Symmetry Adapted Orbitals

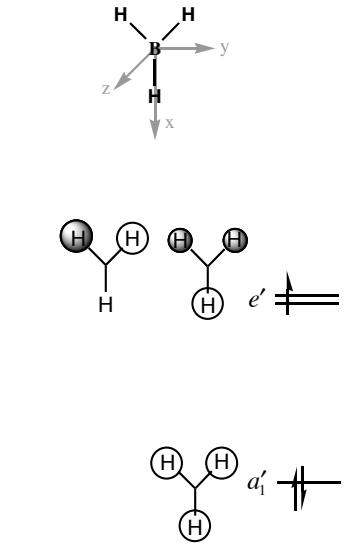


Figure 1 Symmetry adapted fragment orbitals for H_3

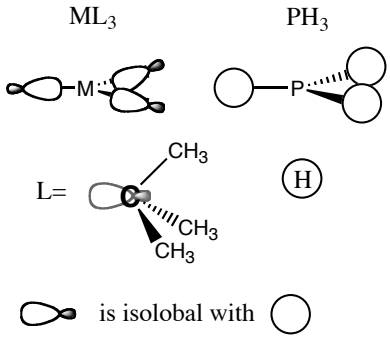


Figure 2 Isolobal relationship

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 H_3 fragment orbitals provided for the tutorial problem on BH_3 (**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:
  - generate a reducible representation
  - use the reduction formula
  - use the projection formula
- We will start with the fragment you have already seen and used, that of H_3, **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 (sp^x) valence AOs arranged in a triangle.
  - 6s AOs of gold atoms.
  - 3 sigma type orbitals from R groups
  - 3 sigma type orbitals of ligands L
- the similarity between the donor orbtial of a ligand and the H 1sAO makes them **isolobal**, **Figure 2**.

The symmetry adapted orbitals of H_3

- The point group of the molecule must be known before symmetry adapted orbitals can be derived. We will start with the fragments of D_{3h} BH_3.
- The D_{3h} 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 D_{3h} point group are given in **Figure 3**.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h=12
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E"	2	-1	0	2	1	0	

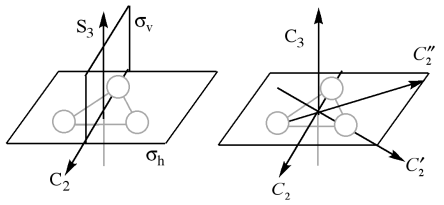


Figure 3 Character table and symmetry elements for D_{3h}

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**)

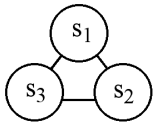


Figure 4 Basis set of 3 sAOs

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma(H_3)$	3	0	1	3	0	1

Figure 5 Representation table

- Determine how the all in-phase orbitals (basis functions) transform under each symmetry operation. For **each orbital that does not move**, we add +1 if the phase remains the same, or -1 if the phase changes.

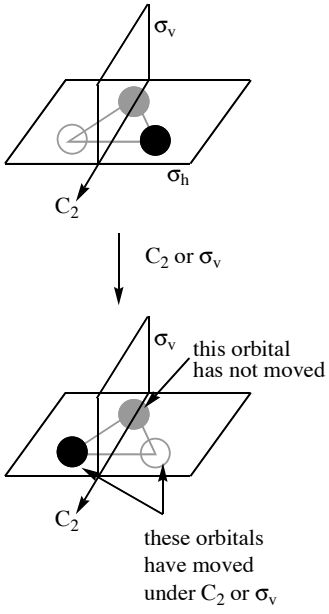


Figure 6 generating a reducible representation

- For H_3
  - under E => all 3 orbitals don't move, and there is no phase change=3
  - under C_3 => 0 orbitals don't move
  - under C_2 => 1 (only the orbital on the axis doesn't move, and it's phase stays the same, see **Figure 6**)
  - under σ_h => all 3 orbitals don't move
  - under S_3 => 0 orbitals don't move
  - under σ_v => 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

IMPORTANT

The Reduction Formula

- Every reducible representation (Γ^R) can be written as a sum of the irreducible representations (Γ^{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 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, ie $v = x\hat{i} + y\hat{j} + z\hat{k}$.
- think of Γ^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.

The Reduction formula

$$n_{IR} = \frac{1}{h} \sum_{Q} k \bullet \chi^{IR}(Q) \bullet \chi^{R}(Q)$$

h	= number of operations in the group
Q	= a particular symmetry operation
k	= the number of operations of Q
$\chi^{IR}(Q)$	= the character of the **I**rreducible **R**epresentation under Q
$\chi^{R}(Q)$	= the character of the **R**educible **R**epresentation under Q

- component terms of the reduction formula are shown for the C_{3v} character table in **Figure 7**
  - h=the number of operations in the point group and for C_{3v} this is $1E+2C_3+3\sigma_v=6$ operations

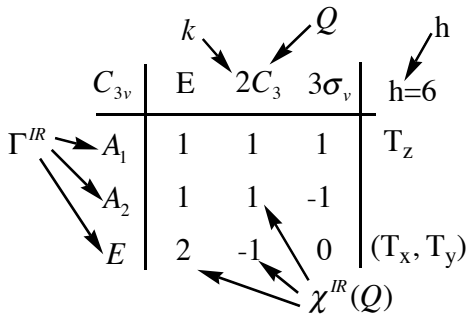


Figure 7 Components of the reduction formula

- we start by working out the number of times ($n_{A_1'}$) the irreducible representation A_1' contributes to the reducible representation of H_3:

$$n_{IR} = \frac{1}{h}\sum_{\mathrm{R}} k\chi^{IR}(Q)\chi^{\mathrm{R}}(Q)$$

$$n_{A_1'} = \frac{1}{12}\left[\begin{array}{l} 1\chi^{A_1'}(E)\chi^{R}(E) + 2\chi^{A_1'}(C_3)\chi^{R}(C_3) + 3\chi^{A_1'}(C_2)\chi^{R}(C_2) \\ +1\chi^{A_1'}(\sigma_h)\chi^{R}(\sigma_h) + 2\chi^{A_1'}(S_3)\chi^{R}(S_3) + 3\chi^{A_1'}(\sigma_v)\chi^{R}(\sigma_v) \end{array}\right]$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
$\Gamma[H_3]$	3	0	1	3	0	1

$$n_{A_1'} = \frac{1}{12}\left[\underbrace{1\bullet 1\bullet 3}_{E} + \underbrace{2\bullet 1\bullet 0}_{C_3} + \underbrace{3\bullet 1\bullet 1}_{C_2} + \underbrace{1\bullet 1\bullet 3}_{\sigma_h} + \underbrace{2\bullet 1\bullet 0}_{S_3} + \underbrace{3\bullet 1\bullet 1}_{\sigma_v}\right]$$

$$n_{A_1'} = \frac{1}{12}\left[3+0+3+3+0+3\right] = \frac{12}{12}$$

$$n_{A_1'} = 1$$

- then we work through the symmetry labels for the group. For example, I've shown that for A_2' below:

$$n_{A_2'} = \frac{1}{12}\left[\underbrace{1\bullet 1\bullet 3}_{E} + \underbrace{2\bullet 1\bullet 0}_{C_3} + \underbrace{3\bullet -1\bullet 1}_{C_2} + \underbrace{1\bullet 1\bullet 3}_{\sigma_h} + \underbrace{2\bullet 1\bullet 0}_{S_3} + \underbrace{3\bullet -1\bullet 1}_{\sigma_v}\right]$$

$$n_{A_2'} = \frac{1}{12}\left[3+0-3+3+0-3\right] = \frac{0}{12} = 0$$

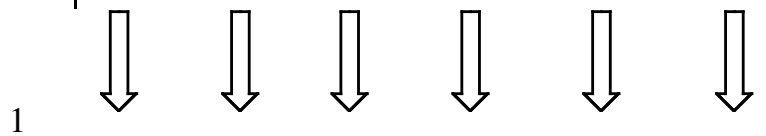
IMPORTANT

- 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.

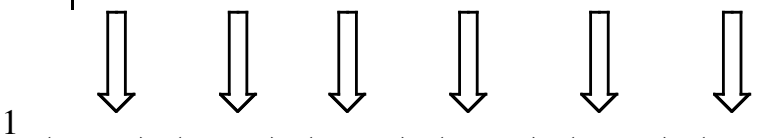
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1''						
$\Gamma(H_3)$						



$$n_{A_1''} = \frac{1}{12}(\quad)+(\quad)+(\quad)+(\quad)+(\quad)+(\quad)$$

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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'						
$\Gamma(H_3)$						



$$n_{E'} = \frac{1}{12}(\quad)+(\quad)+(\quad)+(\quad)+(\quad)+(\quad)$$

$$n_{E'} = \frac{1}{12}[\qquad\qquad\qquad\qquad\qquad\qquad] =$$

- 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:

$$n_{A_1'}=1 \;\; n_{A_2'}=0 \;\; n_{E'}=1 \;\; n_{A_1''}=0 \;\; n_{A_2''}=0 \;\; n_{E''}=0$$

- 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 a_1' symmetry and one doubly degenerate orbital of e' symmetry (**Figure 8**).

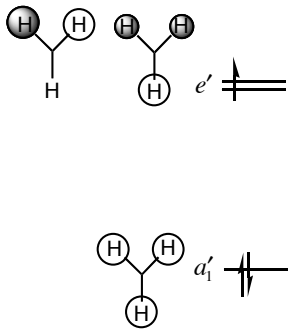


Figure 8 Symmetry adapted fragment orbitals for H_3

$$\Gamma(H_3)=a_1'+e'$$

IMPORTANT

Marks are allocated for checking the answer!

- 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**.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
+						
E'	2	-1	0	2	-1	0
$\Gamma(H_3)$	3	0	1	3	0	1

Figure 9 Checking the answer

IMPORTANT

Marks are allocated for taking the short-cuts!

- **Short-cuts should be used**, for example once you know that A_1' is one of the irreducible representations it is easy to see that the other one must be E' , **Figure 10**, without having to go through all of the other symmetry labels.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma(H_3)$	3	0	1	3	0	1
A_1'	1	1	1	1	1	1
$\Gamma(H_3)$-A_1' = E'	2	-1	0	2	-1	0

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).

$$\psi_{a_1'} = C_1^{a_1'}\varphi_{s_1} + C_2^{a_1'}\varphi_{s_2} + C_3^{a_1'}\varphi_{s_3}$$
$$\psi_{e'(1)} = C_1^{e'(1)}\varphi_{s_1} + C_2^{e'(1)}\varphi_{s_2} + C_3^{e'(1)}\varphi_{s_3}$$
$$\psi_{e'(2)} = C_1^{e'(2)}\varphi_{s_1} + C_2^{e'(2)}\varphi_{s_2} + C_3^{e'(2)}\varphi_{s_3}$$

- 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.

The Projection Operator

$$P_\Gamma[\psi] = \frac{1}{h}\sum_Q \chi^{IR}(Q) \bullet Q[\psi]$$

h	= number of operations in the group
Q	= a particular symmetry operation
$[\psi]$	= operate on an orbital function
$\chi^{IR}(Q)$	= the character of the **I**rreducible **R**epresentation 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.

IMPORTANT

Marks are allocated for labelling the basis

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

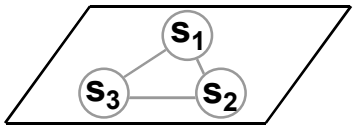


Figure 11 Label the orbitals

IMPORTANT

Marks are allocated for showing all the symmetry elements

- 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

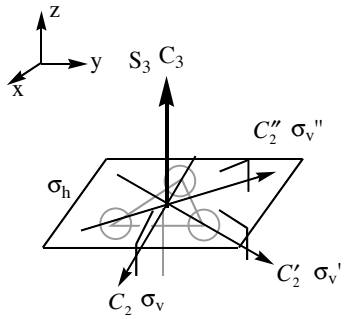


Figure 12 Explicitly identify all the symmetry elements

IMPORTANT

Marks are allocated for showing the expanded table

- set up a **projection table**, this is more complex than the reduction table because each of the symmetry operations has to be explicitly identified.

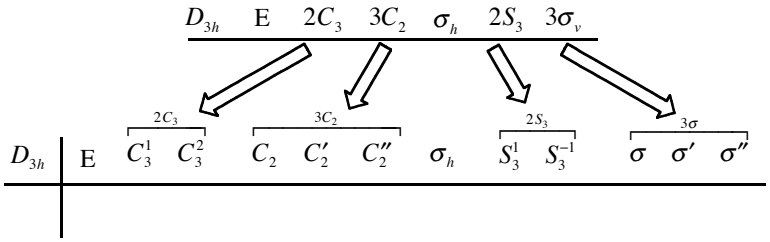
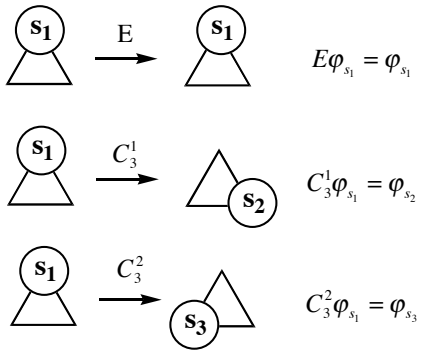


Figure 13 Empty projection table

  - 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.**



$\Gamma(H_3)=a_1'+e'$

Figure 14 Using the projection operator

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

D_{3h}	E	$2C_3$		$3C_2$			σ_h	$2S_3$		3σ		
		C_3^1	C_3^2	C_2	C_2'	C_2''		S_3^1	S_3^{-1}	σ	σ'	σ''
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2	s_1	s_2	s_3	s_1	s_3	s_2
A_1'	1	1	1	1	1	1	1	1	1	1	1	1
$\chi^{A_1'}(Q)\bullet Q\bullet[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2	s_1	s_2	s_3	s_1	s_3	s_2

Figure 15 the a_1' projection table

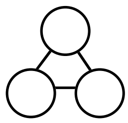
- I do not expect you to reproduce diagrams like **Figure 14**, unless I specifically request you to show the effect of a symmetry operation, I **DO** expect to see a projection table, **Figure 15**, in the exam.
- The projection table generates components of the projection operator, here $\psi=s_1$.

$$P_\Gamma[\psi] = \frac{1}{h}\sum_Q \chi^{IR}(Q)\bullet Q[\psi]$$

- And so the last row of the table has produced the product $\chi^{IR}(Q)\bullet Q\bullet[s_1]$ for each value of Q (the symmetry operations)
- The projection operator actually calls for the sum of these entries as shown below:

$$P_{A_1'}[s_1]=\frac{1}{12}[s_1+s_2+s_3+s_1+s_3+s_2+s_1+s_2+s_3+s_1+s_3+s_2]$$
$$=\frac{1}{12}[4s_1+4s_2+4s_3]=\frac{1}{3}[s_1+s_2+s_3]$$

- 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



$$\psi_{1a_1'}=\frac{1}{3}[\varphi_{s_1}+\varphi_{s_2}+\varphi_{s_3}]$$

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
  - fill in the projection table:

		2C_3		3C_2				2S_3		3σ		
D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ	σ'	σ''
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2	s_1	s_2	s_3	s_1	s_3	s_2
E'												
$\chi^{E'}(Q)\bullet Q\bullet[s_1]$												

  - Then form the sum:

$$P_{E'}[s_1]=\frac{1}{12}[\qquad\qquad\qquad\qquad]$$

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

  - 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' 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.

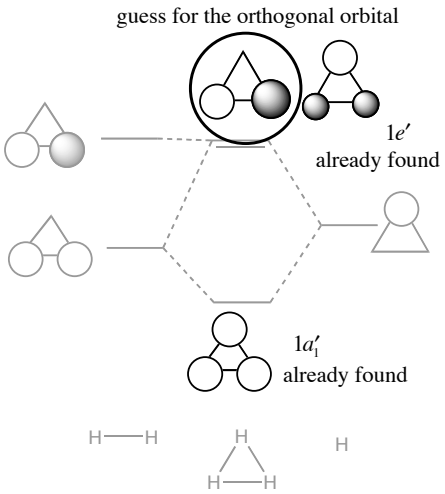


Figure 17 Possible degenerate orbitals

- 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:

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

where f_i and f_j are any functions and $d\tau$ represents integration over all space

- thus we need to evaluate:

$$\int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau \text{ where } \begin{matrix} \psi^1_{1e'} = 2\varphi_{s_1} - \varphi_{s_2} - \varphi_{s_3} \\ \psi^2_{1e'} = \varphi_{s_2} - \varphi_{s_3} \end{matrix}$$

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

$$\int \phi_i \bullet \phi_j d\tau = s_{ij} \quad and \quad \int \phi_i \bullet \phi_i d\tau = 1$$

  - overlap is reciprocal and thus $s_{ij}=s_{ji}$
  - 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.

$$\begin{aligned} \int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau &= \int (2\varphi_{s_1} - \varphi_{s_2} - \varphi_{s_3}) \bullet (\varphi_{s_2} - \varphi_{s_3}) d\tau \\ &= \underbrace{\int 2\varphi_{s_1}\varphi_{s_2} d\tau}_{=2s} - \underbrace{\int 2\varphi_{s_1}\varphi_{s_3} d\tau}_{=s} - \underbrace{\int \varphi_{s_2}\varphi_{s_2} d\tau}_{=1} + \underbrace{\int \varphi_{s_2}\varphi_{s_3} d\tau}_{=s} - \underbrace{\int \varphi_{s_3}\varphi_{s_2} d\tau}_{=s} + \underbrace{\int \varphi_{s_3}\varphi_{s_3} d\tau}_{=1} \\ &= 2s - 2s - 1 + s - s + 1 \end{aligned}$$

$$\int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau = 0$$

- the two fragment orbitals are orthogonal, $\int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau = 0$ and thus the guessed fragment orbital is a valid one.
- if you want to know more details about orthogonally 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 H_3, **Figure 18**.

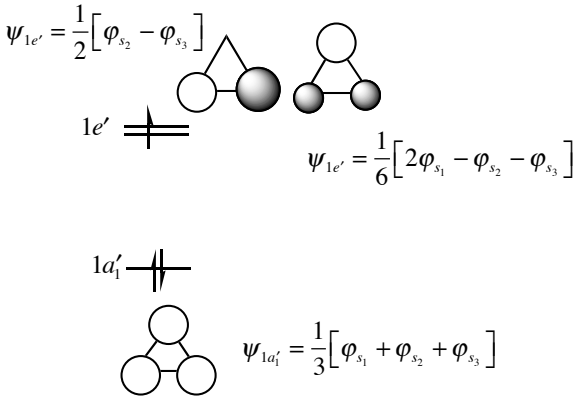


Figure 18 Final fragment orbitals

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

$$n_{IR} = \frac{1}{h}\sum_{Q} k \bullet \chi^{IR}(Q) \bullet \chi^{R}(Q)$$

5. determine the orbital coefficients using the projection operator and a projection table

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

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

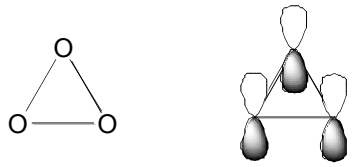
Key Points:

- 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}:



i) Determine the reducible representation for the three p_π 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_π based molecular orbitals. Show your working.

(3 marks)

iv) Use the projection formula to determine the wave function of the p_π 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_π 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