

I will be away Mon and Wed (Mar 4 and Mar 6).

There will be a take home Midterm Exam available Friday, Mar 1 and due Friday Mar 8.

TABLE 16.1 H₂O Calculations That Include Correlation^a

Reference ^b	Method ^c / Basis Set	Energy / E _h	μ / D	θ	R _{OH}	α
Harrison, Handy	CISD/DZ	-76.150				
Harrison, Handy	FCI/DZ	-76.158				
CCCBDB	MP2(FC)/6-31G*	-76.197	2.24	104.0°	0.969	
CCCBDB	CISD(FC)/6-31G*	-76.198	2.24	104.2°	0.966	
CCCBDB	MP2(full)/6-31G*	-76.199	2.24	104.0°	0.969	
CCCBDB	CCSD(FC)/6-31G*	-76.206	2.25	103.9°	0.969	
CCCBDB	MP4(FC)/6-31G*	-76.207	2.25	103.8°	0.970	
CCCBDB	CCSD(T)(FC)/6-31G*	-76.208	2.25	103.8°	0.971	
CCCBDB	MP2(FC)/6-31G**	-76.220	2.20	103.8°	0.961	
CCCBDB	CISD(FC)/6-31G**	-76.221	2.19	104.2°	0.958	
CCCBDB	MP2(FC)/cc-pVDZ	-76.229	2.10	101.9°	0.965	
CCCBDB	CCSD(T)(FC)/cc-pVDZ	-76.241	2.10	101.9°	0.966	
Scuseria, Schaefer	CISDTQ/DZP	-76.270	2.13	104.5°	0.965	
Schaefer et al.	CISD/TZ2P	-76.312	1.94	104.9°	0.952	
CCCBDB	CISD(FC)/cc-pVTZ	-76.314	2.03	104.2°	0.955	
CCCBDB	MP2(FC)/6-31+G(3df,2p)	-76.318	2.02	104.5°	0.959	
CCCBDB	MP2(FC)/cc-pVTZ	-76.319	2.04	103.5°	0.959	
CCCBDB	CCSD(T)(FC)/cc-pVTZ	-76.332	2.04	103.6°	0.959	
Cortez et al.	CCSD(T)(FC)/cc-pV6Z	-76.372		104.4°	0.958	
Kim et al.	CISD(full)/(13s...2d) ^d	-76.382		104.8°	0.952	
Kim et al.	MP2(full)/(13s...2d)	-76.391		104.2°	0.959	
Kim et al.	CCSD(full)/(13s...2d)	-76.396		104.4°	0.956	
Kim et al.	CCSD(T)(full)/(13s...2d)	-76.406		104.1°	0.959	
Kim et al.	MP4(full)/(13s...2d)	-76.407		104.1°	0.960	
CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969	
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965	
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969	
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e				
Gurtubay, Needs	FN-DQMC	-76.428 ^e				
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	0.961	
Nonrelativistic fixed-nuclei energy		-76.438				
Experimental values		-76.480	1.85	104.5°	0.958	

^aSee footnote a to Table 15.2 in Section 15.6.^bR. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theor. Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.^d(13s...2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.^eCalculated at a geometry close to the experimental geometry.

If electron-correlation is added to the wavefunction, all properties converge to experimentally observed values.

CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e			
Gurtubay, Needs	FN-DQMC	-76.428 ^e			
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5°	0.961
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B3LYP is the most popular DFT method;

B3LYP/cc-pVTZ

99.87% of experiment;

Takes 5 sec on a PC (1 sec if SP)

CCCBDB	B3LYP/6-31G*	-76.409	2.10	103.6°	0.969
CCCBDB	B3LYP/6-31G**	-76.420	2.04	103.7°	0.965
CCCBDB	B3LYP/cc-pVDZ	-76.421	1.94	102.7°	0.969
Lüchow et al.	MRCISD/aug-cc-pCV5Z	-76.427 ^e			
Gurtubay, Needs	FN-DQMC	-76.428 ^e			
CCCBDB	B3LYP/cc-pVTZ	-76.460	1.92	104.5	0.961
<i>Nonrelativistic fixed-nuclei energy</i>		-76.438			
<i>Experimental values</i>		-76.480	1.85	104.5°	0.958

^aSee footnote a to Table 15.2 in Section 15.6.

^bR. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983); cccbdb.nist.gov; G. E. Scuseria and H. F. Schaefer, III, *Chem. Phys. Lett.*, **146**, 23 (1988); H. F. Schaefer, III et al., in *Yarkony*, Chapter 1; M. H. Cortez et al., *J. Chem. Theory Comput.*, **3**, 1267 (2007); J. Kim et al., *J. Chem. Phys.*, **102**, 310 (1995); A. Lüchow, J. B. Anderson, and D. Feller, *J. Chem. Phys.*, **106**, 7706 (1997); I. G. Gurtubay and R. J. Needs, *J. Chem. Phys.*, **127**, 124306 (2007).

^cFC denotes frozen-core calculations and full indicates that the frozen-core approximation is not used.

^d(13s . . . 2d) is an uncontracted (13s8p4d2f/8s4p2d) set with 131 basis functions.

^eCalculated at a geometry close to the experimental geometry.

Water B3LYP/cc-pVTZ

highest occupied MOs

Eigenvalues --				(A1)--O	(A1)--O	(B2)--O	(A1)--O	(B1)--O
1	1	O	1S	0.97322	-0.20503	0.00000	-0.07789	0.00000
2			2S	-0.00948	0.46648	0.00000	0.18513	0.00000
3			3S	0.05111	0.14123	0.00000	0.06005	0.00000
4			4S	0.00530	0.26510	0.00000	0.27685	0.00000
5			5PX	0.00000	0.00000	0.00000	0.00000	0.37000
6			5PY	0.00000	0.00000	0.29791	0.00000	0.00000
7			5PZ	-0.00157	-0.06592	0.00000	0.32240	0.00000
8			6PX	0.00000	0.00000	0.00000	0.00000	0.42182
9			6PY	0.00000	0.00000	0.32623	0.00000	0.00000
10			6PZ	-0.00027	-0.07862	0.00000	0.36176	0.00000
11			7PX	0.00000	0.00000	0.00000	0.00000	0.38755
12			7PY	0.00000	0.00000	0.15452	0.00000	0.00000
13			7PZ	-0.00087	-0.01589	0.00000	0.29150	0.00000
14			8D 0	0.00005	0.00142	0.00000	-0.00559	0.00000
15			8D+1	0.00000	0.00000	0.00000	0.00000	-0.00540
16			8D-1	0.00000	0.00000	-0.01142	0.00000	0.00000
17			8D+2	-0.00031	-0.00412	0.00000	0.00171	0.00000
18			8D-2	0.00000	0.00000	0.00000	0.00000	0.00000
19			9D 0	-0.00014	0.00335	0.00000	-0.01848	0.00000
20			9D+1	0.00000	0.00000	0.00000	0.00000	-0.01877
21			9D-1	0.00000	0.00000	-0.01521	0.00000	0.00000
22			9D+2	-0.00013	-0.00749	0.00000	0.00318	0.00000
23			9D-2	0.00000	0.00000	0.00000	0.00000	0.00000
24			10F 0	0.00009	0.00035	0.00000	0.00084	0.00000
25			10F+1	0.00000	0.00000	0.00000	0.00000	0.00140

		(A1)--O	(A1)--O	(B2)--O	(A1)--O	(B1)--O
	Eigenvalues --	-19.12112	-1.00831	-0.52771	-0.38542	-0.30952
25	10F+1	0.00000	0.00000	0.00000	0.00000	0.00149
26	10F-1	0.00000	0.00000	-0.00040	0.00000	0.00000
27	10F+2	0.00009	0.00182	0.00000	-0.00239	0.00000
28	10F-2	0.00000	0.00000	0.00000	0.00000	0.00000
29	10F+3	0.00000	0.00000	0.00000	0.00000	-0.00370
30	10F-3	0.00000	0.00000	-0.00258	0.00000	0.00000
31	2 H 1S	0.00041	0.09582	0.14975	-0.08763	0.00000
32	2S	-0.00188	0.08076	0.21228	-0.12074	0.00000
33	3S	-0.00037	0.01096	0.07888	-0.03201	0.00000
34	4PX	0.00000	0.00000	0.00000	0.00000	0.01032
35	4PY	0.00012	-0.01119	-0.00915	0.00914	0.00000
36	4PZ	-0.00017	0.00744	0.01270	0.00143	0.00000
37	5PX	0.00000	0.00000	0.00000	0.00000	0.03388
38	5PY	0.00078	-0.01197	-0.01400	0.01323	0.00000
39	5PZ	-0.00065	0.00571	0.02078	0.02105	0.00000
40	6D 0	-0.00011	-0.00010	0.00207	0.00230	0.00000
41	6D+1	0.00000	0.00000	0.00000	0.00000	0.00270
42	6D-1	0.00078	-0.00275	-0.00610	0.00046	0.00000
43	6D+2	0.00039	-0.00225	-0.00314	0.00319	0.00000
44	6D-2	0.00000	0.00000	0.00000	0.00000	-0.00414
45	3 H 1S	0.00041	0.09582	-0.14975	-0.08763	0.00000
46	2S	-0.00188	0.08076	-0.21228	-0.12074	0.00000
47	3S	-0.00037	0.01096	-0.07888	-0.03201	0.00000
48	4PX	0.00000	0.00000	0.00000	0.00000	0.01032

b3lyp/cc-pV6Z

%nproc=16

%mem=1000mw

%chk=Jean-h20-b3lypcc-pV6Z-opt.chk

#p opt b3lyp/cc-pV6Z pop=full

water molecule from Jean Standard pdf

0 1

8 0.000000 0.000000 0.116321

1 0 .000000 0.751155 -0.465285

1 0.000000 -0.751155 -0.465285

Molecular Orbital Coefficients:

b3lyp/cc-pV6Z

		1	2	3	4	5							
		(A1)--O	(A1)--O	(B2)--O	(A1)--O	(B1)--O							
Eigenvalues --		-19.13486	-1.02020	-0.54089	-0.39835	-0.32373							
1	O 1S	-0.42362	-0.08854	0.00000	-0.03273	0.00000	26	14D 0	-0.00001	0.00011	0.00000	-0.00054	0.00000
2	2S	0.45768	0.16731	0.00000	0.06303	0.00000	27	14D+1	0.00000	0.00000	0.00000	0.00000	-0.00053
3	3S	-0.18948	-0.09083	0.00000	-0.03551	0.00000	28	14D-1	0.00000	0.00000	-0.00102	0.00000	0.00000
4	4S	-0.01786	0.12380	0.00000	0.05610	0.00000	29	14D+2	0.00016	-0.00026	0.00000	0.00027	0.00000
5	5S	0.00224	0.36997	0.00000	0.11962	0.00000	30	14D-2	0.00000	0.00000	0.00000	0.00000	0.00000
6	6S	-0.01812	0.35495	0.00000	0.25183	0.00000	31	15D 0	-0.00002	0.00018	0.00000	-0.00085	0.00000
7	7S	-0.00490	0.10222	0.00000	0.25156	0.00000	32	15D+1	0.00000	0.00000	0.00000	0.00000	-0.00078
8	8PX	0.00000	0.00000	0.00000	0.00000	0.10938	33	15D-1	0.00000	0.00000	-0.00170	0.00000	0.00000
9	8PY	0.00000	0.00000	0.08977	0.00000	0.00000	34	15D+2	-0.00017	-0.00036	0.00000	0.00019	0.00000
10	8PZ	0.00112	-0.01940	0.00000	0.09652	0.00000	35	15D-2	0.00000	0.00000	0.00000	0.00000	0.00000
11	9PX	0.00000	0.00000	0.00000	0.00000	0.17454	36	16D 0	0.00008	0.00155	0.00000	-0.00751	0.00000
12	9PY	0.00000	0.00000	0.13847	0.00000	0.00000	37	16D+1	0.00000	0.00000	0.00000	0.00000	-0.00729
13	9PZ	-0.00006	-0.02947	0.00000	0.15148	0.00000	38	16D-1	0.00000	0.00000	-0.01464	0.00000	0.00000
14	10PX	0.00000	0.00000	0.00000	0.00000	0.27136	39	16D+2	-0.00012	-0.00465	0.00000	0.00398	0.00000
15	10PY	0.00000	0.00000	0.22858	0.00000	0.00000	40	16D-2	0.00000	0.00000	0.00000	0.00000	0.00000
16	10PZ	-0.00111	-0.05045	0.00000	0.24567	0.00000	41	17D 0	0.00016	0.00223	0.00000	-0.00315	0.00000
17	11PX	0.00000	0.00000	0.00000	0.00000	0.29499	42	17D+1	0.00000	0.00000	0.00000	0.00000	-0.00653
18	11PY	0.00000	0.00000	0.23350	0.00000	0.00000	43	17D-1	0.00000	0.00000	-0.02027	0.00000	0.00000
19	11PZ	0.00695	-0.05610	0.00000	0.23171	0.00000	44	17D+2	0.00341	-0.01071	0.00000	-0.00307	0.00000
20	12PX	0.00000	0.00000	0.00000	0.00000	0.20238	45	17D-2	0.00000	0.00000	0.00000	0.00000	0.00000
21	12PY	0.00000	0.00000	0.13388	0.00000	0.00000	46	18D 0	-0.00001	0.00045	0.00000	0.00447	0.00000
22	12PZ	0.00346	-0.02223	0.00000	0.11517	0.00000	47	18D+1	0.00000	0.00000	0.00000	0.00000	-0.00220
23	13PX	0.00000	0.00000	0.00000	0.00000	0.14066	48	18D-1	0.00000	0.00000	-0.00767	0.00000	0.00000
24	13PY	0.00000	0.00000	0.02908	0.00000	0.00000	49	18D+2	0.00151	-0.00380	0.00000	-0.00694	0.00000
25	13PZ	0.00015	-0.00114	0.00000	0.08782	0.00000	50	18D-2	0.00000	0.00000	0.00000	0.00000	0.00000
							51	19F 0	-0.00003	0.00004	0.00000	0.00001	0.00000

109	26H+2	0.00000	0.00002	0.00000	-0.00008	0.00000
110	26H-2	0.00000	0.00000	0.00000	0.00000	0.00000
111	26H+3	0.00000	0.00000	0.00000	0.00000	-0.00007
112	26H-3	0.00000	0.00000	-0.00009	0.00000	0.00000
113	26H+4	-0.00001	-0.00003	0.00000	0.00003	0.00000
114	26H-4	0.00000	0.00000	0.00000	0.00000	0.00000
115	26H+5	0.00000	0.00000	0.00000	0.00000	0.00003
116	26H-5	0.00000	0.00000	0.00004	0.00000	0.00000
117	27H 0	0.00002	0.00015	0.00000	-0.00016	0.00000
118	27H+1	0.00000	0.00000	0.00000	0.00000	-0.00008
119	27H-1	0.00000	0.00000	-0.00045	0.00000	0.00000
120	27H+2	0.00003	0.00012	0.00000	-0.00014	0.00000
121	27H-2	0.00000	0.00000	0.00000	0.00000	0.00000
122	27H+3	0.00000	0.00000	0.00000	0.00000	-0.00025
123	27H-3	0.00000	0.00000	-0.00044	0.00000	0.00000
124	27H+4	0.00006	-0.00034	0.00000	-0.00008	0.00000
125	27H-4	0.00000	0.00000	0.00000	0.00000	0.00000
126	27H+5	0.00000	0.00000	0.00000	0.00000	0.00020
127	27H-5	0.00000	0.00000	0.00025	0.00000	0.00000
128	28I 0	-0.00001	0.00001	0.00000	0.00003	0.00000
129	28I+1	0.00000	0.00000	0.00000	0.00000	0.00001
130	28I-1	0.00000	0.00000	0.00007	0.00000	0.00000
131	28I+2	0.00000	0.00003	0.00000	0.00002	0.00000
132	28I-2	0.00000	0.00000	0.00000	0.00000	0.00000
133	28I+3	0.00000	0.00000	0.00000	0.00000	0.00002
134	28I-3	0.00000	0.00000	0.00002	0.00000	0.00000
135	28I+4	0.00001	0.00008	0.00000	-0.00003	0.00000
136	28I-4	0.00000	0.00000	0.00000	0.00000	0.00000
137	28I+5	0.00000	0.00000	0.00000	0.00000	-0.00010
138	28I-5	0.00000	0.00000	-0.00011	0.00000	0.00000
139	28I+6	0.00000	-0.00002	0.00000	-0.00002	0.00000
140	28I-6	0.00000	0.00000	0.00000	0.00000	0.00000

**Last 32 CGTF coefficients
for the O atom**

321 (B2)--V 40.787038 43.939263
322 (A1)--V 105.789410 195.525732

Total kinetic energy from orbitals= 7.617168527125D+01

No NMR shielding tensors so no spin-rotation constants.

Leave Link 601 at Sat Mar 4 11:53:51 2017, MaxMem= 1048576000 cpu: 18.8

(Enter /g09/g09/l9999.exe)

1\1\GINC-MFRUITS\FOpt\RB3LYP\CC-pV6Z\H2O1\CALLIS\04-Mar-2017\0\#p opt
b3lyp/cc-pV6Z pop=full\water molecule from Jean Standard pdf\0,1\O,
0.,0.,0.1175449502\H,0.,0.7626351801,-0.4658969751\H,0.,-0.7626351801,
-0.4658969751\Version=AS64L-G09RevD.01\State=1-A1\ **HF=-76.4740629** \RMSD
=1.093e-09\RMSF=7.226e-05\Dipole=0.,0.,-0.7348709\Quadrupole=-1.131291
7,1.3222066,-0.1909149,0.,0.,0.\PG=C02V [C2(O1),SGV(H2)]\@

THE POLHOLDE ROLLS WITHOUT SLIPPING ON THE HERPOLHOLDE LYING IN
THE INVARIABLE PLANE.

H.GOLDSTEIN, "CLASSICAL MECHANICS", PG 161

Job cpu time: 0 days 3 hours 36 minutes 53.4 seconds. Clock time = 3.6 hrs/16 cpus
= **13.5 minutes with 16 cpus.** 3.6 hours (at least) on personal computer

File lengths (MBytes): RWF= 67 Int= 0 D2E= 0 Chk= 8 Scr= 1

Normal termination of Gaussian 09 at Sat Mar 4 11:53:51 2017.

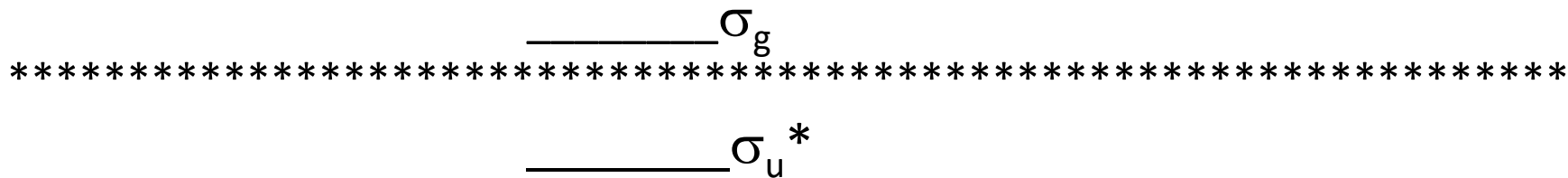
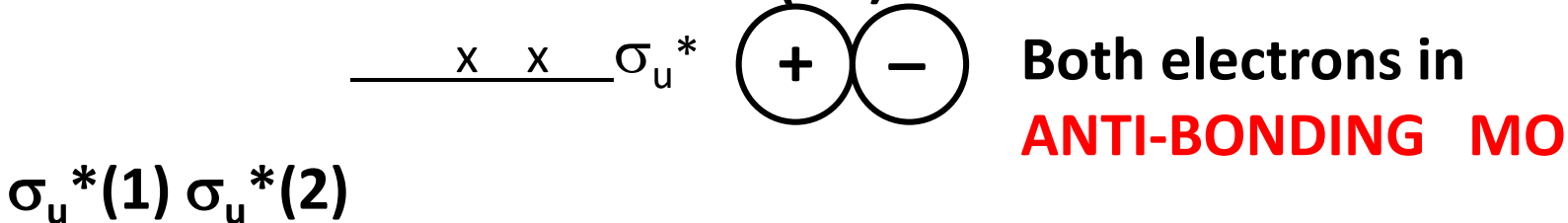
.out file was 87403 lines

How can CI (mixing higher energy state with ground state cause correlation???)

Higher states have more nodes. Squaring the linear combination gives cross terms (interference terms), which are negative when 2 electrons are on different sides of a nodal surface.

$\Psi^*\Psi$ is thereby *reduced*.

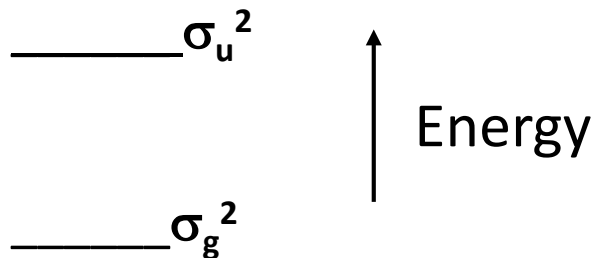
Example: The H_2 molecule (ionic and covalent terms, difference between the MO and Valence Bond (VB) methods



H₂ Molecule Configuration State Functions (CSFs)

A(1) = 1s(1) on Nucleus A B(1) = 1s(1) on Nucleus B

Doubly excited CSF



Ground CSF

$$\sigma_u^2 = [A(1) - B(1)] [A(2) - B(2)] = AA + BB - AB - BA \quad (\text{not normalized})$$

$$\sigma_g^2 = [A(1) + B(1)] [A(2) + B(2)] = AA + BB + AB + BA \quad (\text{not normalized})$$

ionic + covalent = molecular orbital method

covalent* = AB + BA = valence bond method

*Heitler-London (1927) the ***first*** wavefunction proposed for H₂ at the dawn of quantum mechanics.

Do a linear variation calculation:

$$H = \langle \sigma_g^2 | H | \sigma_g^2 \rangle \quad \langle \sigma_g^2 | H | \sigma_u^2 \rangle$$

$$\langle \sigma_u^2 | H | \sigma_g^2 \rangle \quad \langle \sigma_u^2 | H | \sigma_u^2 \rangle$$



$$\text{Ground} = c_{Lg} | \sigma_g^2 \rangle + c_{Lu} | \sigma_u^2 \rangle$$

Will $| \sigma_u^2 \rangle$ be added or subtracted from $| \sigma_g^2 \rangle$?

Depends on the sign of $\langle \sigma_g^2 | H | \sigma_u^2 \rangle$

$$|1\rangle = |\sigma_g^2\rangle = \sigma_g(1)\sigma_g(2) \equiv |gg\rangle$$

$$|2\rangle = \sigma_u(1)\sigma_u(2) \equiv |uu\rangle$$

$$g = 0.707 |A + B\rangle$$

$$u = 0.707(A - B) \text{ where } A = 1s_A, B = 1s_B$$

$$\langle 1 | H | 2 \rangle = \langle gg | h_1 + h_2 + 1/r_{12} | uu \rangle$$

$$= 2 \langle g | h | u \rangle \langle g | u \rangle = 0$$

$$\langle 1 | H | 2 \rangle = \langle gg | 1/r_{12} | uu \rangle \equiv (gg | uu)$$

in Parr notation

$$= 1/4(A + B)(A + B) | (A - B)(A - B)$$

$$= 1/4[(AA + BB + AB + BA | AA + BB - AB - BA)$$

$$= 1/4[(AA | AA) + (AA | BB) - (AA | AB) - (AA | BA) +$$

$$(BB | AA) + (BB | BB) - (BB | AB) - (BB | BA) +$$

$$(AB | AA) + (AB | BB) - (AB | AB) - (AB | BA) +$$

$$(BA | AA) + (BA | BB) - (BA | AB) - (BA | BA)]$$

$$\langle 1 | H | 2 \rangle =$$

$$\langle 1 | 1/r_{12} | 2 \rangle = \frac{1}{2}[(AA | AA) + (AA | BB) - (AA | AB) - (AA | BA) + (BB | AA) + (BB | BB) - (BB | AB) - (BB | BA) + (AB | AA) + (AB | BB) - (AB | AB) - (AB | BA) + (BA | AA) + (BA | BB) - (BA | AB) - (BA | BA)]$$

(where the $1/r_{12}$ is left out in the Parr notations)

Note that almost all of the terms with AB are NEGATIVE

But r_{12} is large when the two electrons are on different atoms,

which means anything involving AB will be negligible relative to $(AA | AA)$, $(BB | BB)$, and $(AA | BB)$. Therefore,

$\langle 1 | H | 2 \rangle$ is clearly **positive**.

$\Psi = |gg\rangle - c|uu\rangle$, where c is positive

$$\Psi = |gg\rangle - c|uu\rangle$$

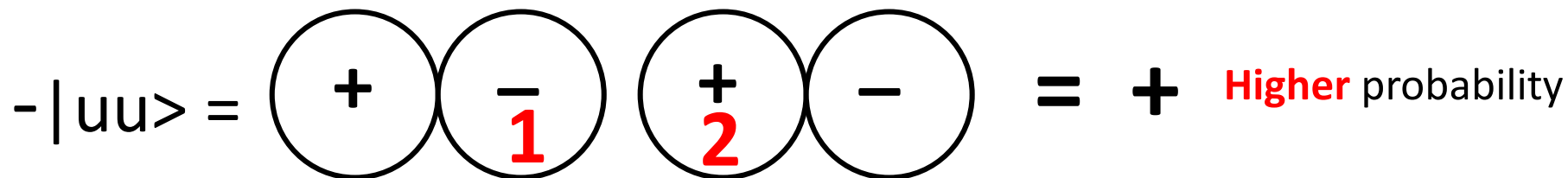
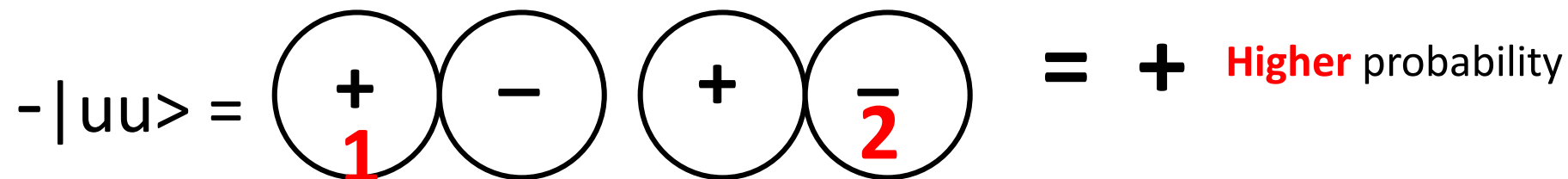
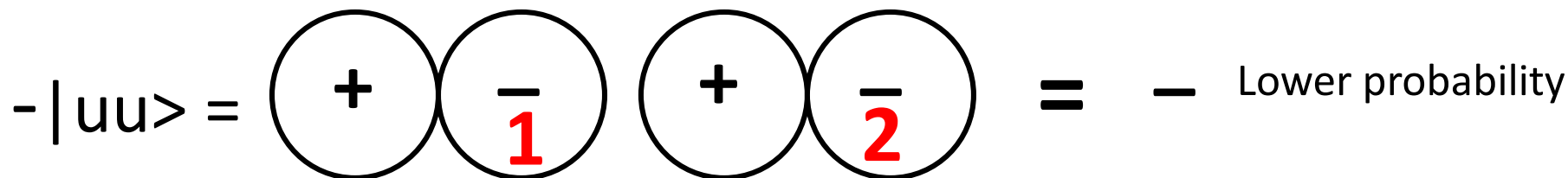
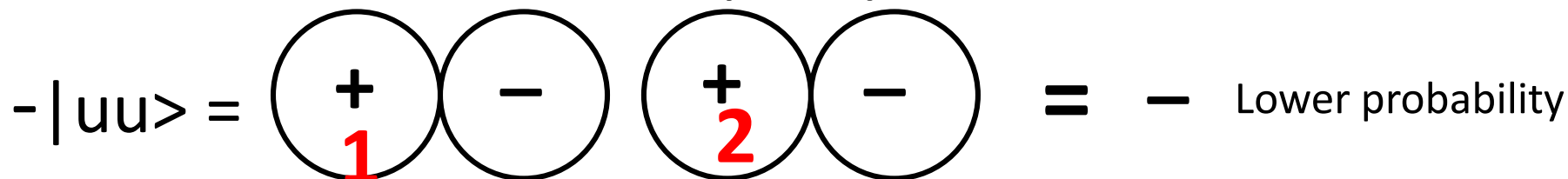
$$\Psi^2 \text{ is proportional to } [|gg\rangle - c|uu\rangle]^2$$

$$= |gg\rangle^2 + c^2|uu\rangle^2 - 2c|gg\rangle|uu\rangle$$

$|uu\rangle$ can be positive or negative, depend on where electrons 1 and 2 are located.

If e1 and e2 are in same lobe $-2c|uu\rangle$ is neg. and Ψ^2 is reduced

If e1 and e2 are in different lobes, $-2c|uu\rangle$ is positive, and Ψ^2 is increased

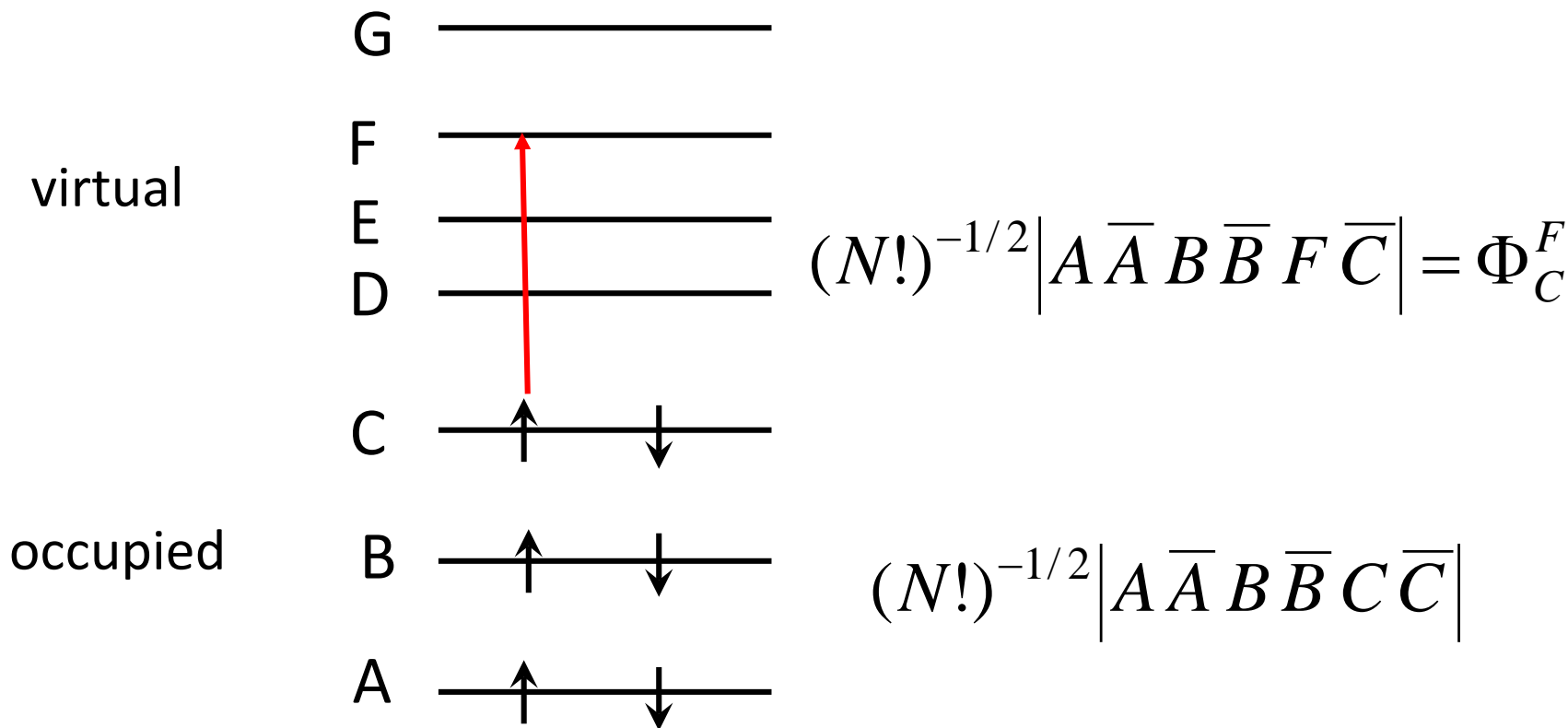


CI-singles (CIS) (important for understanding spectra)

$$(N!)^{-1/2} |A \bar{A} B \bar{B} C \bar{C}|$$

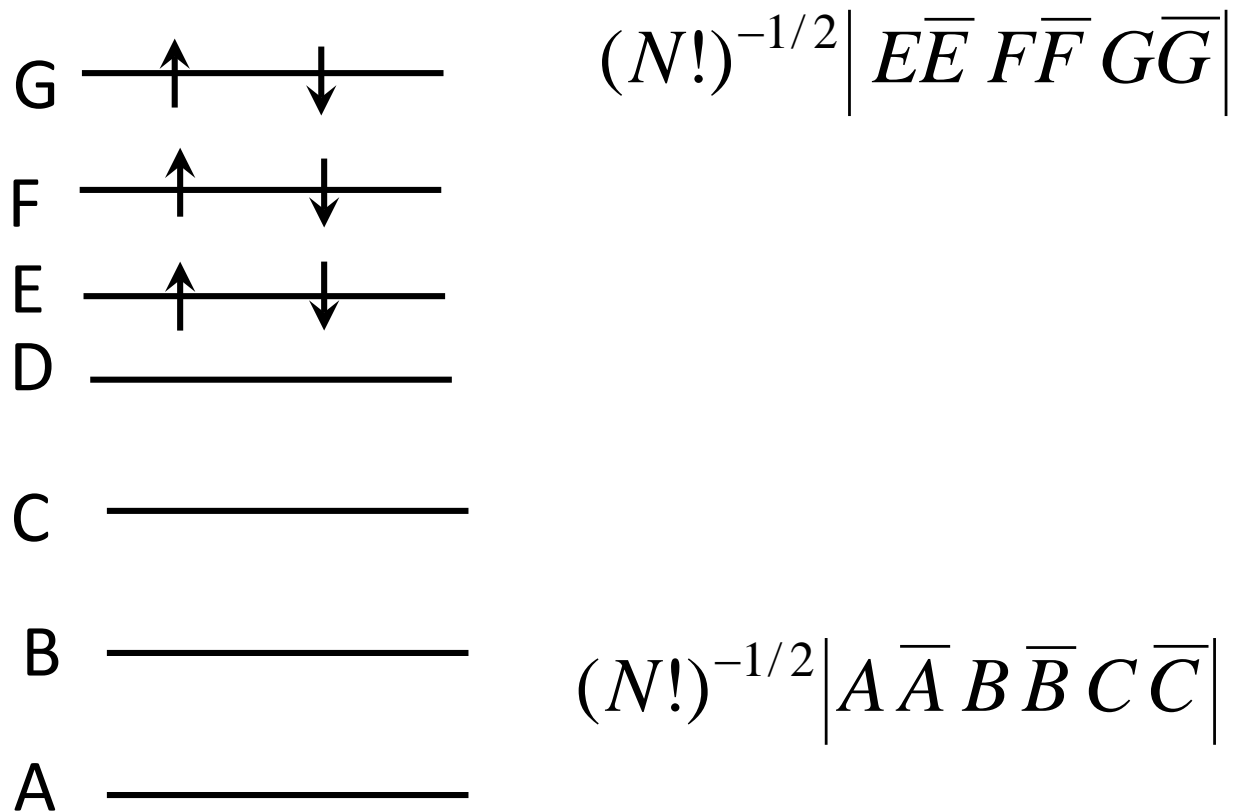
If ground state is

$$\Psi_{CIS} = \sum_{o=A,C}^{v=D-G} \Phi_o^v$$



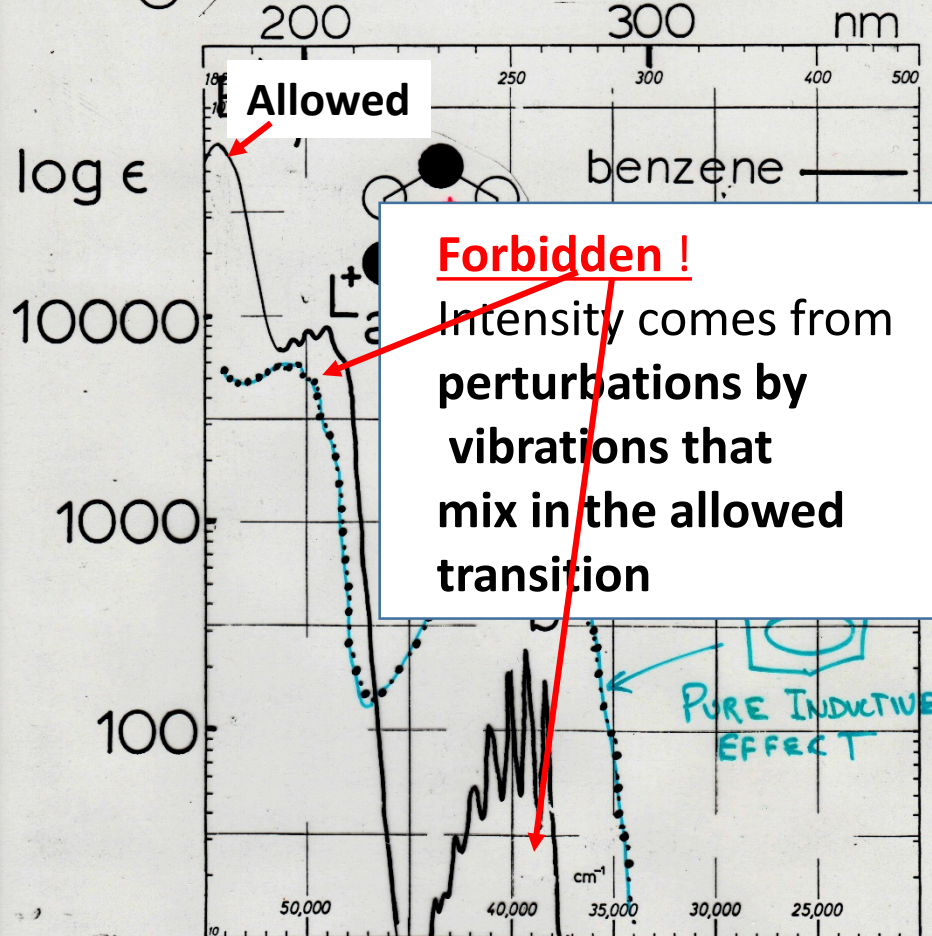
Example of Full CI (FCI)

High energy CSF for six electrons and 7 basis functions



$$(N!)^{-1/2} |A\bar{A} B\bar{B} C\bar{C}|$$

If the basis set is *complete*, and if we include *all possible configurations*, the eigenvalues and eigenstates will be **exact**.



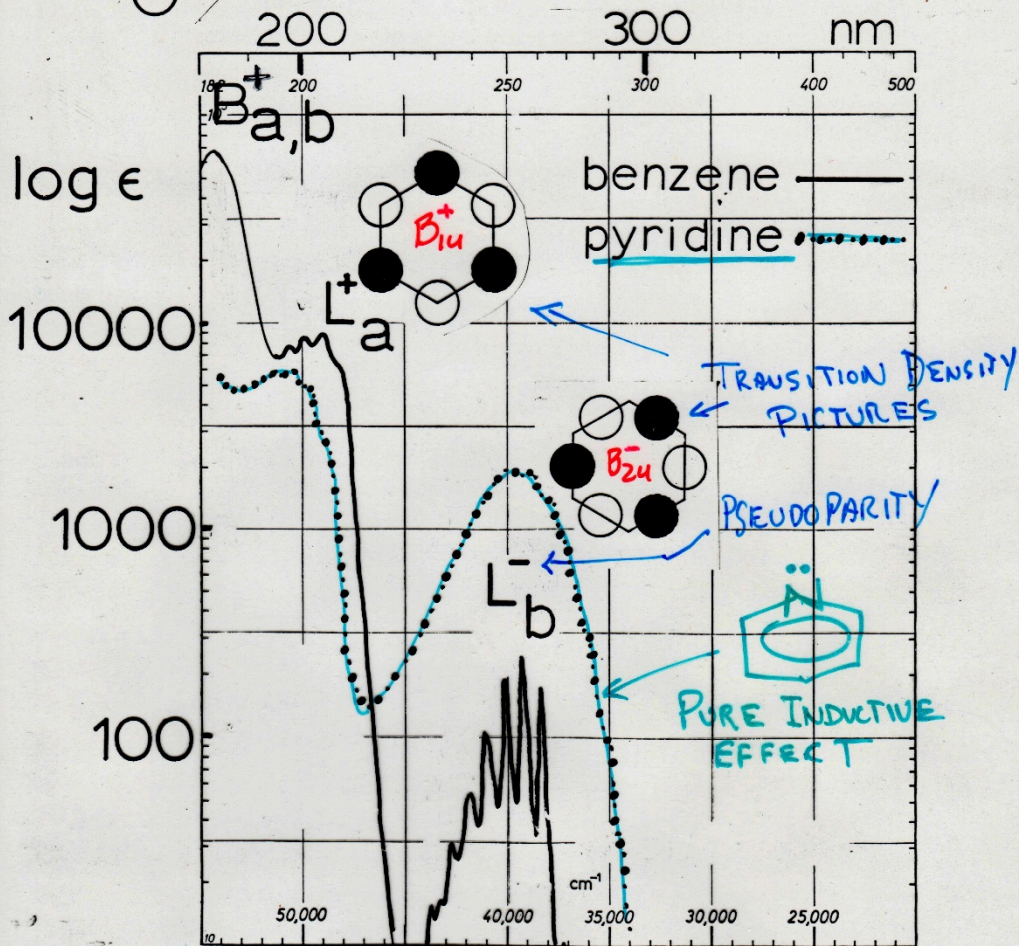
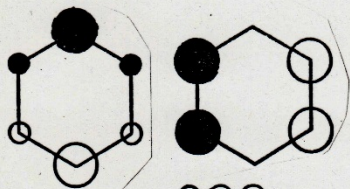
200 nm 250 nm

Just look at spectra on
LOG SCALE

$$40000 \text{ cm}^{-1} = 250 \text{ nm}$$

E_{1u}^+ _{a,b}

ONE-PHOTON ABS.
(LOG SCALE)



L_b^- AND L_a^+ FORBIDDEN FOR BENZENE
ALLOWED FOR PYRIDINE

(Reduced) 1st order
Transition Density is
Product of Ground
and Excited state
wavefunctions

(integrated over all but one
electron)

Example of G09 CIS calculation for benzene

CIS = Configuration Interaction Singly-Excited (configurations)

```
%chk=C:\564-17\benzene1.chk
```

```
# cis=nstates=5/ 3-21g pop=reg density=current
```

```
( method )/(basis set) (needed to get excited  
state density)
```

```
Title Card Required
```

```
0 1
```

C	1.20809735	0.69749533	-0.00000000
C	0.00000000	1.39499067	-0.00000000
C	-1.20809735	0.69749533	-0.00000000
C	-1.20809735	-0.69749533	-0.00000000
C	0.00000000	-1.39499067	-0.00000000
C	1.20809735	-0.69749533	-0.00000000
H	2.16038781	1.24730049	-0.00000000
H	0.00000000	2.49460097	-0.00000000
H	-2.16038781	1.24730049	-0.00000000
H	-2.16038781	-1.24730049	-0.00000000
H	0.00000000	-2.49460097	-0.00000000
H	2.16038781	-1.24730049	-0.00000000

 Excited states from <AA,BB:AA,BB> singles matrix:

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.0000	0.0000	0.0000	0.0000	0.0000
3	0.0172	-2.2976	0.0000	5.2793	1.1398
4	-2.2976	-0.0172	0.0000	5.2793	1.1398
5	0.0000	0.0000	0.0000	0.0000	0.0000

Ground to excited state transition velocity dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.0000	0.0000	0.0000	0.0000	0.0000
3	-0.0015	0.1978	0.0000	0.0391	0.0806
4	0.1978	0.0015	0.0000	0.0391	0.0806
5	0.0000	0.0000	0.0000	0.0000	0.0000

Ground to excited state transition magnetic dipole moments (Au):

state	X	Y	Z
1	0.0000	0.0000	0.0000
2	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000
5	0.0000	0.0000	0.0000

Excited state symmetry could not be determined.

Excited State 2: Singlet-?Sym 6.7916 eV 182.55 nm

f=0.0000 <S**2>=0.000

20 -> 22 -0.49024

21 -> 23 0.49024

Excited state symmetry could not be determined.

Excited State 3: Singlet-?Sym 8.8123 eV 140.70 nm

f=1.1398 <S**2>=0.000

20 -> 22 0.48350

21 -> 23 0.48350

Excited state symmetry could not be determined.

Excited State 4: Singlet-?Sym 8.8123 eV 140.70 nm

f=1.1398 <S**2>=0.000

20 -> 23 0.48350

21 -> 22 -0.48350

Excited state symmetry could not be determined.

Excited State 5: Singlet-?Sym 9.5510 eV 129.81 nm

f=0.0000 <S**2>=0.000

14 -> 30 0.16335

18 -> 22 0.47542

19 -> 23 0.47542

Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.

Excited State 1: Singlet-?Sym 6.5521 eV 189.23 nm f=0.0000
 <S**2>=0.000 exp 40,000 cm⁻¹ = 265 nm
 20 -> 23 0.49957
 21 -> 22 0.49957

Excited State 2: Singlet-?Sym 6.7916 eV 182.55 nm f=0.0000
 <S**2>=0.000 exp =50,000 cm⁻¹ = 200 nm
 20 -> 22 -0.49024
 21 -> 23 0.49024

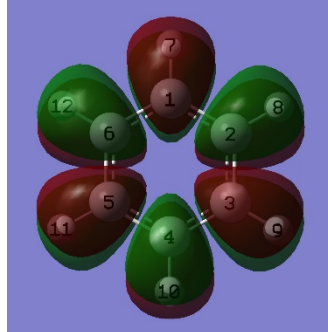
Excited State 3: Singlet-?Sym 8.8123 eV 140.70 nm f=1.1398
 <S**2>=0.000 exp 54,000 cm⁻¹ = 185 nm
 20 -> 22 0.48350
 21 -> 23 0.48350

Excited State 4: Singlet-?Sym 8.8123 eV 140.70 nm f=1.1398
 <S**2>=0.000 exp 54,000 cm⁻¹ = 185 nm
 20 -> 23 0.48350
 21 -> 22 -0.48350

Excited state symmetry could not be determined.

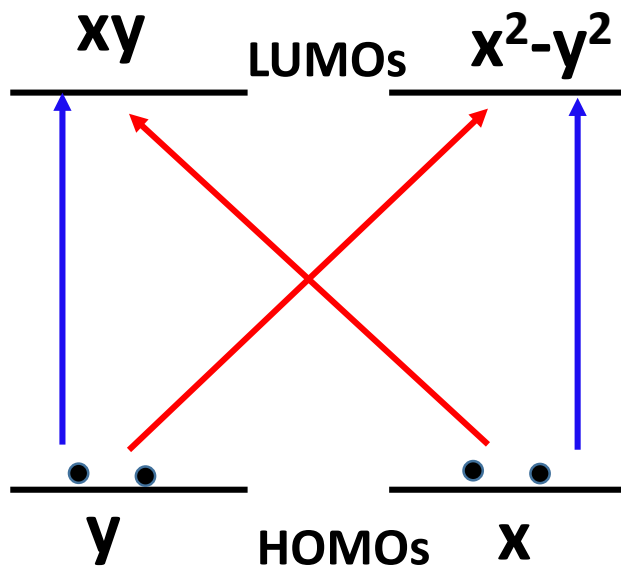
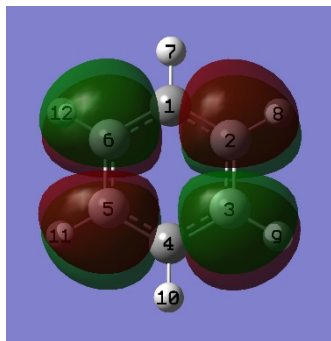
Excited State 5: Singlet-?Sym 8.5510 eV 129.81 nm f=0.0000

π MOs of Benzene

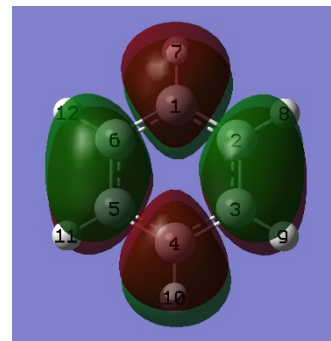


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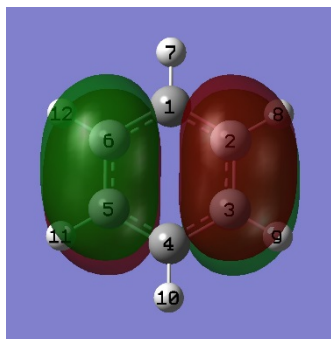
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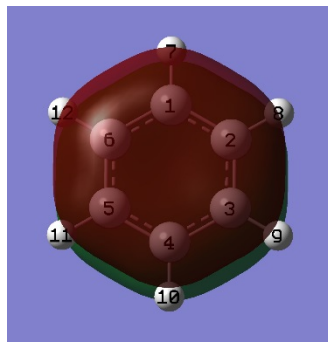
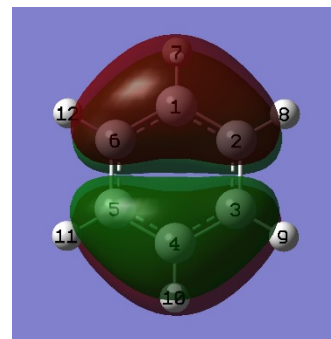
22



21



20



S