

1. (a) What is the order Q of the point group O_h . The character table is given in Problem 2 of this exam. **Solution:** If we add up the squares of the degeneracies (going down the first column of characters) we have

$$1^2 + 1^2 + 2^2 + 3^2 + 3^2 + 1^2 + 1^2 + 2^2 + 3^2 + 3^2 = \boxed{48.}$$

We get the same answer if we add up all the symmetry elements:

$$1 + 8 + 6 + 6 + 3 + 1 + 6 + 8 + 3 + 6 = 48.$$

- (b) Give the bond order for the Al_2 molecule, which has MO configuration (including core electrons)

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4 4\sigma_g^2 4\sigma_u^2 2\pi_u^2.$$

Solution: For homonuclear diatomics, σ_g and π_u are bonding MOs whereas σ_u and π_g are antibonding. Therefore, the bond order would be

$$b = \frac{14 - 12}{2} = \boxed{1.}$$

- (c) The Cartesian d orbitals are labeled d_{z^2} (lies along z axis), d_{xz} (lies in xz plane), d_{yz} (lies in yz plane), $d_{x^2+y^2}$, and $d_{x^2-y^2}$ (which both lie in xy plane). When we combine these five d orbitals centered on different atoms to form MOs, what is the symmetry of each MO that is formed? The same question is solved for the p orbitals as an example. **Solution:** The z^2 is symmetric under rotation about the z axis, so has σ symmetry. The xz and yz must both change sign under 180° rotation about the z axis, so they have π symmetry. The last two must have two angular nodes, being d orbitals, and because they lie in the xy plane those nodes must be along ϕ , so they change sign twice under a 180° rotation about the z axis and have δ symmetry. (Or we could look at the correlation diagram and see that the d orbitals in the united atom limit correlate to σ , π , and δ .)

- $d_{z^2} \rightarrow \boxed{\sigma_g, \sigma_u}$
- $d_{xz}, d_{yz} \rightarrow \boxed{\pi_g, \pi_u}$
- $d_{x^2-y^2}, d_{xy} \rightarrow \boxed{\delta_g, \delta_u}$

- (d) The C_2 molecule has a $X^1\Sigma_g^+$ ground state. The lowest energy bound excited electronic states are listed below. Write **F** next to any of these states that will fluoresce to return to the ground state and **P** for any that will phosphoresce. **Solution:** Transitions from the two triplet states are spin-forbidden, so must be phosphorescence. The product $\Sigma_g^+ \otimes \Pi_u = \Pi_u$ means that the $A \rightarrow X$ transition is electric dipole allowed, so corresponds to fluorescence.

- i. $a^3\Pi_u$ **P**

- ii. $b^3\Sigma_g^-$ P
- iii. $A^1\Pi_u$ F

2. There is an allowed transition from the ${}^3T_{1u}$ state to an upper state Y for a molecule in the point group O_h . If the representation for Y is Γ_Y , we find

$$T_{1u} \otimes \Gamma_Y = A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}.$$

- (a) Find the term symbol for state Y . **Solution:** The characters for the reducible representation, obtained by summing the characters for the righthand side of our equation, are

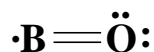
$$\begin{array}{l} O_h \\ A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u} \\ \text{divide by } T_{1u} \end{array} \left| \begin{array}{cccccc} \hat{E} & 8\hat{C}_3 & 6\hat{C}_2 & 6\hat{C}_4 & 3\hat{C}_2(=\hat{C}_4^2) & \hat{I} \\ 9 & 0 & -1 & -1 & 1 & -9 \\ 3 & 0 & 1 & -1 & -1 & 3 \end{array} \right| \begin{array}{l} 6\hat{S}_4 \\ 8\hat{S}_6 \\ 3\hat{\sigma}_h \\ 6\hat{\sigma}_d \\ = T_{2g}. \end{array}$$

So the symmetry of the upper state is T_{2g} . For the transition to be allowed, the spin must be unchanged, so the upper state term symbol is ${}^3T_{2g}$.

- (b) Is the transition allowed by electric dipole selection rules, Raman, or both? **Solution:** Because the T_{1u} representation corresponds to the x , y , and z functions, the transition is electric dipole allowed.
- (c) The ${}^3T_{1u}$ state has a molecular orbital configuration in which all the orbitals are filled except two, which have one electron each. One of those is an a_{2u} MO, fill in the missing symmetry representation:

$$[\text{filled MOs}] a_{2u}^1 \text{ } t_{2g}^1 \text{.}$$

3. (a) Draw the best Lewis structure you can for the diatomic molecule BO. Boron does not normally take an octet in Lewis structures. **Solution:** The only viable Lewis structure without any formal charges and with an octet on the O atom is this one:

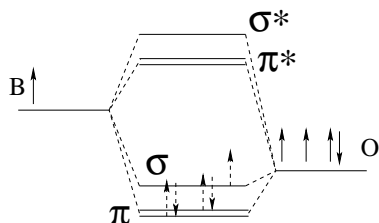


- (b) From this Lewis structure, write an MO configuration for the valence electrons (skip the core electrons). Don't worry about the energy ordering of the orbitals, except for the highest energy MO which you should put last. **Solution:** The molecule is in the point group $C_{\infty v}$, and there are only σ and π MOs in this MO configuration. There are $3+6=9$ valence electrons. Of the four electrons in the double bond, the σ -bond MO must be σ symmetry and the π -bond MO must be π . Of the non-bonding electrons, the lone pairs on the oxygen should be formed from a combination of $2s$ and $2p_x$ or $2p_y$ atomic orbitals. (One way to see this is using VSEPR theory, which predicts that the bond and the two lone pairs must be trigonal planar, or sp^2 hybridized. Another is to see that since oxygen has an octet, all its $2s$ and $2p$ atomic orbitals must be involved. The σ -bond can only use $2p_z$, because it must lie on the z axis, and the π -bond can only use one of the remaining $2p$ orbitals.) The $2s$ atomic orbital has σ symmetry in this point group, and $2p_x$ and $2p_y$ have π symmetry, so

the lone pairs correspond to σ and π MOs. Finally, the unpaired electron (which must be in the highest energy occupied MO) has σ symmetry, because the only way to get π symmetry would be from an unhybridized p atomic orbital, which will be higher energy. $\boxed{\sigma^2 \sigma^2 \pi^4 \sigma^1}$.

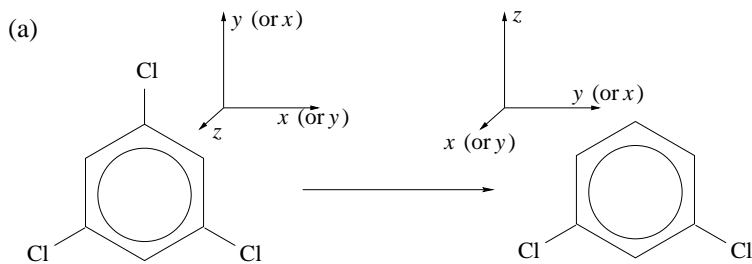
- (c) Complete the MO diagram started below for the $2p$ orbitals of the B and O atoms.

Solution: (It was not necessary to add the electrons or the “”s.)



4. We start with 1,3,5-trichlorobenzene, which has D_{3h} symmetry, and use a laser to break one of the C–Cl bonds, to form 1,3-dichlorobenzene, which has C_{2v} symmetry. We could draw a correlation diagram connecting the MOs in each case. In the space below:

- Label the coordinate axes for both molecules (more than one correct answer).
- Write the symmetry elements that are preserved from one side to the other of this correlation diagram. (If the label changes from one side to the other, give both labels with the D_{3h} label on the left and the C_{2v} label on the right.)
- For each of the MOs listed on one side, write the representation(s) that it correlates to on the other side.



- (b) preserved symmetry elements

$$\begin{array}{ll} \hat{C}_2(y) & \hat{C}_2(z) \\ \hat{\sigma}_{yz} = \hat{\sigma}_v & \hat{\sigma}_{xz} \\ \hat{\sigma}_{xy} = \hat{\sigma}_h & \hat{\sigma}_{yz} \end{array}$$

