L5 MO Diagram Construction Details

The Splitting Energy

- "input" are fragment orbitals ϕ_a & ϕ_b with of energy ε_a & ε_b
  - the energy difference between the FOs is $\Delta\varepsilon=\varepsilon_b-\varepsilon_a$
- "output" are the MOs ψ_+ & ψ_- with energy E_+ & $E-$
  - ΔE_s is the energy of stabilisation from ε_a
  - ΔE_d is the energy of destabilisation from ε_b

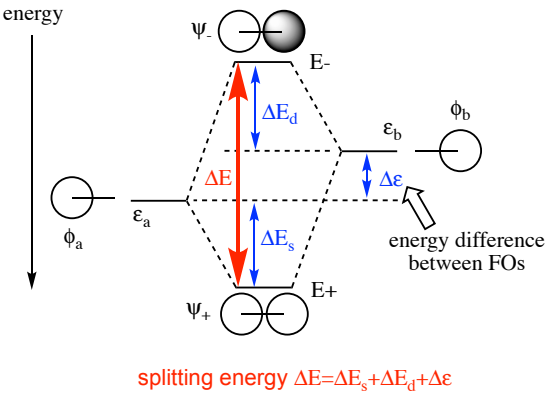


Figure 1 Splitting energy definition

- the **splitting energy** (ΔE) is the energy between E+ and E-
  - The splitting energy is dependent on:
    - the *energy difference* between orbitals: $\Delta\varepsilon=\varepsilon_b-\varepsilon_a$
    - and the *extent of orbital overlap*: $S_{ab} =< \phi_a|\phi_b >= \int \phi_a\phi_b dr$
    - the orbital coupling: $H_{ab} =< \phi_a|H|\phi_b >$

important

- S_{ab} recovers the direct spatial overlap of orbitals, **Figure 2**

$$S_{ab} = \int \phi_a\phi_b dr$$

  - break the equation down!
  - we have two wavefunctions and are multiplying them together $\psi=\phi_a\phi_b$
  - then we are taking the integral of this new function and an integral is just the area under the function
  - S is a number the magnitude of which tells us how much AOs overlap
- H_{ab} recovers the Hamiltonian mediated overlap of orbitals
  - H includes all the nuclear-electronic and electron-electron interactions within a molecule, thus you can think of H_{ab} as an orbital "overlap" modified by the local environment within the molecule, **Figure 3**

$$H_{ab} = \langle\phi_a|H|\phi_b\rangle = \int \phi_a H \phi_b \, dr$$

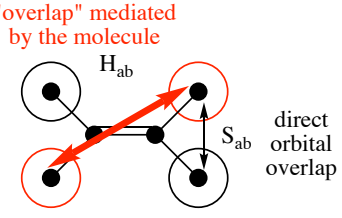


Figure 3 H_{ab} and S_{ab}

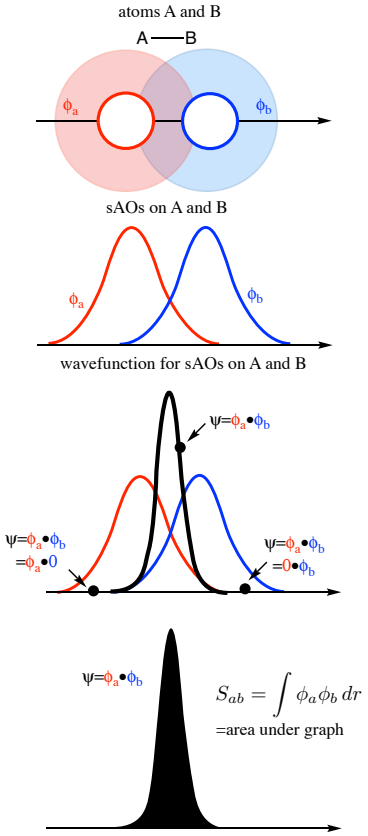


Figure 2 understanding S_{ab}

FO Energy Difference impact on ΔE

important

- *qualitatively* there is a sliding scale of **splitting energies (ΔE)**
  - degenerate orbitals have a large splitting energy and then as the fragment orbitals shift apart in energy the splitting energy decreases, a point will be reached when Δε is sufficiently large that the fragment orbitals do not interact at all (the system is now ionic and not covalent!) **Figure 4**

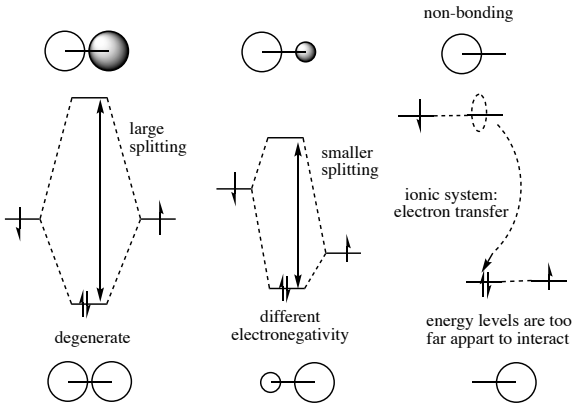


Figure 4 Increasing energy difference between the fragment orbitals

Orbital Overlap impact on ΔE

important

- qualitatively the larger the **orbital overlap** the greater the energy splitting, **Figure 5**
  - for clarity we don't always draw the orbitals actually overlapping
- orbital overlap depends on the *distance*
  - orbitals that are close together interact strongly with each other through electron-electron interactions and also interact with the positive nuclei and also have a large H_{ab}

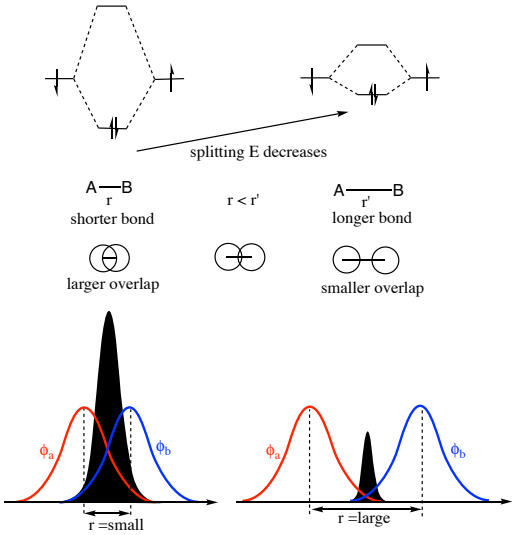


Figure 5 distance dependence of S_{ab}

- orbital overlap also depends on *orientation and directionality*
  - sAOs are spherical, the angle of overlap is not important
  - for pAOs the angle of overlap is important, for example if a sAO overlaps with a pAO in-line then the overlap is good, as the sAO moves out-of-line the overlap decays, **Figure 6**

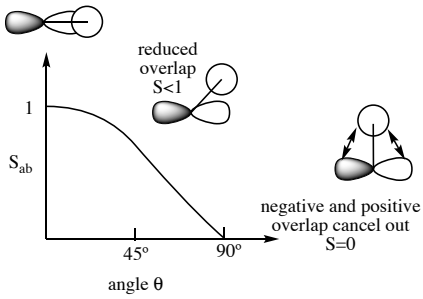


Figure 6 angular dependence of S_{ab}

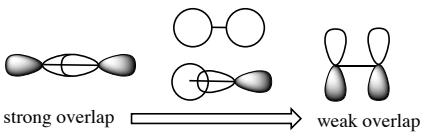


Figure 7 directional dependence of S_{ab}

- the more directed an interaction the better the overlap, for example p_σ orbitals have their lobes directed toward each other have very good overlap, when the orbitals are side-by-side as in p_π the overlap is smaller.
- directed interactions decrease $p_\sigma > s_\sigma \approx sp_\sigma > p_\pi$, where the *orientation* of p orbitals in p-s interactions is important, **Figure 7**

- orbital overlap depends on the *diffusivity* of the orbital, **Figure 8**
  - in general the more diffuse an orbital the weaker the interactions
  - inner AOs are very dense and *decay quickly*. At short distances the overlap is very strong, but at larger distances overlap is weak
  - thus some s-s interactions can be stronger than directed p_σ interactions
  - outer AOs are diffuse and *decay more slowly*, thus the maximum overlap is lower, but overlap is still moderate at larger distances
  - hence at a longer distance p_σ overlap can be stronger than s-s

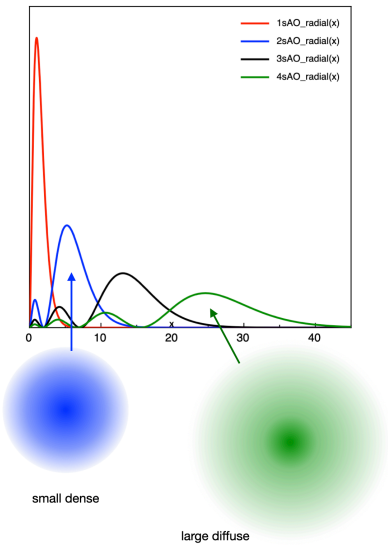


Figure 8 decay dependence of S_{ab}

- overall the magnitude of the orbital overlap depends on an interplay between the relative *distance, orientation, directionality and diffusivity* of the orbitals

Introduction to symmetry adapted fragment orbitals

- symmetry fragments are often used in MO theory because we can use generic **symmetry adapted fragment orbitals**
- the easiest way to explain the process of generating symmetry adapted orbitals is to show you with an example.
- we will generate the symmetry adapted fragments for of H_3, **Figure 9** (in BH_3)

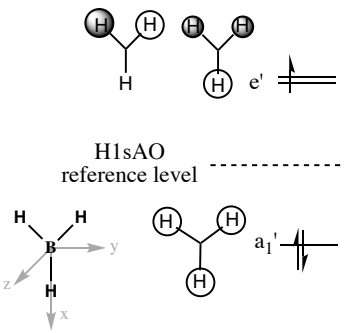


Figure 9 Symmetry adapted fragment orbitals for H_3

- the fragment orbitals we derive will apply to ANY system which has a set of 3 sigma-type (sp^x) valence AOs arranged in a triangle, **Figure 10**.
  - 6s AOs of gold atoms.
  - 3 sigma type orbitals from R groups
  - 3 sigma type orbitals of ligands L
- the similarity between the donor orbital of a ligand and the H 1sAO makes them **isolobal**, **Figure 10**.

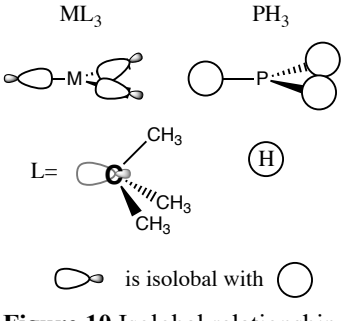


Figure 10 Isolobal relationship

The symmetry adapted orbitals of H_3

- The point group of the molecule must be known before symmetry adapted orbitals can be derived.
- BH_3 belongs to the D_{3h} point group, the character table is given below, along with a reminder of the symmetry elements. **Figure 11**.

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	

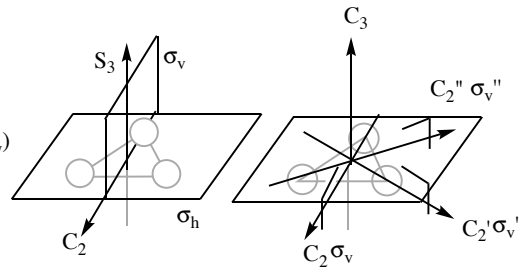


Figure 11 Character table and symmetry elements for D_{3h}

Reducible Representations

- first identify the **basis set** of symmetry related orbitals, in this case they are *three sAOs*, **Figure 12**
  - this is NOT a MO, this is 3 separate AOs

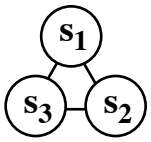


Figure 12 Basis set of 3 sAOs

- The reducible representation is found by forming a representation table (Figure 13)
  - determine how the orbitals (basis functions) transform under each operation of the point group.

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

Figure 13 Representation table

  - for *each basis orbital* that does not move, we add +1 if the phase remains the same, or -1 if the phase changes.
- For H_3
  - under E => all 3 orbitals don't move, and there is no phase change, E=3
  - under C_3 => 0 all orbitals move
  - under C_2 => 1 (only the orbital on the axis doesn't move, and it's phase stays the same, see **Figure 14**)
  - under σ_h => all 3 orbitals don't move
  - under S_3 => 0 all orbitals move
  - under σ_v => 1 (only the orbital in the mirror plane doesn't move, **Figure 14**)
- 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 three* sAOs

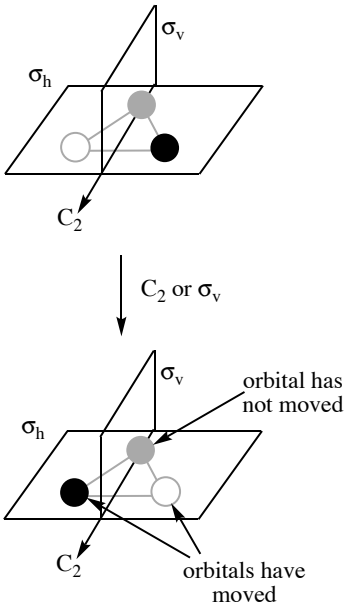


Figure 14 generating a reducible representation

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.

important

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 (simpler!) C_{3v} character table in **Figure 15**
  - h=the number of operations in the point group and for C_{3v} this is $1E+2C3+3\sigma_v$=6 operations

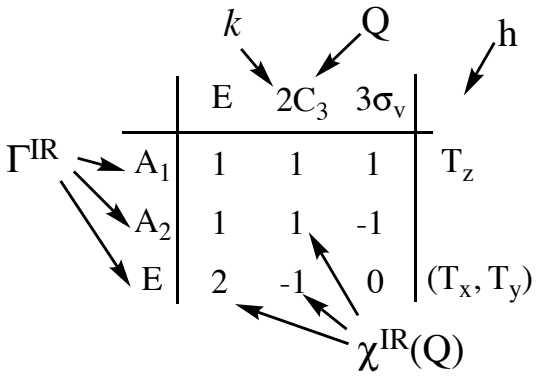


Figure 15 Components of the reduction formula

- start by working out the number of times ($n_{A_1'}$) the irreducible representation A_1' contributes to the reducible representation of H_3 **Figure 16**

important
show your working

$\mathbf{D_{3h}}$	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

$$n_{A_1'} = \frac{1}{12}\left[\underbrace{1\bullet 1\bullet 3}_{E} + \underbrace{2\bullet 1\bullet 0}_{C_3} + \underbrace{3\bullet 1\bullet 1}_{C_2} + \underbrace{1\bullet 1\bullet 3}_{\sigma_h} + \underbrace{2\bullet 1\bullet 0}_{S_3} + \underbrace{3\bullet 1\bullet 1}_{\sigma_3}\right]$$

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

Figure 16 Reduction table for A_1'

- This is the kind of working that is **expected** (as shown for A_1' above). You only need to show the full working **ONCE**, after which, for the other irreducible representations, you can simplify the working.
- then we work through the symmetry labels for the group.

In-Class Activity P1

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

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

$$n_{A_1''} = \frac{1}{12}\left[(\quad)+(\quad)+(\quad)+(\quad)+(\quad)+(\quad)\right]$$

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

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

$$n_{E'} = \frac{1}{12}\left[(\quad)+(\quad)+(\quad)+(\quad)+(\quad)+(\quad)\right]$$

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

Figure 17 In class practice reduction tables

- 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 $\Gamma(H_3)=a_1'+e'$, and tells us how many fragment orbitals need to be found, and what their symmetry will be.
  - in this case one non-degenerate orbital of a_1' symmetry and one doubly degenerate orbital of e' symmetry **Figure 18**.

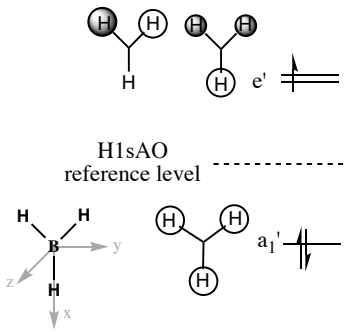


Figure 18 Symmetry determined

- It is easy to make simple mistakes! n is always a positive integer, so fractions or negative numbers indicate a mistake.

important

- you can also check your answer by adding the irreducible representations to make sure you regenerate the reducible representation
- **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 19**, 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 19 Taking short-cuts

The Projection Operator

- now that we have 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 numerical values that represent the size of an AO contribution to each MO, these are found using the **projection operator**. You must be able to write this equation and define each of the symbols.
- 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".

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

important

- 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*, as shown in **Figure 20**

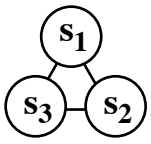


Figure 20 Label the orbitals

important

- make sure you *explicitly identify all of the symmetry elements*, as shown in **Figure 21**
  - 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

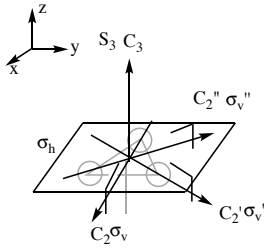


Figure 21 Explicitly identify all the symmetry elements

- 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 22**

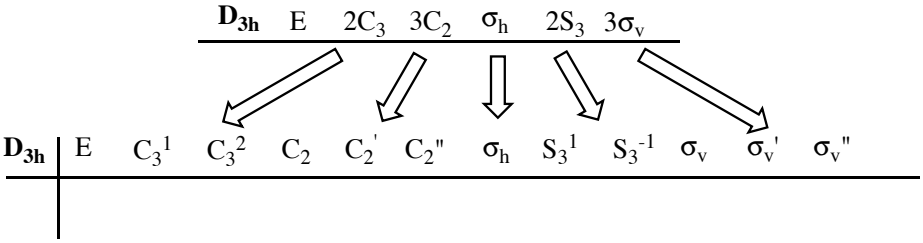
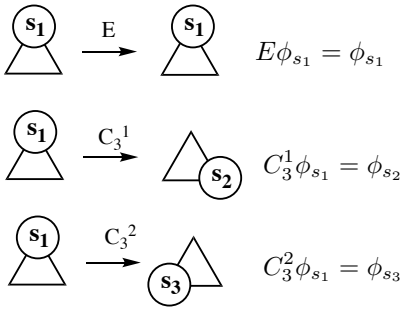


Figure 22 Empty projection table

- 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 23.**

Figure 23 Using the projection operator

- This data is filled in on a projection table as shown below, **Figure 24**.

D_{3h}	E	$2C_3$: C_3^1	C_3^2	$3C_2$: C_2	C_2'	C_2''	σ_h	$2S_3$: S_3^1	S_3^{-1}	3σ: 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 24 the a_1' projection table

- I do not expect you to reproduce diagrams like **Figure 23**, unless I specifically request you to show the effect of a symmetry operation, I **DO** expect to see a projection table, **Figure 24**, in assignments/tests.
- The projection table generates components of the projection operator

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

- 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), we then need to sum these entries:

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

- thus we have derived the first fragment orbital, **Figure 25**, 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

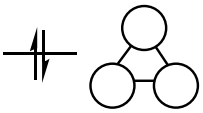
a_1'  $\psi_{a_1'} = \frac{1}{3}\left[\phi_{s_1}+\phi_{s_2}+\phi_{s_3}\right]$

Figure 25 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.
- when drawing the orbitals be careful to make each the *correct size and phase* according to your original assignment.
- producing the two wavefunctions for the degenerate fragment orbitals is slightly more difficult, but we start in exactly the same way

In-Class Activity P2

- You try! Determine the wavefunction for one of the components of the degenerate e' MOs using a 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:

The Other Degenerate FO

- the following is for completeness and your interest you will not be asked to find the orthogonal orbitals in the test
- to obtain the second fragment orbital a process called Gram Schmidt orthogonalization is normally undertaken, I don't have time to teach you this method, however it is also easy to make a guess "from inspection" and then confirm that the 2 degenerate fragment orbitals are *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 26**.
  - 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.

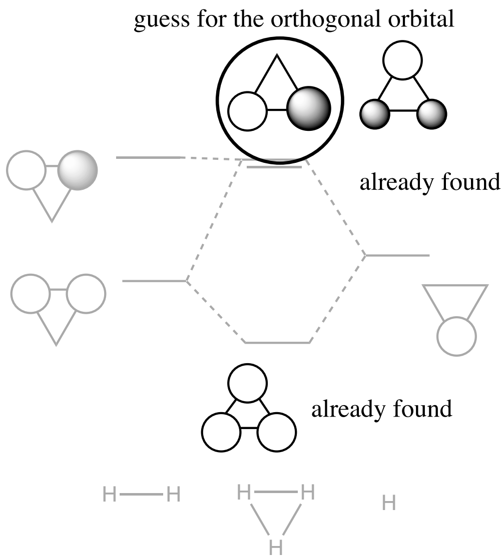


Figure 26 Possible degenerate orbitals

- 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:

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

  - we also know that overlap is reciprocal and thus $s_{ij}=s_{ji}$
  - and that all our sAOs are equidistant and thus $s_{12}=s_{13}=s_{23}$

- thus we have all the information we need to evaluate the integral.

$$\int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau = \int (2\varphi_{s_1} - \varphi_{s_2} - \varphi_{s_3}) \bullet (\varphi_{s_2} - \varphi_{s_3}) d\tau$$

$$= \underbrace{\int 2\varphi_{s_1}\varphi_{s_2} d\tau}_{=2s} - \underbrace{\int 2\varphi_{s_1}\varphi_{s_3} d\tau}_{=s} - \underbrace{\int \varphi_{s_2}\varphi_{s_2} d\tau}_{=1} + \underbrace{\int \varphi_{s_2}\varphi_{s_3} d\tau}_{=s} - \underbrace{\int \varphi_{s_3}\varphi_{s_2} d\tau}_{=s} + \underbrace{\int \varphi_{s_3}\varphi_{s_3} d\tau}_{=1}$$

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

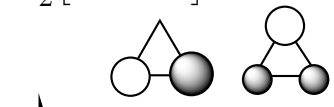
$$\int \psi^1_{1e'} \bullet \psi^2_{1e'} d\tau = 0$$

- 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.

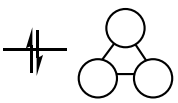
Bring everything together!

- by combining all of the information obtained during this lecture we are now ready to produce the fragment orbitals for H_3, **Figure 27**.

$$\psi_{e'} = \frac{1}{2}\left[\phi_{s_2} - \phi_{s_3}\right]$$

e' 

$$\psi_{e'} = \frac{1}{6}\left[2\phi_{s_1} - \phi_{s_2} - \phi_{s_3}\right]$$

a_1' 

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

Figure 27 Final fragment orbitals

  - 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.

Key Points:

- be able to define and illustrate the splitting energy
- be able employ equations, diagrams and examples discussing $\Delta\varepsilon$, S_{ab} and H_{ab}
- be able to employ this knowledge in forming MO diagrams
- be able to explain and predict the relative size of AO contributions to MOs
- be able to rationalise the relative position of fragment orbital energy levels
- 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 form a MO diagram for small molecules and analyse the MO diagram for information relating to structure and bonding

Self-Study Problems / Test Preparation

- **Q1** Where would you put the FOs for a MO diagram of $MgCl_2$? Draw out the fragments and the FOs (don't complete the diagram, just set it up). Use the fragments "Cl_2" Cl–•–Cl and •–Mg–• for Cl–Mg–Cl
- **Q2** The transition metal (M) complex ML_4 with 4 sigma ligands (L) belongs to the D_{4h} point group and is aligned as shown in **Figure 28**. In the following show your working.
  - Determine the reducible representation ($\Gamma_{L\sigma}$) for the basis set consisting of 4 ligand σ-orbitals.
  - The reducible representation $\Gamma_{L\sigma}$ has three irreducible components, one of which is E_u. Use the reduction formula and appropriate "short-cuts" to determine the remaining irreducible components of $\Gamma_{L\sigma}$.
  - Use the projection formula to determine the wave function of the totally symmetric irreducible representation. The wavefunction does not need to be normalised.

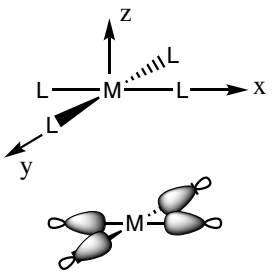


Figure 28 L_4 ligand σ-orbitals