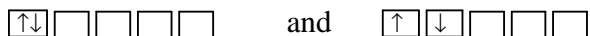


CH 342 Handin Homework 7

1. Determine the atomic terms that correspond to a d^2 configuration. Specify the total orbital angular momentum and the spin multiplicity. Use the following steps:

(a). Draw all the possible explicit singlet states. For example, two of the explicit singlet states are:



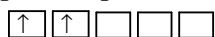
(b). Calculate M_L for each of the states.

(c). Find $L = |M_L|_{\max}$. Remove the M_L states from the list from part (b) corresponding to this L .

(d). Find $L = |M_L|_{\max}$ for the remaining states. Remove the M_L states from the list corresponding to this L .

(e). Repeat part (d) until all the M_L states are accounted for. Write the term symbols for each of the different L values that you have found (for example, 1D or 3P).

(f). Repeat steps (a) through (e) for all possible explicit triplet states. For example one of the explicit triplet states is:



(g). Verify that the Clebsch-Gordan series applied to the total orbital angular momentum gives the same results.

Answer: (a). All the possible singlet arrangements are, in no particular order:

	M_L		M_L		M_L		M_L																
	2	1	0	-1	-2		2	1	0	-1	-2		2	1	0	-1	-2		2	1	0	-1	-2
$\boxed{\uparrow\downarrow}\boxed{}\boxed{}\boxed{}\boxed{}$	4					$\boxed{}\boxed{\uparrow\downarrow}\boxed{}\boxed{}\boxed{}$	2					$\boxed{}\boxed{}\boxed{\uparrow\downarrow}\boxed{}\boxed{}$	0					$\boxed{}\boxed{}\boxed{}\boxed{}\boxed{\uparrow\downarrow}$	-4				
$\boxed{\uparrow}\boxed{\downarrow}\boxed{}\boxed{}\boxed{}$	3					$\boxed{}\boxed{\uparrow}\boxed{\downarrow}\boxed{}\boxed{}$	1					$\boxed{}\boxed{}\boxed{\uparrow}\boxed{\downarrow}\boxed{}$	-1										
$\boxed{\uparrow}\boxed{}\boxed{\downarrow}\boxed{}\boxed{}$	2					$\boxed{}\boxed{\uparrow}\boxed{}\boxed{\downarrow}\boxed{}$	0					$\boxed{}\boxed{}\boxed{\uparrow}\boxed{}\boxed{\downarrow}$	-2										
$\boxed{\uparrow}\boxed{}\boxed{}\boxed{\downarrow}\boxed{}$	1					$\boxed{}\boxed{\uparrow}\boxed{}\boxed{}\boxed{\downarrow}$	-1					$\boxed{}\boxed{}\boxed{}\boxed{\uparrow\downarrow}$	-2										
$\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{\downarrow}$	0											$\boxed{}\boxed{}\boxed{}\boxed{\uparrow}\boxed{\downarrow}$	-3										

(b). The full list is then:

$$M_L = \{4, 3, 2, 2, 1, 1, 0, 0, 0, -1, -1, -2, -2, -3, -4\}$$

(c). With $L = |M_L|_{\max} = 4$, the first term is a G term based on the definitions of the term symbols:

L:	0	1	2	3	4
Term:	S	P	D	F	G

Removing $M_L = \{4, 3, 2, 1, 0, -1, -2, -3, -4\}$ from the full list leaves:

$$M_L = \{2, 1, 0, 0, -1, -2\}$$

(d). Repeating the process, $L = |M_L|_{\max} = 2$ and the second term is a D term. Removing $M_L = \{2, 1, 0, -1, -2\}$ leaves: $M_L = \{0\}$.

(e). The last term is an S term. The final singlet terms are 1G , 1D , 1S .

(f). All the possible triplet arrangements are, in no particular order:

2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L
↑	↑	□	□	□	3	□	↑	↑	□	□	1	□	□	↑	↑	□	-1
↑	□	↑	□	□	2	□	↑	□	↑	□	0	□	□	↑	□	↑	-2
↑	□	□	↑	□	1	□	↑	□	□	↑	-1	□	□	□	↑	↑	-3
↑	□	□	□	↑	0												

The full list is then: $M_L = \{3, 2, 1, 1, 0, 0, -1, -1, -2, -3\}$

With $L = |M_L|_{\max} = 3$, the first term is an F term. Removing $M_L = \{3, 2, 1, 0, -1, -2, -3\}$ leaves:

$$M_L = \{1, 0, -1\}$$

Repeating the process, $L = |M_L|_{\max} = 1$ and the second term is a P term, which corresponds to $M_L = \{1, 0, -1\}$. In summary, the resulting triplet terms are then ${}^3F, {}^3P$.

(g). Using the Clebsch-Gordon series for the total orbital angular momentum for a d^2 configuration corresponds to $l_1 = 2$ and $l_2 = 2$ so that:

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2| = 4, 3, 2, 1, 0$$

giving G, F, D, P, and S terms as listed above.

2. Use the Clebsch-Gordon series and the Russell-Saunders coupling scheme to find the possible total angular momentum J states for the terms that result from the d^2 configuration. See the previous problem for the terms.

Answer: The plan is to use the Clebsch-Gordon series for $\vec{J} = \vec{L} + \vec{S}$ giving:

$J = L + S, L + S - 1, \dots, |L - S|$. In the previous problem, the Clebsch-Gordon series was applied to the coupling of the orbital angular momenta of the different electrons for the given configuration. In this problem, the Clebsch-Gordon series is applied to the coupling of the total orbital angular momentum and the total spin angular momentum.

Since the total spin quantum number for the singlet states is 0, then $J = L$ and the full singlet terms are ${}^1G_4, {}^1D_2, {}^1S_0$. Next consider the triplet terms. Applying the Clebsch-Gordon series for the total angular momentum results in the J values:

$$\begin{aligned} {}^3F: L = 3, S = 1: J = 3 + 1, \dots, |3 - 1| = 4, 3, 2 & \text{ giving } {}^3F_4, {}^3F_3, {}^3F_2 \\ {}^3P: L = 1, S = 1: J = 1 + 1, \dots, |1 - 1| = 2, 1, 0 & \text{ giving } {}^3P_2, {}^3P_1, {}^3P_0 \end{aligned}$$

3. Write an EXCEL spreadsheet to calculate the total amplitude of the normalized bonding LCAO-MO that is formed from two H1s orbitals at a separation of 1.06 Å. Plot the two amplitudes for positions along the internuclear axis both inside and outside the internuclear region. The overlap integral required for the normalization constant is given by the expression

$$S = \left(1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right) e^{-R/a_0} \quad \text{with } R = \text{internuclear distance}$$

[Hint: Let x be the distance along the bond axis. Then along this axis $r_A = |x|$ and $r_B = |1.06 \text{ \AA} - x|$. Then make up a spreadsheet with x , r_A , r_B , $\Psi_{1s,A}$, $\Psi_{1s,B}$, and Ψ_{MO} . Use a_0 in \AA.]

Answer: The normalized bonding LCAO-MO that is formed from two $1s$ orbitals is given by:

$$\Psi_{MO} = \frac{1}{\sqrt{2+S}} (\Psi_{1s,A} + \Psi_{1s,B}) = \frac{1}{\sqrt{2+S}} \left(\frac{1}{\sqrt{\pi}} \left(\frac{Z_{\text{eff}}}{a_0} \right)^{3/2} e^{-Z_{\text{eff}} r_A/a_0} + \frac{1}{\sqrt{\pi}} \left(\frac{Z_{\text{eff}}}{a_0} \right)^{3/2} e^{-Z_{\text{eff}} r_B/a_0} \right)$$

The variationally optimized effective nuclear charge is $Z_{\text{eff}} = 1.197$. In the spreadsheet, below, the Ψ_{1s} normalization is:

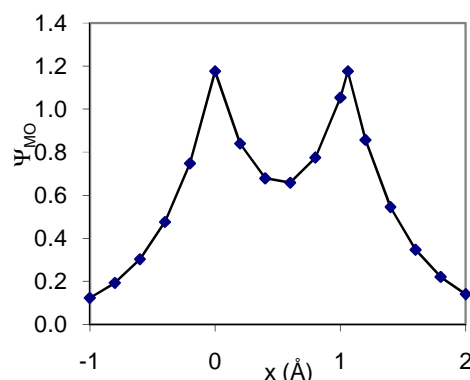
$$N_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z_{\text{eff}}}{a_0} \right)^{3/2} \quad \text{or C4} \text{ “} =1/\text{SQRT}(\text{PI}()) * (\text{F2}/\text{C2})^{1.5} \text{”}$$

and the molecular orbital normalization is:

$$N_{MO} = \frac{1}{\sqrt{2+S}} \quad \text{with S given by F3 “} = (1 + \text{C3}/\text{C2} + 1/3 * \text{C3}^2/\text{C2}^2) * \text{EXP}(-\text{C3}/\text{C2}) \text{”}$$

The radii for the electron are given by $r_A = x$ and $r_B = |1.06 \text{ \AA} - x|$ as A7 “ $=\text{ABS}(\text{\$C\$3}-\text{B7})$ ”.

A1	B	C	D	E	F	G
2	$a_0 =$	0.529	\AA	$Z_{\text{eff}} =$	1.197	
3	$R_{AB} =$	1.06	\AA	$S =$	0.585	
4	$1s$ normalization	1.920		MO normalization	0.562	
5						
6	x (\AA)	r_A (\AA)	r_B (\AA)	$\psi(1s_A)$	$\psi(1s_B)$	Ψ_{MO}
7	-2	2	3.06	0.021	0.002	0.013
8	-1.8	1.8	2.86	0.033	0.003	0.020
9	-1.6	1.6	2.66	0.051	0.005	0.031
10	-1.4	1.4	2.46	0.081	0.007	0.050
11	-1.2	1.2	2.26	0.127	0.012	0.078
12	-1	1	2.06	0.200	0.018	0.122
13	-0.8	0.8	1.86	0.314	0.029	0.192
14	-0.6	0.6	1.66	0.494	0.045	0.303
15	-0.4	0.4	1.46	0.777	0.071	0.476
16	-0.2	0.2	1.26	1.221	0.111	0.748
17	0	0	1.06	1.920	0.174	1.176
18	0.2	0.2	0.86	1.221	0.274	0.840
19	0.4	0.4	0.66	0.777	0.431	0.678
20	0.6	0.6	0.46	0.494	0.678	0.658
21	0.8	0.8	0.26	0.314	1.066	0.775
22	1	1	0.06	0.200	1.677	1.054
23	1.06	1.06	0	0.174	1.920	1.176
24	1.2	1.2	0.14	0.127	1.399	0.857



If $Z_{\text{eff}} = Z = 1$ is used, the wave function maxima are 0.935.

4. For the H_2^+ ion, show that for the bonding orbital $c_A = c_B$ using E_+ and for the anti-bonding orbitals

$c_A = -c_B$ using E_- .

Answer: The first of the two secular equations (either one would do) is:

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

For a homonuclear molecule, $H_{AA} = H_{BB}$ and normalized atomic orbitals give $S_{AA} = S_{BB} = 1$.

(a). Substituting $E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$ into the secular equation gives:

$$c_A(H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S}) + c_B(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} S) = 0$$

Multiplying the last equation by $1 + S$ gives:

$$c_A H_{AA}(1 + S) - c_A H_{AA} - c_A H_{AB} + c_B H_{AB}(1 + S) - c_B H_{AA} S - c_B H_{AB} S = 0$$

After cancelling common terms the result is:

$$c_A H_{AA} S - c_A H_{AB} + c_B H_{AB} - c_B H_{AA} S = 0$$

Collecting terms in c_A and c_B :

$$c_A (H_{AA} S - H_{AB}) + c_B (H_{AB} - H_{AA} S) = 0$$

which rearranges to give:

$$c_A (H_{AA} S - H_{AB}) = c_B (H_{AA} S - H_{AB})$$

The common term cancels to give: $c_A = c_B$

(b). Substituting $E_- = \frac{H_{AA} - H_{AB}}{1 - S}$ into the secular equation gives:

$$c_A (H_{AA} - \frac{H_{AA} - H_{AB}}{1 - S}) + c_B (H_{AB} - \frac{H_{AA} - H_{AB}}{1 - S} S) = 0$$

Multiplying the last equation by $1 - S$ gives:

$$c_A H_{AA}(1 - S) - c_A H_{AA} + c_A H_{AB} + c_B H_{AB}(1 - S) - c_B H_{AA} S + c_B H_{AB} S = 0$$

After cancelling common terms the result is:

$$-c_A H_{AA} S + c_A H_{AB} + c_B H_{AB} - c_B H_{AA} S = 0$$

Collecting terms in c_A and c_B :

$$c_A (-H_{AA} S + H_{AB}) + c_B (H_{AB} - H_{AA} S) = 0$$

which rearranges to give:

$$c_A (-H_{AA} S + H_{AB}) = c_B (H_{AA} S - H_{AB})$$

The common term cancels to give $c_A = -c_B$.

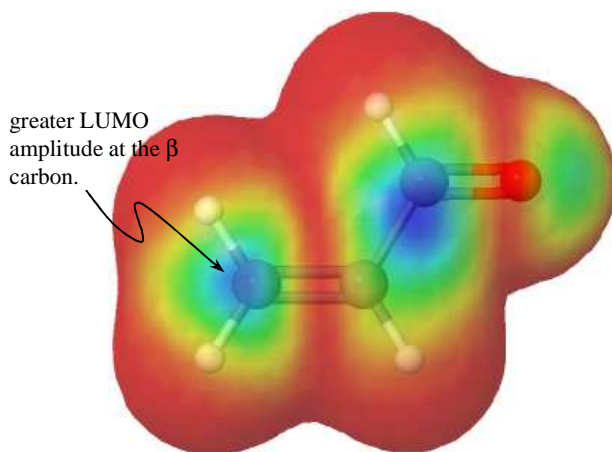
For *trans*-Acrolein:

1. Is the LUMO of acrolein consistent with experimental evidence for reactivity of α,β -unsaturated carbonyl compounds?

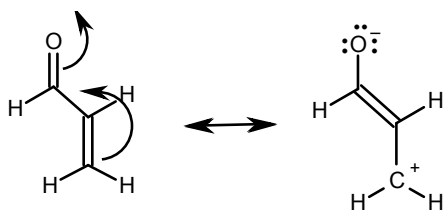
2. Draw the resonance structure that predicts the position of nucleophilic attack on the alpha or beta carbon of the C=C double bond. Show the shifts in the electron pairs with arrows.

3. Does this resonance structure agree with the LUMO map intensity distribution? Explain how you know that they agree or disagree with reference to attack at the alpha or beta carbon of the C=C double bond.

Answer: 1. The LUMO intensity is greater above the β -carbon than the α , which is consistent with the preference for Michael addition at the β -olefin position.



2. The resonance structure that predicts the position of nucleophilic attack on the beta carbon of the C=C double bond is:



3. This resonance structure agrees with the LUMO map intensity distribution. The resonance structure predicts nucleophilic attack at the β -carbon of the C=C double bond, since the β -carbon develops a partial positive charge.