Tutorial problem:
• This is an old exam question, Model answers from your tutors, or the web-site

Consider three oxygen atoms arranged in an equilateral triangle, the point group is $D_{3h}$:

i) Determine the reducible representation for the three $p_x$ orbitals

ii) Write down the reduction and projection formulae. Briefly explain each of the terms in both formulae.

iii) Use the reduction formula to determine the symmetry of the $p_x$ based molecular orbitals. Show your working.

iv) Use the projection formula to determine the wave function of the $p_x$ based molecular orbitals. Show your working. The molecular orbital wavefunctions do not need to be normalised.

v) Draw an energy level diagram for the $p_x$ based orbitals. Draw the molecular orbital and write the associated equation beside each energy level. Label the symmetry of each orbital.

Symmetry adapted MOs for $p$-orbitals of $D_{3h}$ (model answers)

Consider three oxygen atoms arranged in an equilateral triangle, the point group is $D_{3h}$:

i) Determine the reducible representation for the three $p_x$ orbitals

use all three $p$ orbitals as a basis
thus determine the number of orbitals that don't shift from one atomic center to another under the symmetry operations of the group, if the phase is unchanged an orbital contributes $+1$, if the phase changes the orbital contributes $(-1)$. For example under $C_2$ two of the orbitals move, and one inverts $=0-1=-1$ for the character.

these orbitals move atomic center

this orbital inverts $C_2$
ii) Write down the reduction and projection formulae. Briefly explain each of the terms in both formulae.

reduction formula  
projection formula

\[
n_{IR} = \frac{1}{h} \sum_{Q} k \cdot \chi^{IR}(Q) \cdot \chi^{R}(Q)
\]

\[
P_{\Gamma} [\psi] = \frac{1}{h} \sum_{Q} \chi^{IR}(Q) \cdot Q[\psi]
\]

\( n_{IR} \) = number of times the irreducible representation IR contributes to the reducible representation R

\( h \) = number of operations in the point group

\( Q \) = a particular symmetry operation

\( k \) = the number of operations of \( Q \) in the point group

\( \chi^{IR}(Q) \) = character of the irreducible representation (IR) under \( Q \)

\( \chi^{R}(Q) \) = the character of the reducible representation (R) under \( Q \)

\( \psi \) = basis function on which the projection operator acts

\( P_{\Gamma} [\psi] \) = the molecular orbital wavefunction

\( Q[\psi] \) = an operator acting on the basis function \( \psi \)

iii) Use the reduction formula to determine the symmetry of the \( \pi \) based molecular orbitals. Show your working.

(3 marks)

\[ D_{3h} \]

\[ \Gamma \{ \begin{array}{ccccc} 3 & 0 & -1 & -3 & 0 & 1 \\ \end{array} \} \]

Be smart! do not just go through all the Irreducible Representations sequentially you WILL run out of time!

look at the character table

(a) cannot be \( A_1' \) since under \( \sigma_h \) the pAOs will invert giving -1 character

(b) the orbitals all have the same phase as the z-axis try the \( A_2'' \) first

\[ D_{3h} \]

\[ \Gamma \{ \begin{array}{ccccc} 3 & 0 & -1 & -3 & 0 & 1 \\ \end{array} \} \]

Reducible rep= \( \Gamma(3\pi) \)

\[ D_{3h} \]

\[ \begin{array}{cccccc} E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
A_1' & 1 & 1 & 1 & 1 & 1 & 1 \\
A_2' & 1 & 1 & -1 & 1 & 1 & -1 \\
E' & 2 & -1 & 0 & 2 & -1 & 0 \\
A_1'' & 1 & 1 & 1 & -1 & 1 & -1 \\
A_2'' & 1 & 1 & -1 & -1 & 1 & 1 \\
E' & 2 & -1 & 0 & -2 & 1 & 0 \\
\end{array} \]

show your working ONLY for the first example:
now we know that there is $1a_2''$ component we subtract this from the reducible representation:

$$
\begin{array}{cccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 \\
\hline
A_2'' & 1 & 1 & -1 & -1 & -1 \\
\Gamma(3p\pi) & 3 & 0 & -1 & -3 & 0 \\
\hline
n_{\Delta_1'} = \frac{1}{12} \left[ 1 \cdot 1 + 2 \cdot 0 + 3 \cdot -1 \cdot -1 + 1 \cdot -1 \cdot -3 + 2 \cdot -1 \cdot 0 + 3 \cdot 1 \cdot 1 \right] \\
\end{array}
$$

now we know that there is $1a_2''$ component we subtract this from the reducible representation:

$$
\begin{array}{cccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 \\
\hline
\Gamma(3p\pi) & 3 & 0 & -1 & -3 & 0 \\
A_2'' & 1 & 1 & -1 & -1 & -1 \\
\hline
n_{\Delta_1'} = \frac{1}{12} \left[ 3 + 0 + 3 + 0 + 3 \right] = \frac{12}{12} = 1 \\
\end{array}
$$

this tells us that

$$
\Gamma(3p\pi) = a_2'' + e''
$$

we can check our answer by adding the irreducible representations, make sure we get the reducible representation back!

$$
\begin{array}{cccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 \\
\hline
A_2'' & 1 & 1 & -1 & -1 & -1 \\
E'' & 2 & -1 & 0 & -2 & 1 \\
\hline
\Gamma(3p\pi) = A_2'' + E'' & 3 & 0 & -1 & -3 & 0 \\
\end{array}
$$
iv) Use the projection operator to determine the equation of the $p_{\pi}$ based molecular orbitals, show your working. The molecular orbital wavefunctions do not need to be normalised.

(5 marks)

First define your basis:

then define where all the symmetry elements are:

and a $C_2$ and $\sigma_v$ through the $p_1$ corner

then construct a projection table

Remember there is no “k” in the projection operator, you must "expand" out the top line to determine the effect of every operation on your chosen basis function!

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
D_{3h} & E & C_3 & C_3' & C_2 & C_2' & C_2'' & \sigma_v \\
\hline
\chi^{A''}(Q) \cdot Q \cdot [p_1] & p_1 & p_2 & p_3 & -p_1 & -p_3 & -p_2 & -p_1 \ 
\chi^{E''}(Q) \cdot Q \cdot [p_1] & 2p_1 & -p_2 & -p_3 & 0 & 0 & 0 & -2p_1 \ 
\hline
\end{array}
\]

Now you need to guess an orthogonal partner, you already know the orbital shapes for the $H_3$ system:
if you look directly down from above on the pAO system it looks just like the sAO system, (except that in the pAO system reflection in the σh plane alters the phase!). The first two orbitals have already been derived, we guess that the third will look like the last sAO MO but with a node in σh plane and a change of phase.

ψ_e′(1) = \frac{1}{3} \left[ p_1 + p_2 + p_3 \right]  
ψ_e′(2) = \frac{1}{6} \left[ 2p_1 - p_2 - p_3 \right]  
ψ_e′(3) = \frac{1}{2} \left[ p_2 - p_3 \right] 

so we guess that ψ_e′(2) = \frac{1}{2} \left[ p_2 - p_3 \right] 

now check that the two e" MOs are orthogonal:

\langle ψ_e′(1) | ψ_e′(2) \rangle = \frac{1}{3} \sum_{i=1}^{3} \langle p_i | p_i \rangle = 1

\langle ψ_e′(1) | ψ_e′(3) \rangle = \frac{1}{3} \sum_{i=1}^{3} \langle p_i | p_i \rangle = 1

\langle ψ_e′(2) | ψ_e′(3) \rangle = \frac{1}{6} \sum_{i=1}^{3} \langle p_i - p_i | p_i - p_i \rangle = 0

which is true!

v) Draw an energy level diagram for the \( p_\pi \) based orbitals. Draw the molecular orbital and write the associated equation beside each energy level. Label the symmetry of each orbital. (2 marks)

ψ_e′(1) = \frac{1}{6} \left[ 2p_1 - p_2 - p_3 \right]  
ψ_e′(2) = \frac{1}{2} \left[ p_2 - p_3 \right]  
ψ_e′(3) = \frac{1}{3} \left[ p_1 + p_2 + p_3 \right]