PROBLEM SHEET – MOLECULAR SYMMETRY, GROUP THEORY, & APPLICATIONS

Q1. Draw sketches to illustrate the following symmetry elements:

a) a vertical mirror plane and a C_2 axis in O_3 (ozone)
b) a horizontal mirror plane in CO_2
c) an S_4 axis in methane
d) all of the symmetry elements in CH_3F (point group C_{3v})
e) all of the symmetry elements in ethene (point group D_{2h})

Q2. Determine the symmetry elements possessed by an s orbital, a p orbital, a d_z^2 orbital, and a d_{xy} orbital

Q3. Which of the following molecules has i) a centre of inversion and ii) an S_4 axis?

a) CO_2
b) C_2H_2
c) BF_3
d) SO_4^{2-}

Q4. Identify the symmetry elements in the following molecules, and assign each one to a point group (use the flow diagram in the lecture notes if you find this helpful).

a) NH_2Cl
b) SiF_4
c) H-C≡N
d) SiFClBrI
e) NO_2
f) H_2O_2

Q5. a) What are the symmetry elements that prevent a molecule from being polar? Which of the molecules in Q4 are polar?

b) What are the symmetry elements that exclude chirality? Which (if any) of the molecules in Q4 may be chiral?

Q6. What are the symmetry operations in the point group C_{2v}? Identify a molecule that belongs to the group. By examining the effect of sequential application of the various symmetry operations in the group, construct the group multiplication table.

Q7. a) How can group theory be used to determine whether an integral can be non-zero?

b) Use group theory to determine whether the following integrals are non-zero (use the tables of direct products provided in the lecture handout).

i) the overlap integral between a p_x orbital and a p_z orbital in the point group C_{2v}
ii) the overlap integral between a p_x orbital and a d_{xz} orbital in the point group C_{3v}
iii) the overlap integral between a p_y orbital and a d_z^2 orbital in the point group T_d
iv) the overlap integral between a p_z orbital and a d_z^2 orbital in the point group D_{2h}

c) Which of the following electronic transitions are symmetry allowed?

i) a transition from a state of A_1 symmetry to a state of E_1 symmetry excited by z-polarised light in a molecule belonging to the point group C_{5v}.

ii) a transition from a state of A_{1g} symmetry to a state of A_{2u} symmetry excited by z-polarised light in a molecule belonging to the point group $D_{\infty h}$.

iii) a transition from a state of B_2 symmetry to a state of B_1 symmetry excited by y-polarised light in a molecule belonging to the point group C_{2v}.

Q8. Consider the hydronium ion H_3O^+. This ion has a pyramidal structure with one HOH bond angle smaller than the other two, and belongs to the point group C_S.

a) Using a basis set consisting of a 1s orbital on each H atom and 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on the O atom (i.e. (s_O,p_x,p_y,p_z,s_1,s_2,s_3)), construct a matrix representation.

b) What are the characters of each of the matrix representatives?

c) What are the irreps spanned by the basis?

d) Use the basis to construct a set of SALCs.

e) Write down the general form of the molecular orbitals of H_3O^+.

Q9. Consider the chlorobenzene molecule C_6H_5Cl.

a) What is the molecular point group?

b) Use a basis made up of a p orbital on each carbon atom (pointing perpendicular to the benzene ring) to construct the π molecular orbitals using the following steps:
   i) determine the character of each symmetry operation
   ii) determine the irreps spanned by the basis
   iii) construct a set of SALCs and take linear combinations to form the molecular orbitals of each symmetry species.

Q10. a) Use the 3N Cartesian basis and the character table for the C_{3v} point group to determine the symmetries of the vibrational modes of NH_3.

b) Use a basis of internal coordinates to determine the symmetries of the *stretching* vibrations *only*. Hence classify each of the vibrational modes found in a) as a bending or a stretching vibration.

c) Construct SALCs using the internal coordinate basis to determine the atomic displacements associated with each stretching mode. Draw each mode, and label it as a symmetric or asymmetric stretching vibration. It is quite complicated to use the 3N Cartesian basis to construct SALCs in this case (though you are welcome to try). What do you think the A_1 bending vibration looks like? Identify the A_1 and E bending vibrations as symmetric or antisymmetric.

d) Which vibrational modes could be excited by i) a one-photon process ii) a two-photon process? What are the polarisations of the photons involved in each case?