Symmetry Adapted Orbitals

Introduction
• so far the fragments used in forming the MOs have been atomic orbitals, those for a diatomic, or I have provided them for you. In this section you will learn how to derive symmetry adapted fragment orbitals for use in MO diagrams
• for example the H₃ fragment orbitals provided for the tutorial problem on BH₃ (Figure 1) are symmetry adapted orbitals. Symmetry adapted orbitals are the fragment orbitals of symmetry fragments (as opposed to molecular fragments)
• the easiest way to explain the process of generating symmetry adapted orbitals is to show you with an example. The key steps taken in this process will then be highlighted so that you have a general method which can be applied to an "unknown" system. In this section we will:
  o generate a reducible representation
  o use the reduction formula
  o use the projection formula
• We will start with the fragment you have already seen and used, that of H₃, Figure 1.
• In fact the fragment orbitals we will derive will not apply to only H₃ but to ANY system which has a set of 3 sigma-type (sp²) valence AOs arranged in a triangle.
  o 6s AOs of gold atoms.
  o 3 sigma type orbitals from R groups
  o 3 sigma type orbitals of ligands L
• the similarity between the donor orbital of a ligand and the H 1sAO makes them isolobal, Figure 2.
The symmetry adapted orbitals of H₃

- The point group of the molecule must be known before symmetry adapted orbitals can be derived. We will start with the fragments of D₃h BH₃.
- The D₃h character table is given to the left below. When deriving symmetry adapted orbitals it is important you know where all the symmetry elements are located. A quick reminder of the symmetry elements for the D₃h point group are given in Figure 3.

<table>
<thead>
<tr>
<th>D₃h</th>
<th>E</th>
<th>2C₃</th>
<th>3C₂</th>
<th>σᵥ</th>
<th>2σₕ</th>
<th>3σₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A'₂</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>A''₁</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>A''₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E''</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3 Character table and symmetry elements for D₃h

Reducible Representations

- A reducible representation is determined for a basis set of symmetry related orbitals on the fragment, in this case there are three sAOs, Figure 4
- The reducible representation is found by forming a representation table (Figure 5)
- Determine how the orbital that does not move, we add +1 if the phase remains the same, or -1 if the phase changes.

For H₃
- under E => all 3 orbitals don't move, and there is no phase change =3
- under C₃ => 0 orbitals don't move
- under C₂ => 1 (only the orbital on the axis doesn't move, and it's phase stays the same, see Figure 6)
- under σᵥ => all 3 orbitals don't move
- under Sᵥ => 0 orbitals don't move
- under σₕ => 1 (only the orbital in the mirror plane doesn't move, Figure 6)

- previously we used a representation table to determine the symmetry of a SINGLE MO composed of 3 sAOs (bonding MO)
- NOW we are using as a basis, the SET OF 3 sAOs

Figure 6 generating a reducible representation

IMPORTANT
The Reduction Formula

- Every reducible representation (\( \Gamma^R \)) can be written as a sum of the irreducible representations (\( \Gamma^{IR} \)) of a point group, where \( n_{IR} \) = the number of times a particular irreducible representation occurs:

\[
\Gamma^R = \sum_{IR} n_{IR} \Gamma^{IR}
\]

- for example, any vector can be described as a sum of components in the x, y, and z directions. The x, y, and z components are represented by unit vectors \( \hat{i}, \hat{j} \) and \( \hat{k} \) and the coefficients multiply each of the unit vectors, i.e. \( v = x\hat{i} + y\hat{j} + z\hat{k} \).

- think of \( \Gamma^R \) as a vector in the space spanned by the D\(_{3h}\) point group (like \( v \) is a vector in the space spanned by Cartesian coordinates). The irreducible representations are the unit vectors for a point group and the \( n_{IR} \) are the coefficients that describe the vector in this space.

- we use the reduction formula to determine \( n_{IR} \) (see the box). You must be able to write this equation and define each of the symbols.

\[
\begin{align*}
\text{The Reduction formula} \\
n_{IR} &= \frac{1}{h} \sum_{Q} k \cdot \chi^{IR}(Q) \cdot \chi^R(Q) \\
\h &= \text{number of operations in the group} \\
Q &= \text{a particular symmetry operation} \\
k &= \text{the number of operations of } Q \\
\chi^{IR}(Q) &= \text{the character of the Irreducible Representation under } Q \\
\chi^R(Q) &= \text{the character of the Reducible Representation under } Q
\end{align*}
\]
component terms of the reduction formula are shown for the $C_{3v}$ character table in Figure 7.

- $h$ is the number of operations in the point group and for $C_{3v}$ this is $1E+2C_3+3\sigma_v=6$ operations.

- We start by working out the number of times ($n_{\chi'}$) the irreducible representation $A'_1$ contributes to the reducible representation of $H_3$:

$$n_{\chi'} = \frac{1}{h} \sum_R k \chi'^R(Q) \chi^R(Q)$$

$$n_{\chi'} = \frac{1}{12} \left[ 1 \chi'^R(E) \chi^R(E) + 2 \chi'^R(C_3) \chi^R(C_3) + 3 \chi'^R(C_2) \chi^R(C_2) + \chi'^R(\sigma_v) \chi^R(\sigma_v) + 2 \chi'^R(S_3) \chi^R(S_3) + 3 \chi'^R(\sigma_v) \chi^R(\sigma_v) \right]$$

<table>
<thead>
<tr>
<th>$\Gamma[H_3]$</th>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_v$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$$n_{\chi'} = \frac{1}{12} \left[ 1 \cdot 1 + 2 \cdot 1 + 3 \cdot 1 + 1 \cdot 1 + 2 \cdot 1 + 3 \cdot 1 \right] = \frac{12}{12}$$

$$n_{\chi'} = 1$$

- Then we work through the symmetry labels for the group. For example, I've shown that for $A'_2$ below:

$$n_{\chi'} = \frac{1}{12} \left[ 1 \cdot 1 + 2 \cdot 1 + 3 \cdot 1 + 1 \cdot 1 + 2 \cdot 1 + 3 \cdot 1 \right]$$

$$n_{\chi'} = \frac{1}{12} \left[ 3 + 0 + 3 + 0 + 3 + 0 \right] = 0$$

- This is the kind of working that is expected in the exam (as shown for $A'_2$ above) when I ask you to "Show your working". You only need to show the full working ONCE, after which, for the other irreducible representations, you can simply state the answer, or show as much working as you like. BUT people often make simple errors at this stage, I would advise showing the some working for each representation calculated in this way as it reduces the chances of making such an error. (See short-cuts below for why you might choose to do it another way.)
**Practice:**

Your turn, please determine the number of times the $E'$ and $A_1''$ irreducible representations contribute to the reducible representation of $H_3$. Show your working.

<table>
<thead>
<tr>
<th></th>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1''$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma(H_3)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$n_{A_1''} = \frac{1}{12} [\quad + \quad + \quad + \quad + \quad + \quad + \quad ] = \quad$  

$n_{E'} = \frac{1}{12} [\quad + \quad + \quad + \quad + \quad + \quad + \quad ] = \quad$
• I will leave it up to you to practice the rest at home, the results of applying this method to all of the irreducible representations is:

\[ n_{\mathcal{A}_1} = 1 \quad n_{\mathcal{A}_2} = 0 \quad n_{\mathcal{E}} = 1 \quad n_{\mathcal{E}'} = 0 \quad n_{\mathcal{E}''} = 0 \]

• This information is normally presented as shown below, and tells us how many fragment orbitals need to be found, and what their symmetry will be. One non-degenerate orbital of \( \mathcal{A}_1' \) symmetry and one doubly degenerate orbital of \( \mathcal{E}' \) symmetry (Figure 8).

\[ \Gamma(H_3) = \mathcal{A}_1' + \mathcal{E}' \]

• It is easy to make simple mistakes! \( n \) is always a positive integer, so fractions or negative numbers indicate a mistake. It is important that you check your answer by adding the irreducible representations to make sure you regenerate the reducible representation, Figure 9.

\[
\begin{array}{c|cccccc}
& E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
\mathcal{A}_1' & 1 & 1 & 1 & 1 & 1 & 1 \\
+ &  &  &  &  &  &  \\
\mathcal{E}' & 2 & -1 & 0 & 2 & -1 & 0 \\
\hline
\Gamma(H_3) & 3 & 0 & 1 & 3 & 0 & 1 \\
\end{array}
\]

Figure 9 Checking the answer

• Short-cuts should be used, for example once you know that \( \mathcal{A}_1' \) is one of the irreducible representations it is easy to see that the other one must be \( \mathcal{E}' \), Figure 10, without having to go through all of the other symmetry labels.

\[
\begin{array}{c|cccccc}
& E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
\Gamma(H_3) & 3 & 0 & 1 & 3 & 0 & 1 \\
\mathcal{A}_1' & 1 & 1 & 1 & 1 & 1 & 1 \\
\hline
\Gamma(H_3) - \mathcal{A}_1' = \mathcal{E}' & 2 & -1 & 0 & 2 & -1 & 0 \\
\end{array}
\]

Figure 10 Taking short-cuts
The Projection Operator

• Now we know the symmetry of the fragment orbitals, we need to determine the "picture" for each fragment orbital. This requires us to determine the orbital coefficients (or the C's in the equations below).

\[
\psi'_{a_1} = C_1' \phi_{s_1} + C_2' \phi_{s_2} + C_3' \phi_{s_3}
\]

\[
\psi_{e'(1)} = C_1 e'(1) \phi_{s_1} + C_2 e'(1) \phi_{s_2} + C_3 e'(1) \phi_{s_3}
\]

\[
\psi_{e'(2)} = C_1 e'(2) \phi_{s_1} + C_2 e'(2) \phi_{s_2} + C_3 e'(2) \phi_{s_3}
\]

• The orbital coefficients are just a numerical value that represents the size of the AO contributions to each MO, these are found using the projection operator, which is given below. You must be able to write this equation and define each of the symbols.

\[
P_G [\psi] = \frac{1}{h} \sum_Q \chi^R(Q) \cdot Q[\psi]
\]

- \( h \) = number of operations in the group
- \( Q \) = a particular symmetry operation
- \([\psi]\) = operate on an orbital function
- \( \chi^R(Q) \) = the character of the Irreducible Representation under \( Q \)

• the reduction formula produced a number (\( n_{IR} \)), while the projection operator produces a function (the wavefunction of the fragment orbital). An operator always acts on something, normally an atomic orbital function, hence the wavefunction in square brackets [\( \psi \)] does not mean "multiply by" it means "operate on".

• like the reduction formula it is easiest to show you how the projection operator works with an example.

• first set up the problem: **label each of the basis orbitals**, this is very important as you will see shortly, Figure 11

• then **explicitly identify all of the symmetry elements**, for example as shown in Figure 12
  - it is very important to know which elements each basis function lies on
  - for example, that \( s_1 \) lies on the \( C_2' \) axis and not on either of the \( C_2' \) or \( C_2'' \) axes
• set up a **projection table**, this is more complex than the reduction table because each of the symmetry operations has to be explicitly identified.

$$\begin{array}{c|cccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
D_{3h} & E & C_3^1 & C_3^1 & C_2' & C_2' & C_{2''} & \sigma_h & S_3^1 & S_3^1 & \sigma & \sigma' & \sigma'' \\
\end{array}$$

Figure 13 Empty projection table

- up until now we have not differentiated between operations that have been grouped together. For example, we have just used "2C_3" however now we must compute the effect of each operation C_3^1 and C_3^2 explicitly.
- This is why there is no "k" in the projection operator equation

• pick **ONE** of the orbitals (s_1 say) and work out what happens to this orbital under **ALL** of the symmetry operations of the point group, I've shown the first few for the E and the two C_3 operations, **Figure 14**.

$$\begin{array}{cccc}
s_1 & \rightarrow & s_1 & \rightarrow & s_1 \\
\end{array}$$

Figure 14 Using the projection operator

• This data is filled in on a projection table as shown below, **Figure 15**.

$$\begin{array}{c|cccccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
Q[s_1] & s_1 & s_2 & s_3 & s_1 & s_2 & s_3 & s_2 & s_3 & s_2 & s_1 & s_3 & s_2 \\
A_{1}' & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\chi'^K(Q) \bullet Q [s_1] & s_1 & s_2 & s_3 & s_1 & s_2 & s_3 & s_2 & s_3 & s_2 & s_1 & s_3 & s_2 \\
\end{array}$$

Figure 15 The a_1' projection table

• I do not expect you to reproduce diagrams like **Figure 14**, unless I specifically request you to show the effect of a symmetry operation, I **DO** expect to see a projection table, **Figure 15**, in the exam.

• The projection table generates components of the projection operator, here \( \psi = s_1 \).

\[ P_1[\psi] = \frac{1}{\hbar} \sum_Q \chi'^K(Q) \bullet Q [\psi] \]
• And so the last row of the table has produced the product $\chi^{IR}(Q) \cdot Q \cdot [s_1]$ for each value of $Q$ (the symmetry operations)

• The projection operator actually calls for the sum of these entries as shown below:

$$P_{s_1} = \frac{1}{12} \left[ s_1 + s_2 + s_3 + s_1 + s_2 + s_3 + s_1 + s_2 + s_3 + s_1 + s_2 + s_3 \right]$$

$$= \frac{1}{12} \left[ 4s_1 + 4s_2 + 4s_3 \right] = \frac{1}{3} \left[ s_1 + s_2 + s_3 \right]$$

• thus we have derived the first fragment orbital (Figure 16) this equation tells us that each orbital contributes an equal third to the whole fragment orbital which is a totally positive combination of all the s AOs

$$\psi_{1a_1} = \frac{1}{3} \left[ \phi_{s_1} + \phi_{s_2} + \phi_{s_3} \right]$$

Figure 16 the $a_1'$ fragment orbital of $H_3$

• an advantage is that once the first projection table has been generated, the $Q[s_1]$ components don't change. But the IR being considered does.

• producing the two wavefunctions for the degenerate fragment orbitals is slightly more difficult, but we start in exactly the same way

In-Class Activity
• You try! Determine the wavefunction for one of the components of the degenerate e' MOs
  o fill in the projection table:

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$C_3^1$</th>
<th>$C_3^2$</th>
<th>$C_2$</th>
<th>$C_2'$</th>
<th>$C_2''$</th>
<th>$\sigma_h$</th>
<th>$S_3^1$</th>
<th>$S_3^2$</th>
<th>$\sigma'$</th>
<th>$\sigma''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q[s_1]$</td>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$s_3$</td>
<td>$s_1$</td>
<td>$s_3$</td>
<td>$s_2$</td>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$s_3$</td>
<td>$s_1$</td>
<td>$s_3$</td>
</tr>
<tr>
<td>$E'$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi^{e'}(Q) \cdot Q \cdot [s_1]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

  o Then form the sum:

$$P_{E}[s_1] = \frac{1}{12} \left[ \right]$$

$$P_{E}[s_1] =$$

  o finally draw the orbital:
• when drawing the orbitals be careful to make each the correct size and phase according to your original assignment.
• to obtain the second fragment orbital make a guess "from inspection" for the form of the orbital and then check it against the requirement that **degenerate fragment orbitals must be orthogonal.**
• How do you make a guess from inspection? In this case H$_3$ can be thought of as being made up from H$_2$ and H. H$_2$ will have a bonding and antibonding combination and the single H will be just a plain sAO, **Figure 17.** The bonding orbital of H$_2$ will interact with the H s atomic orbital because they both have a $1_g$ symmetry. The antibonding orbital of H$_2$ will remain non-bonding and is therefore a good candidate for the other part of the e' pair.
• now we need to establish if the "guessed" fragment orbital is orthogonal to the one we found using the projection operator. Orbitals are orthogonal when:

$$S_{ij} = \int f_i \cdot f_j \, d\tau = 0$$

where $f_i$ and $f_j$ are any functions and $d\tau$ represents integration over all space
• thus we need to evaluate:

$$\int \psi_{i\prime}^1 \cdot \psi_{i\prime}^2 \, d\tau$$

where

$$\psi_{i\prime}^1 = 2\varphi_{i\prime} - \varphi_{j\prime} - \varphi_{k\prime}$$

$$\psi_{i\prime}^2 = \varphi_{j\prime} - \varphi_{k\prime}$$

• two pieces of information simplify matters significantly:
  o atomic orbitals overlap where
  o atomic orbitals are normalized

$$\int \varphi_i \cdot \varphi_j \, d\tau = s_{ij} \quad \text{and} \quad \int \varphi_i \cdot \varphi_i \, d\tau = 1$$

  o overlap is reciprocal and thus $s_{ij} = s_{ji}$
  o sAOs are equidistant and thus $s_{12} = s_{13} = s_{23}$
• thus we have all the information we need to evaluate the integral for the two fragment orbitals.

$$\int \psi_{i\prime}^1 \cdot \psi_{i\prime}^2 \, d\tau = \int (2\varphi_{i\prime} - \varphi_{j\prime} - \varphi_{k\prime}) \cdot (\varphi_{i\prime} - \varphi_{j\prime}) \, d\tau$$

$$= \int (2\varphi_{i\prime} \varphi_{i\prime} - \varphi_{j\prime} \varphi_{i\prime} - \varphi_{k\prime} \varphi_{i\prime}) + \int (\varphi_{j\prime} \varphi_{i\prime} - \varphi_{k\prime} \varphi_{i\prime}) \, d\tau$$

$$= 2s - 2s - 1 + s - s + 1$$

$$\int \psi_{i\prime}^1 \cdot \psi_{i\prime}^2 \, d\tau = 0$$
• the two fragment orbitals are orthogonal, \( \int \psi_{\nu'}^1 \cdot \psi_{\nu'}^2 \, d\tau = 0 \) and thus the guessed fragment orbital is a valid one.
• if you want to know more details about orthogonality there is additional information available on my web-site.

Final symmetry adapted orbitals
• by combining all of the information obtained during this lecture we are now ready to produce the fragment orbitals for \( \text{H}_3 \), Figure 18.

\[
\psi_{\nu'} = \frac{1}{2} [ \varphi_{s_1} - \varphi_{s_2} ] \\
\psi_{\nu'} = \frac{1}{6} [ 2 \varphi_{s_1} - \varphi_{s_2} - \varphi_{s_3} ]
\]

Figure 18 Final fragment orbitals

**IMPORTANT**
• Always ensure you plot the energy levels, label them with the correct symmetry, draw the fragment orbitals and then write the correct equation next to each orbital.

Kolb Cycle Abstraction: How to construct symmetry adapted orbitals
• summarise the steps used to produce symmetry adapted orbitals

**Finding Symmetry Adapted Orbitals**
1. determine the basis orbitals for the fragment
2. identify the point group and locate all of the symmetry operations of the molecule
3. take the all in-phase combination of the basis orbitals and produce a representation table
4. find the contributing irreducible representations using the reduction formula and a reduction table
\[
n_{IR} = \frac{1}{h} \sum_{Q} k \cdot \chi^R(Q) \cdot \chi^R(Q)
\]
5. determine the orbital coefficients using the projection operator and a projection table
\[
P_r[\psi] = \frac{1}{h} \sum_{Q} \chi^R(Q) \cdot Q \cdot [\psi]
\]
6. if there are any degenerate orbitals find the second orbital by guessing and then testing for orthogonally
7. produce the full fragment orbital diagram
Key Points:
- be able to find the reducible representation for a given set of basis orbitals
- be able to write down the reduction formula and define all the terms
- be able to use the reduction formula, be able to show all your working for at least one example and be able to use all the short-cuts identified
- be able to write down the projection operator and define all the terms
- be able to set up and use a projection table and hence find the coefficients for fragment orbitals
- be able to predict and prove the orthogonally of two orbitals for a degenerate set
- be able to produce a clear fragment orbital diagram containing all of the key elements (energy levels, symmetry labels, orbital pictures, associated wavefunction)

Homework and/or 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 $D_{3h}$:

![Oxygen molecule](image)

i) Determine the reducible representation for the three $p_{\pi}$ orbitals (1 mark)

ii) Write down the reduction and projection formulae. Briefly explain each of the terms in both formulae. (4 marks)

iii) Use the reduction formula to determine the symmetry of the $p_{\pi}$ based molecular orbitals. Show your working. (3 marks)

iv) Use the projection formula to determine the wave function of the $p_{\pi}$ based molecular orbitals. Show your working. The molecular orbital wavefunctions do not need to be normalised. (5 marks)

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)

Optional reading is detailed on the web-site