

SOLUTION TO ASSIGNMENT 8

1. A student has given you the table below, for the molecular orbitals of formaldehyde. The MO's are represented as columns, with the energy at the top. The coefficients of each of the atomic orbitals are given by the elements down the column. Sketch each of the occupied orbitals, and label it properly according to the group theory designation.

Remember the orbitals are numbered in ascending order within their group designation. We can describe some of the orbitals approximately as follows:

- $1a_1$: oxygen 2s (almost entirely)
 $2a_1$: carbon 2s (carbon is less electronegative) + C-H bonds
 $1b_2$: antisymmetric combination of C-H bonds
 $1b_1$: C=O π bond
 $3a_1$: oxygen lone pair
 $2b_2$: oxygen lone pair
 $2b_1$: C=O antibonding π orbital (unoccupied)

Energy	44.2	20.1	19.2	-9.8	-13.8	-15.2	-15.4	-16.6	-22.1	-34.7
Desig.	$5a_1$	$4a_1$	$3b_2$	$2b_1$	$2b_2$	$3a_1$	$1b_1$	$1b_2$	$2a_1$	$1a_1$
C 2S	-0.744	0.065	0.000	0.000	0.000	0.000	0.000	0.000	-0.642	0.337
C Py	0.000	0.000	0.683	0.000	-0.262	0.000	0.000	-0.559	0.000	0.000
C Px	0.000	0.000	0.000	0.871	0.000	0.000	0.371	0.000	0.000	0.000
C Pz	-0.043	-0.719	0.000	0.000	0.000	-0.268	0.000	0.000	0.348	0.152
H 1S	0.401	-0.314	-0.509	0.000	-0.304	0.166	0.000	-0.398	-0.328	0.027
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O 2S	0.268	0.428	0.000	0.000	0.000	0.143	0.000	0.000	0.414	0.927
O Py	0.000	0.000	-0.120	0.000	0.864	0.000	0.000	-0.609	0.000	0.000
O Px	0.000	0.000	0.000	-0.491	0.000	0.000	0.929	0.000	0.000	0.000
O Pz	-0.226	-0.313	0.000	0.000	0.000	0.923	0.000	0.000	0.281	0.042

2. Is the LUMO a π or a σ orbital? Is it bonding (π , σ) or antibonding (π^* , σ^*)? Explain briefly.

The LUMO is the $2b_1$ orbital, which is an antibonding (π^*) orbital; note the different signs of the carbon and oxygen p_x orbitals. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the UV spectra of ketones go to this orbital.

3. For the following partial electronic configurations, list the possible electronic states (including spin multiplicity). Any unspecified orbitals are filled. Make sure you use the proper group-theoretical symbols. The table in the back of Harris on direct products of group representations will be useful.

This is simple, since the product of a_1 (totally symmetric) is trivial

- a) water: $(a_1)^2(a_1)^1(b_1)^1$ 3B_1 , 1B_1

- b) water: $(a_1)^2(b_2)^1(b_1)^1$ $^3A_2, ^1A_2$ (page 479 in Harris shows $b_2 \times b_1 = a_2$)
- c) square planar complex: $(b_{2g})^1(b_{1g})^1$ $^3A_{2g}, ^1A_{2g}$ (page 480 in Harris shows $b_2 \times b_1 = a_2$ in D_{4h} also, and we must include $g \times g = g$)
- d) square planar complex: $(e_g)^2$ (optional, for bonus marks)

In this case, we must include the Pauli principle, and worry about overall asymmetry. Triplet states are symmetrical, and singlets antisymmetrical. See page 323 in Harris, and following pages. The tables on page 480 give the product of $e_g \times e_g = a_{1g} + a_{2g} + b_{1g} + b_{2g}$. a_1, b_1 and b_2 are symmetrical and a_2 is antisymmetric. Therefore the possible states are $^1A_1, ^1B_1$ and 1B_2 and 3A_2 .

4. The triplet combination, with z component of +1, of two spins (1/2) is given by $\alpha\alpha$, where α is the wavefunction of a single spin with total angular momentum of 1/2 and a z component of +1/2. Show that this is an eigenfunction (with the correct eigenvalue) of the total angular momentum operator, L^2 , which is equal to $(I+J)^2$, where I and J are the individual angular momentum operators.

Hint: Remember that $(I+J)^2$ is the dot product of $(I+J)$ with itself and

$$I \cdot I = I_x^2 + I_y^2 + I_z^2 = \frac{1}{2}(I_+ I_- + I_- I_+) + I_z^2$$

First of all, remember

$$I^2 \mathbf{a} = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \mathbf{a}$$

and

$$I_z \mathbf{a} = \frac{1}{2} \mathbf{a}$$

Therefore

$$(I+J)^2 \mathbf{a} \mathbf{a} = (I \cdot I + I \cdot J + J \cdot I + J \cdot J) \mathbf{a} \mathbf{a}$$

Since I and J commute

$$= (I^2 + 2I \cdot J + J^2) \mathbf{a} \mathbf{a}$$

$$= (I^2 + I_+ J_- + I_- J_+ + 2I_z J_z + J^2) \mathbf{a} \mathbf{a}$$

The I operators act on the left-hand \mathbf{a} and the J operators act on the right-hand \mathbf{a} . This means the following.

$$I^2 \mathbf{aa} = \frac{3}{4} \mathbf{aa}$$

$$J^2 \mathbf{aa} = \frac{3}{4} \mathbf{aa}$$

$$I_+ J_- \mathbf{aa} = 0 \quad (I_+ \text{ can't raise } \mathbf{a}), \text{ similarly}$$

$$I_- J_+ \mathbf{aa} = 0$$

$$\begin{aligned} 2I_z J_z \mathbf{aa} &= 2 \left(\frac{1}{2} \right) \left(\frac{1}{2} \right) \mathbf{aa} \quad \text{since both operators operate} \\ &= \left(\frac{1}{2} \right) \mathbf{aa} \end{aligned}$$

Therefore

$$\begin{aligned} (I+J)^2 \mathbf{aa} &= \left(\frac{3}{4} + \frac{3}{4} + \frac{1}{2} \right) \mathbf{aa} \\ &= 2 \mathbf{aa} \\ &= 1(1+1) \mathbf{aa} \end{aligned}$$

This is the appropriate eigenvalue for an angular momentum of 1 unit.