TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

Lecture 5 of 6

TEXAS A&M UNIVERSITY
## Division of Research

Excited State Methods

If the excited state has a different spin or symmetry, you can perform a Single Point Energy (SPE) or Geometry Optimization using the correct spin and/or orbital occupation.

O_2 triplet ground state

singlet excited state

OsC_2^+ in C_{2v} symmetry:

$^2A_1$, $^2A_2$, $^2B_1$, or $^2B_2$

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

Symmetry and Excited States
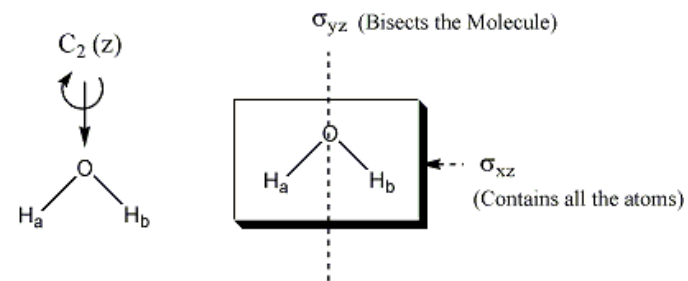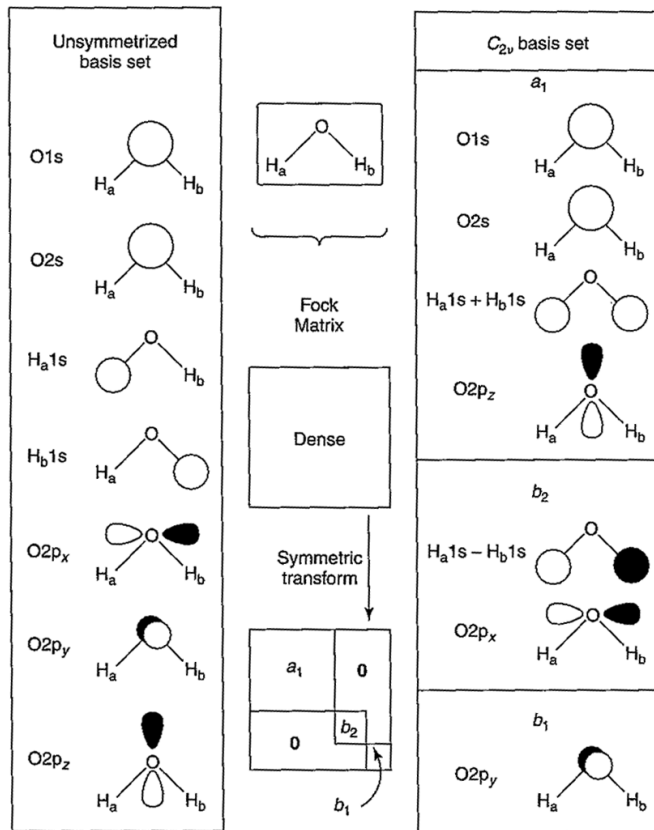
| C_{2v}	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
$a_1 x b_1$	1x1	1x(−1)	1x(1)	1x(−1)
b_1	1	−1	1	−1
$b_1 x b_2$	1x1	−1x(−1)	1x(−1)	−1x(1)
a_2	1	1	−1	−1

```
Orbital symmetries:
Alpha Orbitals:
    Occupied  (A1) (A1) (B2) (B1) (A1) (A1)
    Virtual   (B2)
Beta  Orbitals:
    Occupied  (A1) (A1) (B2) (A1)
    Virtual   (B1) (A1) (B2)
The electronic state is 3-B1.
Alpha  occ. eigenvalues --  -20.43372  -1.43457  -0.70542  -0.63599  -0.62365
Alpha  occ. eigenvalues --    0.02368
Alpha virt. eigenvalues --    0.56142
 Beta  occ. eigenvalues --  -20.38194  -1.19468  -0.62529  -0.50668
 Beta virt. eigenvalues --    0.27727   0.63457   0.70966
    Alpha Molecular Orbital Coefficients
                            1          2          3          4          5
                          (A1)--O    (A1)--O    (B2)--O    (B1)--O    (A1)--O
      EIGENVALUES --     -20.43372   -1.43457   -0.70542   -0.63599   -0.62365
  1 1   O  1S            0.99408   -0.24869    0.00000    0.00000   -0.07293
  2        2S            0.02635    0.93457    0.00000    0.00000    0.36237
  3        2PX           0.00000    0.00000    0.00000    1.00000    0.00000
  4        2PY           0.00000    0.00000    0.63670    0.00000    0.00000
  5        2PZ          -0.00306   -0.13811    0.00000    0.00000    0.87907
  6 2   H  1S           -0.00560    0.08032    0.41335    0.00000   -0.18056
  7 3   H  1S           -0.00560    0.08032   -0.41335    0.00000   -0.18056
                            6          7
                          (A1)--O    (B2)--V
      EIGENVALUES --       0.02368    0.56142
  1 1   O  1S            0.11965    0.00000
  2        2S           -0.80891    0.00000
  3        2PX           0.00000    0.00000
  4        2PY           0.00000    0.95591
  5        2PZ           0.58523    0.00000
  6 2   H  1S            0.81596   -0.81581
  7 3   H  1S            0.81596    0.81581
    Beta Molecular Orbital Coefficients.
                            1          2          3          4          5
                          (A1)--O    (A1)--O    (B2)--O    (A1)--O    (B1)--V
      EIGENVALUES --     -20.38194   -1.19468   -0.62529   -0.50668    0.27727
  1 1   O  1S            0.99466   -0.24048    0.00000   -0.06484    0.00000
  2        2S            0.02379    0.88678    0.00000    0.35254    0.00000
  3        2PX           0.00000    0.00000    0.00000    0.00000    1.00000
  4        2PY           0.00000    0.00000    0.72027    0.00000    0.00000
  5        2PZ          -0.00255   -0.03603    0.00000    0.85179    0.00000
  6 2   H  1S           -0.00495    0.13466    0.33814   -0.22974    0.00000
  7 3   H  1S           -0.00495    0.13466   -0.33814   -0.22974    0.00000
```

$b_1 \times a_1 \rightarrow {}^3B_1$

If we want the ${}^3A_1$ state, we will need to swap β orbitals 4 and 5 using the guess=(read,alter) keyword
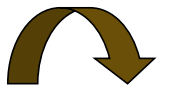
```
%chk=h2o.chk
#p hf/sto-3g pop=full guess=(read,alter)
b1
title
b1
0 3
O
H 1 b1
H 1 b1 2 a1
b1
b1 1.0
a1 109.5
b1
b1                        ← Alpha orbital swap section
4 5                       ← Beta orbital swap section
b1
```

Alpha Molecular Orbital Coefficients

				1	2	3	4	5
				(A1)--O	(A1)--O	(A1)--O	(B2)--O	(B1)--O
		EIGENVALUES --		-20.35050	-1.37970	-0.68279	-0.68060	-0.49934
1	1	O	1S	0.99410	-0.24739	-0.06231	0.00000	0.00000
2			2S	0.02615	0.92150	0.32104	0.00000	0.00000
3			2PX	0.00000	0.00000	0.00000	0.00000	1.00000
4			2PY	0.00000	0.00000	0.00000	0.59599	0.00000
5			2PZ	-0.00220	-0.07595	0.88247	0.00000	0.00000
6	2	H	1S	-0.00541	0.10043	-0.18707	0.44725	0.00000
7	3	H	1S	-0.00541	0.10043	-0.18707	-0.44725	0.00000

				6	7
				(A1)--O	(B2)--V
		EIGENVALUES --		0.03115	0.57703
1	1	O	1S	-0.12783	0.00000
2			2S	0.84074	0.00000
3			2PX	0.00000	0.00000
4			2PY	0.00000	0.98180
5			2PZ	-0.59145	0.00000
6	2	H	1S	-0.81226	-0.79773
7	3	H	1S	-0.81226	0.79773

Beta Molecular Orbital Coefficients.

				1	2	3	4	5
				(A1)--O	(A1)--O	(B2)--O	(B1)--O	(A1)--V
		EIGENVALUES --		-20.30251	-1.16482	-0.59165	-0.42211	0.15055
1	1	O	1S	0.99450	-0.24181	0.00000	0.00000	-0.09597
2			2S	0.02448	0.89422	0.00000	0.00000	0.53599
3			2PX	0.00000	0.00000	0.00000	1.00000	0.00000
4			2PY	0.00000	0.00000	0.72450	0.00000	0.00000
5			2PZ	-0.00204	-0.06820	0.00000	0.00000	0.70571
6	2	H	1S	-0.00508	0.12513	0.33411	0.00000	-0.38197
7	3	H	1S	-0.00508	0.12513	-0.33411	0.00000	-0.38197

				6	7
				(A1)--V	(B2)--V
		EIGENVALUES --		0.70643	0.74863
1	1	O	1S	0.11385	0.00000
2			2S	-0.75648	0.00000
3			2PX	0.00000	0.00000
4			2PY	0.00000	0.89120
5			2PZ	0.79476	0.00000
6	2	H	1S	0.73709	-0.85134
7	3	H	1S	0.73709	0.85134

```
No Alpha orbitals switched.
 Pairs of Beta  orbitals switched:
   4   5
Initial guess orbital symmetries:
Alpha Orbitals:
     Occupied  (A1) (A1) (B2) (B1) (A1) (A1)
     Virtual   (B2)
Beta  Orbitals:
     Occupied  (A1) (A1) (B2) (B1)
     Virtual   (A1) (A1) (B2)
The electronic state of the initial guess is 3-A1.

Alpha Orbitals:
     Occupied  (A1) (A1) (A1) (B2) (B1) (A1)
     Virtual   (B2)
Beta  Orbitals:
     Occupied  (A1) (A1) (B2) (B1)
     Virtual   (A1) (A1) (B2)
The electronic state is 3-A1.
Alpha  occ. eigenvalues --  -20.35050  -1.37970  -0.68279  -0.68060  -0.49934
Alpha  occ. eigenvalues --    0.03115
Alpha virt. eigenvalues --    0.57703
 Beta  occ. eigenvalues --  -20.30251  -1.16482  -0.59165  -0.42211
 Beta virt. eigenvalues --    0.15055   0.70643   0.74863
```

Excited State Methods

CIS – Configuration Interaction Singles. CIS gives HF quality results for excited states.

RPA – Random Phase Approximation. Similar to CIS but includes double excitations in the calculation of the excited state energies.

CIS(D) – Configuration Interaction Singles with 2nd order Perturbative correction for the excitation energies.

Time-Dependent Density Functional Theory (TD-DFT)

Excited State Methods

- CIS – Configuration Interaction Singles.
  - CIS gives HF quality results for excited states

TABLE III. Lowest lying singlet states of C_6H_6 at the 6-31+G* level of theory using various theoretical methods.

Symmetry	CIS	RPA	B3LYP	BPW91	LSDA	Experiment
B_{2u} $(\pi \to \pi^*)$	6.15	5.96	5.40	5.19	5.31	4.9
B_{1u} $(\pi \to \pi^*)$	6.31	6.01	6.06	5.93	6.10	6.2
E_{1g} $(\pi \to 3s)$	7.13	7.12	6.34	6.34	6.36	6.33
A_{2u} $(\pi \to 3p)$	7.45	7.43	6.84	6.87	6.99	6.93
E_{2u} $(\pi \to 3p)$	7.75	7.74	6.88	6.85	6.98	6.95
E_{1u} $(\pi \to \pi^*)$	7.94	7.52	6.96	6.84	6.94	7.0

J. Chem. Phys., Vol. 109, 1998, 8218

Excited State Methods

- CIS
  - Oscillator strengths are proportional to extinction coefficient

Excitation energies and oscillator strengths:

Excited State   1:   Singlet-A   6.1546 eV 201.45 nm f=0.0000 <S**2>=0.000
    20 -> 27   0.47187
    20 -> 38   -0.15934
    21 -> 28   0.47187
    21 -> 39   -0.15934
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:   Singlet-A   6.3056 eV 196.63 nm f=0.0000 <S**2>=0.000
    20 -> 28   -0.46761
    20 -> 39   0.14725
    21 -> 27   0.46763
    21 -> 38   -0.14725

Excited State   3:   Singlet-A   7.1275 eV 173.95 nm f=0.0000 <S**2>=0.000
    21 -> 22   0.65758
    21 -> 34   -0.11577
    21 -> 48   0.11247

Benzene CIS output

- ## Excitation 1 $\pi \rightarrow \pi^*$

Excited State   1:   Singlet-A   6.1546 eV   201.45 nm   f=0.0000   <S**2>=0.000

     20 -> 27   0.47187

     20 -> 38   -0.15934

     21 -> 28   0.47187

     21 -> 39   -0.15934

27   28

20 (HOMO-1)   21 (HOMO)
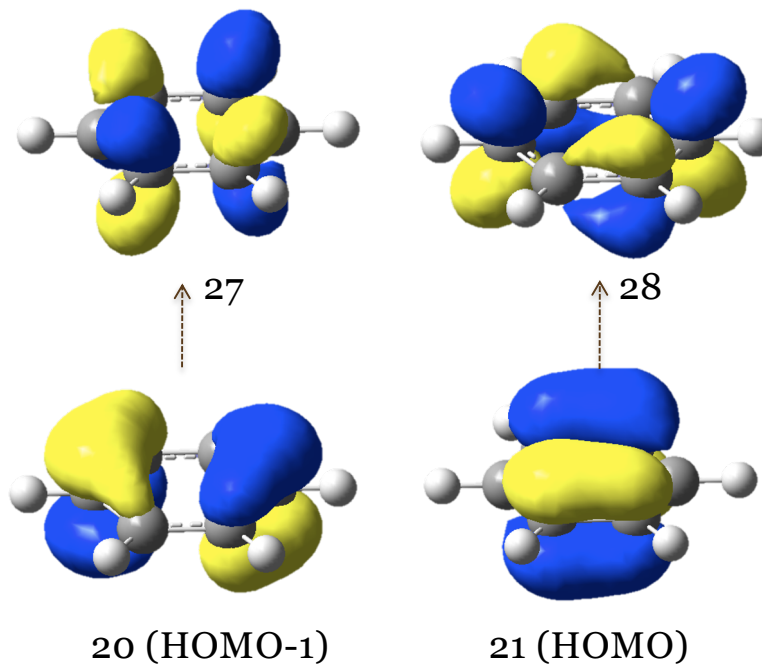
UV/Vis spectra via TD-DFT
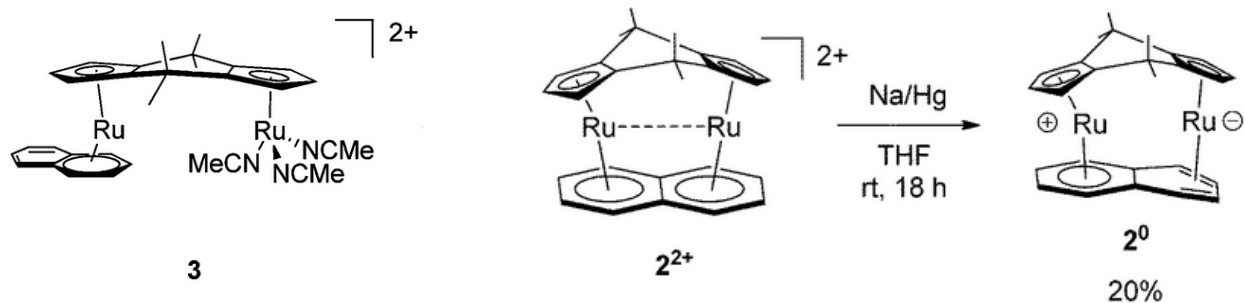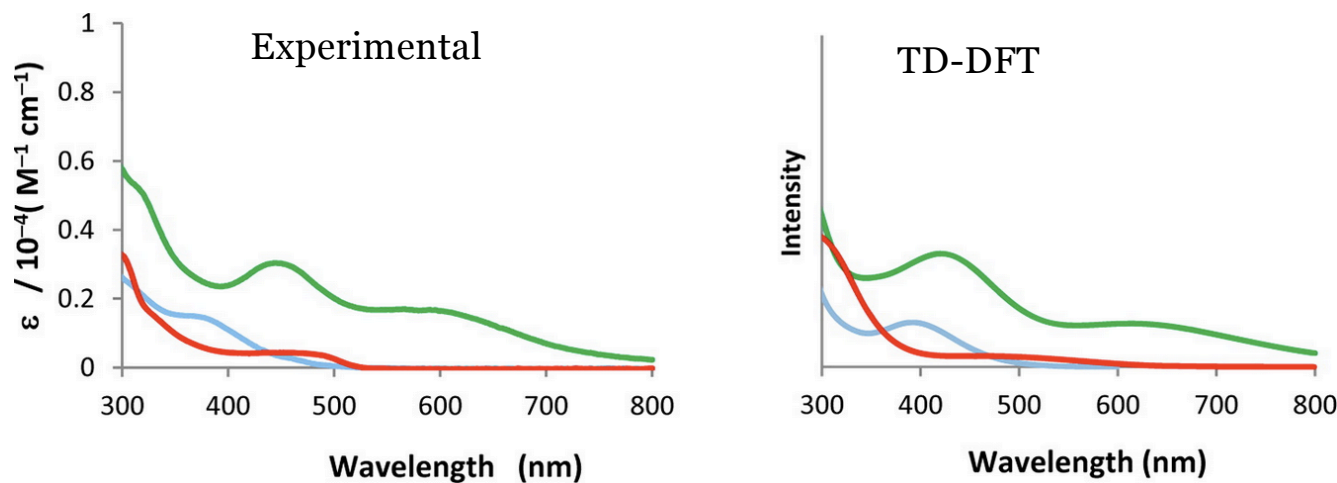
Excited State Methods

SAC-CI – Symmetry Adapted Cluster Configuration Interaction

EOM-CCSD – Equation of Motion – Coupled Cluster Singles and Doubles.

Multi-Reference Excited State Methods:

CASSCF – Complete Active Space Self-Consistent Field. Multi-reference Hartree-Fock.

CAS-PT2 – Complete Active Space Self- Consistent Field with MP2 corrected energies.

MRCI – Multi-Reference Configuration Interaction.

Semi-empirical Calculations

- Based on HF formulism – $FC = SC\varepsilon$
  - Iterative
- core e^- are not treated explicitly
- each atom is described by 1STO
- 2e$^-$ integrals are replaced with parameters (V_{ee})
- Parameterized to reproduce Heats of Formation
- Commonly used semi-empirical models
  - AM1 – austin model 1 (Dewar)
  - PM3 – 3rd parameterization of MNDO (Stewart)
  - PM7 – 7th parameterization of MNDO which includes more transition metals (http://openmopac.net/PM7_accuracy/PM7_accuracy.html).
  - ZINDO/S – parameterized to calculate electronic spectra (primarily for organic species)

Semi-Empirical

- AM1 – Austin Model 1
  - Heavily used for organic compound containing 1st row main group elements (ie C, N, O)
  - Reasonable geometries
  - Poor for hydrogen bonding
  - heavier elements are often represented with MNDO

- PM3 – Parameter Model 3
  - Also heavily used with a wider range of elements available
  - utilizes an extra molecular mechanics

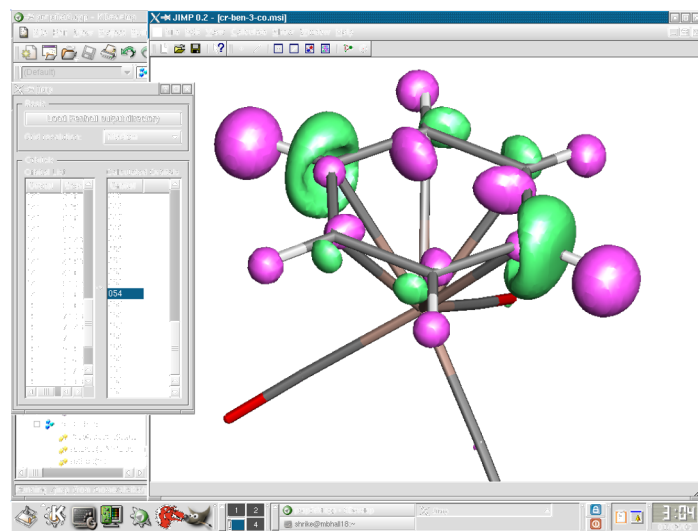 term to accurately describe peptide bonds
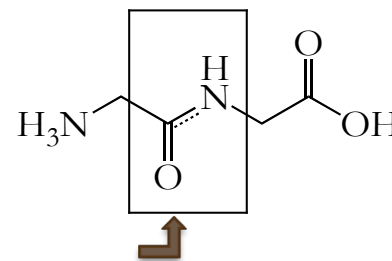
ZINDO/S
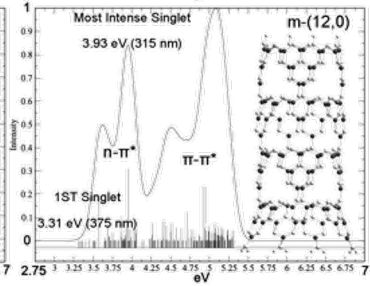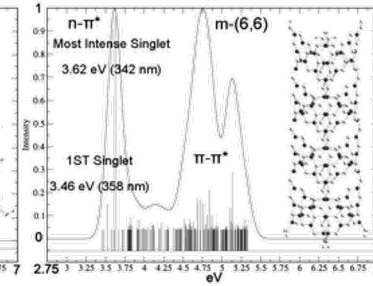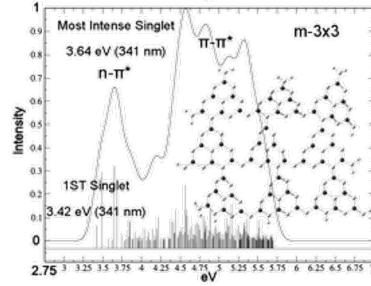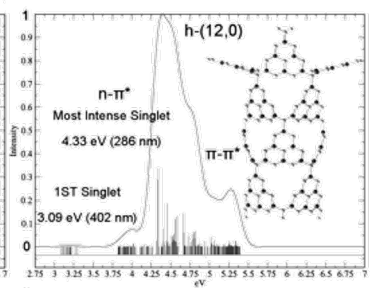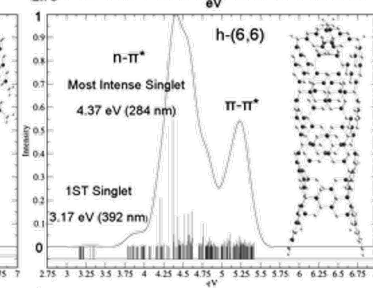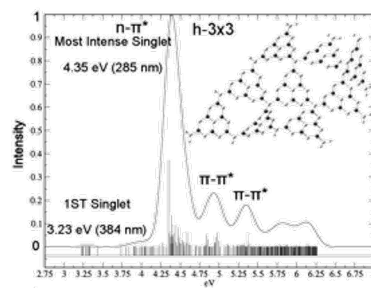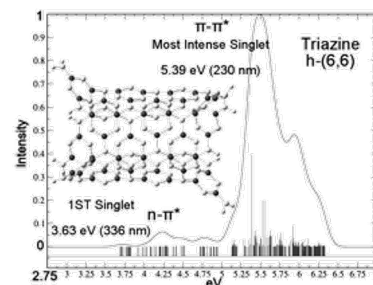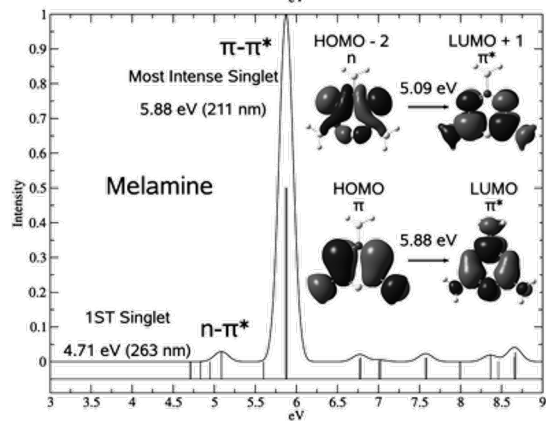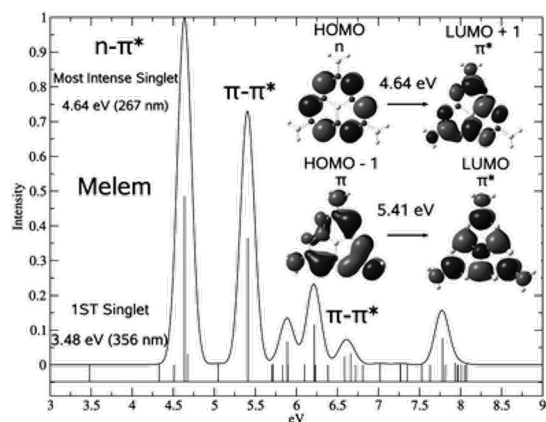
Fenske-Hall (FH)
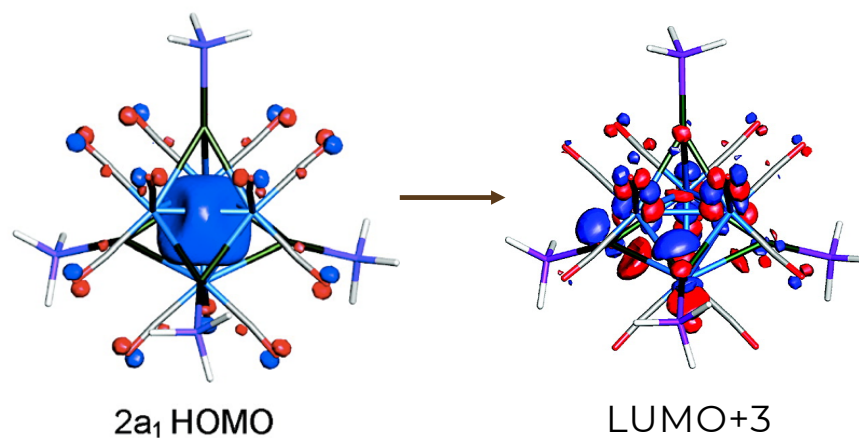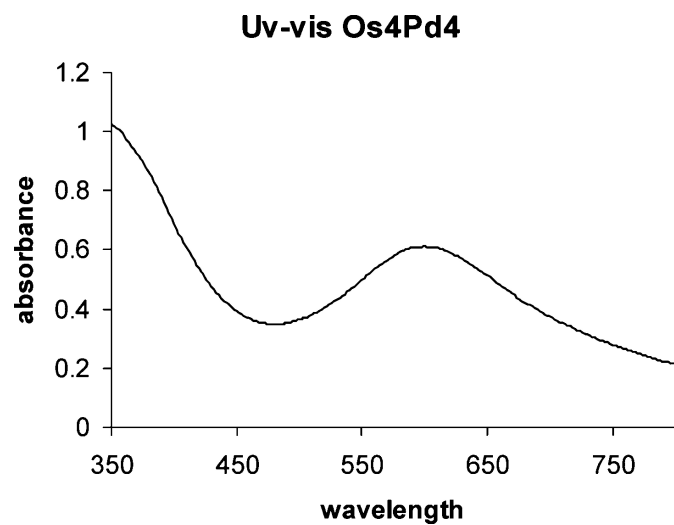
Uv-vis Os4Pd4
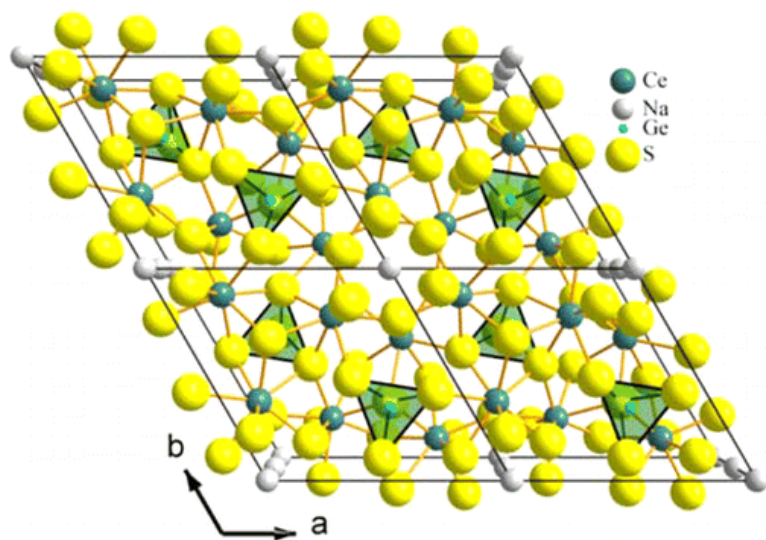

2a₁ HOMO → LUMO+3

http://www.chem.tamu.edu/jimp2

Fenske-Hall (FH)

- Based on Extended Hückel Theory
- Replaces the diagonal terms ($H_{\mu\mu}$) with an adjustable parameter to account for partial charge changes in molecules.
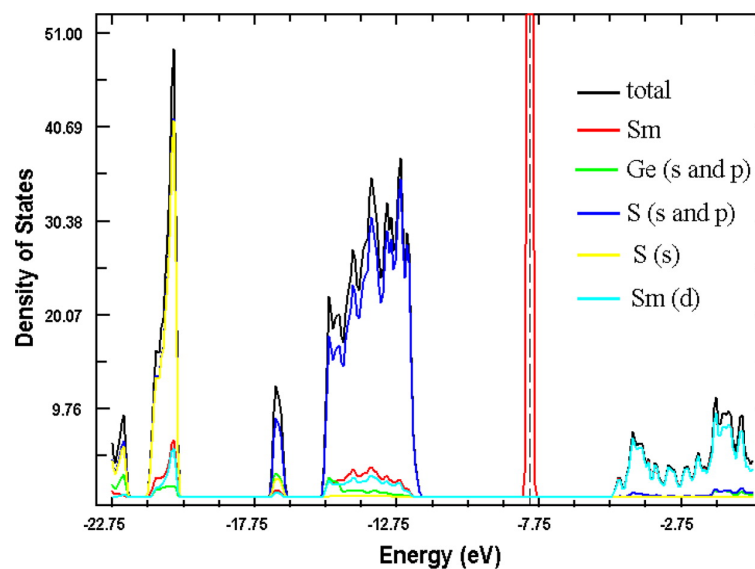- Iterative

- Available in Jimp2:
  http://www.chem.tamu.edu/jimp2

Extended Hückel Theory (EHT)

Total and partial (Sm, Ge, and S) DOSs calculated for **III**. The dashed line indicates the position of the Fermi level.

Composite/Compound/extrapolation Methods

Methods that try to extrapolate to the energy obtained using an infinite basis set and full electron correlation. Designed to accurately calculate thermochemical data.
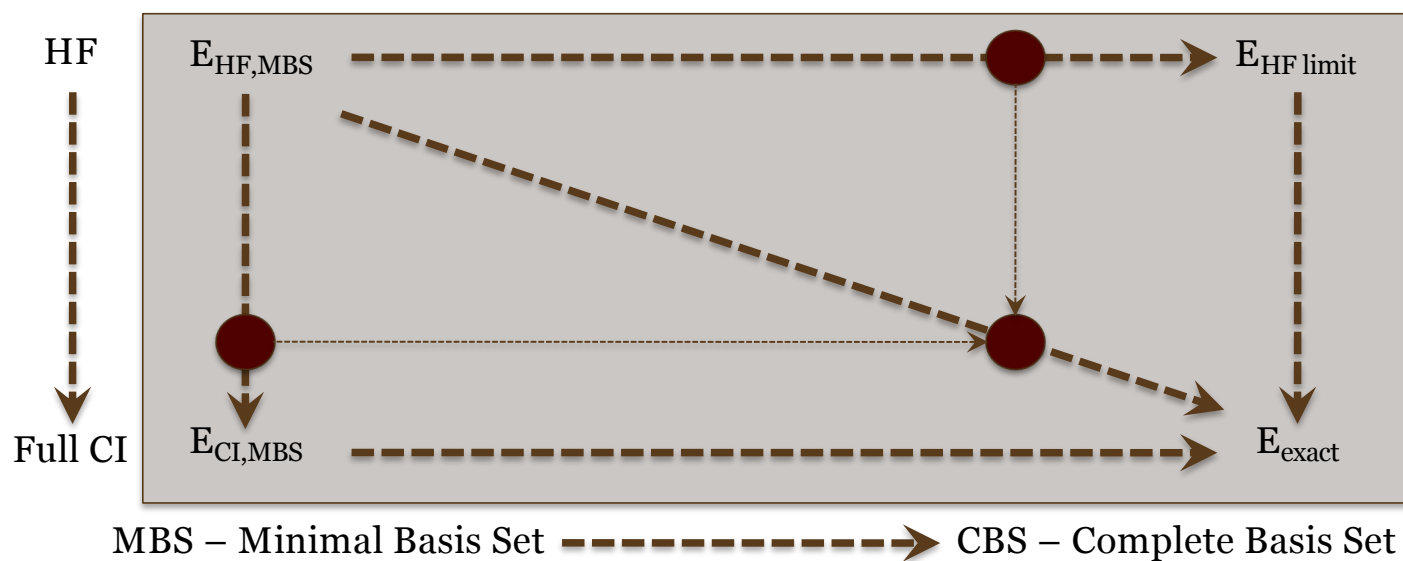
Composite/Compound/extrapolation Methods

Basic Method:

- Select a level of theory for the Geometry (optimization)

- Select a level of theory for the zero-point energy (optimize and frequency calculation)

- Select a level of theory for the reference energy calculation (single point energy)

- Perform a variety of single point energy calculations with increasing basis set size and increasing level of theory to estimate basis set effects and dynamic electron correlation.

- Estimate the spin-paired correlation error

G1-4 Accuracy
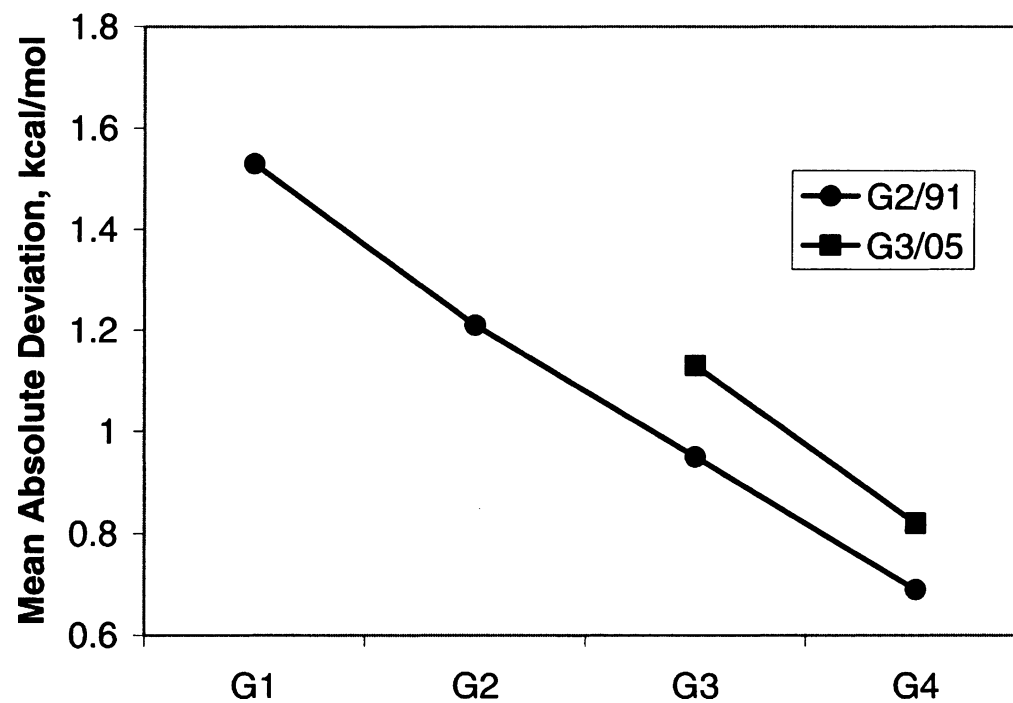
J. Chem. Phys. **126, 084108 (2007)**

Koopmans Theorem

- The energy required to remove an electron from a closed shell atom or molecule is well approximated by the negative of the orbital energy that it is being removed from:

$$1^{st} \text{ Ionization Energy} \cong -\varepsilon_{HOMO}$$

- Electron Affinity $\neq \varepsilon_{LUMO}$
- Unoccupied orbitals are not well treated. The coefficient matrix is optimized for the occupied orbitals.