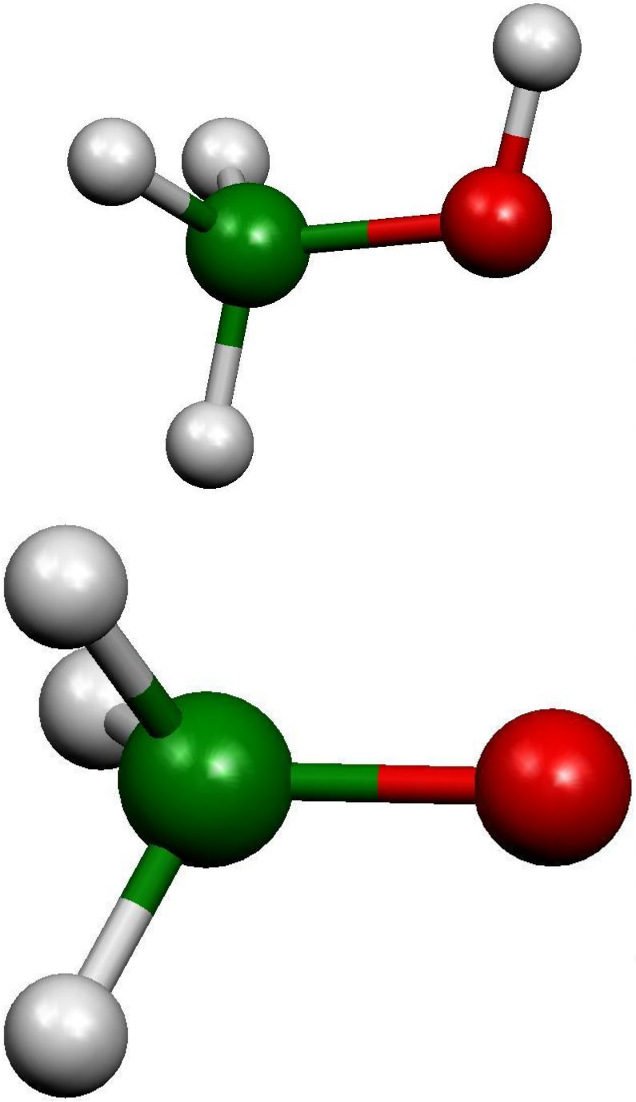
Picking Basis Set

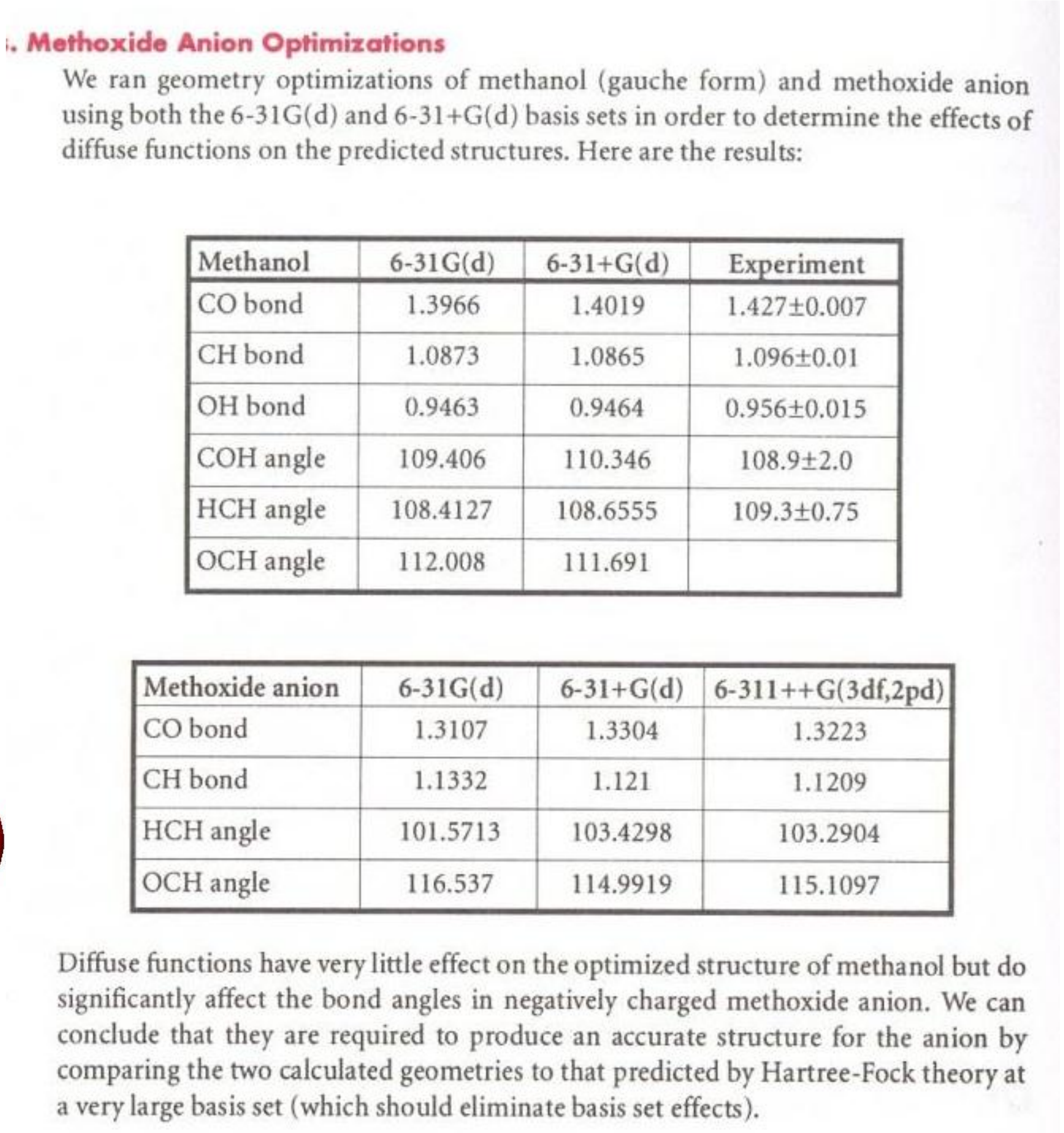
Basis Sets

- Minimal Basis: only those in atomic orbital so one 1S orbital for hydrogen, one 1S, 2S, 2P for carbon, oxygen
  - STO-3G
- Split Valence: valence orbital has two, for hydrogen two 1S orbital, one 1S and two 2S, 2P for carbon oxygen
  - 6-31G, 3-21G
- Diffuse: large version of valence orbital
  - +, ++
- Polarization: higher angular momentum add 2P for hydrogen, add 3D for carbon, oxygen
  - *,**, (d), (d,p)

Geometry

Hartree Fock





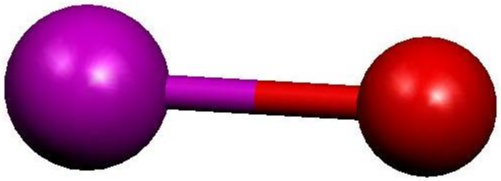
. Methoxide Anion Optimizations

We ran geometry optimizations of methanol (gauche form) and methoxide anion using both the 6-31G(d) and 6-31+G(d) basis sets in order to determine the effects of diffuse functions on the predicted structures. Here are the results:

Methanol	6-31G(d)	6-31+G(d)	Experiment
CO bond	1.3966	1.4019	1.427±0.007
CH bond	1.0873	1.0865	1.096±0.01
OH bond	0.9463	0.9464	0.956±0.015
COH angle	109.406	110.346	108.9±2.0
HCH angle	108.4127	108.6555	109.3±0.75
OCH angle	112.008	111.691	

Methoxide anion	6-31G(d)	6-31+G(d)	6-311++G(3df,2pd)
CO bond	1.3107	1.3304	1.3223
CH bond	1.1332	1.121	1.1209
HCH angle	101.5713	103.4298	103.2904
OCH angle	116.537	114.9919	115.1097

Diffuse functions have very little effect on the optimized structure of methanol but do significantly affect the bond angles in negatively charged methoxide anion. We can conclude that they are required to produce an accurate structure for the anion by comparing the two calculated geometries to that predicted by Hartree-Fock theory at a very large basis set (which should eliminate basis set effects).



PO bond length

B3LYP

Basis Set	Bond Length (Å)
6-31G(d)	1.4986
6-311G(d)	1.4914
6-311G(2d)	1.4818
6-311G(2df)	1.4796
6-311G(3df)	1.4758

Experiment 1.476

Pick Basis Set Convergence

Dipole moment of H_2O

Method	# of basis	Debye
B3LYP/STO-3G	7	1.5936
B3LYP/6-31G	13	2.3986
B3LYP/6-31+G	17	2.5458
B3LYP/6-31+G(d,p)	29	2.1951
B3LYP/6-311G	19	2.4296
B3LYP/6-311++G	25	2.5240
B3LYP/6-311++G(d,p)	37	2.1592
B3LYP/6-311++G(3d,3p)	61	1.8963
B3LYP/6-311++G(3df,3pd)	83	1.8897
B3LYP/aug-cc-pVTZ	105	1.8473
B3LYP/aug-cc-pVQZ	215	1.8458
Exp		1.8550

Computational time ~ $(\text{\# of basis})^2$

Beyond Hartree Fock:
Electron Correlation Methods

Hartree Fock Review

- Hatree Fock Results=By considering one slater determinant we obtained the best results

Molecular Orbital $$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua}\theta_u \qquad a = 1,2,\ldots Nbasis$$

Spin Orbital $$\psi_i(\mathbf{x}) = \phi_a(\mathbf{r}_1)\sigma_m(\mathrm{s}) \qquad i = 1,2,\ldots Nbasis, Nbasis+1\ldots 2Nbasis$$

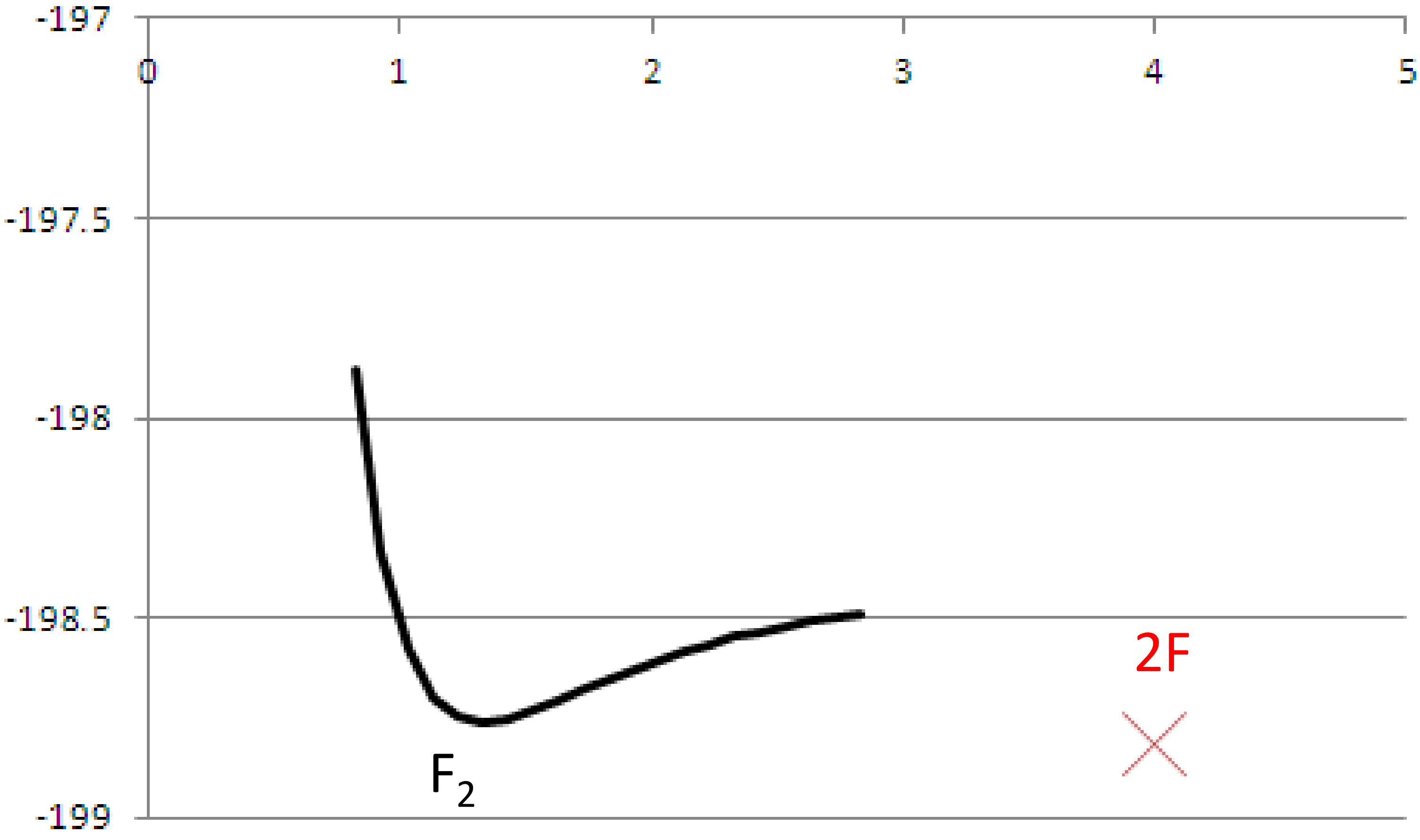
$$\mathrm{a} = 1,2\ldots Nbasis; \quad m = \alpha, \beta$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \cdots\cdots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \cdots\cdots & \psi_n(\mathbf{x}_2) \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \cdots\cdots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

$$= \left\| \psi_i \quad \psi_j \quad \cdots\cdots \quad \psi_n \right\|$$

One Slater Determinant

Failure of Hartree Fock



The cross is the energy for two F atoms.
For Hartree Fock the minimum energy for F2 molecule at 1.2 angstrom is higher then the energy for two F atoms = no bond???

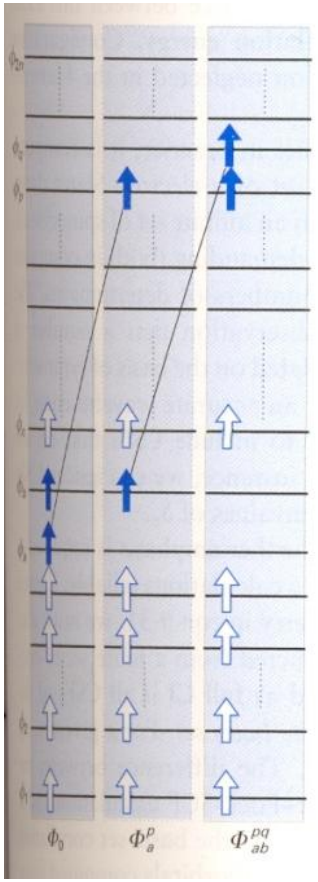
So to go beyond Hartree Fock

- Use more than one slater determinant
    - CISD: Configuration Interaction Singles and Doubles
    - CCSD: Coupled Cluster Singles and Doubles
    - MCSCF: Multiconfigurational Self Consistent Field
    - MR-CISD: Multireference CISD
- Add in Corrections to Hartree Fock Energy
    - MP2,3,4: Mollar Plesset perturbation theory
- Explicitly Correlated methods F12
- Totally Change the Hamiltonian
    - Density Functional Theory Method B3LYP
- Mixed methods G3, CBS

Configuration Interaction SD

n-electron system HF solution $D_0 = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_i \psi_j \cdots\cdots \quad \psi_n \right\|$

You have 2Nbasis-n unoccupied orbitals so you can use them



Single excitation from HF solution

$$D_i^a = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_a \psi_j \cdots\cdots \quad \psi_n \right\|$$

Double excitation from HF solution

$$D_{ij}^{ab} = \left\| \psi_1 \quad \psi_2 \quad \cdots\cdots\psi_a \psi_b \cdots\cdots \quad \psi_n \right\|$$

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

H_2 Potential Curve Revisited Review

This is equivalent to using CI double excitation for the wave function

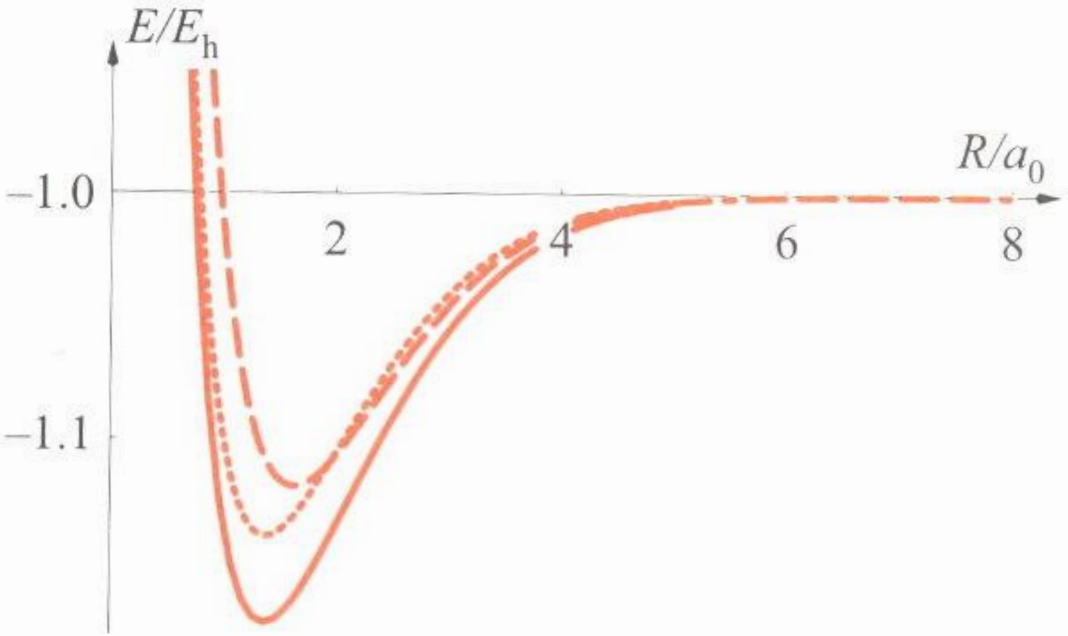


FIGURE 10.25
The configuration-interaction energy E_{CI} of the ground-state energy of H_2 for $\zeta = 1$ (dashed curve) and for an optimized value of ζ (dotted curve) plotted against R. The "exact" results of Kolos and Wolniewicz (solid curve) are shown for comparison.

H2 Configuration Interaction Review

Two 1S orbitals can make TWO molecular orbitals
Why not use the two and make combinations

$$\left|\Psi_1\right\rangle = C_1\begin{vmatrix}\alpha(1)\left|+\right\rangle_1 & \beta(1)\left|+\right\rangle_1 \\ \alpha(2)\left|+\right\rangle_2 & \beta(2)\left|+\right\rangle_2\end{vmatrix} \qquad \left|\Psi_2\right\rangle = C_2\begin{vmatrix}\alpha(1)\left|-\right\rangle_1 & \beta(1)\left|-\right\rangle_1 \\ \alpha(2)\left|-\right\rangle_2 & \beta(2)\left|-\right\rangle_2\end{vmatrix}$$

$$\left|\Psi_1\right\rangle \approx \left|++\right\rangle(\alpha\beta-\beta\alpha) \qquad \left|\Psi_2\right\rangle \approx \left|--\right\rangle(\alpha\beta-\beta\alpha)$$

Configuration 1: two electron in bonding orbital

$$\left|\Psi_1\right\rangle \approx \left|++\right\rangle(\alpha\beta-\beta\alpha)$$

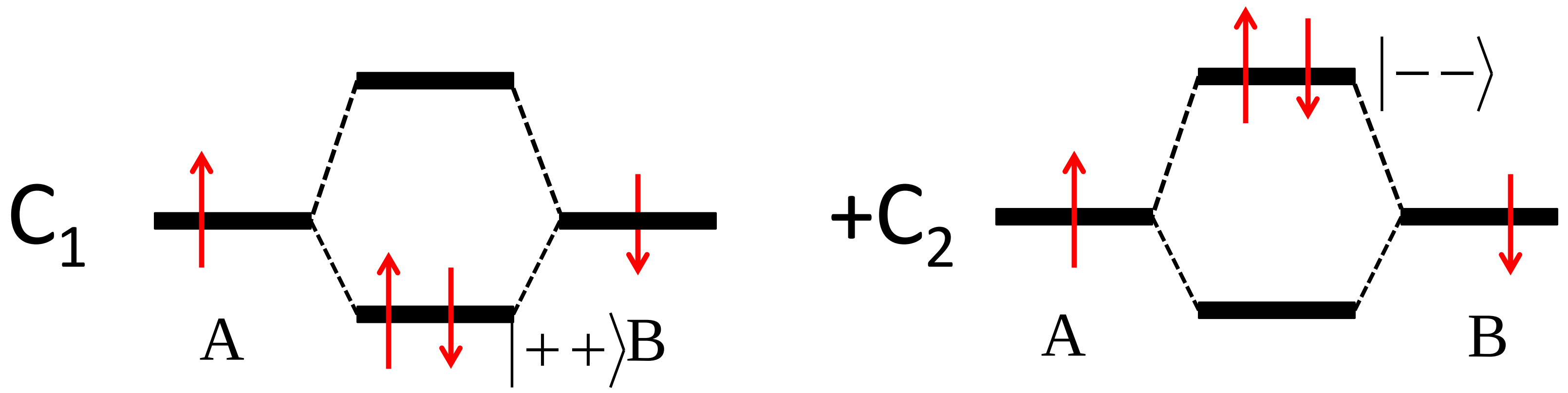
Configuration 2: two electron in antibonding orbital

$$\left|\Psi_2\right\rangle \approx \left|--\right\rangle(\alpha\beta-\beta\alpha)$$

$$\left|\Psi_{CI}\right\rangle = C_1\left|\Psi_1\right\rangle + C_2\left|\Psi_2\right\rangle = C_1\left|++\right\rangle + C_2\left|--\right\rangle$$

What we did in H2 is minimal basis CID

Using two 1S orbitals you can get two molecular orbitals



Hartree Fock Solution

Double excitation from Hartree Fock Solution

Use variational theory to calculate the values of C_1 and C_2

In most cases due to limitation of computational power we cut at the double excitation CISD, MRCISD, CCSD

Brillouin's Theorem

Interaction between the Hartree Fock solution and the one electron excitation determinant is zero

$$\left\langle D_0 \middle| H \middle| D_i^a \right\rangle = \left\langle i \middle| h \middle| a \right\rangle + \sum_{j=1}^{n_{electron}} \left\langle ij \mid aj \right\rangle - \left\langle ij \mid ja \right\rangle = h_{ia} + \sum_{j=1}^{n_{electron}} \left\langle i \middle| J_j \middle| a \right\rangle + \left\langle i \middle| K_j \middle| a \right\rangle$$

$$= \left\langle i \middle| f \middle| a \right\rangle = \delta_{ij}$$

Interaction energy is the cross term of the Fock matrix and by definition it is zero in the cannonical Hartree Fock

However two one electron excitations can have interaction and the one electron excitation and two electron interaction can have interaction, so if Hartree Fock is a good solution the two electron excitation contribution is the greatest

One Electron Operator Matrix Element (two electron system)

$$\left\langle D_0 \middle| h_1 \middle| D_i^a \right\rangle = 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^*$$

$$\times h(\mathbf{r}_1)\left(\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2)\right)$$

$$= 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \left[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2) h(\mathbf{r}_1)\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right.$$

$$+ \psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2) h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2)$$

$$- \psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2) h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2)$$

$$\left. - \psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2) h(\mathbf{r}_1)\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right]$$

Due to orthonormality of the spin orbitals last three terms are zero with integration with respect to $\mathbf{x}_2$

One Electron Operator 2

$$\left\langle D_0 \middle| h_1 \middle| D_i^a \right\rangle = 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \left[\psi_i^{\ *}(\mathbf{x}_1) \psi_j^{\ *}(\mathbf{x}_2) h(\mathbf{r}_1) \psi_a(\mathbf{x}_1) \psi_j(\mathbf{x}_2) \right]$$

$$= 2^{-1} \int \psi_i^{\ *}(\mathbf{x}_1) h(\mathbf{r}_1) \psi_a(\mathbf{x}_1) d\mathbf{x}_1$$

$$= 2^{-1} \left(\left\langle \psi_i \middle| h \middle| \psi_a \right\rangle \right)$$

$$\left\langle D_0 \middle| h_2 \middle| D_i^a \right\rangle = 2^{-1} \left(\left\langle \psi_i \middle| h \middle| \psi_a \right\rangle \right)$$

Two Electron Operator Matrix Element

$$\begin{aligned}
\left\langle D_0 \middle| |\mathbf{r}_{12}|^{-1} \middle| D_i^a \right\rangle &= 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)-\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^* \\
&\quad\times|\mathbf{r}_{12}|^{-1}\left(\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2)-\psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2)\right) \\
&= 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \Big[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2) \\
&\quad+\psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2) \\
&\quad-\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_1)\psi_a(\mathbf{x}_2) \\
&\quad-\psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_a(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\Big]
\end{aligned}$$

Since $|\mathbf{r}_{12}|$ is equal to $|\mathbf{r}_{21}|$ perform interchange of electron 1 and electron 2 and first and second are the same and third and fourth are the same

Two Electron Operator 2

$$\left\langle D_0 \middle| |\mathbf{r}_{12}|^{-1} \middle| D_i^a \right\rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \Big[\psi_i^{\,*}(\mathbf{x}_1) \psi_j^{\,*}(\mathbf{x}_2) |\mathbf{r}_{12}|^{-1} \psi_a(\mathbf{x}_1) \psi_j(\mathbf{x}_2)$$

$$- \psi_i^{\,*}(\mathbf{x}_1) \psi_j^{\,*}(\mathbf{x}_2) |\mathbf{r}_{12}|^{-1} \psi_j(\mathbf{x}_1) \psi_a(\mathbf{x}_2) \Big]$$

$$= \langle ij \mid aj \rangle - \langle ij \mid ja \rangle$$

Coupled Cluster

- Coupled cluster is a smarter way to do CI

We have Hartree Fock solution

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

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

$$T = T_1 + T_2 + T_3 + \ldots$$

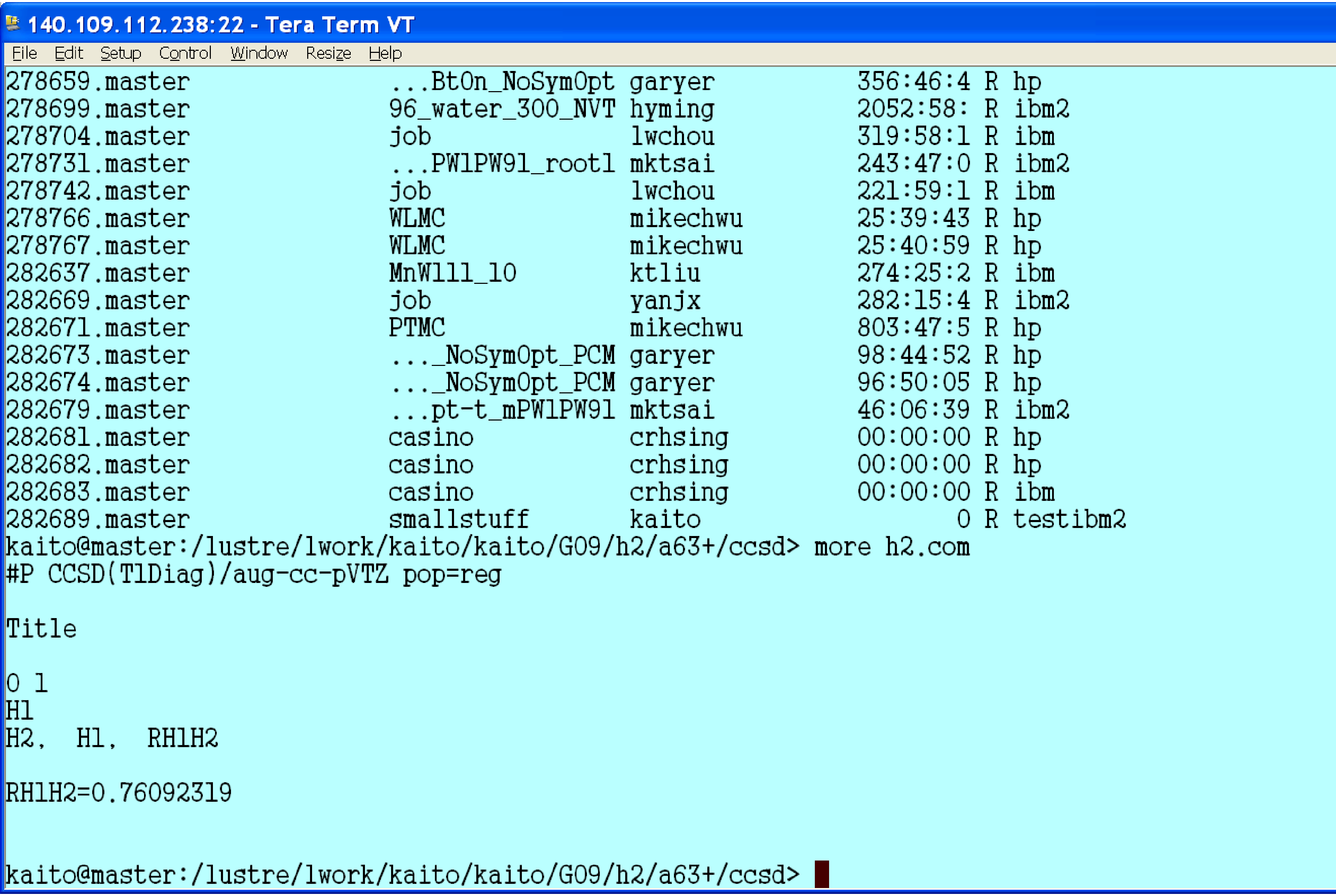
T_n is n electron excitation operator

$$T_2 D_0 = \sum_{i<j,a<b} C_{ij}^{ab} D_{ij}^{ab}$$

When using Couple cluster or CCSD or CCSD(T) what do you have to be careful for?

CC assumes Hartree Fock is a good answer so if Hatree Fock is a bad answer CCSD is bad! CHECK T1 DIAGONOSTIC (tells you how much one electron excitation is contributing to the wave function)

T1 Diagnostic in Gaussian

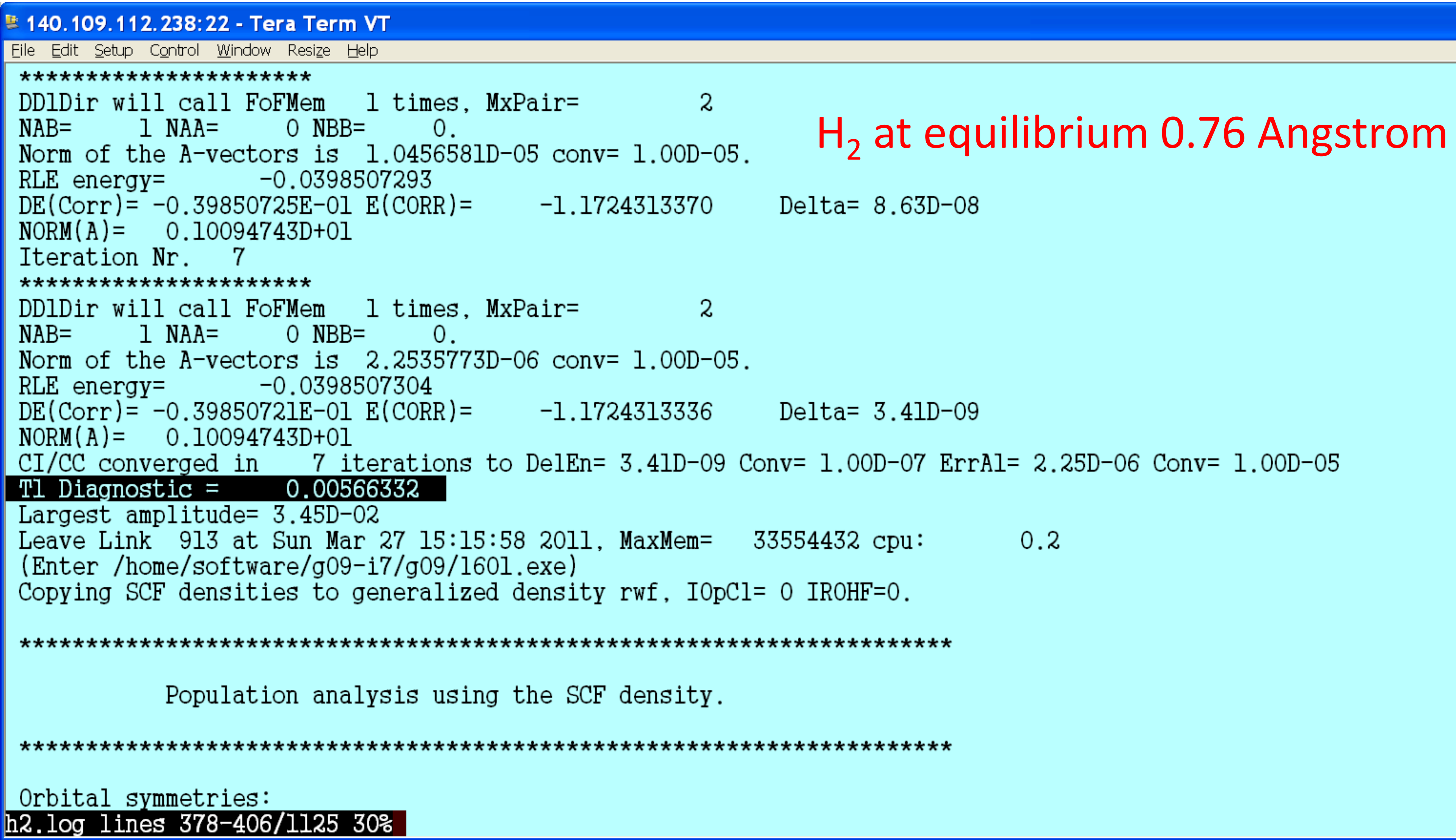


```
278659.master           ...BtOn_NoSymOpt garyer       356:46:4 R hp
278699.master           96_water_300_NVT hyming       2052:58: R ibm2
278704.master           job              lwchou       319:58:1 R ibm
278731.master           ...PW1PW91_root1 mktsai       243:47:0 R ibm2
278742.master           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>
```

T1 Diagnostic for H2

If T1 diagonostic greater than 0.03 means Hartree Fock in not a good starting point

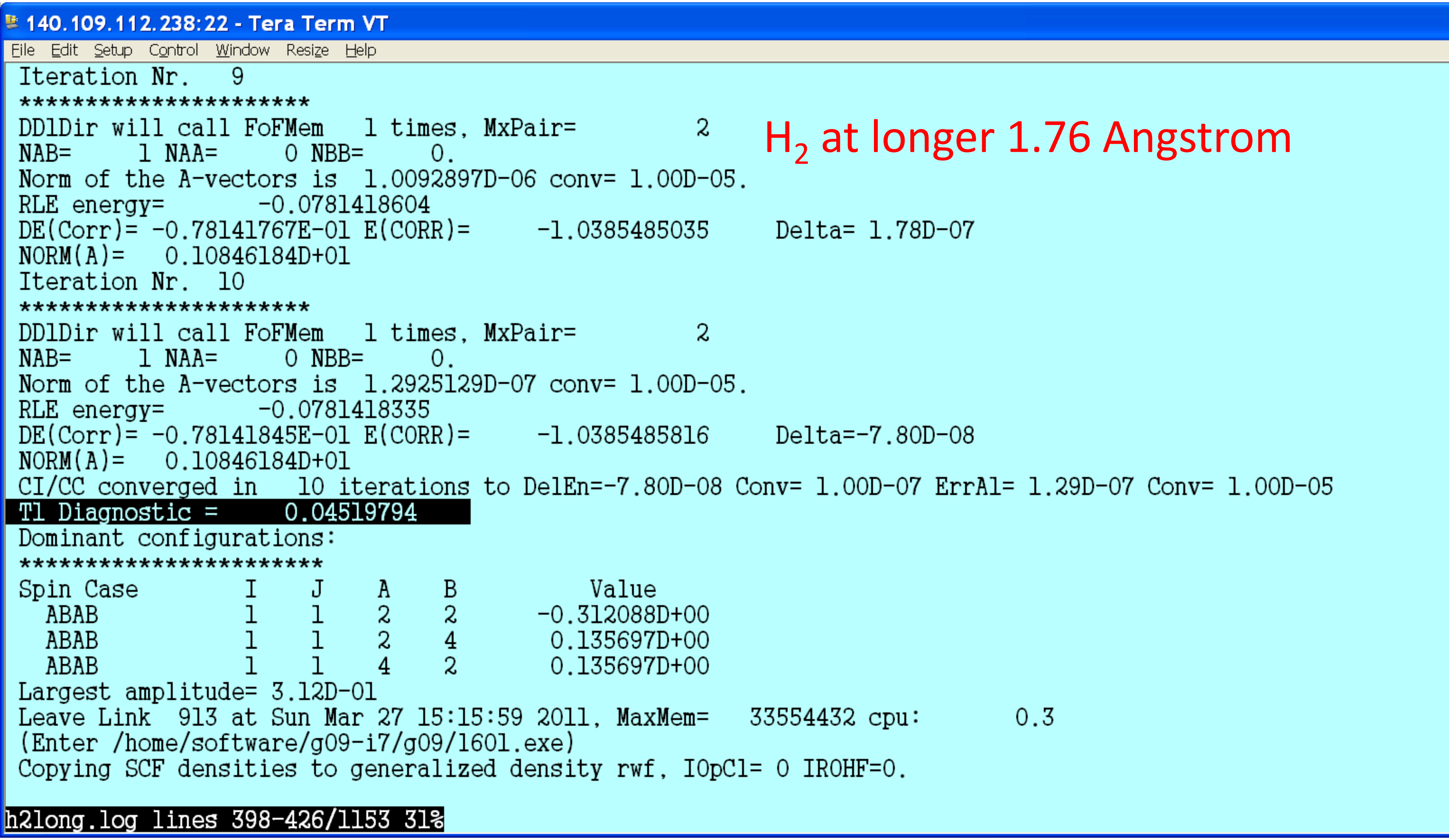
Last time we show that Hartree Fock is not good for long distances



```
**********************
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%
```

H_2 at equilibrium 0.76 Angstrom

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

CASSCF/MRCI

- You pick which configuration you want to put into the summation of configuration interaction
- CASSCF optimizes the orbitals in each determinant as well as the coefficient

Why Use?

1. If you know the problem correctly, you can choose only the important configuration more efficiently

MP2, 3, 4

- Perturbation Theory: Add in correction one by one

$$E^{MP2} = E^{HF} + E^{correction2}$$

$$E^{MP3} = E^{MP2} + E^{correction3}$$

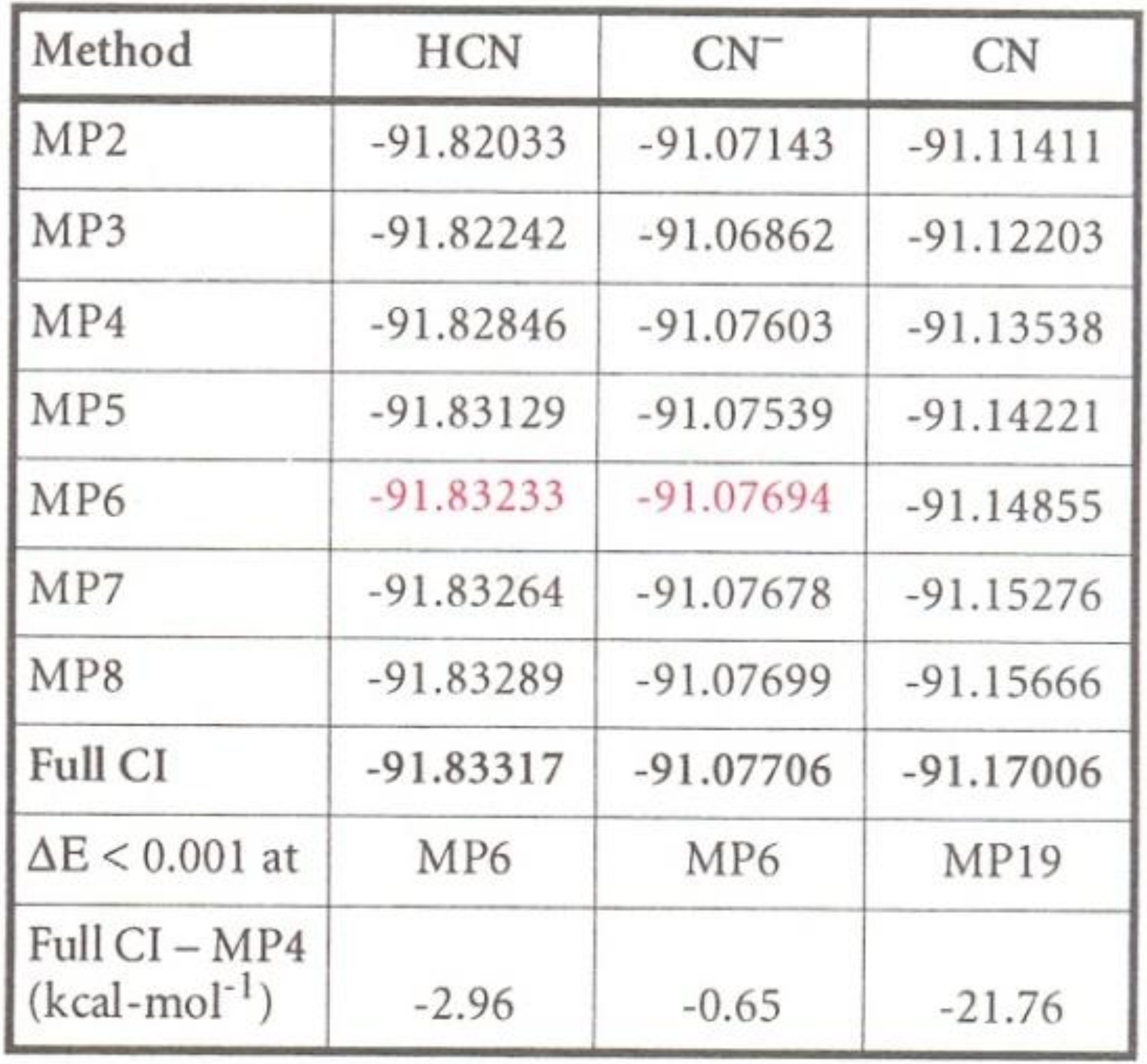
$$E^{MP4} = E^{MP3} + E^{correction4}$$

Why Use?

1. Easy to do after SCF results
2. Can get good accuracy for van der waals interactions

Perturbation Convergence

STO-3G



Method	HCN	CN^-	CN
MP2	-91.82033	-91.07143	-91.11411
MP3	-91.82242	-91.06862	-91.12203
MP4	-91.82846	-91.07603	-91.13538
MP5	-91.83129	-91.07539	-91.14221
MP6	-91.83233	-91.07694	-91.14855
MP7	-91.83264	-91.07678	-91.15276
MP8	-91.83289	-91.07699	-91.15666
Full CI	-91.83317	-91.07706	-91.17006
$\Delta E < 0.001$ at	MP6	MP6	MP19
Full CI – MP4 (kcal-mol^{-1})	-2.96	-0.65	-21.76

CCD(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.

Valance and Full Correlation

- Usually most post-Hartree Fock calculation are performed for only the valance electrons, since valance electrons are most important
- However to get high accuracy one has to consider the core correlation energy in that case one is recommended to use basis set that also include core correlation using usual basis that was made for valance correlation is not good

Aug-ccpCVXZ basis

Density Function Theory

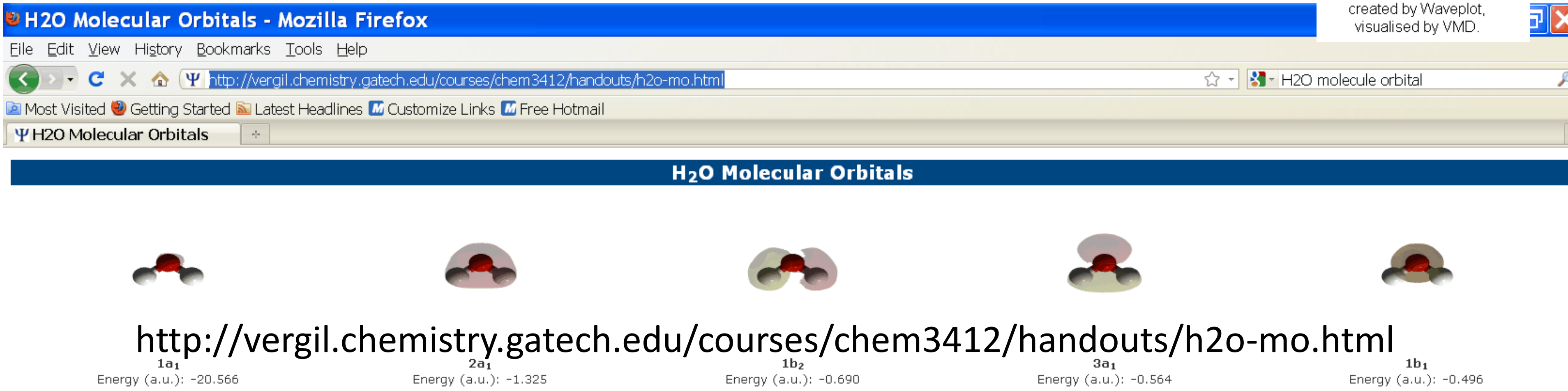
- Instead of getting the wavefunction let’s get the correct density

$$H\Psi = E\Psi \Rightarrow E[\rho] \qquad \rho(r) = \Psi^*(r)\Psi(r)$$

Problem is no one knows this relationship
Many people have thought of approximate solution: B3LYP, PBE, BLYP…..

Why?
1. Can get good answer with SCF
2. Density is much easier to calculate than orbital

Figure 1: Total charge density for the H2O molecule, created by Waveplot, visualised by VMD.

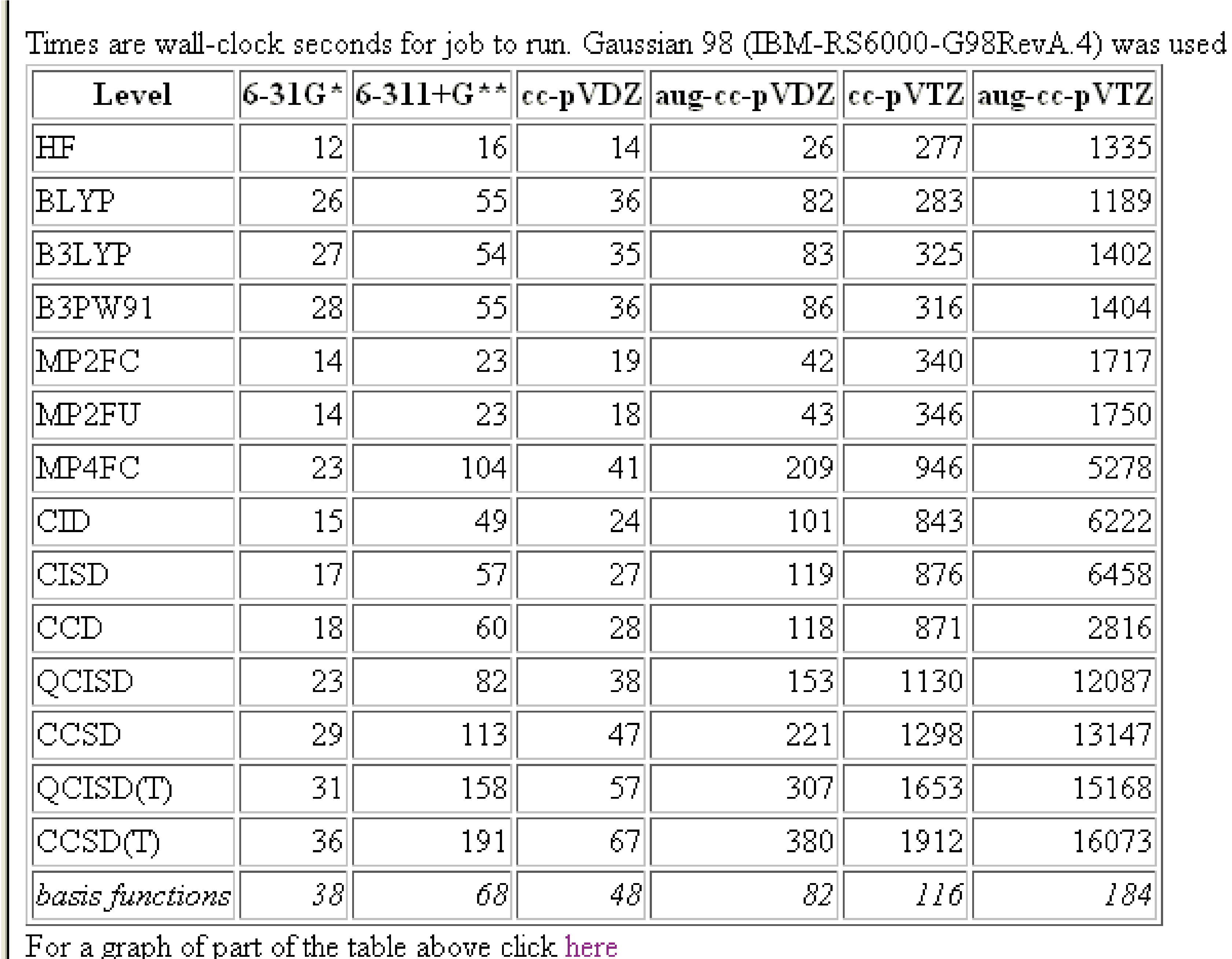


H_2O Molecular Orbitals

http://vergil.chemistry.gatech.edu/courses/chem3412/handouts/h2o-mo.html

$1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
Energy (a.u.): -20.566	Energy (a.u.): -1.325	Energy (a.u.): -0.690	Energy (a.u.): -0.564	Energy (a.u.): -0.496

Single Point of Methanol Time

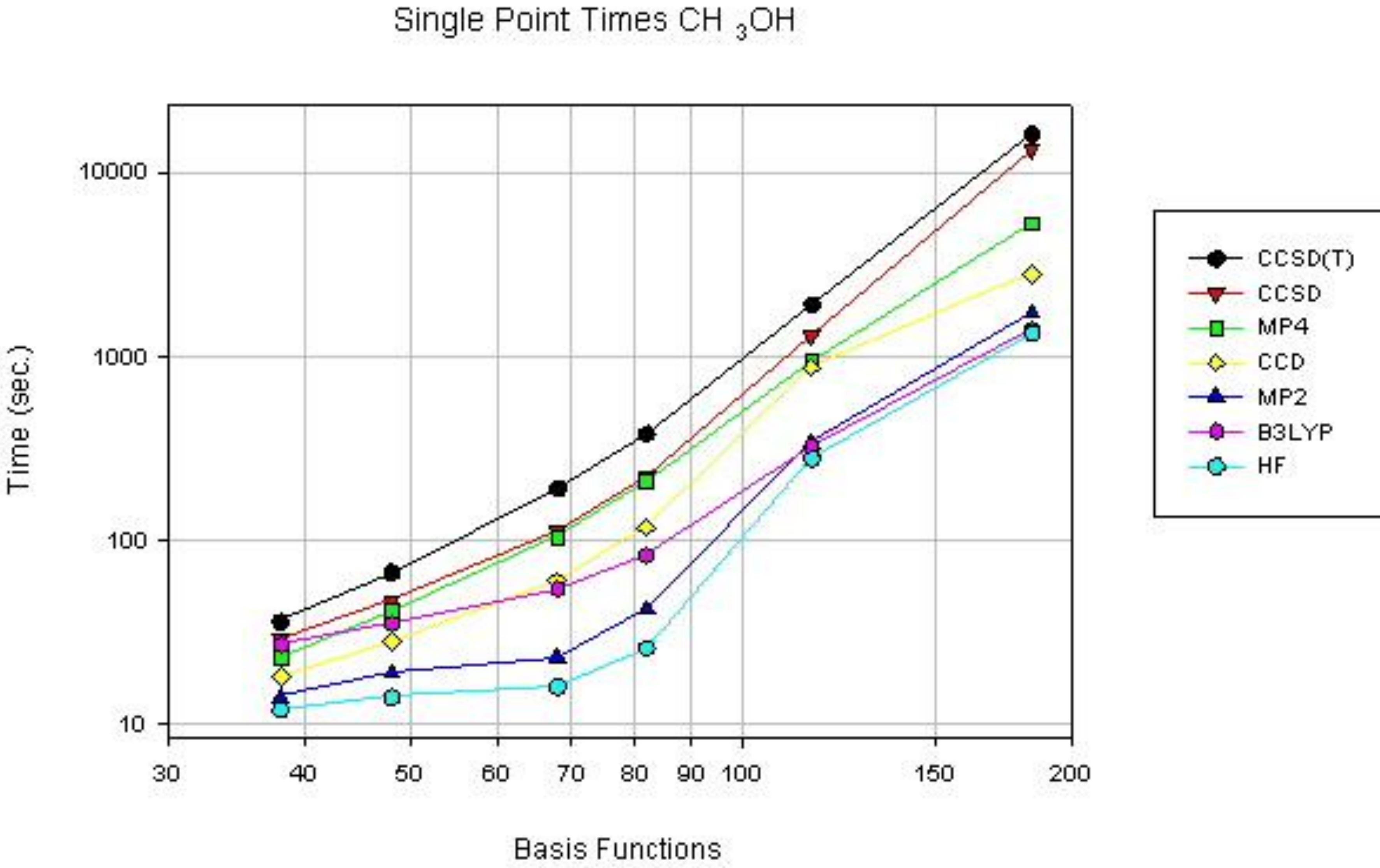


Times are wall-clock seconds for job to run. Gaussian 98 (IBM-RS6000-G98RevA.4) was used

Level	**6-31G***	**6-311+G****	**cc-pVDZ**	**aug-cc-pVDZ**	**cc-pVTZ**	**aug-cc-pVTZ**
HF	12	16	14	26	277	1335
BLYP	26	55	36	82	283	1189
B3LYP	27	54	35	83	325	1402
B3PW91	28	55	36	86	316	1404
MP2FC	14	23	19	42	340	1717
MP2FU	14	23	18	43	346	1750
MP4FC	23	104	41	209	946	5278
CID	15	49	24	101	843	6222
CISD	17	57	27	119	876	6458
CCD	18	60	28	118	871	2816
QCISD	23	82	38	153	1130	12087
CCSD	29	113	47	221	1298	13147
QCISD(T)	31	158	57	307	1653	15168
CCSD(T)	36	191	67	380	1912	16073
basis functions	*38*	*68*	*48*	*82*	*116*	*184*

For a graph of part of the table above click here

Single Point of Methanol Time



Present State of Art Gas Phase Water results: using time independent

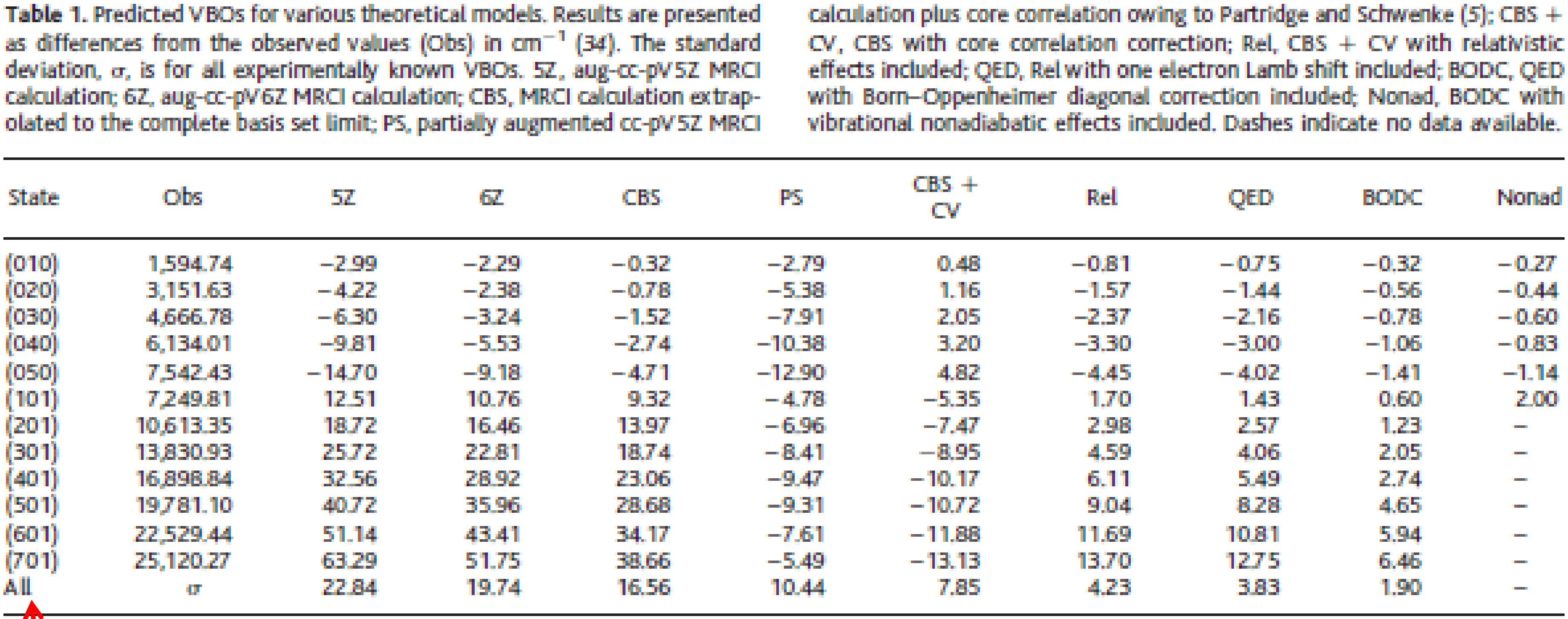
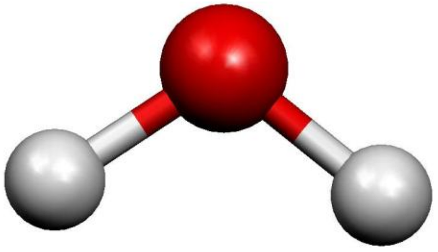


Table 1. Predicted VBOs for various theoretical models. Results are presented as differences from the observed values (Obs) in cm^{-1} (34). The standard deviation, σ, is for all experimentally known VBOs. 5Z, aug-cc-pV5Z MRCI calculation; 6Z, aug-cc-pV6Z MRCI calculation; CBS, MRCI calculation extrapolated to the complete basis set limit; PS, partially augmented cc-pV5Z MRCI calculation plus core correlation owing to Partridge and Schwenke (5); CBS + CV, CBS with core correlation correction; Rel, CBS + CV with relativistic effects included; QED, Rel with one electron Lamb shift included; BODC, QED with Born–Oppenheimer diagonal correction included; Nonad, BODC with vibrational nonadiabatic effects included. Dashes indicate no data available.

State	Obs	5Z	6Z	CBS	PS	CBS + CV	Rel	QED	BODC	Nonad
(010)	1,594.74	−2.99	−2.29	−0.32	−2.79	0.48	−0.81	−0.75	−0.32	−0.27
(020)	3,151.63	−4.22	−2.38	−0.78	−5.38	1.16	−1.57	−1.44	−0.56	−0.44
(030)	4,666.78	−6.30	−3.24	−1.52	−7.91	2.05	−2.37	−2.16	−0.78	−0.60
(040)	6,134.01	−9.81	−5.53	−2.74	−10.38	3.20	−3.30	−3.00	−1.06	−0.83
(050)	7,542.43	−14.70	−9.18	−4.71	−12.90	4.82	−4.45	−4.02	−1.41	−1.14
(101)	7,249.81	12.51	10.76	9.32	−4.78	−5.35	1.70	1.43	0.60	2.00
(201)	10,613.35	18.72	16.46	13.97	−6.96	−7.47	2.98	2.57	1.23	–
(301)	13,830.93	25.72	22.81	18.74	−8.41	−8.95	4.59	4.06	2.05	–
(401)	16,898.84	32.56	28.92	23.06	−9.47	−10.17	6.11	5.49	2.74	–
(501)	19,781.10	40.72	35.96	28.68	−9.31	−10.72	9.04	8.28	4.65	–
(601)	22,529.44	51.14	43.41	34.17	−7.61	−11.88	11.69	10.81	5.94	–
(701)	25,120.27	63.29	51.75	38.66	−5.49	−13.13	13.70	12.75	6.46	–
All	σ	22.84	19.74	16.56	10.44	7.85	4.23	3.83	1.90	–

Complete basis set gets you to 15 cm-1 accuracy
Addition of core valence gets you to 8 cm-1
Relativistic lowers 4 cm-1, QED does not change much
and addition of nonBO gets you to 2cm-1



Include transitions to 30,000cm-1

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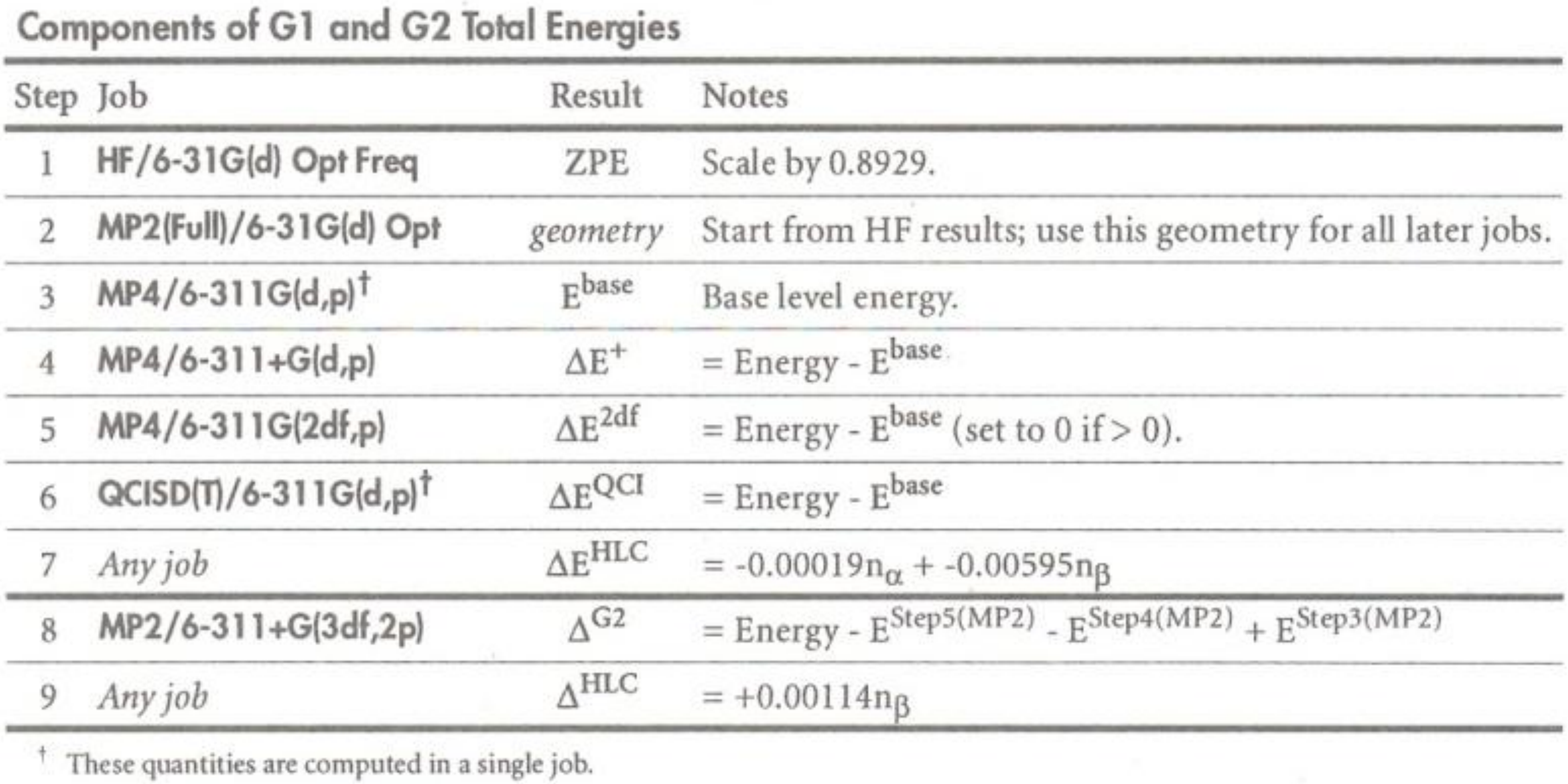
Mixed Methods G2



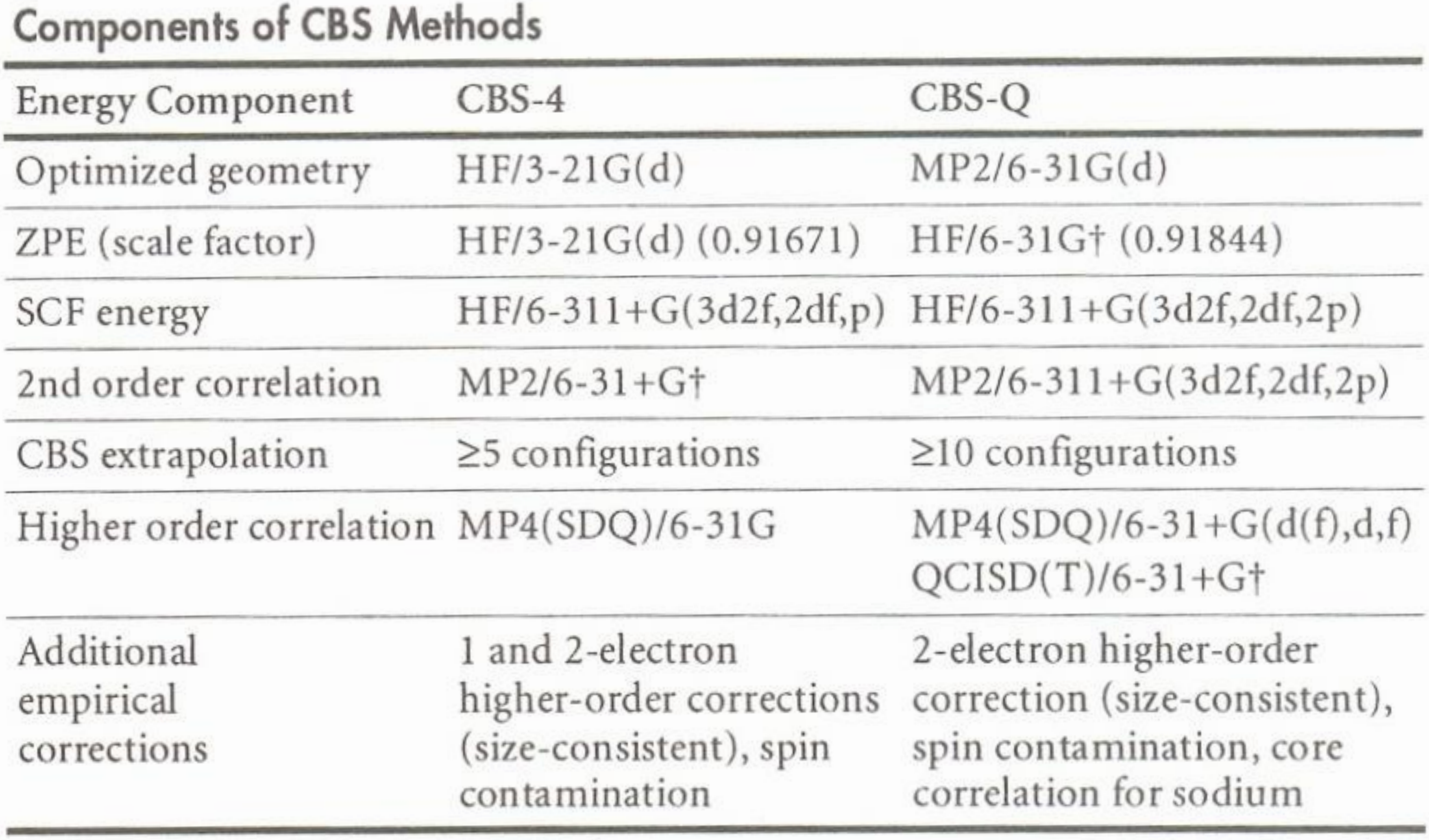
Components of G1 and G2 Total Energies

Step	Job	Result	Notes
1	**HF/6-31G(d) Opt Freq**	ZPE	Scale by 0.8929.
2	**MP2(Full)/6-31G(d) Opt**	*geometry*	Start from HF results; use this geometry for all later jobs.
3	**MP4/6-311G(d,p)**†	E^{base}	Base level energy.
4	**MP4/6-311+G(d,p)**	ΔE^{+}	$=$ Energy - E^{base}
5	**MP4/6-311G(2df,p)**	ΔE^{2df}	$=$ Energy - E^{base} (set to 0 if > 0).
6	**QCISD(T)/6-311G(d,p)**†	ΔE^{QCI}	$=$ Energy - E^{base}
7	*Any job*	ΔE^{HLC}	$= -0.00019 n_{\alpha} + -0.00595 n_{\beta}$
8	**MP2/6-311+G(3df,2p)**	Δ^{G2}	$=$ Energy - $E^{Step5(MP2)} - E^{Step4(MP2)} + E^{Step3(MP2)}$
9	*Any job*	Δ^{HLC}	$= +0.00114 n_{\beta}$

† These quantities are computed in a single job.

Use different methods to obtain values and add up contributions that are estimated by small basis set

Mixed Methods CBS-Q

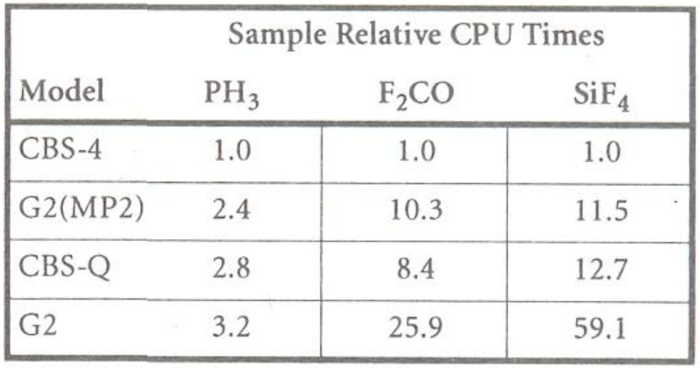


Components of CBS Methods

Energy Component	CBS-4	CBS-Q
Optimized geometry	HF/3-21G(d)	MP2/6-31G(d)
ZPE (scale factor)	HF/3-21G(d) (0.91671)	HF/6-31G† (0.91844)
SCF energy	HF/6-311+G(3d2f,2df,p)	HF/6-311+G(3d2f,2df,2p)
2nd order correlation	MP2/6-31+G†	MP2/6-311+G(3d2f,2df,2p)
CBS extrapolation	≥5 configurations	≥10 configurations
Higher order correlation	MP4(SDQ)/6-31G	MP4(SDQ)/6-31+G(d(f),d,f) QCISD(T)/6-31+G†
Additional empirical corrections	1 and 2-electron higher-order corrections (size-consistent), spin contamination	2-electron higher-order correction (size-consistent), spin contamination, core correlation for sodium

Level of Accuracy and time

Model Chemistry	MAD	Standard Deviation	Absolute Max. Error
CBS-Q	1.0	0.8	3.8
G2	1.2	0.9	5.1
G2(MP2)	1.5	1.2	6.2
G1	1.6	1.4	9.2
CBS-4	2.0	1.5	7.0
B3LYP/6-311+G(3df,2df,2p) // B3LYP/6-31G(d)	2.7	2.6	12.5
B3LYP/6-311+G(2d,p) // B3LYP/6-311+G(2d,p)	3.1	3.0	19.7
B3LYP/6-311+G(2d,p) // B3LYP/6-31G(d)	3.2	3.0	20.1
B3LYP/6-311+G(2d,p) // HF/3-21G(d)	3.2	3.0	21.2
BLYP/6-31+G(d,p) // BLYP/6-31+G(d,p)	3.9	3.2	15.2
BLYP/6-311+G(2d,p) // BLYP/6-311+G(2d,p)	3.9	3.2	15.9
B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p)	3.9	4.2	33.8
B3LYP/6-31+G(d,p) // B3LYP/6-31G(d)	4.0	4.2	33.9
B3LYP/6-31G(d) // B3LYP/6-31G(d)	7.9	9.5	54.2
B3LYP/6-31G(d) // HF/3-21G(d)	8.0	9.4	54.2
MP2/6-311+G(2d,p) // B3LYP/6-31G(d)	8.9	7.8	39.2
MP2/6-311+G(2d,p) // MP2/6-311+G(2d,p)	8.9	7.8	39.2
B3LYP/6-31G(d) // AM1	10.5	11.3	54.2
MP2/6-31+G(d,p) // MP2/6-31+G(d,p)	11.4	8.1	44.0
MP2/6-31+G(d,p) // HF/6-31G(d)	11.8	8.2	43.2
PM3 // PM3	17.2	14.0	69.9
SVWN5/6-311+G(2d,p) // SVWN5/6-311+G(2d,p)	18.1	19.8	81.0
AM1 // AM1	18.8	16.9	95.5
SVWN/6-311+G(2d,p) // SVWN/6-311+G(2d,p)	24.9	19.2	89.3
HF/6-311+G(2d,p) // HF/6-31G(d)	46.1	40.0	173.8
HF/6-311+G(2d,p) // B3LYP/6-31G(d)	46.6	40.5	174.6
HF/6-31+G(d,p) // HF/6-31G(d)	46.6	40.7	179.9
HF/6-31+G(d,p) // HF/6-31+G(d,p)	46.7	40.6	179.8
HF/6-31+G(d,p) // AM1	49.4	43.1	206.1
HF/6-31G(d) // HF/6-31G(d)	51.0	41.2	184.2
HF/6-31G(d) // AM1	54.2	43.1	207.2
HF/3-21G(d) // HF/3-21G(d)	58.4	50.1	215.2
HF/STO-3G // HF/STO-3G	93.3	66.3	313.9

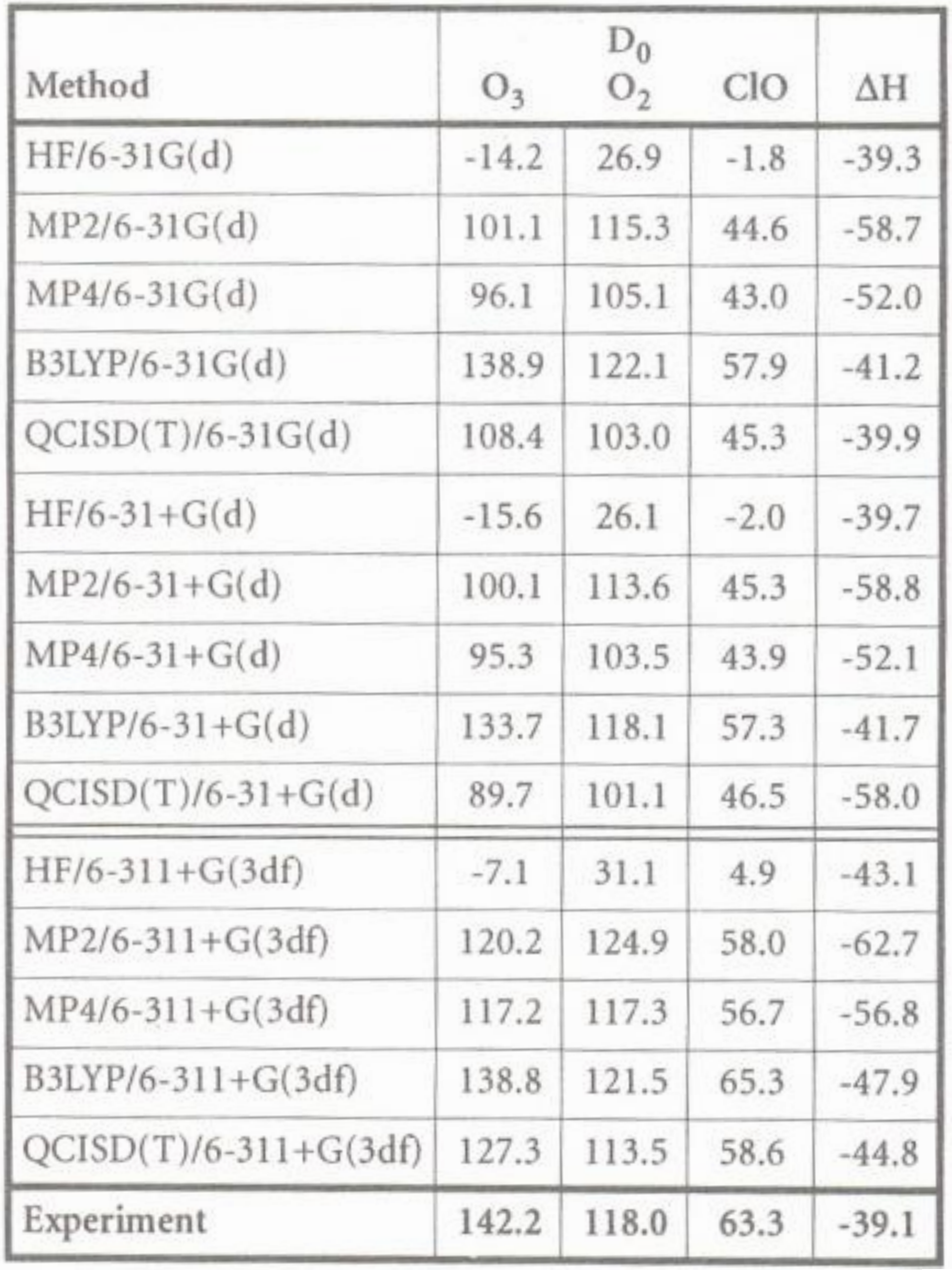


	Sample Relative CPU Times		
Model	PH_3	F_2CO	SiF_4
CBS-4	1.0	1.0	1.0
G2(MP2)	2.4	10.3	11.5
CBS-Q	2.8	8.4	12.7
G2	3.2	25.9	59.1

Ozone Hole Problem

$O_3 + Cl \rightarrow ClO + O_2$

$O_3 + ClO \rightarrow Cl + 2O_2$



Method	D_0			ΔH
	O_3	O_2	ClO	
HF/6-31G(d)	-14.2	26.9	-1.8	-39.3
MP2/6-31G(d)	101.1	115.3	44.6	-58.7
MP4/6-31G(d)	96.1	105.1	43.0	-52.0
B3LYP/6-31G(d)	138.9	122.1	57.9	-41.2
QCISD(T)/6-31G(d)	108.4	103.0	45.3	-39.9
HF/6-31+G(d)	-15.6	26.1	-2.0	-39.7
MP2/6-31+G(d)	100.1	113.6	45.3	-58.8
MP4/6-31+G(d)	95.3	103.5	43.9	-52.1
B3LYP/6-31+G(d)	133.7	118.1	57.3	-41.7
QCISD(T)/6-31+G(d)	89.7	101.1	46.5	-58.0
HF/6-311+G(3df)	-7.1	31.1	4.9	-43.1
MP2/6-311+G(3df)	120.2	124.9	58.0	-62.7
MP4/6-311+G(3df)	117.2	117.3	56.7	-56.8
B3LYP/6-311+G(3df)	138.8	121.5	65.3	-47.9
QCISD(T)/6-311+G(3df)	127.3	113.5	58.6	-44.8
Experiment	**142.2**	**118.0**	**63.3**	**-39.1**

When is Hartree Fock Bad

- WHEN electronic state can not be described by one slater determinant (configuration) Hartree Fock is bad

1. Metal systems with small HOMO LUMO gap
2. Bond dissociation
3. Transition state
4. Intermolecular interaction

Small Rules to Remember

- Equilibrium geometry present day state of art calculation is from CCSD(T)
- Transition metals you should use multireference methods, d orbitals are hard!
- If you want to correctly write the potential energy curve of dissociating problems must use multireference methods
- Van de waals interaction must use MP2, CCSD CI, MRCI methods to accurately get
- You have to do test calculations for your problem to find the best way to do your problem

Quantities other that Energy

- Dipole Moment of the Molecule: Rotational Spectroscopy
- Dipole Derivative of the Molecule: Infrared Absorption Spectroscopy
- Polarizability Derivative of the Molecule: Infrared Raman Spectroscopy
- Nuclear Shielding by the electron related to NMR spectrum