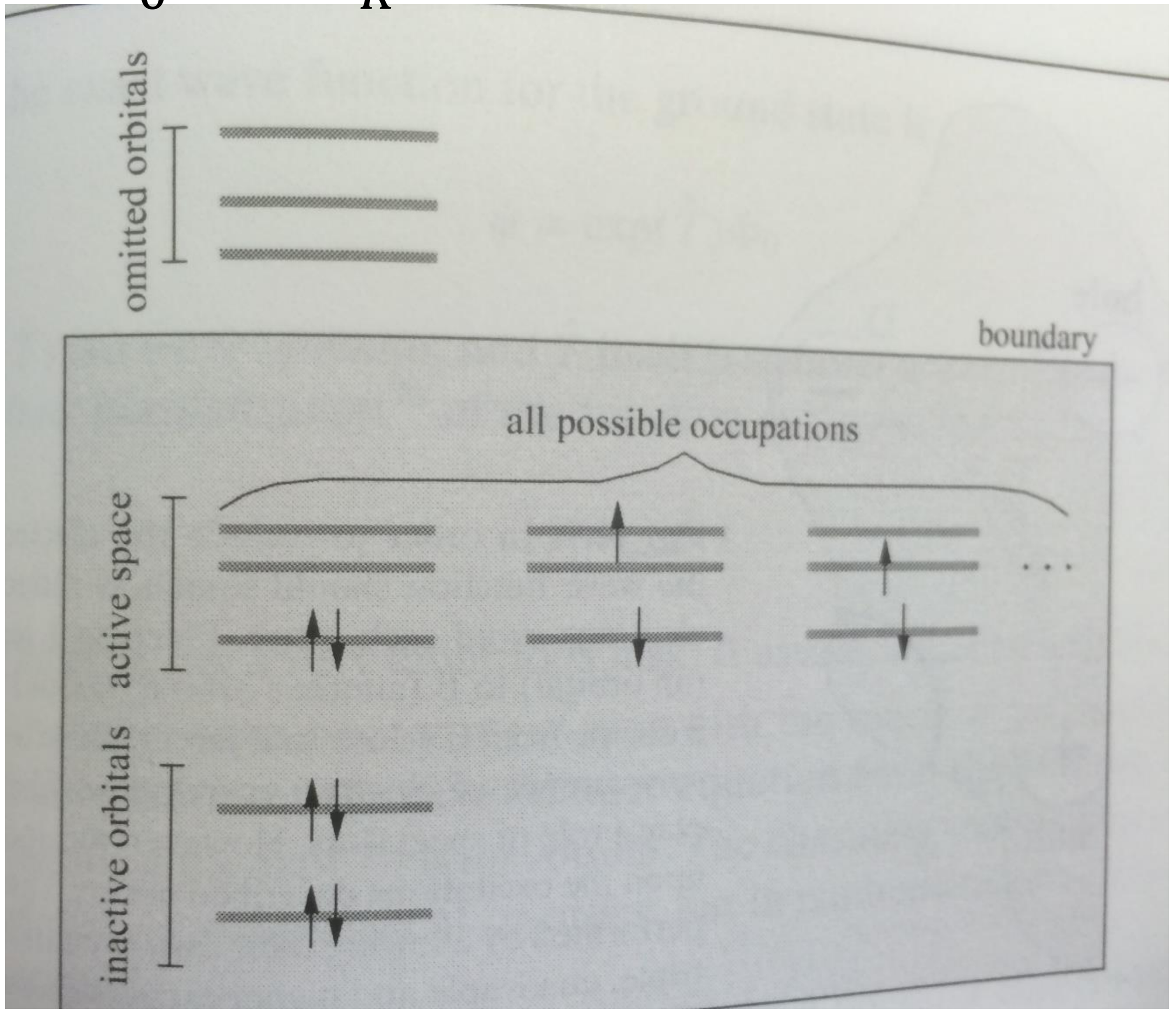
Beyond Hartree Fock: Multireference Methods

MultiReference CI (MRCI)

- In MRCI, you pick which configuration/determinants you want to put into the summation of configuration interaction, use Hartree Fock orbitals and optimize the $C_0\ and C_K$

$$\Psi_{MRCI} = C_0 D_0 + \sum_{K}^{\substack{active \\ space}} C_K D_K$$

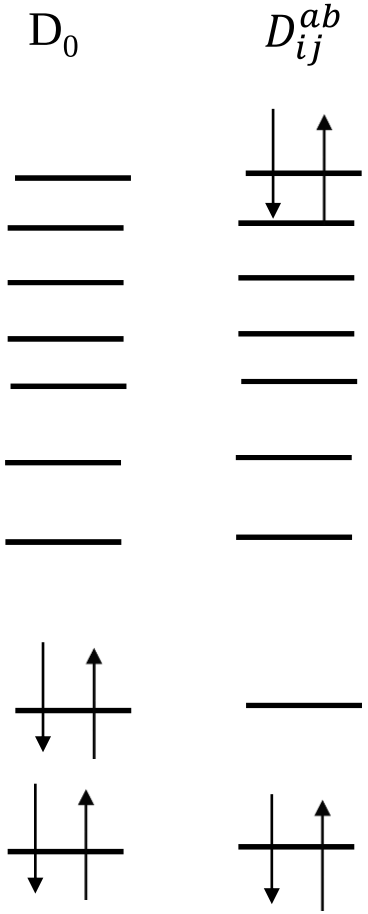
We define an active space and then consider all the excitation within this active space (all singles, doubles, triples …)



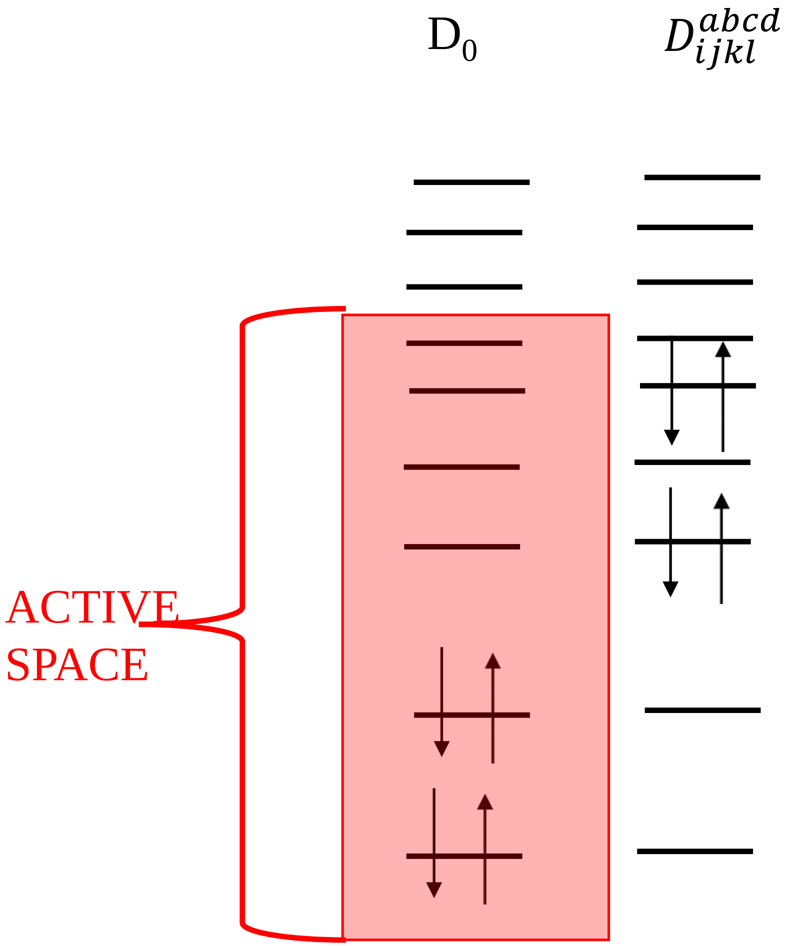
What is the difference between CI and MRCI

- In CISD we add up contribution for all singles and doubles excitations. We have to excite to very high energy MO

- In MRCISD we add up excitation in active space no matter how many electrons are excited



In CID we can have double excitation to very high orbital



In MRCI we can have four electron excitation as long at its in the active space

Complete Active Space Self Consistent Field CASSCF

- CASSCF optimizes the orbitals in each determinant as well as the coefficient: so for 3 state casscf

$$\Psi_{CASSCF} = C_0 D_0 + C_1 D_1' + C_2 D_2''$$

where the ‘ and “ means that the orbital used in the determinant is different from that in the first slater determinant.

- Steps for the calculation:
  1. Calculate Hartree Fock
  2. Use Hartree Fock orbital to calculate C_0, C_1, C_2 then
  3. Keep C_0, C_1, C_2 fixed and optimized the orbitals for D_0, D_1', D_2''
  4. Using the new orbitals calculate C_0, C_1, C_2 again
  5. Do 3 and 4 until converged

Conclusions

- MRCI is useful when you know that one single Slater determinant is not good enough and YOU KNOW WHICH ONES WILL BE IMPORTANT
- In cases where there is degeneracy the wavefunction is described best by the degenerate number of Slater determinants we can select it. (Sometimes this is called static correlation or left right correlation)
- MRCI and CASSCF can be used to calculate excited states as well as ground states.
- When breaking bonds it is important

Excited Electronic States Calculation

Method for Excited States

- Use more than one slater determinant
    - CIS: Configuration Interaction Singles
    - CISD: Configuration Interaction Singles and Doubles
    - MCSCF: Multiconfigurational Self Consistent Field
    - MR-CISD: Multireference CISD
- CAS MP2
    - MP2,3,4: Mollar Plesset perturbation theory
- Equation of Motion CCSD
- Time Dependent DFT

Things to consider: Practical Advice

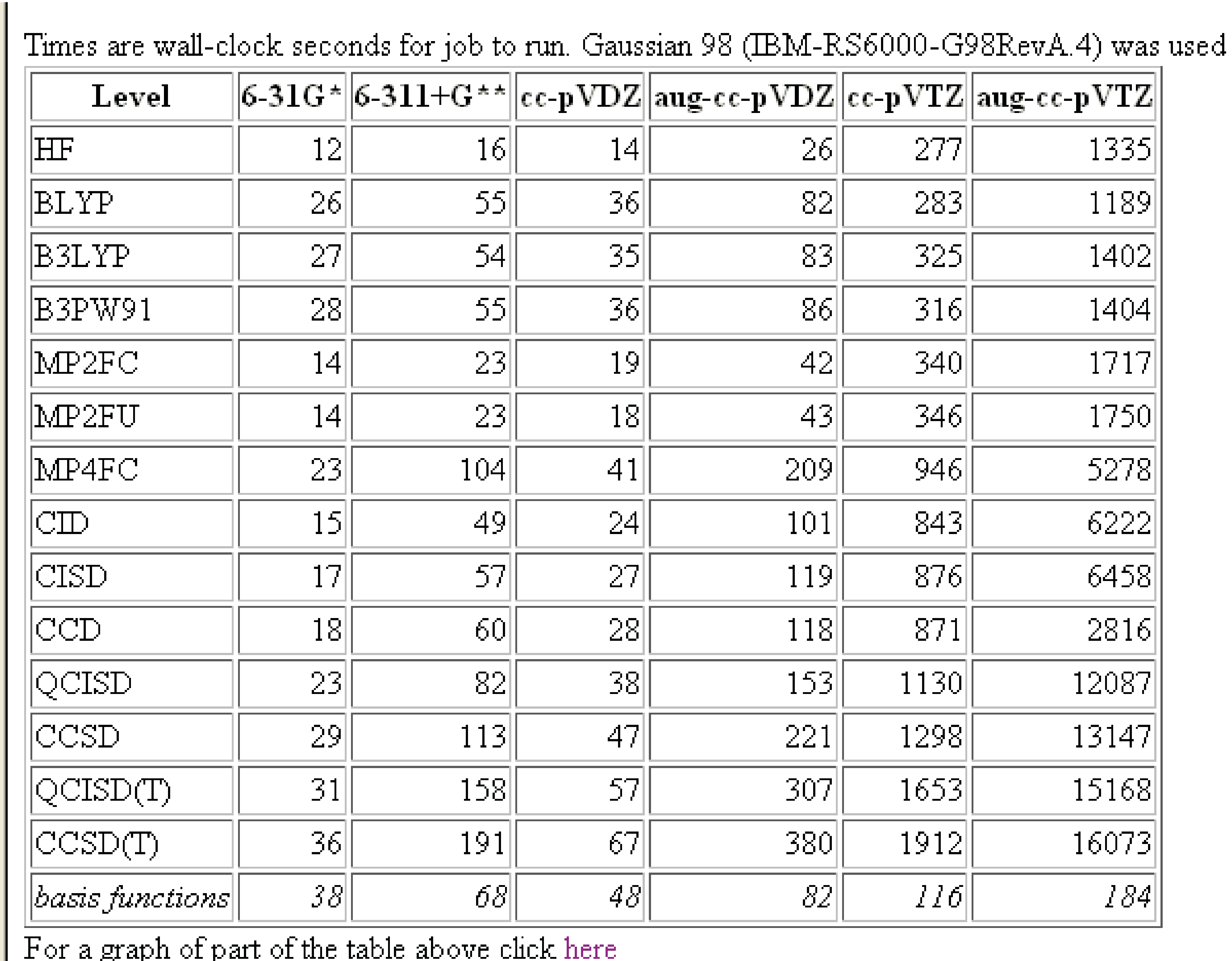
Valance and Full Correlation

- Usually most post-Hartree Fock calculation are performed for only the valance electrons, since valance electrons are most important MP2(Full) versus MP2(FC)

- 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

Single Point of Methanol Time

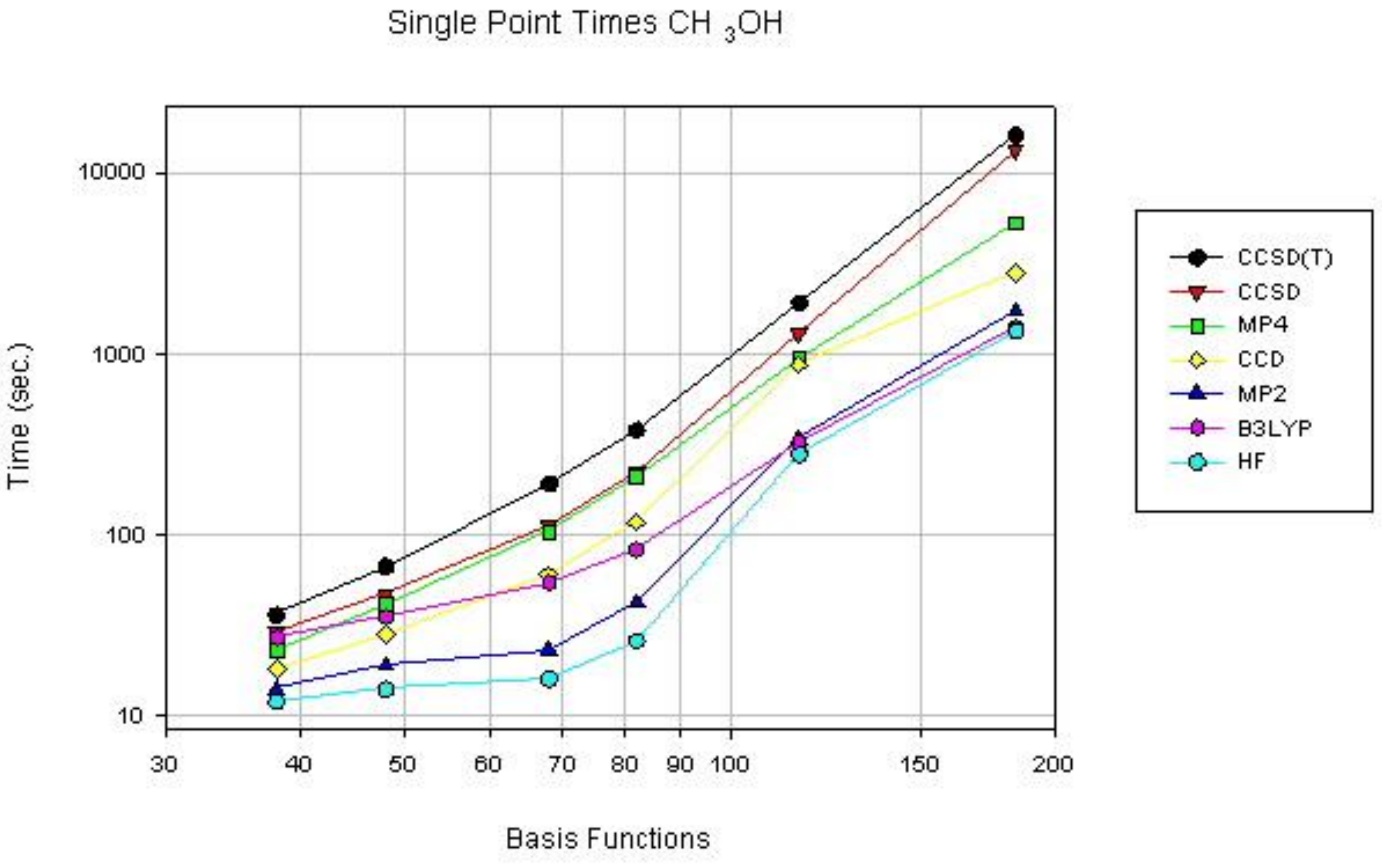


Times are wall-clock seconds for job to run. Gaussian 98 (IBM-RS6000-G98RevA.4) was used

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

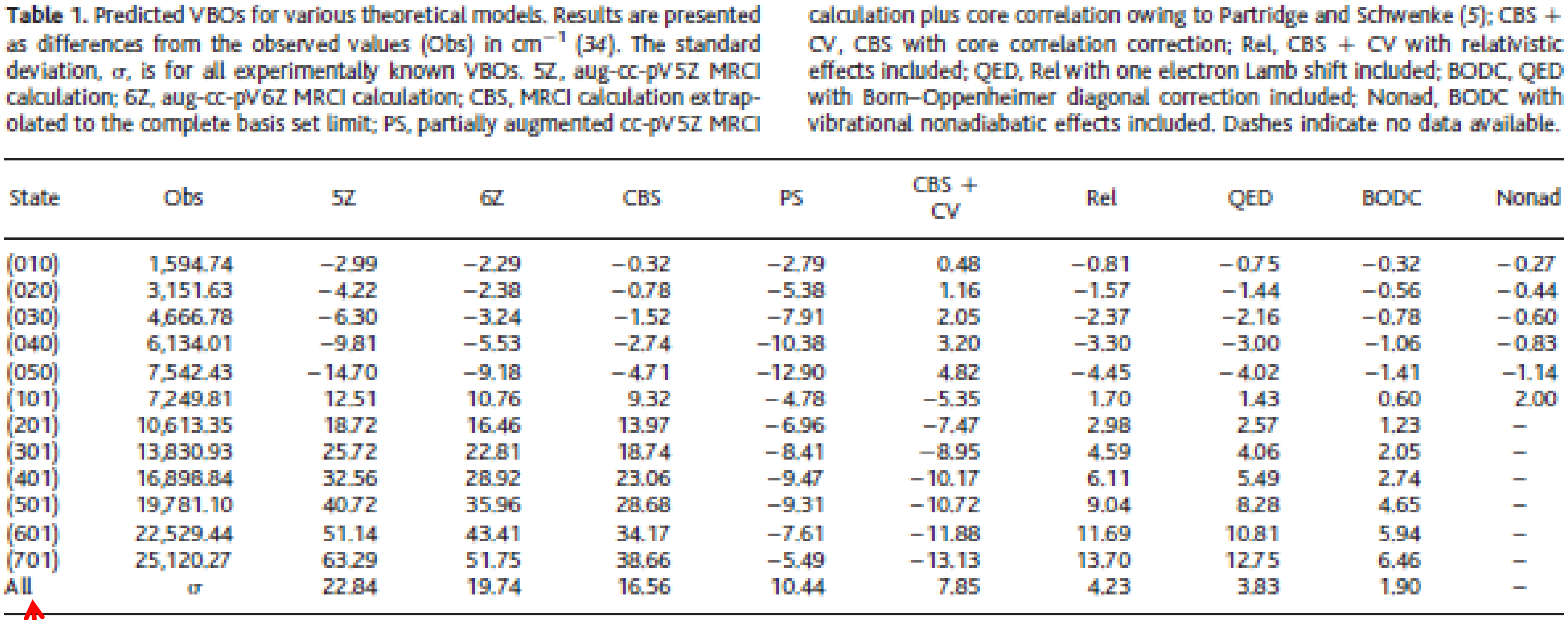
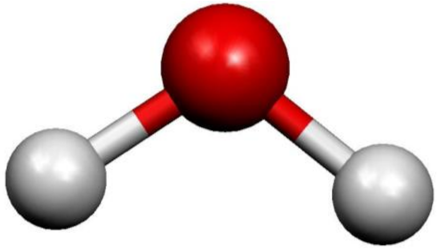


Table 1. Predicted VBOs for various theoretical models. Results are presented as differences from the observed values (Obs) in cm^{-1} (34). The standard deviation, σ, is for all experimentally known VBOs. 5Z, aug-cc-pV5Z MRCI calculation; 6Z, aug-cc-pV6Z MRCI calculation; CBS, MRCI calculation extrapolated 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

O L Polyansky et al. Science 299, 539 (2003)

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 (making/breaking bonds)
4. Intermolecular interaction (van der Waals interaction, protein folding)

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

Choice for basis sets

- Use 6-31G(d) or 6-31+G(d,p) for small test calculations (better than cc-pvdz)
- For higher level use aug-cc-pvtz
- For anions use diffuse functions (aug and +)
- For excited state also use diffuse functions
- Dispersion forces also require diffuse functions
- For alkali or alkali earth metals (row 1 and 2) may be better to use core valance cc-pCVTZ basis

Choice of method

- If you don’t know what to start with do B3LYP
- Do MP2 doing MP3, MP4 will not converge so just use CCSD
- ASK EXPERT FOR bond breaking, 3d metals, and radicals (please help me keep my job)

Common things to check

- Make sure Hartree Fock Self Consistent Field is converged
- Check Virial coefficient is 2
- Geometry optimization is really a minimum? Check frequency
- Are you not starting from a symmetric geometry or not?

Tricks to remember

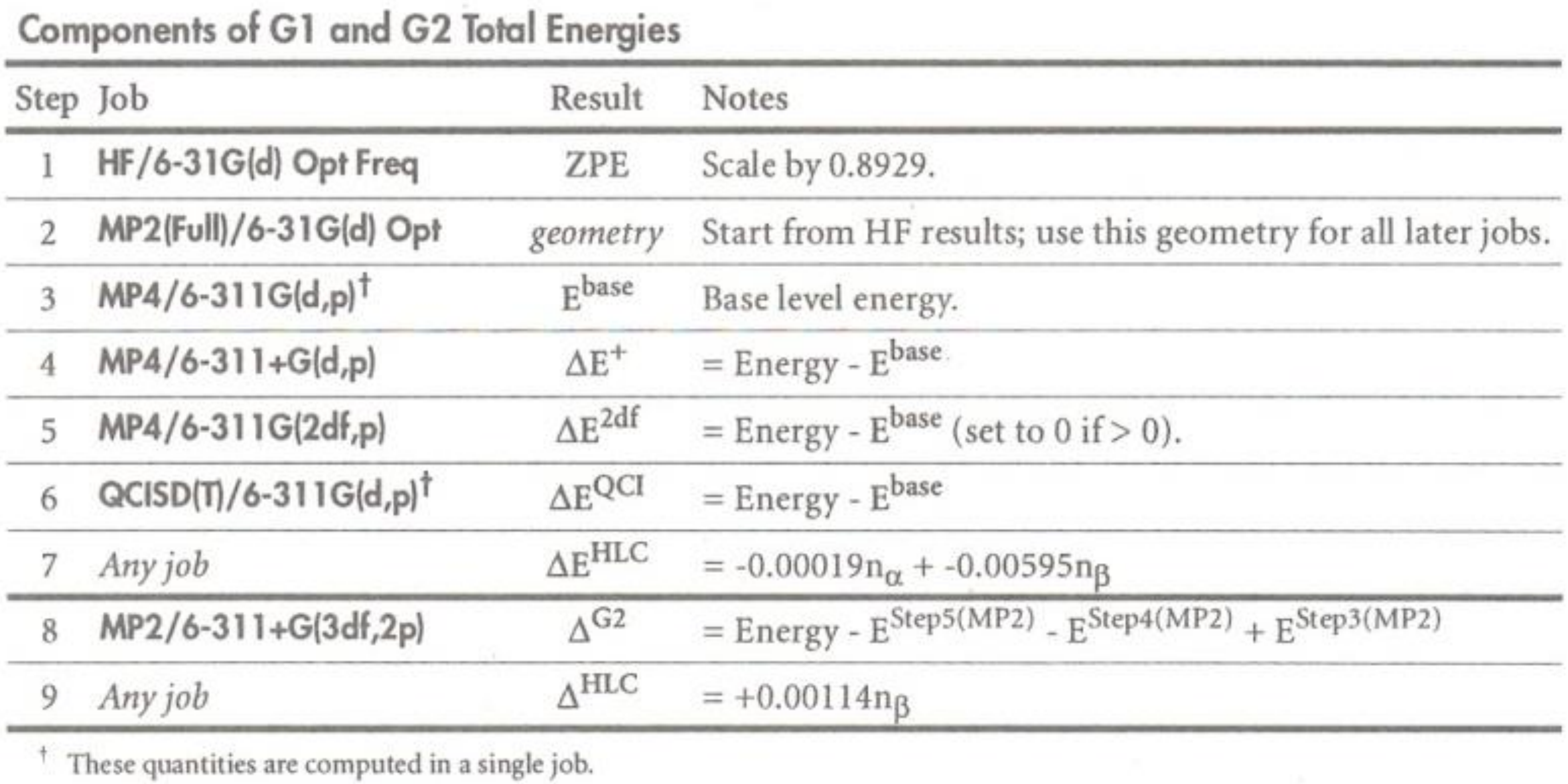
- SCF convergence you can use a small basis set to first let it converge, then use that results to do the calculation for bigger basis sets
- Turn up the SCF cycle number from default
- Look at the SCF energies, make sure it is not flipping between two values. (This is a sign that Hartree Fock might not be good)
- For SCF or radicals, maybe you first calculate the SCF with its cation or anion form to make the orbitals then calculate the neutral radical using those results as input
- If SCF seems weird check its “stability”, or ask a professional

- Geometry optimization for van der Waals complex maybe it is easy to first optimize the relative van der Waals coordinate while keeping the intramolecular coordinate fixed. Then perform the full optimization

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

Mixed Methods G2



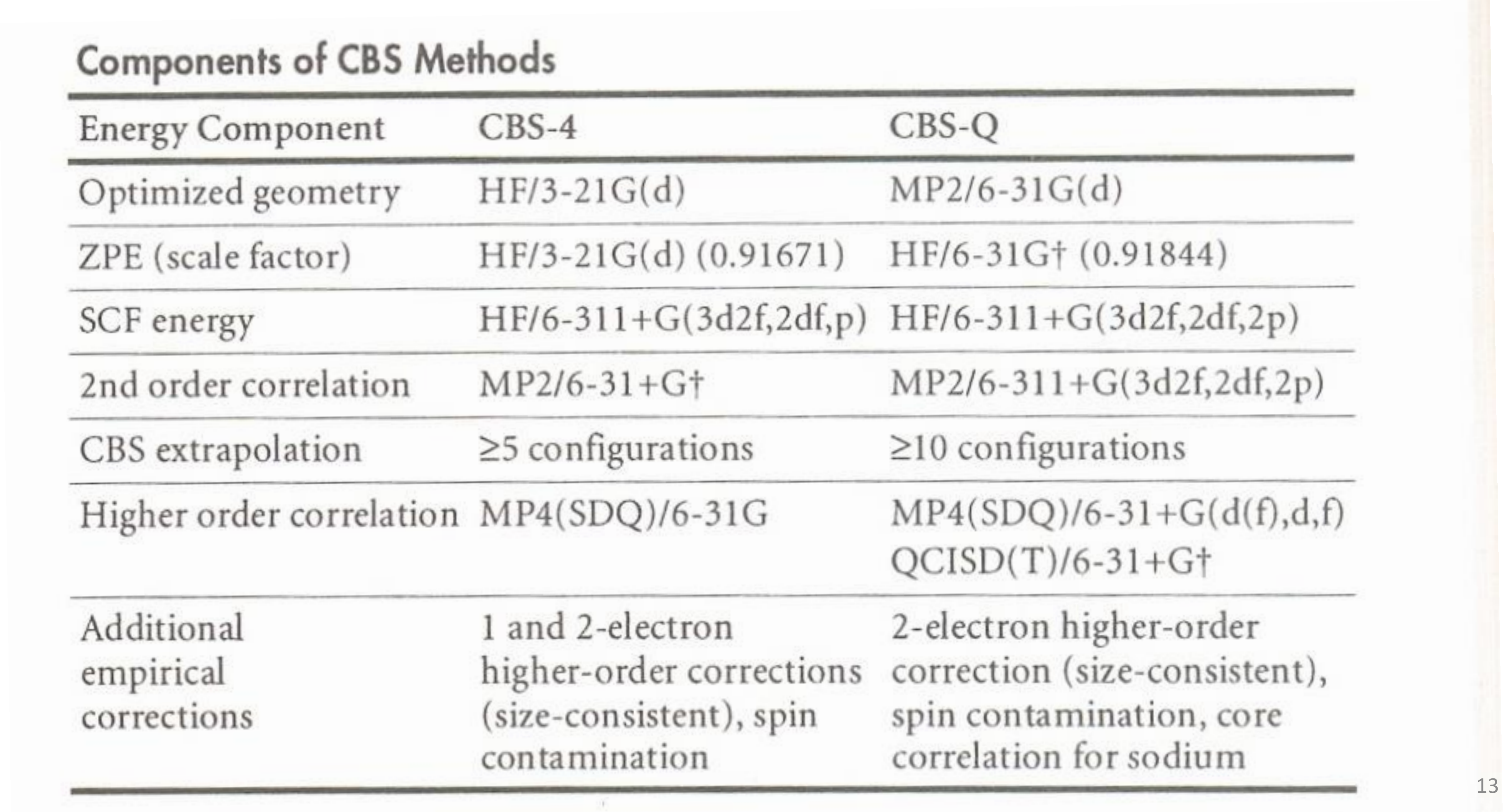
Components of G1 and G2 Total Energies

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



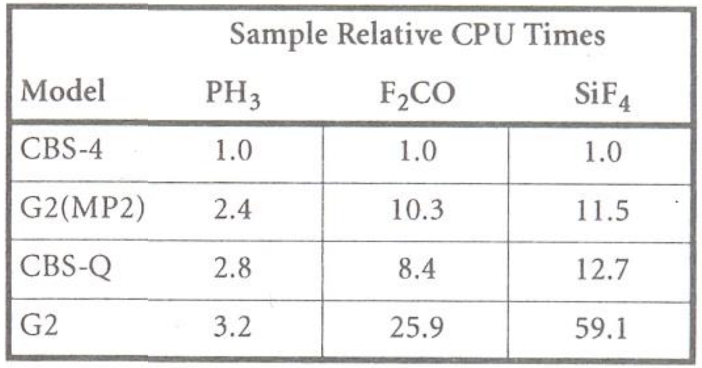
Components of CBS Methods

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

Kcal/mol

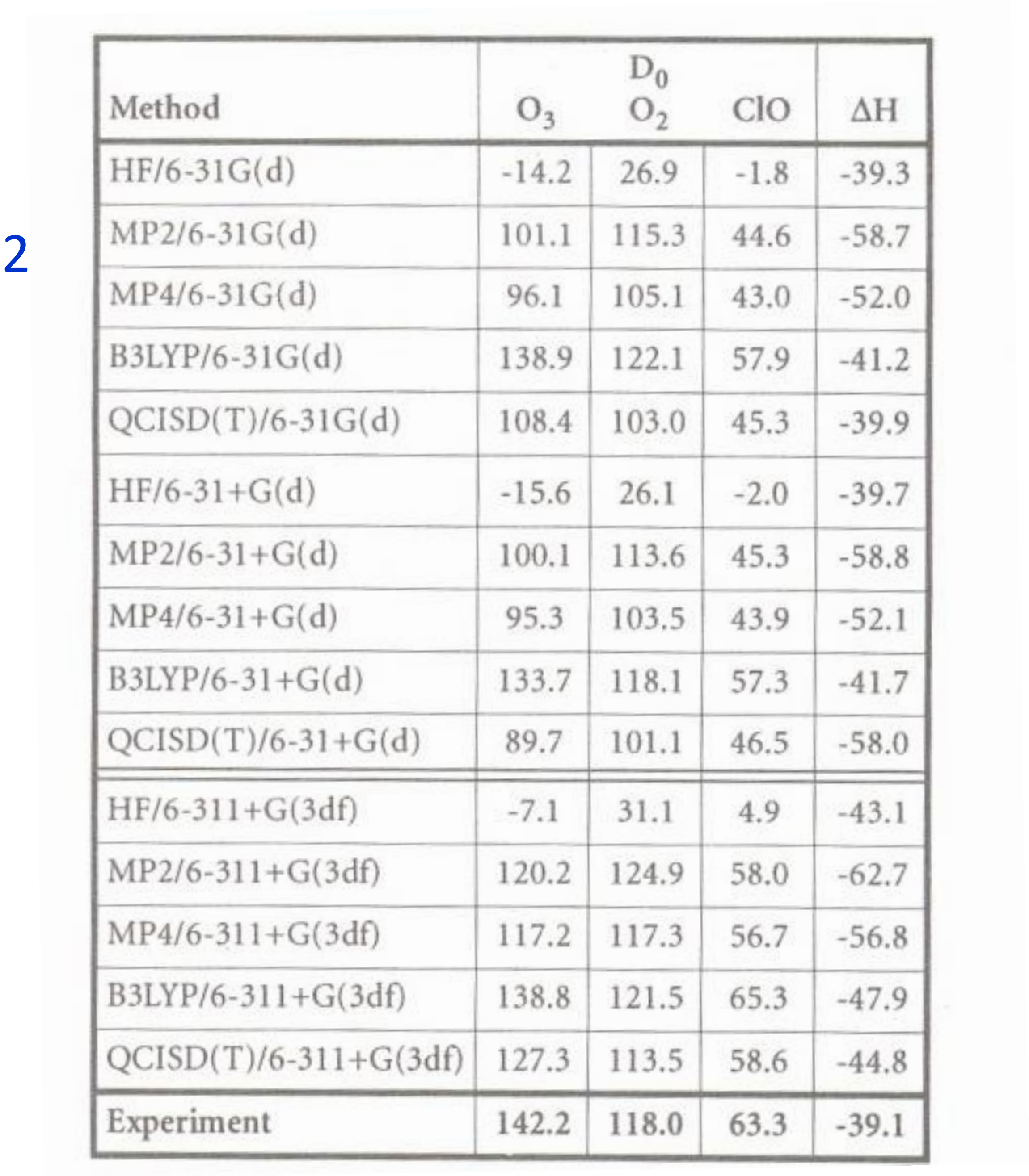


	Sample Relative CPU Times		
Model	PH_3	F_2CO	SiF_4
CBS-4	1.0	1.0	1.0
G2(MP2)	2.4	10.3	11.5
CBS-Q	2.8	8.4	12.7
G2	3.2	25.9	59.1

Ozone Hole Problem

$O_3 + Cl \rightarrow ClO + O_2$

$O_3 + ClO \rightarrow Cl + 2O_2$



Method		D_0		
	O_3	O_2	ClO	ΔH
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