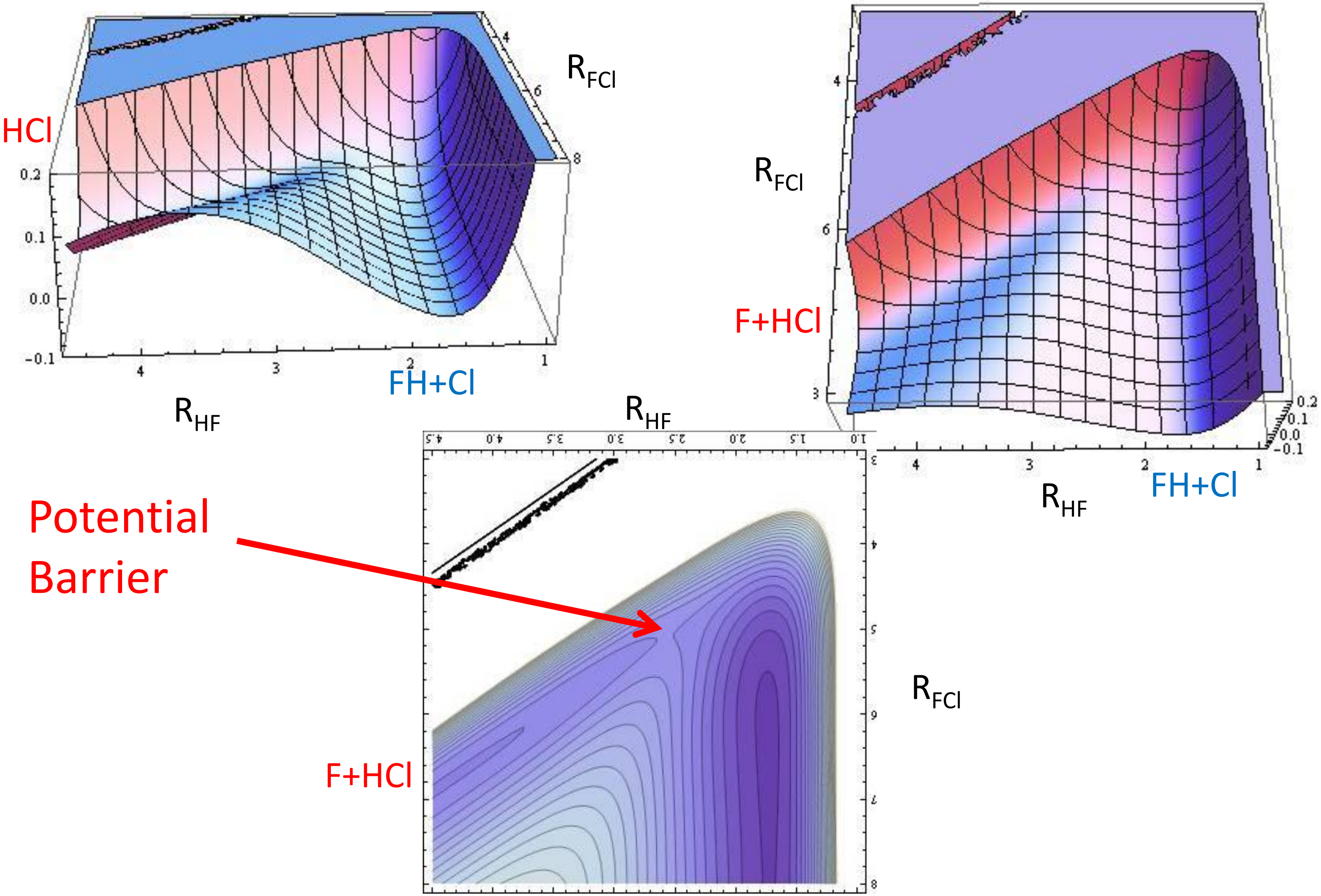
Reaction Barriers

F+HCl→FH+Cl Potential Energy Surface

Hydrogen Abstraction Reaction, break a HCl bond form a HF bond



F+HCl

R_{FCl}

R_{HF}

FH+Cl

R_{FCl}

F+HCl

R_{HF}

FH+Cl

R_{HF}

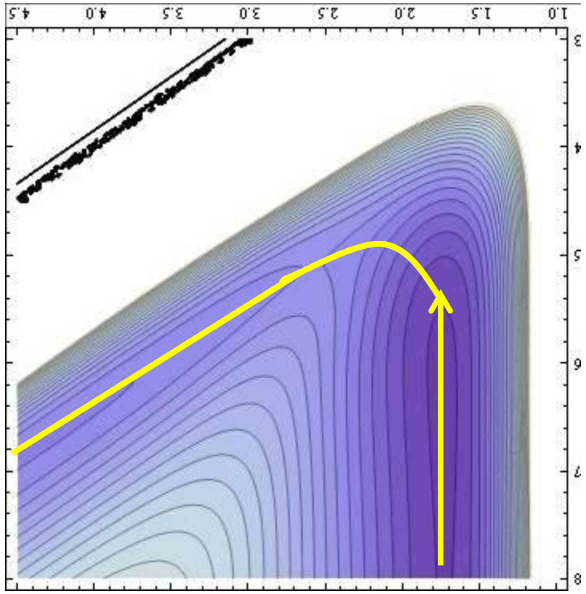
Potential Barrier

R_{FCl}

F+HCl

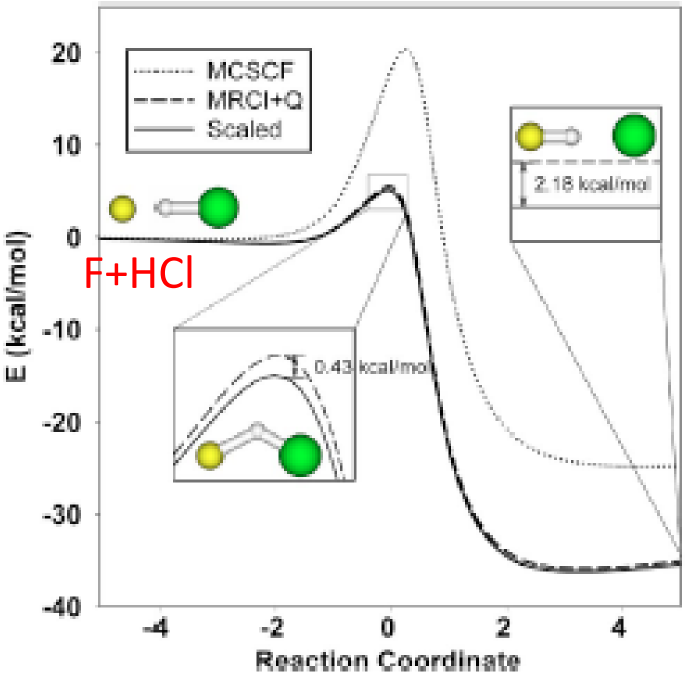
FH+Cl

Potential Energy Curve along IRC



F+HCl

FH+Cl



FH+Cl

You need enough energy to go over the potential barrier to react!

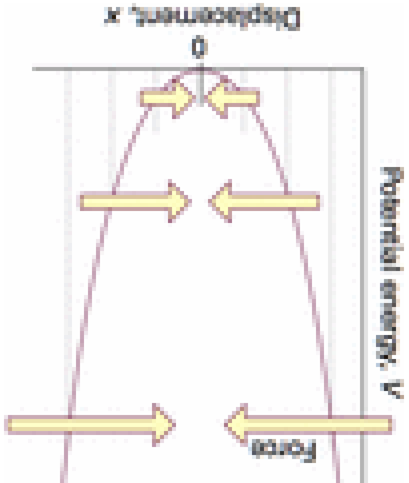
The minimum energy path that connect the barrier with reactant and product is called intrinsic reaction path

For F+HCl case you need about 5 kcal/mol of for reaction to occur

How to quantify Barrier?

- At the barrier the first derivative is zero and the second derivative is negative for one degree of freedom and the rest are always positive. In Gaussian you can use the freq keyword to check if there is imaginary frequency

Harmonic Oscillator approximation at barrier



$$F = m\frac{d^2x}{dt^2} = -kx$$

k: force constant

$$\omega = \sqrt{\frac{k}{m}}$$

In the case of barrier the force constant k is negative so omega is imaginary

Find the potential Barrier

- Input a geometry that is close to the barrier and use the keyword Opt=(ts)
- Check if the optimized structure is a barrier by calculating the frequency by the freq keyword
- Use the IRC keyword to follow the reaction to the reactant and product keyword IRC(forward), IRC(backward)

Transition State Theory

- Once you have the barrier you can estimate the thermal rate constant of the reaction from the calculation results! (Assuming that the reaction proceeds along the IRC)

$$A + B \rightarrow \underset{\uparrow}{(AB)^{+}} \rightarrow \text{product}$$

Activated Complex
(Geomtry at Potential Barrier)

$$-\left(\frac{d[A]}{dt}\right) = \frac{k_B T}{h} K^{+}[A][B]$$

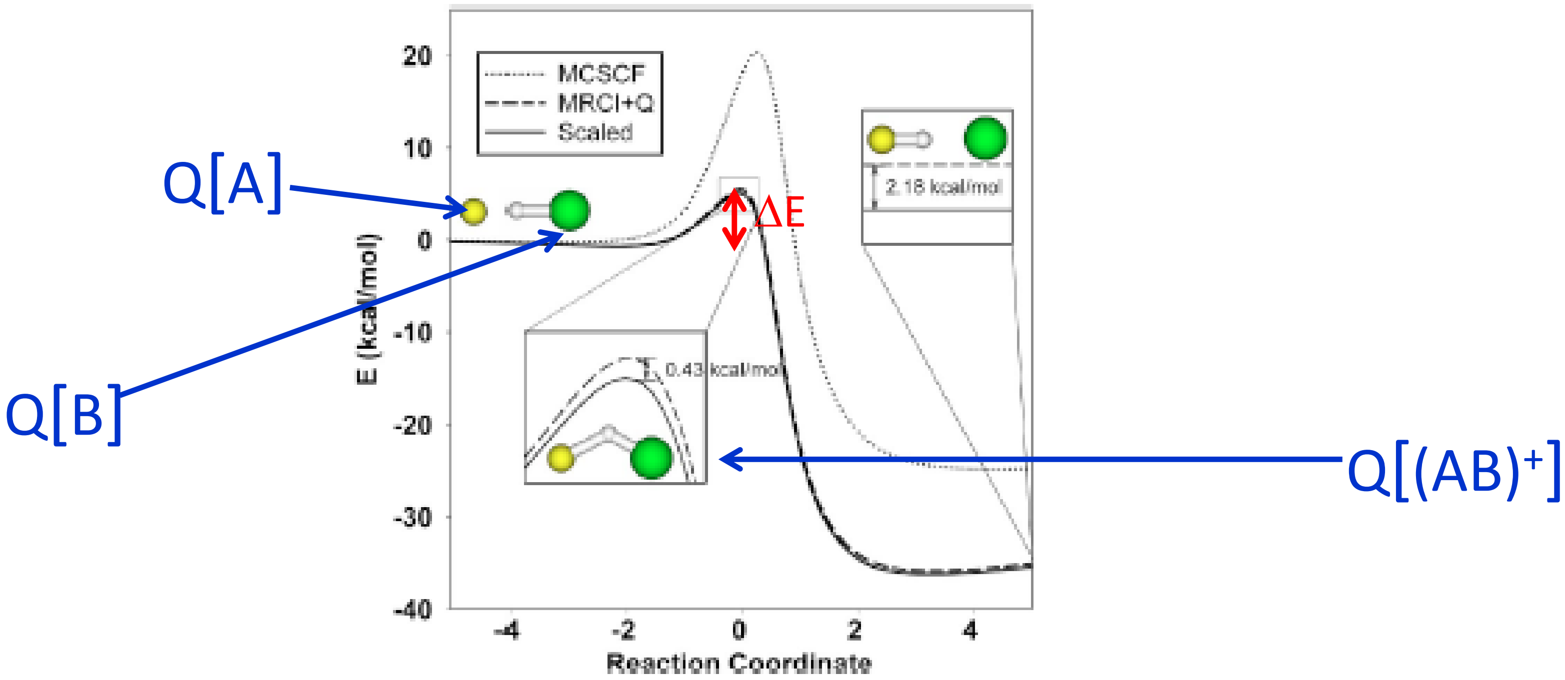
K^{+} is the thermal rate constant that depends on temperature

Things Needed To Calculate Rate Constant

$$K^{+} = \frac{Q\left[(AB)^{+}\right]}{Q[A]Q[B]}\exp\left[-\frac{\Delta E}{k_B T}\right]$$

Q is the partition function of the respective molecules $\sum_{i=1}^{\infty} e^{-\frac{\epsilon_i}{k_B T}}$

ΔE is the energy difference from the reactant to the barrier



Q[A]

Q[B]

ΔE

Q[(AB)$^{+}$]

Partition Function 1

$$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P}$$

Usually you consider 1atm pressure

$$\begin{aligned} Q_{electronic} &= D_0 \exp\left[-\varepsilon_0 / k_B T\right] + D_1 \exp\left[-\varepsilon_1 / k_B T\right] \\ &\quad + D_2 \exp\left[-\varepsilon_2 / k_B T\right] + \ldots \\ &= D_0 \end{aligned}$$

D is the degeneracy of the electronic state, usually only consider ground electronic state

Partition Function 2

$$Q_{rot} = \frac{\pi^{1/2}}{\sigma_r}\left(\frac{T^{3/2}}{(\theta_A\theta_B\theta_C)^{1/2}}\right) \qquad \theta_{A,B,C} = \frac{h^2}{8\pi^2 I_{A,B,C} k_B}$$

I is the moment of inertia around the respective axis

$$Q_{vib} = \prod_{i}^{Nvib} \frac{1}{1 - \exp\left[-\frac{h\nu_i}{k_B T}\right]}$$

ν_i is the vibrational frequency of the i-th vibrational mode

Trial Reactions

- Hydrogen abstraction reaction: F+HCl
- H_2+CO→H_2CO→HCOH(trans)→HCOH(cis) versus H_2+CO→ HCOH(cis)
- H_2COO rotation barrier
- H^+Methanol CH3 internal rotation
- H_2CCH_2 rotation

Beyond Hartree Fock: Coupled Cluster Singles and Doubles

Second quantization
(creation and annihilation operators)

Operators for creating an orbital a is written as $\hat{a}^{\dagger}$

Operators for annihilating (removing) an orbital j is written as $\hat{j}$

So using these operators we can write one electron excitation as

$$D_i^a = \hat{a}^+\hat{i}D_0$$

And the two electron excitation as

$$D_{ij}^{ab} = \hat{b}^+\hat{a}^+\hat{i}\hat{j}D_0$$

*In my notes i,j,k,l will be used for occupied orbital and a,b,c,d will be used for unoccupied orbitals

Coupled Cluster

- Coupled cluster is a smarter way to do CI intended for ground electronic state

We have Hartree Fock solution

$$D_0 = \left\| \psi_1 \quad \psi_2 \quad \ldots\ldots\ldots \psi_i \psi_j \ldots\ldots\ldots\ldots\ldots \quad \psi_n \right\|$$

$$\Psi_{CC} = \exp^{\hat{T}} D_0$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots \hat{T}_{l\max}$$

$\hat{T}_n$ is n electron excitation operator

$$\hat{T}_1 = \sum_i \sum_a t_i^a \hat{a}^\dagger \hat{\imath}$$

t_i^a amplitude/contribution of that excitation

$$\hat{T}_2 = \sum_i \sum_{j \neq i} \sum_a \sum_{b \neq a} t_{ij}^{ab} \hat{a}^\dagger \hat{\imath}$$

We need to find t for all the n electron excitation operators what use

Cluster Expansion

$$exp(\hat{T})D_0 = \left[1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots)^2 + \cdots\right]D_0$$

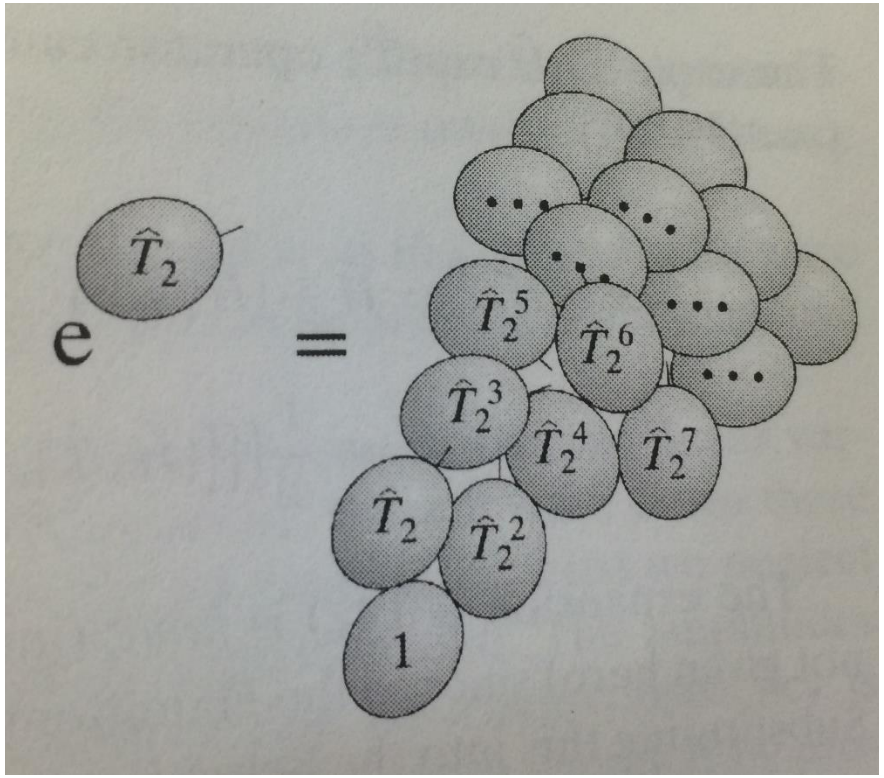
$$= [\hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4]D_0$$

$$\hat{C}_1 = \hat{T}_1$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2$$

$$\hat{C}_3 = \hat{T}_3 + \frac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2$$

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{24}\hat{T}_1^4 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2$$



for each C_n experience says that terms with 2 electron excitation operators contribute the most

Couple Cluster how to solve?

$$\hat{H}\Psi_{CC} = E\Psi_{CC} \quad \Longrightarrow \quad \hat{H}exp(\hat{T})D_0 = Eexp(\hat{T})D_0$$

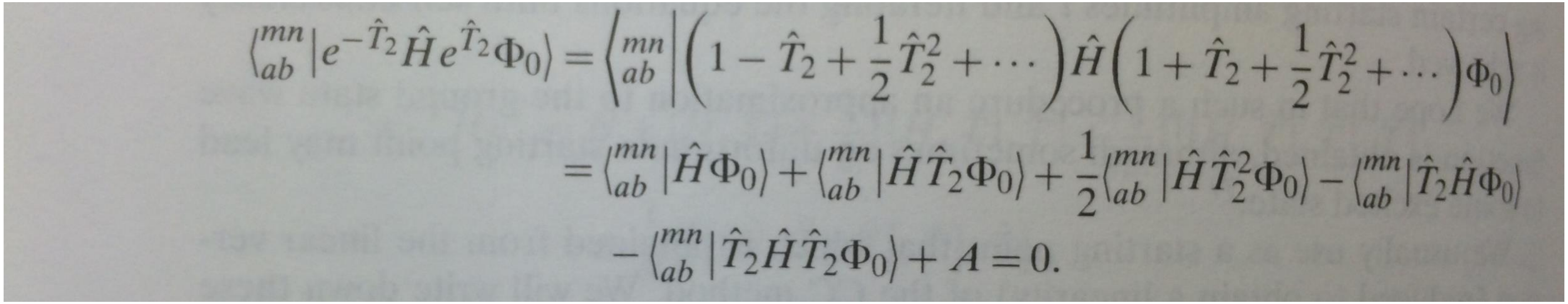
So $exp(-\hat{T})\hat{H}exp(\hat{T})D_0 = ED_0$

If we multiply some electron excited states to the left and integrate what will we get

$$\langle D_{ijkl\ldots}^{abcd\ldots}|exp(-\hat{T})\hat{H}exp(\hat{T})|D_0\rangle = E\langle D_{ijkl\ldots}^{abcd\ldots}|D_0\rangle = 0$$

There are the same number of equations like above as the number of t's that we want to know

CCD working out the equations

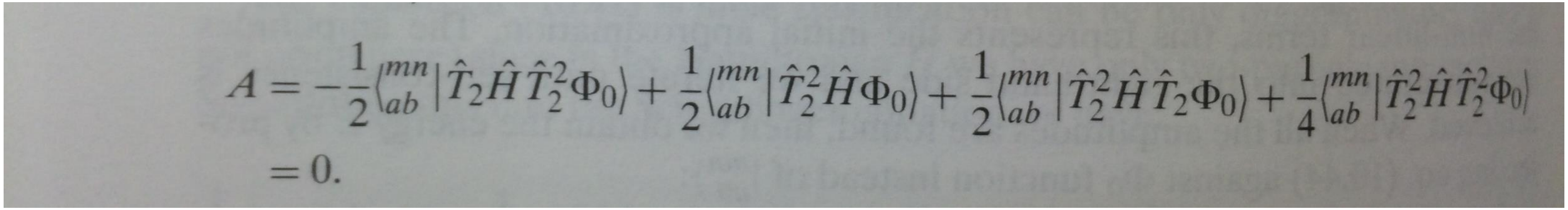


$$\langle {}^{mn}_{ab} | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} \Phi_0 \rangle = \left\langle {}^{mn}_{ab} \middle| \left(1 - \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \cdots\right) \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \cdots\right) \Phi_0 \right\rangle$$

$$= \langle {}^{mn}_{ab} | \hat{H} \Phi_0 \rangle + \langle {}^{mn}_{ab} | \hat{H} \hat{T}_2 \Phi_0 \rangle + \frac{1}{2} \langle {}^{mn}_{ab} | \hat{H} \hat{T}_2^2 \Phi_0 \rangle - \langle {}^{mn}_{ab} | \hat{T}_2 \hat{H} \Phi_0 \rangle$$

$$- \langle {}^{mn}_{ab} | \hat{T}_2 \hat{H} \hat{T}_2 \Phi_0 \rangle + A = 0.$$

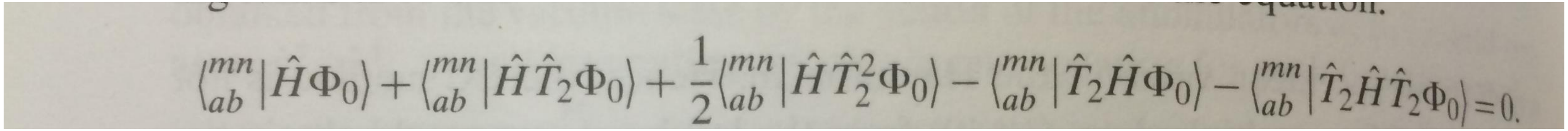
But



$$A = -\frac{1}{2} \langle {}^{mn}_{ab} | \hat{T}_2 \hat{H} \hat{T}_2^2 \Phi_0 \rangle + \frac{1}{2} \langle {}^{mn}_{ab} | \hat{T}_2^2 \hat{H} \Phi_0 \rangle + \frac{1}{2} \langle {}^{mn}_{ab} | \hat{T}_2^2 \hat{H} \hat{T}_2 \Phi_0 \rangle + \frac{1}{4} \langle {}^{mn}_{ab} | \hat{T}_2^2 \hat{H} \hat{T}_2^2 \Phi_0 \rangle$$

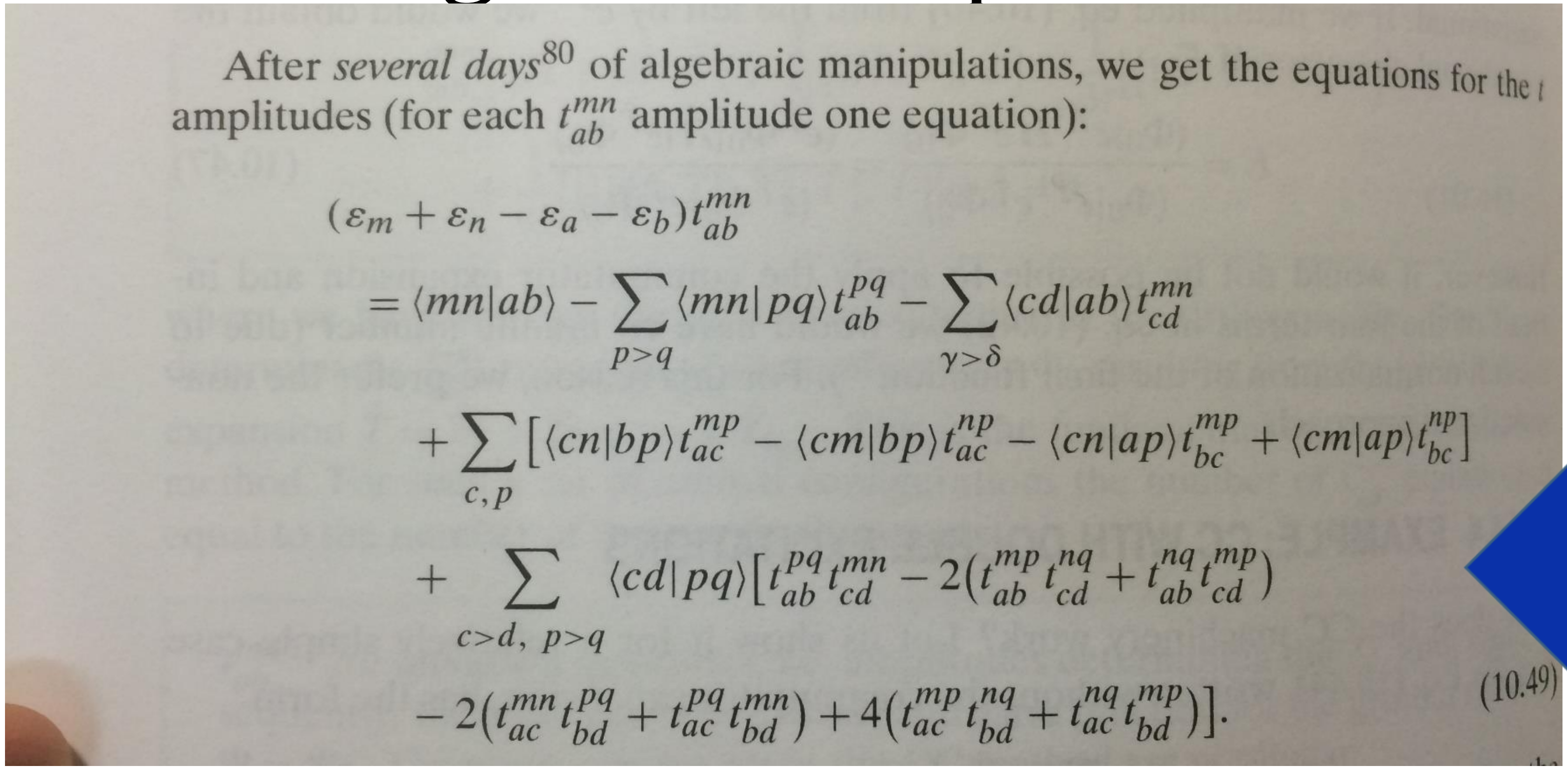
$$= 0.$$

So



$$\langle {}^{mn}_{ab} | \hat{H} \Phi_0 \rangle + \langle {}^{mn}_{ab} | \hat{H} \hat{T}_2 \Phi_0 \rangle + \frac{1}{2} \langle {}^{mn}_{ab} | \hat{H} \hat{T}_2^2 \Phi_0 \rangle - \langle {}^{mn}_{ab} | \hat{T}_2 \hat{H} \Phi_0 \rangle - \langle {}^{mn}_{ab} | \hat{T}_2 \hat{H} \hat{T}_2 \Phi_0 \rangle = 0.$$

CCD working out the equations



After *several days*[80] of algebraic manipulations, we get the equations for the t amplitudes (for each t_{ab}^{mn} amplitude one equation):

$$\begin{aligned}
&(\varepsilon_m+\varepsilon_n-\varepsilon_a-\varepsilon_b)t_{ab}^{mn}\\
&\quad=\langle mn|ab\rangle-\sum_{p>q}\langle mn|pq\rangle t_{ab}^{pq}-\sum_{\gamma>\delta}\langle cd|ab\rangle t_{cd}^{mn}\\
&\qquad+\sum_{c,p}\left[\langle cn|bp\rangle t_{ac}^{mp}-\langle cm|bp\rangle t_{ac}^{np}-\langle cn|ap\rangle t_{bc}^{mp}+\langle cm|ap\rangle t_{bc}^{np}\right]\\
&\qquad+\sum_{c>d,\ p>q}\langle cd|pq\rangle\left[t_{ab}^{pq}t_{cd}^{mn}-2\left(t_{ab}^{mp}t_{cd}^{nq}+t_{ab}^{nq}t_{cd}^{mp}\right)\right.\\
&\qquad\left.-2\left(t_{ac}^{mn}t_{bd}^{pq}+t_{ac}^{pq}t_{bd}^{mn}\right)+4\left(t_{ac}^{mp}t_{bd}^{nq}+t_{ac}^{nq}t_{bd}^{mp}\right)\right].
\end{aligned}\qquad(10.49)$$

Put that into the right hand side and solve

First only consider first term $t_{ab}^{mn}=\dfrac{\langle mn|ab\rangle}{\epsilon_m+\epsilon_n-\epsilon_a-\epsilon_b}$

Repeat until the input t and right side t become same

T1 diagnostic empirical relation ship

$$\Psi_{CI} = C_0 D_0 + \sum_{i,a} C_i^a D_i^a + \sum_{i<j,a<b} C_{ij}^{ab} D_{ij}^{ab} + \sum_{i<j<k,a<b<c} C_{ijk}^{abc} D_{ijk}^{abc} + \ldots$$

When will Hartree Fock be a good solution?

When C_0 is ~1

When Hartee Fock solution is good, Brillouin's theorem says one electron excitation should be small

$$\hat{T}_1 = \sum_i \sum_a t_i^a \hat{a}^{\dagger} \hat{\imath}$$

$$T1\ Diag = \sqrt{\frac{\sum_i^{occ} \sum_a^{unocc} \left(t_i^a\right)^2}{Number\ of\ valence\ electrom}}$$

T1 Diagnostic papers

- TJ Lee et al.Theor. Chim. Acta, 75, 81- (89); Int J Qaunt Chem. Quant Chem Sym. 23, 119- (89) Looked at examples of several molecule’s C_0 and $T1\ diag$ and come up with an empirical number

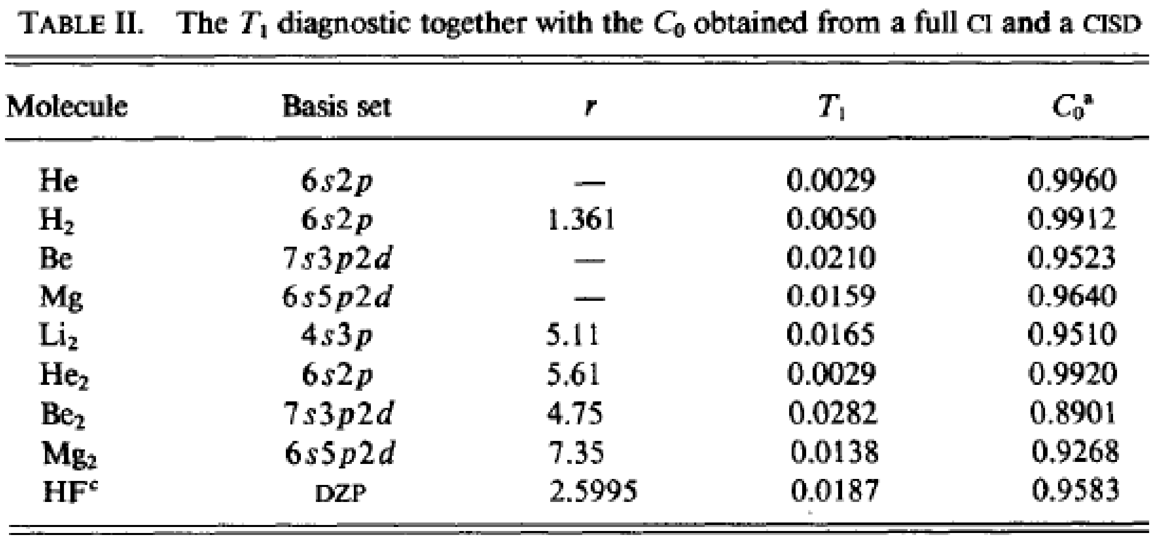


TABLE II. The T_1 diagnostic together with the C_0 obtained from a full CI and a CISD

Molecule	Basis set	r	T_1	C_0[a]
He	$6s2p$	—	0.0029	0.9960
H_2	$6s2p$	1.361	0.0050	0.9912
Be	$7s3p2d$	—	0.0210	0.9523
Mg	$6s5p2d$	—	0.0159	0.9640
Li_2	$4s3p$	5.11	0.0165	0.9510
He_2	$6s2p$	5.61	0.0029	0.9920
Be_2	$7s3p2d$	4.75	0.0282	0.8901
Mg_2	$6s5p2d$	7.35	0.0138	0.9268
HF[c]	DZP	2.5995	0.0187	0.9583

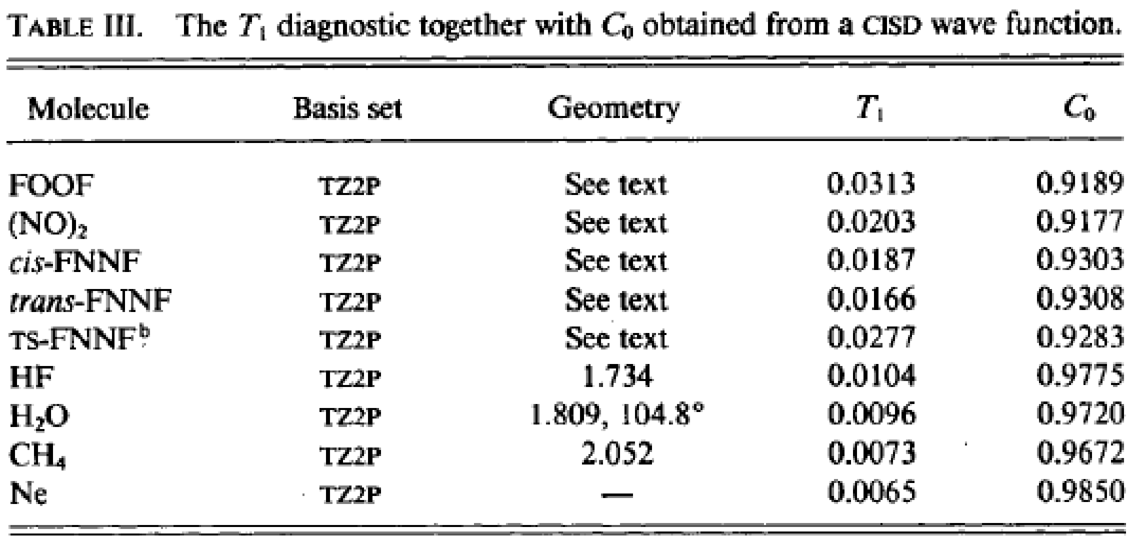
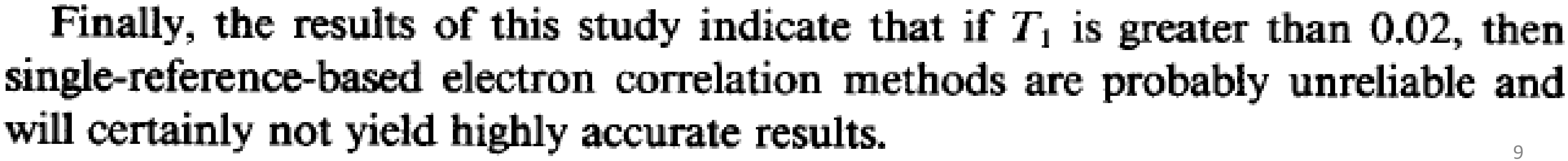


TABLE III. The T_1 diagnostic together with C_0 obtained from a CISD wave function.

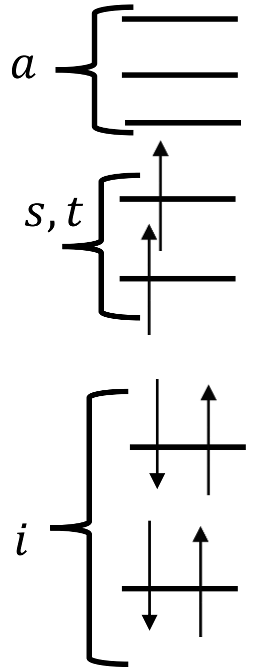
Molecule	Basis set	Geometry	T_1	C_0
FOOF	TZ2P	See text	0.0313	0.9189
$(NO)_2$	TZ2P	See text	0.0203	0.9177
cis-FNNF	TZ2P	See text	0.0187	0.9303
trans-FNNF	TZ2P	See text	0.0166	0.9308
TS-FNNF[b]	TZ2P	See text	0.0277	0.9283
HF	TZ2P	1.734	0.0104	0.9775
H_2O	TZ2P	1.809, 104.8°	0.0096	0.9720
CH_4	TZ2P	2.052	0.0073	0.9672
Ne	TZ2P	—	0.0065	0.9850



Finally, the results of this study indicate that if T_1 is greater than 0.02, then single-reference-based electron correlation methods are probably unreliable and will certainly not yield highly accurate results.

T1 Diagnostics for Open Shell species

$$\frac{1}{2}\sqrt{\frac{\sum_{i}^{D\ occ}\sum_{a}^{D\ unocc}\left[\left(t_{i\alpha}^{a\alpha}\right)^2+\left(t_{i\beta}^{a\beta}\right)^2\right]+\sum_{s}^{S\ occ}\sum_{a}^{D\ unocc}2\left(t_{s\alpha}^{a\alpha}\right)^2+\sum_{i}^{D\ occ}\sum_{t}^{S\ unocc}2\left(t_{i\beta}^{t\beta}\right)^2}{Number\ of\ valence\ electrom}}$$



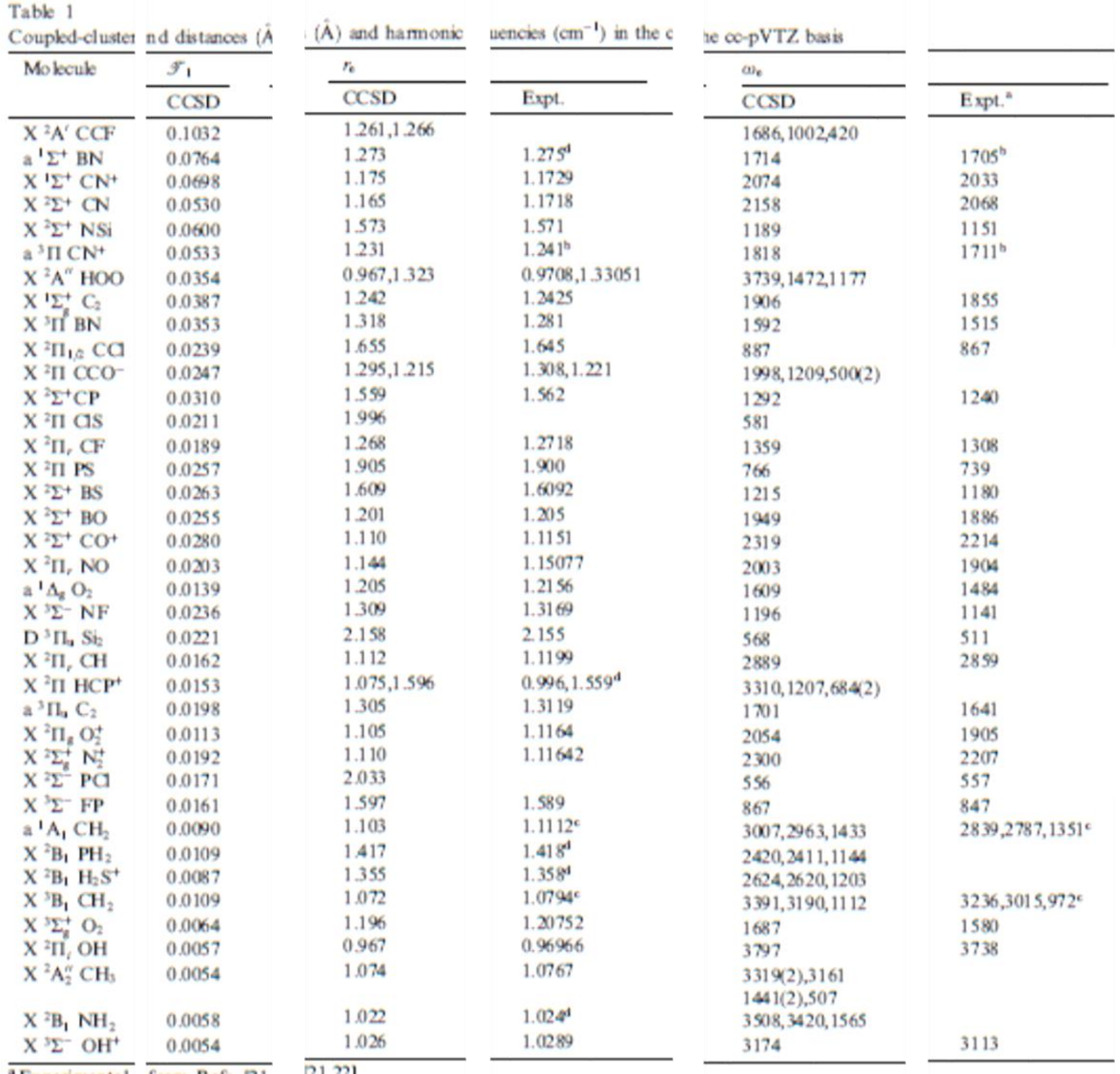
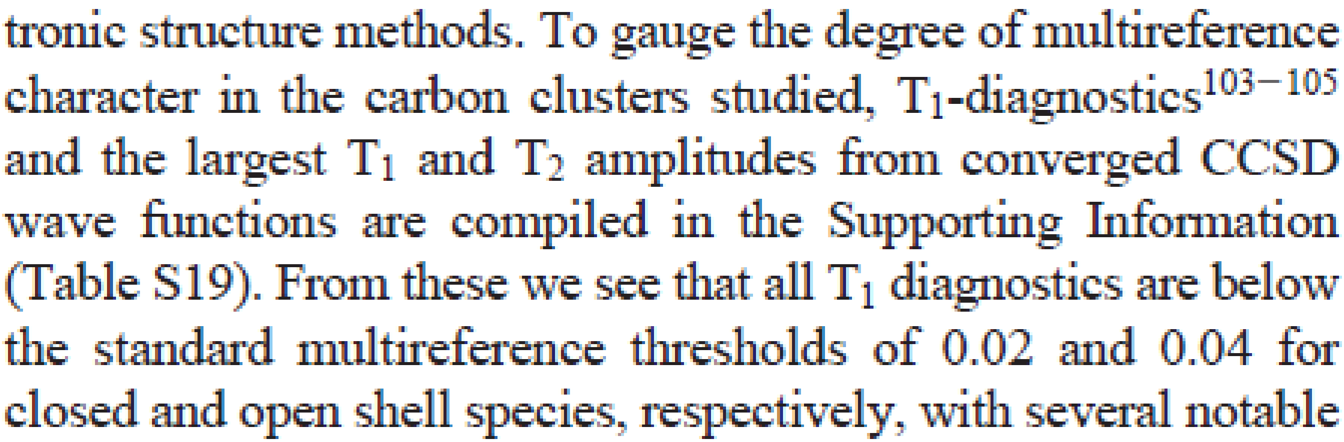


Table 1
Coupled-cluster nd distances (Å (Å) and harmonic uencies (cm^{-1}) in the c he cc-pVTZ basis

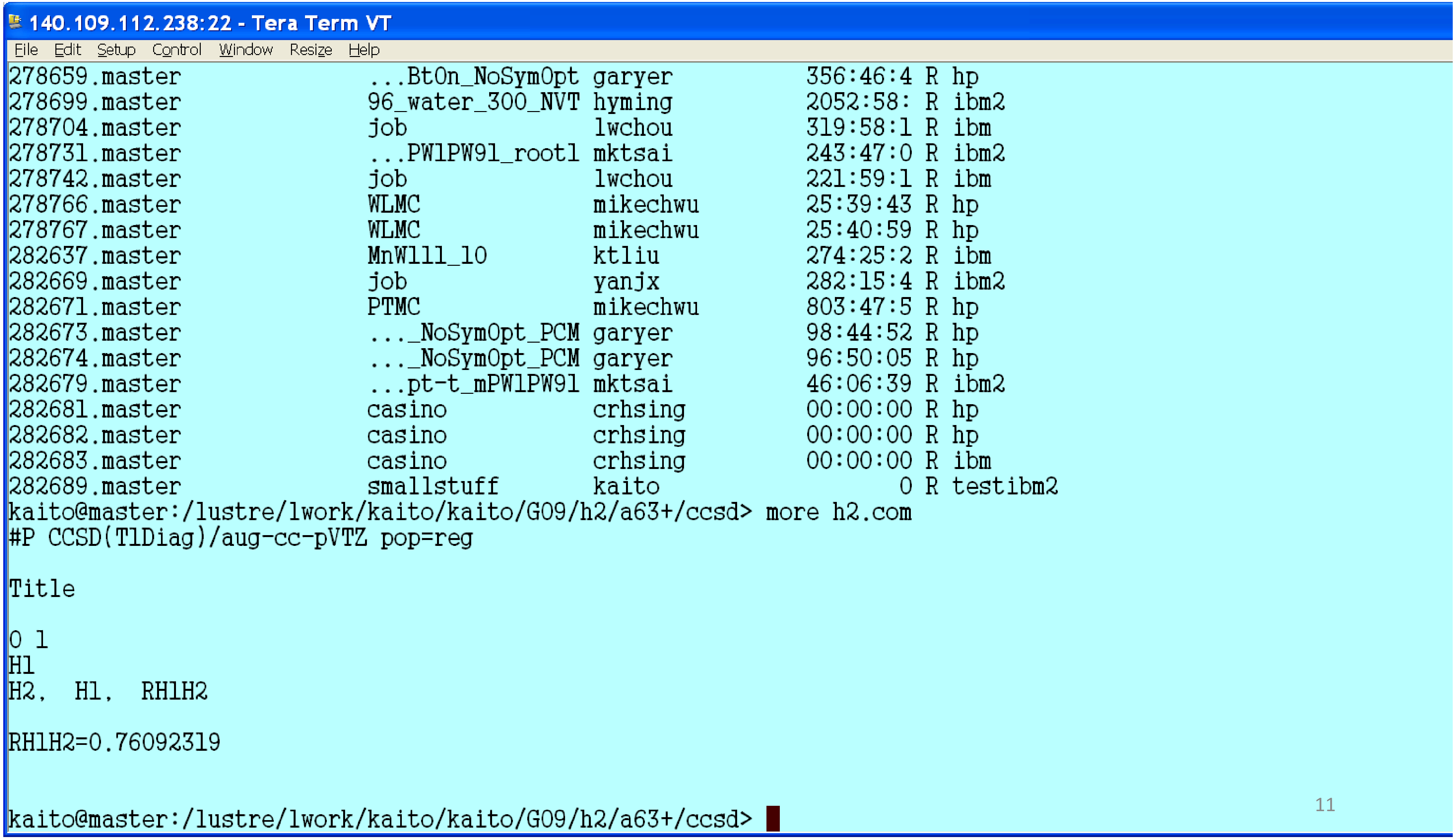
Molecule	$\mathcal{T}_1$	r_e		ω_e	
	CCSD	CCSD	Expt.	CCSD	Expt.^{a}
X $^2A'$ CCF	0.1032	1.261,1.266		1686,1002,420	
a $^1\Sigma^+$ BN	0.0764	1.273	1.275^d	1714	1705^b
X $^1\Sigma^+$ CN$^+$	0.0698	1.175	1.1729	2074	2033
X $^2\Sigma^+$ CN	0.0530	1.165	1.1718	2158	2068
X $^2\Sigma^+$ NSi	0.0600	1.573	1.571	1189	1151
a $^3\Pi$ CN$^+$	0.0533	1.231	1.241^b	1818	1711^b
X $^2A''$ HOO	0.0354	0.967,1.323	0.9708,1.33051	3739,1472,1177	
X $^1\Sigma_g^+$ C$_2$	0.0387	1.242	1.2425	1906	1855
X $^3\Pi$ BN	0.0353	1.318	1.281	1592	1515
X $^2\Pi_{1/2}$ CCl	0.0239	1.655	1.645	887	867
X $^2\Pi$ CCO$^-$	0.0247	1.295,1.215	1.308,1.221	1998,1209,500(2)	
X $^2\Sigma^+$CP	0.0310	1.559	1.562	1292	1240
X $^2\Pi$ ClS	0.0211	1.996		581	
X $^2\Pi_r$ CF	0.0189	1.268	1.2718	1359	1308
X $^2\Pi$ PS	0.0257	1.905	1.900	766	739
X $^2\Sigma^+$ BS	0.0263	1.609	1.6092	1215	1180
X $^2\Sigma^+$ BO	0.0255	1.201	1.205	1949	1886
X $^2\Sigma^+$ CO$^+$	0.0280	1.110	1.1151	2319	2214
X $^2\Pi_r$ NO	0.0203	1.144	1.15077	2003	1904
a $^1\Delta_g$ O$_2$	0.0139	1.205	1.2156	1609	1484
X $^3\Sigma^-$ NF	0.0236	1.309	1.3169	1196	1141
D $^3\Pi_u$ Si$_2$	0.0221	2.158	2.155	568	511
X $^2\Pi_r$ CH	0.0162	1.112	1.1199	2889	2859
X $^2\Pi$ HCP$^+$	0.0153	1.075,1.596	0.996,1.559^d	3310,1207,684(2)	
a $^3\Pi_u$ C$_2$	0.0198	1.305	1.3119	1701	1641
X $^2\Pi_g$ O$_2^+$	0.0113	1.105	1.1164	2054	1905
X $^2\Sigma_g^+$ N$_2^+$	0.0192	1.110	1.11642	2300	2207
X $^2\Sigma^-$ PCl	0.0171	2.033		556	557
X $^3\Sigma^-$ FP	0.0161	1.597	1.589	867	847
a $^1A_1$ CH$_2$	0.0090	1.103	1.1112^c	3007,2963,1433	2839,2787,1351^c
X $^2B_1$ PH$_2$	0.0109	1.417	1.418^d	2420,2411,1144	
X $^2B_1$ H$_2$S$^+$	0.0087	1.355	1.358^d	2624,2620,1203	
X $^3B_1$ CH$_2$	0.0109	1.072	1.0794^c	3391,3190,1112	3236,3015,972^c
X $^3\Sigma_g^+$ O$_2$	0.0064	1.196	1.20752	1687	1580
X $^2\Pi_i$ OH	0.0057	0.967	0.96966	3797	3738
X $^2A_2''$ CH$_3$	0.0054	1.074	1.0767	3319(2),3161 1441(2),507	
X $^2B_1$ NH$_2$	0.0058	1.022	1.024^d	3508,3420,1565	
X $^3\Sigma^-$ OH$^+$	0.0054	1.026	1.0289	3174	3113



tronic structure methods. To gauge the degree of multireference character in the carbon clusters studied, T_1-diagnostics[103−105] and the largest T_1 and T_2 amplitudes from converged CCSD wave functions are compiled in the Supporting Information (Table S19). From these we see that all T_1 diagnostics are below the standard multireference thresholds of 0.02 and 0.04 for closed and open shell species, respectively, with several notable

T J Lee JCP, 98, 9734- (1993), CPL, 372, 362- (2003), D Crawford CPL, 328, 431- (2000), HF Schaefer et al. JACS, 129, 10229- (07).

T1 Diagnostic in Gaussian



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278659.master              ...BtOn_NoSymOpt garyer          356:46:4 R hp
278699.master              96_water_300_NVT hyming          2052:58: R ibm2
278704.master              job              lwchou          319:58:1 R ibm
278731.master              ...PW1PW91_root1 mktsai          243:47:0 R ibm2
278742.master              job              lwchou          221:59:1 R ibm
278766.master              WLMC             mikechwu        25:39:43 R hp
278767.master              WLMC             mikechwu        25:40:59 R hp
282637.master              MnW111_10        ktliu           274:25:2 R ibm
282669.master              job              yanjx           282:15:4 R ibm2
282671.master              PTMC             mikechwu        803:47:5 R hp
282673.master              ..._NoSymOpt_PCM garyer          98:44:52 R hp
282674.master              ..._NoSymOpt_PCM garyer          96:50:05 R hp
282679.master              ...pt-t_mPW1PW91 mktsai          46:06:39 R ibm2
282681.master              casino           crhsing         00:00:00 R hp
282682.master              casino           crhsing         00:00:00 R hp
282683.master              casino           crhsing         00:00:00 R ibm
282689.master              smallstuff       kaito                  0 R testibm2
kaito@master:/lustre/lwork/kaito/kaito/G09/h2/a63+/ccsd> more h2.com
#P CCSD(T1Diag)/aug-cc-pVTZ pop=reg

Title

0 1
H1
H2,  H1,  RH1H2

RH1H2=0.76092319


kaito@master:/lustre/lwork/kaito/kaito/G09/h2/a63+/ccsd> 
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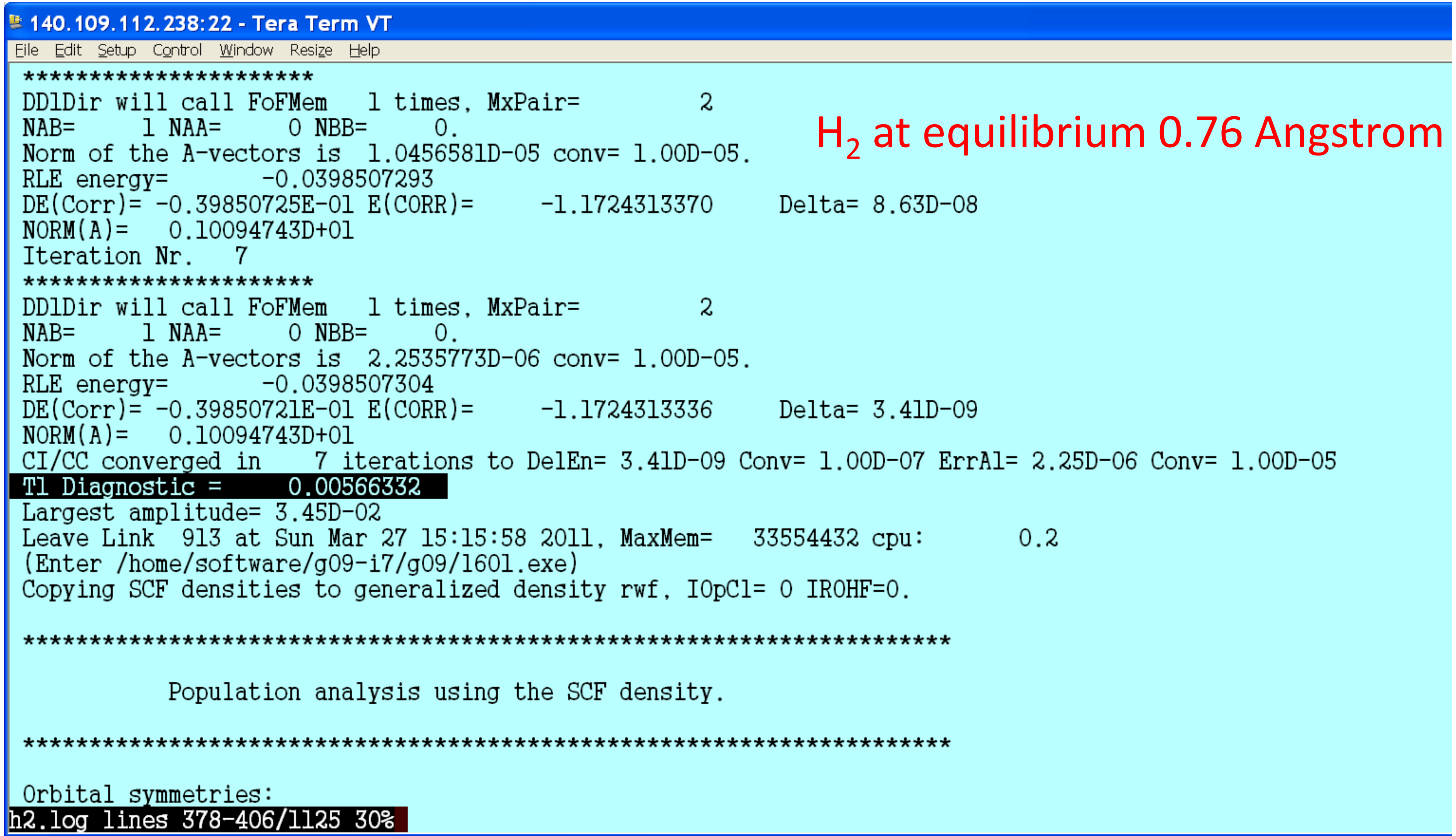
T1 Diagnostic for H2

If T1 diagonostic greater than 0.02 means Hartree Fock in not a good starting point for SINGLET SYSTEMS

Last time we show that Hartree Fock is not good for long distances



H_2 at equilibrium 0.76 Angstrom

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**********************
DD1Dir will call FoFMem   1 times, MxPair=         2
NAB=      1 NAA=      0 NBB=      0.
Norm of the A-vectors is  1.0456581D-05 conv= 1.00D-05.
RLE energy=        -0.0398507293
DE(Corr)= -0.39850725E-01 E(CORR)=     -1.1724313370     Delta= 8.63D-08
NORM(A)=   0.10094743D+01
Iteration Nr.   7
**********************
DD1Dir will call FoFMem   1 times, MxPair=         2
NAB=      1 NAA=      0 NBB=      0.
Norm of the A-vectors is  2.2535773D-06 conv= 1.00D-05.
RLE energy=        -0.0398507304
DE(Corr)= -0.39850721E-01 E(CORR)=     -1.1724313336     Delta= 3.41D-09
NORM(A)=   0.10094743D+01
CI/CC converged in    7 iterations to DelEn= 3.41D-09 Conv= 1.00D-07 ErrA1= 2.25D-06 Conv= 1.00D-05
T1 Diagnostic =       0.00566332
Largest amplitude= 3.45D-02
Leave Link  913 at Sun Mar 27 15:15:58 2011, MaxMem=   33554432 cpu:       0.2
(Enter /home/software/g09-i7/g09/l601.exe)
Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.

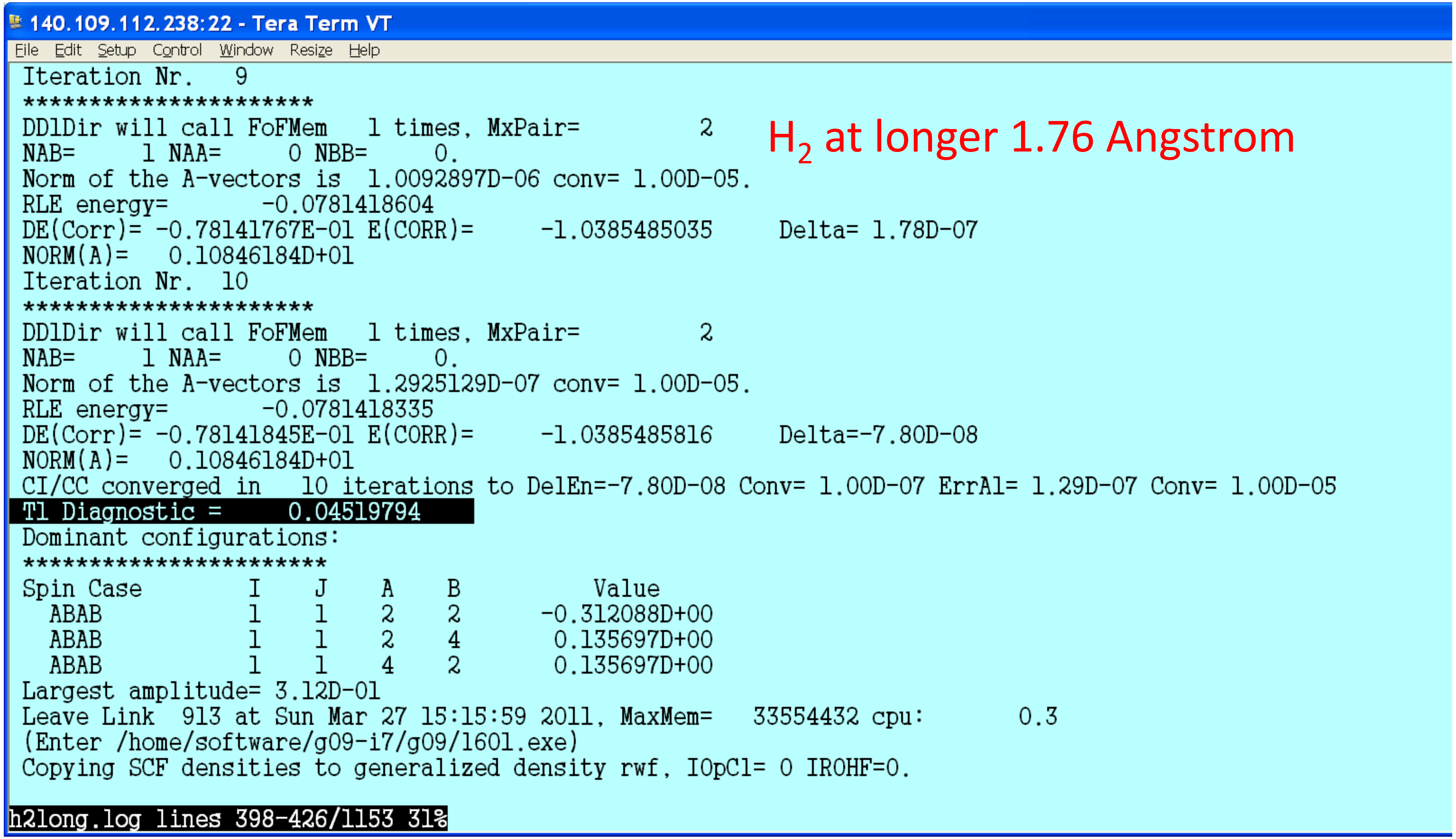
**********************************************************************

           Population analysis using the SCF density.

**********************************************************************

Orbital symmetries:
h2.log lines 378-406/1125 30%
```

T1 Diagnostic for H2



H_2 at longer 1.76 Angstrom

```
Iteration Nr.   9
**********************
DD1Dir will call FoFMem   1 times, MxPair=         2
NAB=      1 NAA=      0 NBB=      0.
Norm of the A-vectors is  1.0092897D-06 conv= 1.00D-05.
RLE energy=       -0.0781418604
DE(Corr)= -0.78141767E-01 E(CORR)=     -1.0385485035     Delta= 1.78D-07
NORM(A)=   0.10846184D+01
Iteration Nr.  10
**********************
DD1Dir will call FoFMem   1 times, MxPair=         2
NAB=      1 NAA=      0 NBB=      0.
Norm of the A-vectors is  1.2925129D-07 conv= 1.00D-05.
RLE energy=       -0.0781418335
DE(Corr)= -0.78141845E-01 E(CORR)=     -1.0385485816     Delta=-7.80D-08
NORM(A)=   0.10846184D+01
CI/CC converged in   10 iterations to DelEn=-7.80D-08 Conv= 1.00D-07 ErrA1= 1.29D-07 Conv= 1.00D-05
T1 Diagnostic =        0.04519794
Dominant configurations:
***********************
Spin Case        I    J    A    B          Value
  ABAB           1    1    2    2      -0.312088D+00
  ABAB           1    1    2    4       0.135697D+00
  ABAB           1    1    4    2       0.135697D+00
Largest amplitude= 3.12D-01
Leave Link  913 at Sun Mar 27 15:15:59 2011, MaxMem=   33554432 cpu:       0.3
(Enter /home/software/g09-i7/g09/l601.exe)
Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.

h2long.log lines 398-426/1153 31%
```

Not very good to use this CCSD results

CCSD(T)

- CCSD with contributions coming from Triples excitation is done by perturbation “golden standard” of quantum chemistry

$$E^{CCSD(T)} = E^{CCSD} + E^{Triples}$$

Explicitly Correlated F12

- MP2-F12, CCSD-F12 are methods where two electron distance r_{ij} is explicitly in the basis set of the calculation. Usually this uses density fitting and resolution of identity approximation so needs to define three basis.