Moleuclar Orbital Theory

Lecture 5

Outline

MO Diagram Construction Details

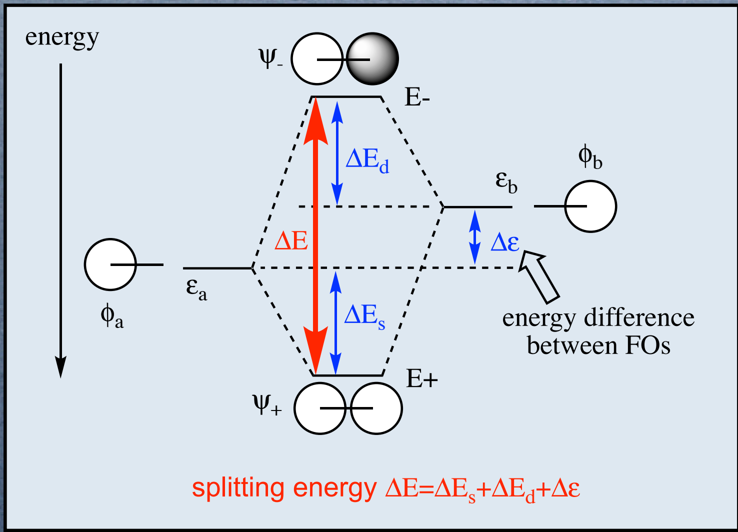
- **the splitting energy**
  - energy
  - coefficients
  - overlap
  - H_{ab}
- **symmetry adapted fragement orbitals**
  - generate fragment orbitals for H3
  - generate a reducible representation
  - introduce and use the Reduction Formula
  - introduce and use the Projection Operator
  - consider degenerate orbitals

Splitting Energy

- **Splitting energy**

$E=\Delta E_s+\Delta E_d+\Delta\varepsilon$

- Φ_a and Φ_b are FOs
- ε_b and ε_a FO energy levels
- $\Delta\varepsilon = \varepsilon_b - \varepsilon_a$ energy difference
- E+ and E- MO energy levels
- ΔE_s=stabilisation energy
- ΔE_d=destabilisation energy



Splitting Energy

Depends on 3 quantities

Important!

- **energy difference between FO:** $\Delta\varepsilon = \varepsilon_i - \varepsilon_j$
- **extent of orbital overlap:** $S_{ab} = \langle \phi_a | \phi_b \rangle$ (direct orbital overlap)
- **orbital coupling:** $H_{ab} = \langle \phi_a | H | \phi_b \rangle$ (molecule mediated orbital overlap)

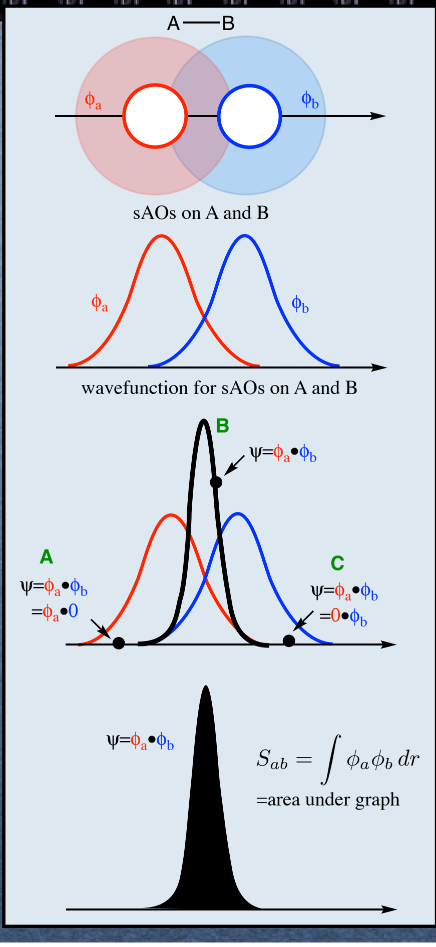
Dirac notation: $\langle \psi | \psi \rangle = \int \psi \psi d\tau$

Overlap

- **S_{ab} recovers direct overalp of orbitals**

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

- **Break this down:**
  - two wavefunctions on different atoms
  - in 2d -> two gaussian curves
  - MULTIPLY them together
  - then we want the AREA under the curve
- **S is a number**
  - large S is good overlap
  - low S is poor overlap

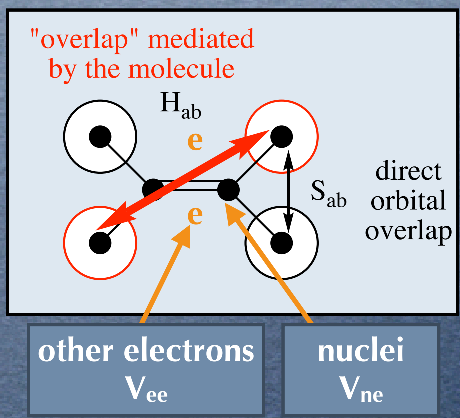


H_{ab} "Overlap"

- **H_{ab} H mediated "overlap" of the orbitals**

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

- **Go back to the Schrödinger equation**
  - solving the wave equation gives the MOs
- **H contains interaction of e with**
  - nuclei (V_{en})
  - other electrons (V_{ee})



$$E\psi = H\psi$$

$$H = T_n + T_e + V_{ee} + V_{en} + V_{nn}$$

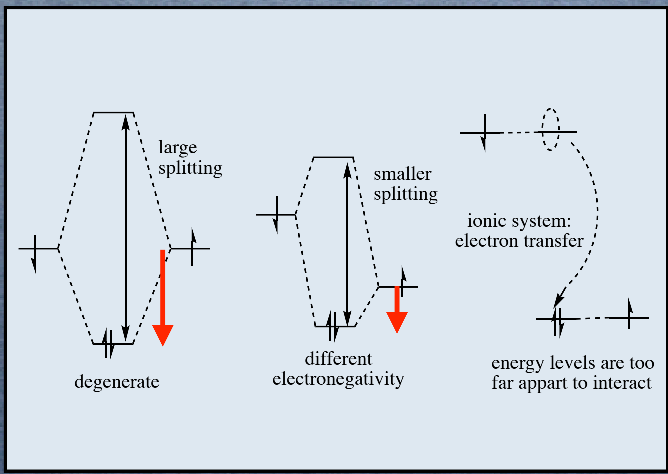
interaction of orbital(a) with orbital(b) modified by the local environment (H)

FO Energy Difference Δε

Important!

- degenerate orbitals have largest splitting
- sliding scale
- as FO shift apart splitting energy is reduced
- point is reached at which there is no interaction

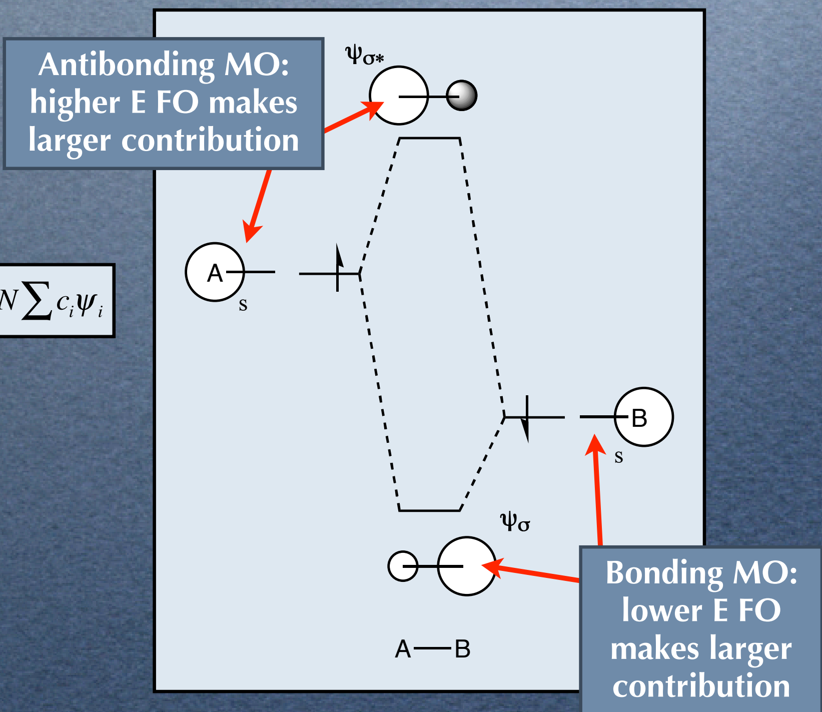
covalent | polar covalent | ionic



FO Energy Difference Δε

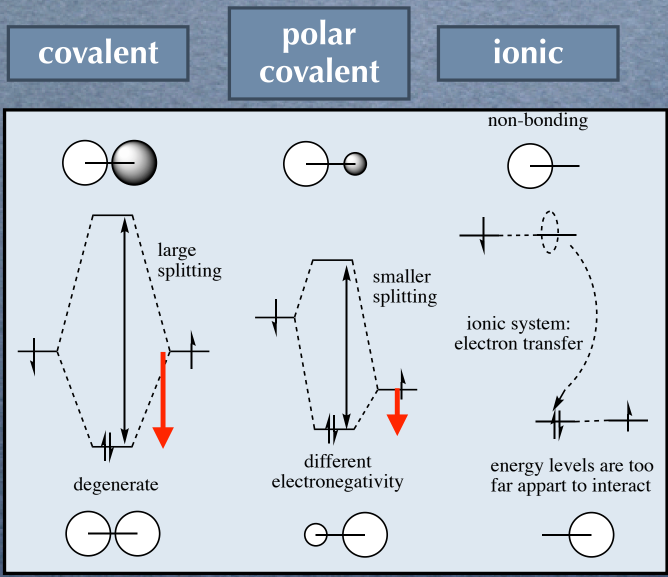
- C's are represented in the size of the AO contributions

$$\psi_\Gamma = N(c_1\psi_1 + c_2\psi_2 + \cdots c_n\psi_n) = N\sum c_i\psi_i$$



FO Energy Difference Δε

- C's are represented in the size of the FOs
  - the larger the energy gap the greater the disparity in FO contributions
  - the larger the energy gap the more polar the bond (more ionic), until eventually there is no covalent interaction, the bond is ionic



Orbital Overlap

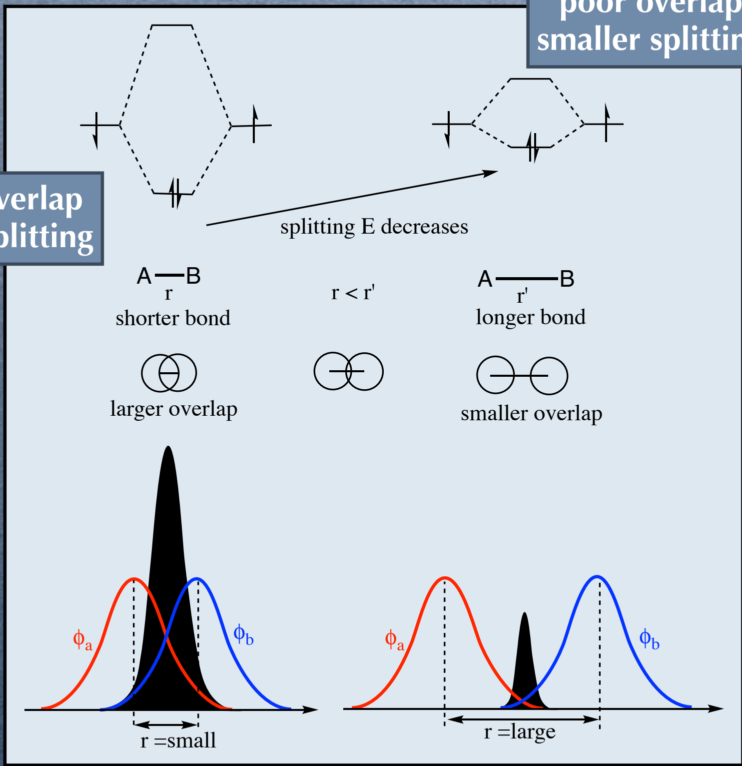
Important!

- Depends on
  - distance
  - orientation and directionality
  - diffusivity
- we don't always draw orbitals explicitly overlapping

Orbital Overlap: Distance

poor overlap
smaller splitting

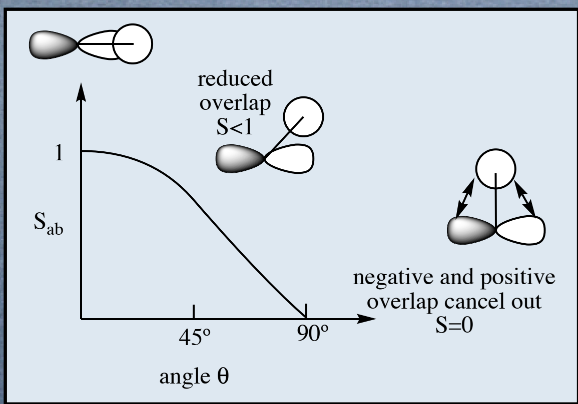
good overlap
larger splitting



- close atoms have more overlap
- larger overlap means greater splitting

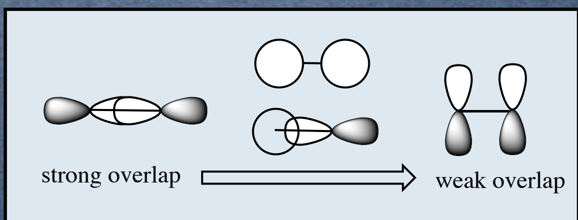
Orbital Overlap: Orientation

- sAO overlap, orientation has no effect
- pAO overlap orientation is important
  - in-line overlap is strong
  - as bending increases overlap rapidly decays
- directed interactions



sigma orbitals overlap better than pi orbitals

overlap: $p_\sigma > s_\sigma \approx sp_\sigma > p_\pi$



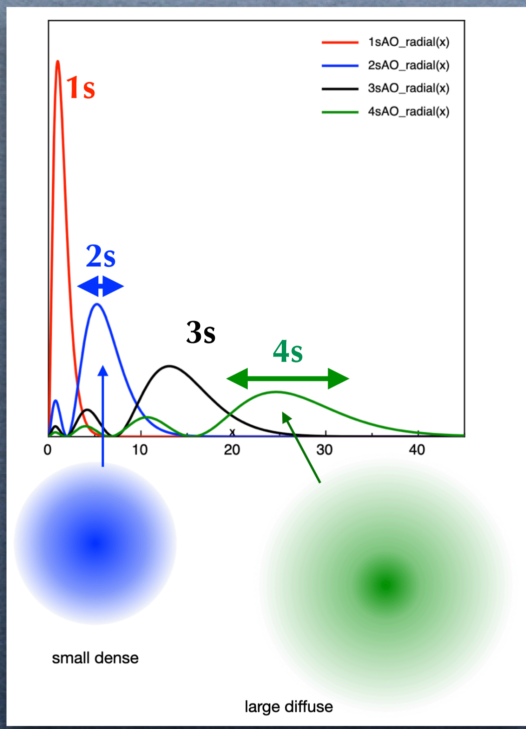
orbitals orientated toward each other overlap better

Orbital Overlap: Diffusivity

- **diffuse orbitals**
  - large (good overlap)
  - slow overlap decay with distance
  - but electron density is low!
- **condensed orbitals**
  - overlap is strong at short distance
  - but overlap decays very quickly
  - s-s overlap can be greater than directed p-p

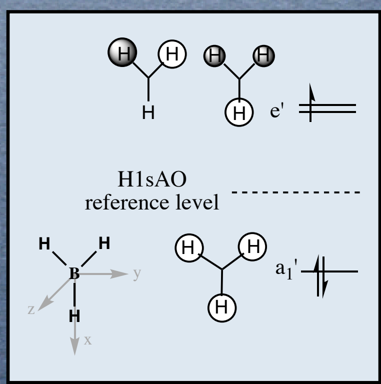
general: more diffuse =weaker S_{ab}

highly system dependent



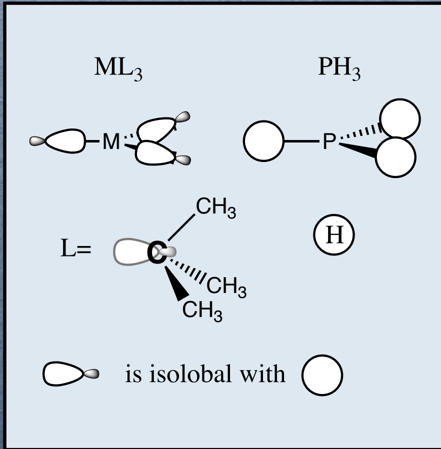
Symmetry Adapted Orbitals

- **symmetry adapted orbitals are the fragment orbitals of symmetry fragments**
  - as opposed to molecular fragments
- **we will use the H_3 fragment orbitals as an example**
- **process**
  - generate a reducible representation
  - use reduction formula
  - use the projection operator
  - draw out and label the symmetry FOs!



Isolobal Orbitals

- apply to any set of three sigma-type FOs
- Isolobal orbitals
  - orbitals with similar symmetry characteristics
- Examples
  - 3 gold atoms and their 6sAOs!
  - 3 substituent sp^x orbitals
  - 3 ligand sp^x orbitals

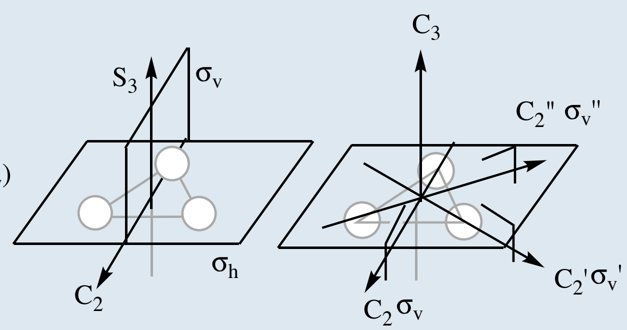


Revision: D_{3h} Point Group

Find the D_{3h} Character table

symmetry operations: D_{3h} E $2C_3$ $3C_2$ σ_h $2S_3$ $3\sigma_v$

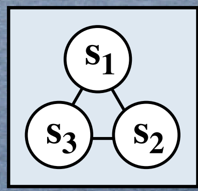
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h=12
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	



symmetry elements

Reducible Representation

- **Identify your "basis set" of orbitals**
  - symmetry related, and all in-phase
  - this is NOT a MO, but three separate AOs



- **Form a representation table**
  - under each operation of the point group
  - for EACH BASIS ORBITAL that DOES NOT MOVE
  - add +1 if the phase is unchanged and -1 if the phase changes

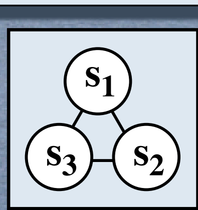
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma(H_3)$	3	0	1	3	0	1

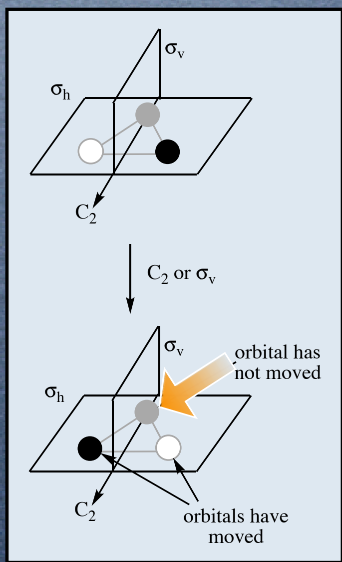
Reducible Representation Γ_R

Representation Table

Reducible Representation

- **Form a representation table**
  - for EACH BASIS ORBITAL that DOES NOT MOVE
  - add +1 if the phase is unchanged and -1 if the phase changes
  - E -> no orbitals move
  - C_3 -> all orbitals move
  - C_2 -> one orbital does not move
  - σ_h -> no orbitals move
  - σ_v -> one orbital does not move





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

Reduce!

- Every reducible representation can be written as a sum of irreducible representations

$$\Gamma_R = \sum_R n_{IR}\Gamma_{IR}$$

Γ_R=reducible representation
Γ_{IR}=irreducible representation
n_{IR}=number
sum over all the irreducible representations

think of Γ_R as a vector in the space of the D_{3h} point group with "axes" defined by the IR

- to determine n_{IR} we use the Reduction Formula

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

Reduction Formula

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

what do all these terms refer to?

use simpler C_{3v} character table to explain each term

Reduction Formula

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

number of symmetry operations in a group

k Q h

Γ^{IR}	E	$2C_3$	$3\sigma_v$	6
A_1	1	1	1	T_z
A_2	1	1	-1	
E	2	-1	0	(T_x, T_y)

$\chi^{IR}(Q)$

Reduction Formula

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

symmetry operations

number of symmetry operations in a group

k Q h

Γ^{IR}	E	$2C_3$	$3\sigma_v$	6
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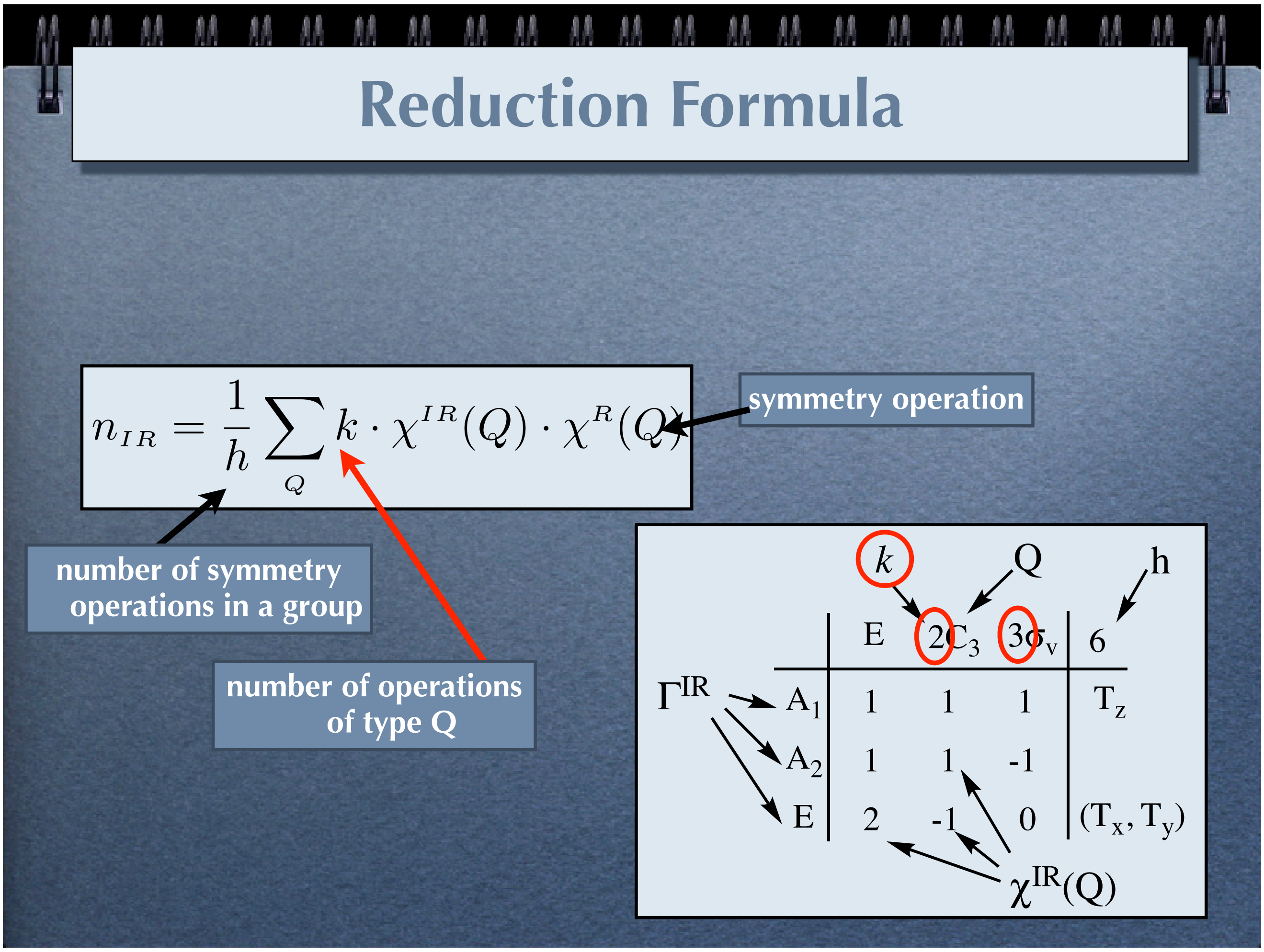
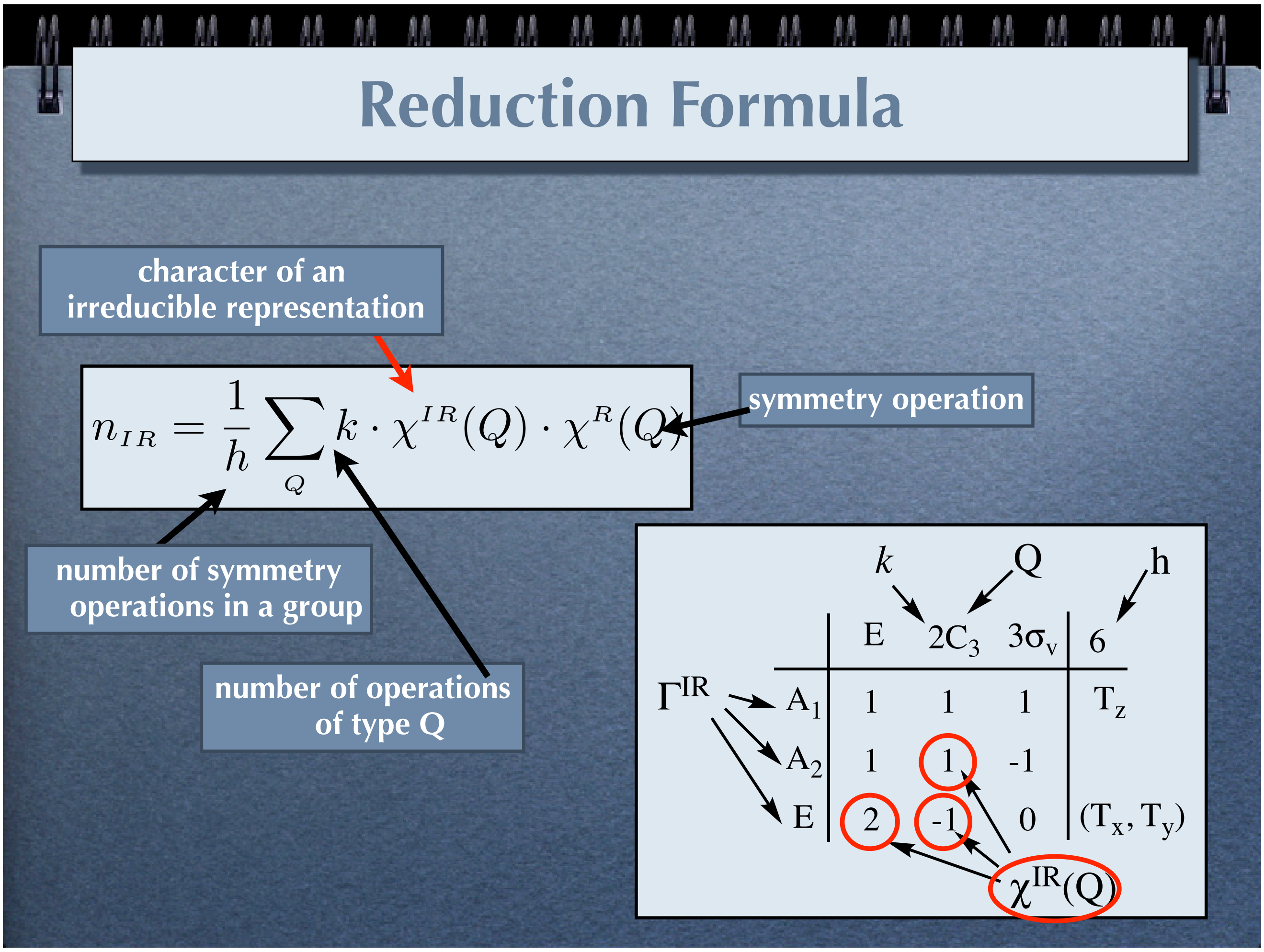
$\chi^{IR}(Q)$


Reduction Formula
$n_{IR} = \frac{1}{h} \sum_{Q} k \cdot \chi^{IR}(Q) \cdot \chi^{R}(Q)$
symmetry operation
number of symmetry operations in a group
number of operations of type Q
k
Q
h
E
2C3
3σv
6
ΓIR
A1
A2
E
1 1 1
1 1 -1
2 -1 0
Tz
(Tx, Ty)
χIR(Q)


Reduction Formula
character of an irreducible representation
$n_{IR} = \frac{1}{h} \sum_{Q} k \cdot \chi^{IR}(Q) \cdot \chi^{R}(Q)$
symmetry operation
number of symmetry operations in a group
number of operations of type Q
k
Q
h
E
2C3
3σv
6
ΓIR
A1
A2
E
1 1 1
1 1 -1
2 -1 0
Tz
(Tx, Ty)
χIR(Q)

Reduction Formula

character of an irreducible representation

character of an reducible representation

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

symmetry operation

number of symmetry operations in a group

number of operations of type Q

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

$\chi^{R}(Q)$

How to Use it!

Form a representation table:

Reduction Formula:

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

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

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

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

How to Use it!

Form a representation table:

Reduction Formula:

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How to Use it!

Form a representation table:

Reduction Formula:

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

number of elements
$=1E+2C_3+3C_2+1\sigma_h$
$+2S_3+3\ \sigma_v$
$=12$

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

$$n_{A_1'} = \frac{1}{12}\left[\underbrace{1\bullet1\bullet3}_{E}+\underbrace{2\bullet1\bullet0}_{C_3}+\underbrace{3\bullet1\bullet1}_{C_2}+\underbrace{1\bullet1\bullet3}_{\sigma_h}+\underbrace{2\bullet1\bullet0}_{S_3}+\underbrace{3\bullet1\bullet1}_{\sigma_3}\right]$$

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

How to Use it!

Form a representation table:

Reduction Formula:

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

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

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

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

How to Use it!

Form a representation table:

Reduction Formula:

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

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

How to Use it!

Form a representation table:

Reduction Formula:

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

this is what I expect to see "Show your working"

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

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

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

In-Class Activity P1

- **determine the number of times the A_1'' and E' and contribute to the reducible representation**

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

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

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

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

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

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

In-Class Activity P1

- determine the number of times the A_1'' and E' and contribute to the reducible representation

Homework is to practice finding the other IR

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

$$n_{A_1''} = \frac{1}{12}\left[(1\bullet1\bullet3)+(2\bullet1\bullet0)+(3\bullet1\bullet1)+(1\bullet\text{-}1\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet\text{-}1\bullet1)\right]$$

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

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

$$n_{E'} = \frac{1}{12}\left[(1\bullet2\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet0\bullet1)+(1\bullet2\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet0\bullet1)\right]$$

$$n_{E'} = \frac{1}{12}\left[6+0+0+6+0+0\right] = 1$$

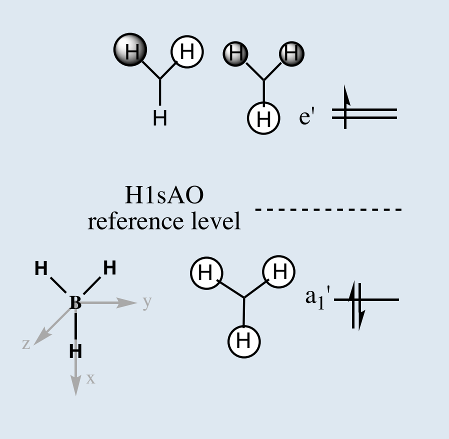
Reduced

- work through for each IR
- only a_1' and e' contribute
- consistent with what we know:

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

easy to make mistakes!

- the values are always integers
- not an integer = a mistake!
- ALSO check your answer



Always Check Your Answer

- Do the irreducible representations add to give the reducible representation?

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

Yes!

Always use Short-Cuts!

- in the test you will not have time to go through ALL of the possible irreducible representations

so be SMART!

Always do totally symmetric first

Then find out what is left

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

Projection Operator

- now we know the symmetry of the fragment orbitals

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

- we need to determine their shape
  - this is the same as determining the orbital coefficients

coefficients are the C's

degenerate orbitals have two components called e′(1) and e′(2) here

$$\psi_{a_1'} = C_1^{a_1'}\phi_{s_1} + C_2^{a_1'}\phi_{s_2} + C_3^{a_1'}\phi_{s_3}$$

$$\psi_{e'(1)} = C_1^{e'(1)}\phi_{s_1} + C_2^{e'(1)}\phi_{s_2} + C_1^{e'(1)}\phi_{s_1}$$

$$\psi_{e'(2)} = C_1^{e'(2)}\phi_{s_1} + C_2^{e'(2)}\phi_{s_2} + C_1^{e'(2)}\phi_{s_1}$$

Projection Operator

character of an irreducible representation

symmetry operation

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

number of symmetry operations in a group

k, Q, h

Γ^{IR}	E	$2C_3$	$3\sigma_v$	6
A_1	1	1	1	T_z
A_2	1	1	-1	
E	2	-1	0	(T_x, T_y)

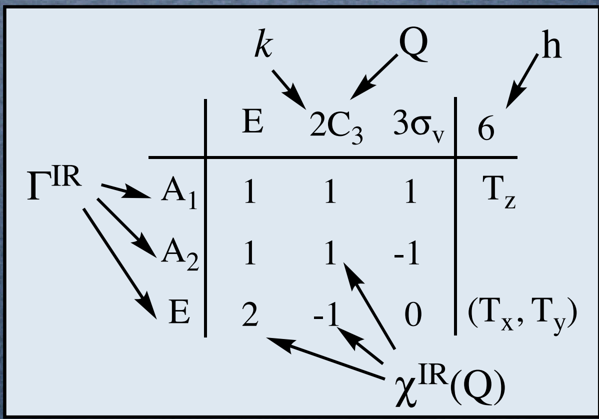
$\chi^{IR}(Q)$

Projection Operator

IMPORTANT: no k (come back to this in a minute)

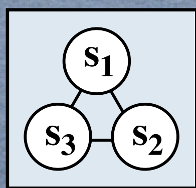
$$P_\Gamma[\psi] = \frac{1}{h}\sum_Q \chi^{IR}(Q)\cdot Q[\psi]$$

- reduction formula produced a number (n_{IR})
- projection operator produces a function (the equation for a MO)

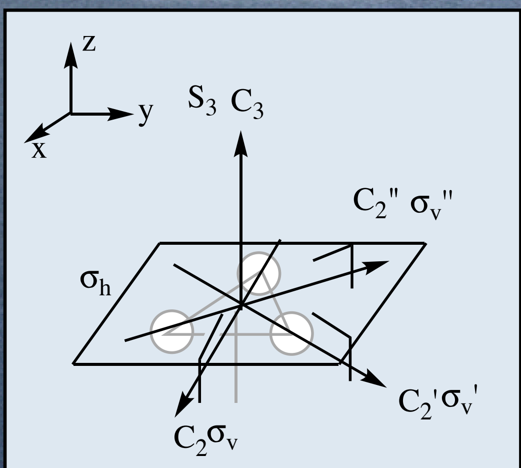


"Setting Up"

- Label orbitals
- Draw ALL of the symmetry elements



Important!



“Setting Up”

Set up the projection table

- No k in the projection operator
- must include EVERY symmetry operation

Important!

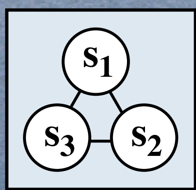
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$

D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ_v	σ_v'	σ_v''

empty projection table

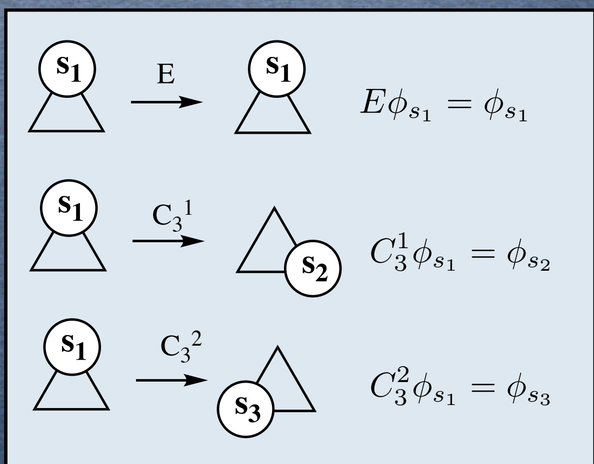
Using the Projection Operator

Work out how ONE orbital (s_1) transforms under EACH of the symmetry operations



- for example: under E s_1 does not move and $Es_1=s_1$

- for example: under the $2C_3$ operations
- after the first rotation s_1 maps onto s_2
- after the second rotation s_1 maps onto s_3



Projection Table

- work out how the orbital transforms under EVERY symmetry operation
- Put the information in a projection table:

D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ_v	σ_v'	σ_v''
		2C₃		3C₂				2S₃		3σ		
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2	s_1	s_2	s_3	s_1	s_3	s_2

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

formed this part of the operator

Projection Table

- now add the irreducible representation

D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ_v	σ_v'	σ_v''
		2C₃		3C₂				2S₃		3σ		
$Q[s_1]$	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

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

add this part of the equation

Projection Table

- then multiply terms in the columns

		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$_v$	σ$_v$'	σ$_v$"
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$_2$

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

carry out the multiplication

Projection Table

- this is a sum so now add all the terms on the bottom line

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

show your working!

		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$_v$	σ$_v$'	σ$_v$"
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$_2$

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

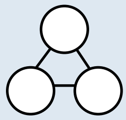
$$P_{A_1'}[s_1] = \frac{1}{12}\left[4s_1 + 4s_2 + 4s_3\right] = \frac{1}{3}\left[s_1 + s_2 + s_3\right]$$

The wave-function!

- the projection operator gives us the wave-function
- this one is 1/3 s_1 plus 1/3 s_2 plus 1/3 s_3
- which is the totally bonding fragment orbital

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

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



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

In-Class Activity P2

- the first line is exactly the same
- second line contains the new irreducible representation

D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ_v	σ_v'	σ_v''
		2C$_3$		3C$_2$				2S$_3$		3σ		
$Q[s_1]$	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'												
$\chi^{E'}(Q) \bullet Q \bullet [s_1]$												

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

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

what is the wave-function?

In-Class Activity P2

- the first line is exactly the same
- second line contains the new irreducible representation

		2C3		3C2				2S3		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_v	σ_v'	σ_v''
$Q[s_1]$	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'	2	-1	-1	0	0	0	2	-1	-1	0	0	0
$\chi^{E'}(Q)\bullet Q\bullet[s_1]$	$2s_1$	$-s_2$	$-s_3$	-	-	-	$2s_1$	$-s_2$	$-s_3$	-	-	-

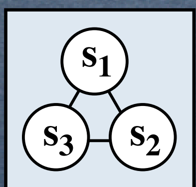
$$P_{E'}[s_1] = \frac{1}{12}\left[2s_1 - s_2 - s_3 + 2s_1 - s_2 - s_3\right]$$

$$P_{E'}[s_1] = \frac{1}{12}\left[4s_1 - 2s_2 - 2s_3\ \right] = \frac{1}{6}\left[2s_1 - s_2 - s_3\right]$$

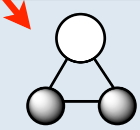
what is the wave-function?

The First e′ Orbital

- draw the orbital
- be careful to represent the correct size and phase of the orbitals
- be consistent with your original labeling!



contribution by s_1 is twice as large as s_2 or s_3



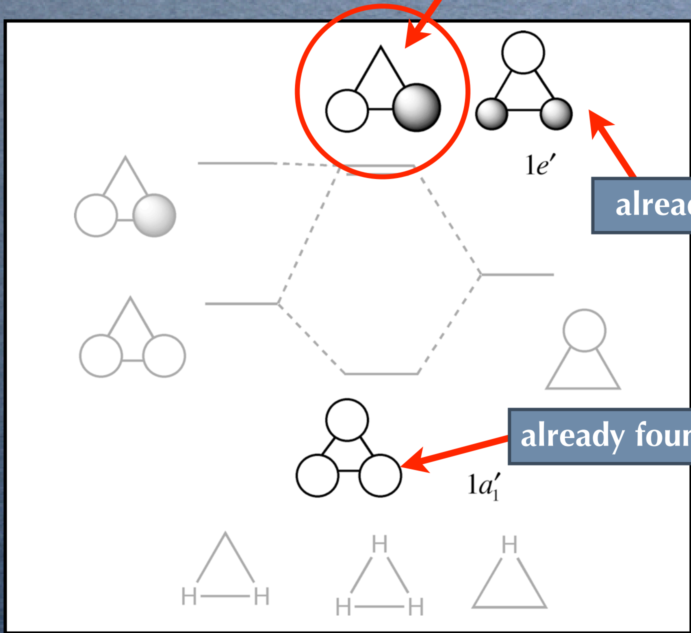
$$\psi_{e'} = \frac{1}{6}\left[2\phi_{s_1} - \phi_{s_2} - \phi_{s_3}\right]$$

s_2 and s_3 have negative phase

The Second e′ Orbital

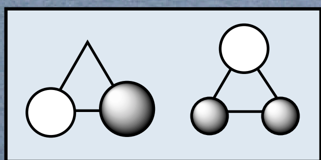
- use orthogonalisation procedure
- OR make a guess “from inspection”

guess from the molecular fragments!



The Second e′ Orbital

- the two e′ orbitals MUST be orthogonal to each other



what is orthogonality?

- two functions are orthogonal when their integral over all space is zero

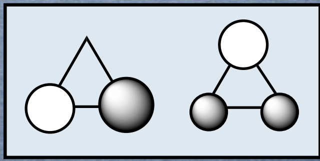
f_1 and f_2 are functions

$$\int f_1 \cdot f_2 d\tau = 0$$

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

The Second e′ Orbital

- **the two e′ orbitals MUST be orthogonal to each other**
- **evaluate:**



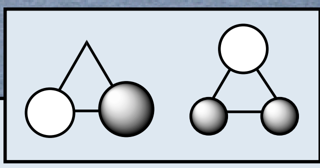
A
$$\int \psi^1_{1e'} \cdot \psi^2_{1e'} d\tau = 0$$

B
$$\psi^1_{1e'} = 2\phi_{s1} - \phi_{s2} - \phi_{s3}$$
$$\psi^2_{1e'} = \phi_{s2} - \phi_{s3}$$

C
$$\int \psi^1_{1e'} \cdot \psi^2_{1e'} d\tau = \int (2\phi_{s1} - \phi_{s2} - \phi_{s3}) \cdot (\phi_{s2} - \phi_{s3}) d\tau$$

The Second e′ Orbital

- **the two e′ orbitals MUST be orthogonal to each other**



$$\int \psi^1_{1e'} \cdot \psi^2_{1e'} d\tau = \int (2\phi_{s1} - \phi_{s2} - \phi_{s3}) \cdot (\phi_{s2} - \phi_{s3}) d\tau$$
$$= \underbrace{\int 2\phi_{s1}\phi_{s2} d\tau}_{=2s} - \underbrace{\int 2\phi_{s1}\phi_{s3} d\tau}_{=2s} - \underbrace{\int \phi_{s2}\phi_{s2} d\tau}_{=1} + \underbrace{\int \phi_{s2}\phi_{s3} d\tau}_{=s} - \underbrace{\int \phi_{s3}\phi_{s2} d\tau}_{=s} + \underbrace{\int \phi_{s3}\phi_{s3} d\tau}_{=1}$$

- **need to know:**
  - atomic orbitals are normalized
  - atomic orbitals can overlap

$$\int \phi_a \cdot \phi_a d\tau = 1$$

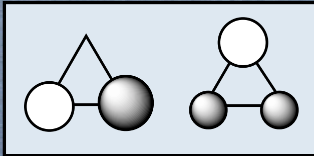
$$\int \phi_a \cdot \phi_b d\tau = S_{ab} = s$$

overalp is reciprocal
$S_{ab}=S_{ba}$
sAOs are equidistant
$S_{12}=S_{13}=S_{23}$

The Second e′ Orbital

- the two e′ orbitals ARE orthogonal to each other

$$\int \psi^1_{1e'} \cdot \psi^2_{1e'} d\tau = 2s - 2s - 1 + s - s + 1 = 0$$

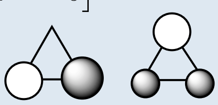


- our guess was a good one

The Symmetry Adapted Orbitals of H_3

- check
  - right energy ordering?
  - orbital pictures?
  - correct equation associated with each orbital?
- these are the orbitals that come out of the Schrödinger equation!

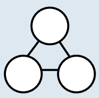
$$\psi_{e'} = \frac{1}{2}\left[\phi_{s_2} - \phi_{s_3}\right]$$



e'

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

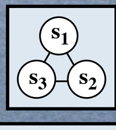
a$_1$'



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

Summary of the Steps:

- determine the basis orbitals of the fragment
- identify point group and locate all symmetry operations
- take all in-phase combination and determine the reducible representation
- find the contributing irreducible representations using a reduction table and the reduction formula
- determine orbital coefficients using the projection operator and table
- if there are degenerate orbitals make a guess and check for orthogonality
- produce your fragment orbital diagram!



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

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

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

$$\int f_1 \cdot f_2 d\tau = 0$$

Key Points

- be able to define and illustrate the splitting energy
- be able to discuss, employing equations, diagrams and examples Δε, Sab and Hab, be able to employ this knowledge in forming MO diagrams
- be able to find the reducible representation for a set of basis orbitals
- be able to write down the reduction formula and the projection operator and define all the terms and relate them to items in a character table
- be able to set up and use a representation table, and a projection table
- be able to find the wave-functions and draw the orbitals for a set of symmetry related orbitals
- be able to produce a clear well-annotated fragment orbital diagram