Part III Symmetry and Bonding

Chapter 2 Representations

第二章（群）表示

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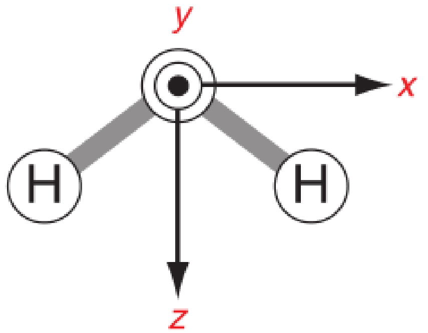
2. Representations

- The key thing about a symmetry operation is that it leaves the molecule in an ***indistinguishable orientation*** to the starting position.

- What effect do these *symmetry operations* have *on functions* ‘within’ the molecule, such as the *atomic orbitals*?

e.g, O the 2s, $2p_z$, $2p_x$, $2p_y$ etc. valence atomic orbitals (VAOs) in H_2O.



- What we will see in this section is that it is very convenient to arrange *for the orbitals to behave* in a way which *reflects the symmetry of the molecule*.

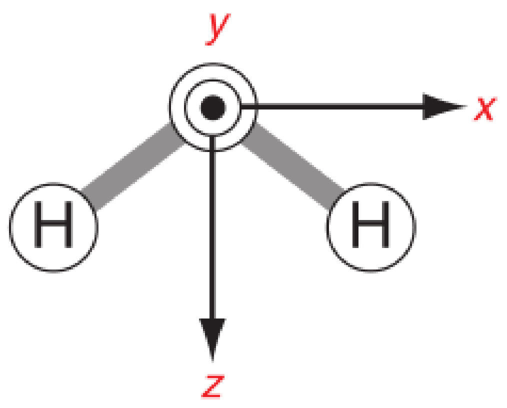
- This discussion will lead us to introduce ***representations*** and the all-important ***irreducible representations*** (of the point groups).

2.1 *Introducing representations*

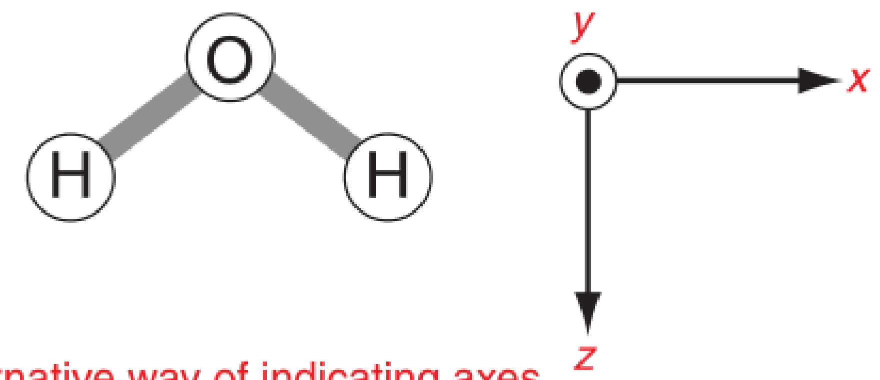
- The idea of a ***representation*** is best introduced using an example: H_2O (C_{2v})

Symmetry elements for H_2O (C_{2v}): the identity (E), a two-fold axis of rotation (the principal axis, C_2) and ***two (vertical) mirror planes (σ_v)***.

- By convention the ***z***-axis is ***coincident with the principal axis***, but we are at liberty to put the ***x***- and ***y***-axes where we like. (i.e., *right handed coordinates!*)



y coming out of plane of paper



alternative way of indicating axes

- ***Symmetry operations** for H_2O (C_{2v}):* E, C_2^z, σ_{xz}, σ_{yz}.

2.1.1 *Behavior of the oxygen AOs in H_2O*

- How are the oxygen atomic orbitals (AOs) affected by the ***symmetry operations*** of the point group: C_2^z, σ^{xz} and σ^{yz}.

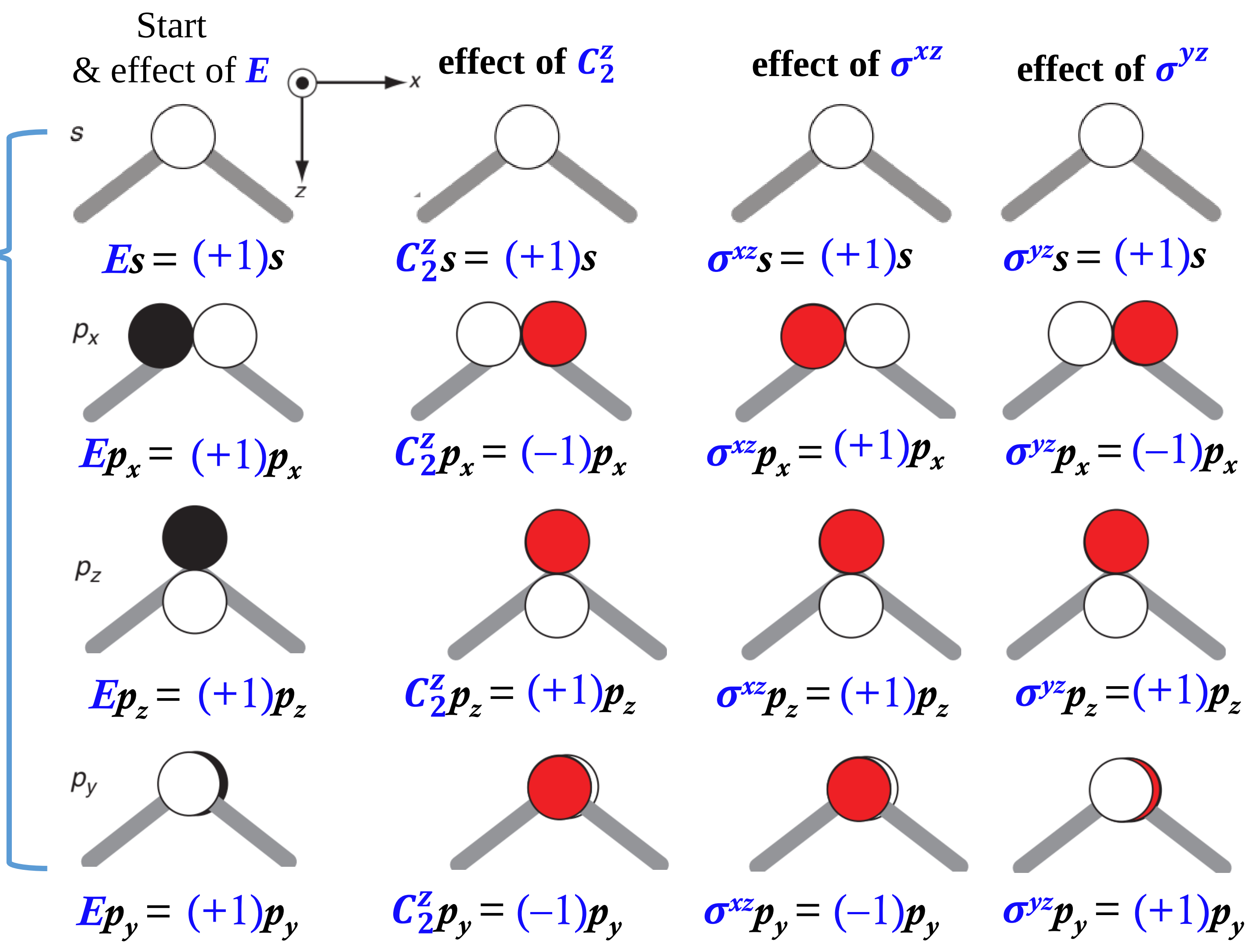
- Under ***the symmetry operations*** these AOs either remain the same or simply change sign; *they neither move to another position nor become other orbital*.

- The effects of ***these symmetry operations*** can be summarized in equations! (Now we need 4 to write out the eqs.!)

- In ***Group Theory*** these AOs are an example of a set of ***basis functions***; they are simply referred to as a ***basis***.

- The effect of the symmetry operations on p_x can be summarized as : **(+1, −1, +1, −1).**

White for + and black/**red** for – value of the wavefunctions.



2.1.1 Behaviour of the oxygen AOs in H_2O

- Taking the O p_x orbital as the basis, the effect of the symmetry operations can be summarized by grouping together as follows : **(+1, −1, +1, −1).**
- In Group Theory this is said to be ***a representation*** of the operations of the group ***in a basis*** consisting of just ***the p_x AO***, and can be found as a row in the character table.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

(+1,−1,+1,−1) in the basis p_x

- In the character table the rows are a very special set of ***representations*** called the ***irreducible representations (IRs)***.

2.1.1 *Behaviour of the oxygen AOs in H_2O* Ex. 5

- Similarly, the ***s***, p_y and p_z AOs each result in a representation:

representation in the basis ***s***: **(+1,+1,+1,+1)**

representation in the basis p_y: **(+1,−1,−1,+1)**

representation in the basis p_z: **(+1,+1,+1,+1)**

- These are all described as ***one-dimensional representations*** since in each case there is only one basis function. They also can be found in the character table of C_{2v}.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

(+1,+1,+1,+1) in the basis *s* or p_z

(+1,−1,+1,−1) in the basis p_x

(+1,−1,−1,+1) in the basis p_y

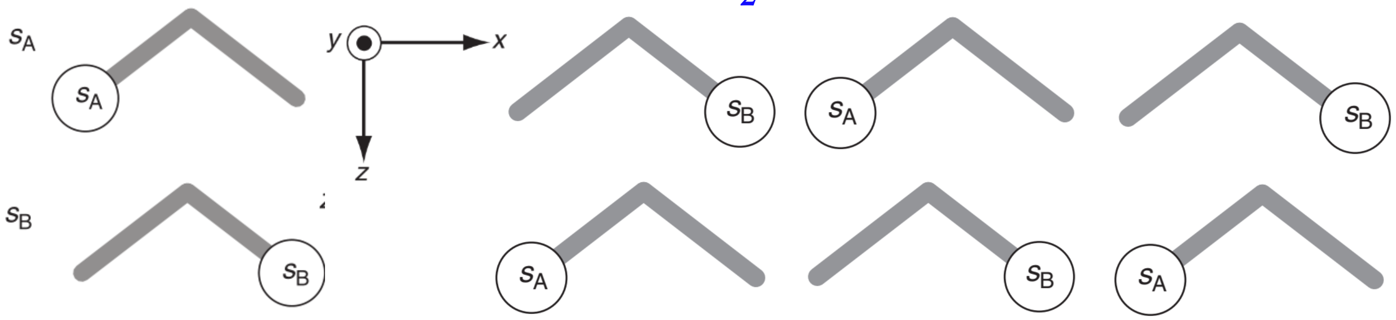
- In the present example, we would say that 'p_x *transforms as the irreducible representation* B_1'. Similarly, p_y transforms as B_2 and p_z transforms as A_1.

2.1.2 Behavior of the hydrogen AOs in H_2O

$$s_A = 1\times s_A + 0\times s_B$$
$$s_B = 0\times s_A + 1\times s_B$$

- Two hydrogen 1s AOs in water (labeled as s_A and s_B).
  We need 2 persons to draw out the effects of operations.

start & effect of E | effect of C_2^z | effect of σ^{xz} | effect of σ^{yz}



$$C_2^z s_A = s_B \qquad C_2^z s_B = s_A \qquad C_2^z\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}s_B\\ s_A\end{pmatrix}=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}s_A\\ s_B\end{pmatrix}$$

$$\sigma^{xz} s_A = s_A \qquad \sigma^{xz} s_B = s_B \qquad \sigma^{xz}\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}s_A\\ s_B\end{pmatrix}$$

$$\sigma^{yz} s_A = s_B \qquad \sigma^{yz} s_B = s_A \qquad \sigma^{yz}\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}s_B\\ s_A\end{pmatrix}=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}s_A\\ s_B\end{pmatrix}$$

$$E s_A = s_A \qquad E s_B = s_B \qquad E\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}s_A\\ s_B\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}s_A\\ s_B\end{pmatrix}$$

- The basis functions s_A and s_B are ***interconverted*** by the operations of the group. (Now in eqs.!)
- The effect of a particular operation on an orbital function is no longer simply to multiply it by ***±1***, but can be expressed as a linear combination of the two AOs.

2.1.2 Behaviour of the hydrogen AOs in H_2O

- These four matrices together form a representation of the operations of the group:

$$\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$$

E $\quad C_2^z$ $\quad \sigma^{xz}$ $\quad \sigma^{yz}$

The character (χ) of a matrix: the sum of the diagonal elements (also known as the trace)

- This is a ***two-dimensional representation***, which is a set of ***2 × 2*** matrices, generated in the basis consisting of ***two*** orbitals (or basis functions), s_A and s_B.
- The ***characters*** of the matrices are more important than the matrices themselves. For the above representation in the s_A and s_B basis, the characters are

$$(2 \;,\; 0 \;,\; 2 \;,\; 0)$$

E $\quad C_2^z$ $\quad \sigma^{xz}$ $\quad \sigma^{yz}$

the ***dimensionality*** of the representation!

◆ The matrix representative of ***E (identity)*** must always be a unit matrix, so its character must be equal to the number of basis functions.

2.1.3 Characters and reducible representations

- The representation with characters ***(2,0,2,0)*** is not one of the IRs in the character table.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
						R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
$\oplus$					y	R_x	yz
	2	**0**	**2**	**0**			

- However, this set of numbers can be obtained by adding together the characters of the **IR** A_1 with those of the **IR** B_1, **i.e.,** $A_1 \oplus B_1$**: (2,0,2,0)**

i.e., the ***representation*** with characters (2,0,2,0) is ***reducible*** and can be ***reduced*** to *the sum of the two* ***IRs*** A_1 *and* B_1, i.e., $A_1 \oplus B_1$.

- The two-dimensional representation formed by the two hydrogen 1s orbitals 'spans the ***IRs*** A_1 and B_1'. In other words, 'these two orbitals transform as $A_1 \oplus B_1$'.

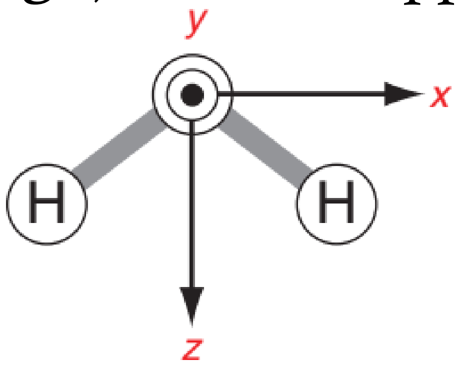
2.1.4 A quick method of finding characters

Since we are only interested in the *characters* of the representative matrices (i.e. the sum of the diagonal elements), then ***we only need to work out their diagonal elements***.

- If *a symmetry operation* moves an orbital to a different position there will be a ***0*** on the diagonal of the matrix. e.g. for the effect of C_2^z on s_A.

- If *the symmetry operation* leaves the orbital in the same place, there will be a ***+1*** on the diagonal, e.g., for the effect of σ^{xz} on s_A.

- Finally, if the orbital remains in the same place but just changes sign, a ***–1*** will appear on the diagonal, e.g., for the effect of C_2^z on the O p_x.



2.1.4 A quick method of finding characters

Simple rules for finding the *character* corresponding to a particular symmetry operation:

1. For each orbital which remains unaffected by the operation, count ***+1***
2. For each orbital which remains in the same position but simply changes sign, count ***–1***
3. All orbitals that are moved by the operation count ***zero***.

In the basis of the two hydrogen 1s orbitals, the procedure is applied in the following way:

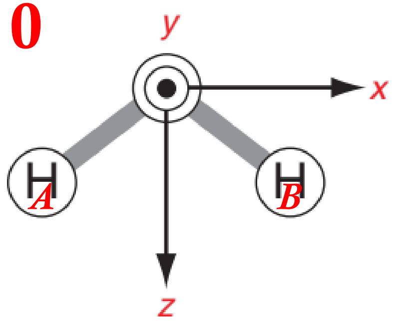
Operation E : both s_A and s_B unaffected, both count +1; character is +1 + 1 = **+2**

Operation C_2^z : both s_A and s_B moved, both count 0; character is 0+0 = **0**

Operation σ^{xz}: both s_A and s_B unaffected, both count +1; character is +1 + 1 = **+2**

Operation σ^{yz}: both s_A and s_B moved, both count 0; character is 0+0 = **0**

→ The characters are therefore *(2,0,2,0)*, as we found before.

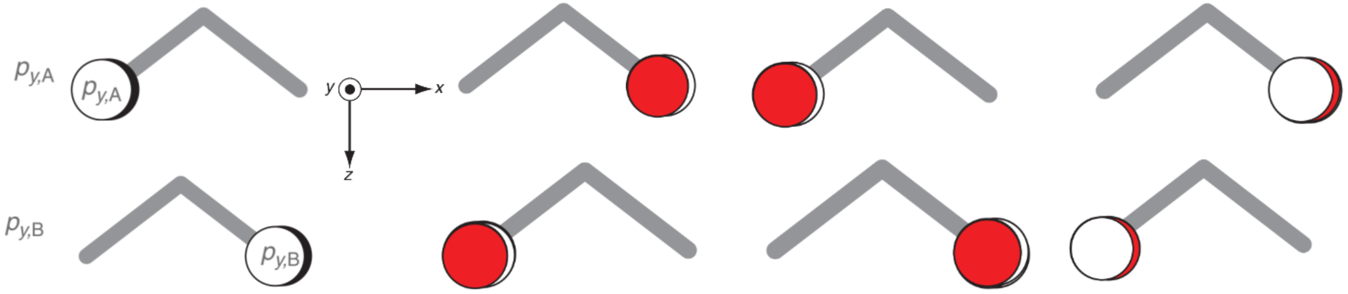


2.1.4 A quick method of finding characters

Example: (somewhat hypothetical) two equivalent p_y orbitals on the hydrogens in H_2O.

two functions in the basis → ***two*** *-dimensional representation.*

Start & effect of E	effect of C_2^z	effect of σ^{xz}	effect of σ^{yz}



$\chi(\hat{R})$ 2   0   -2   0

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Now we need 4 persons to work out the characters for each operation!

E : both unaffected, +1 + 1 = +2

C_2^z : both moved, 0+0 = 0

σ^{xz} : both change sign, -1-1 = -2

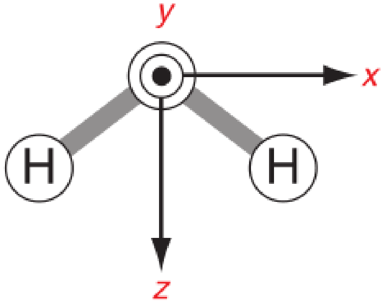
σ^{yz} : both moved, 0 + 0 = 0

→ (2,0,-2,0)   Now reduce it!?

→ $A_2 \oplus B_2$.   ***Ex.6***

2.1.5 *Introducing symmetry orbitals*

- In section 2.1.3, we saw that the two hydrogen 1s AOs in H_2O transform as $\boldsymbol{A_1 \oplus B_1}$. We should be able to find a (linear) combination of the two AOs which transforms just as $\boldsymbol{A_1}$ and another combination which transforms as $\boldsymbol{B_1}$.

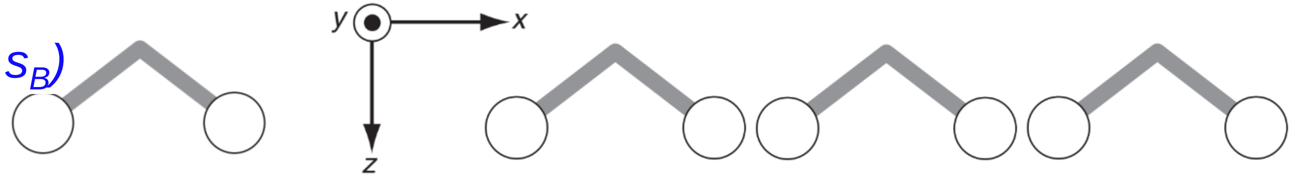


- Let us consider $\boldsymbol{(s_A \pm s_B)}$. Now 2 persons to sketch the effects of operations!

start & effect of ***E*** | effect of $\mathbf{C_2^z}$ | effect of $\boldsymbol{\sigma}^{xz}$ | effect of $\boldsymbol{\sigma}^{yz}$

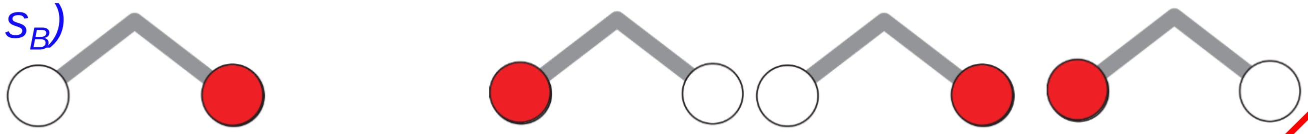
Now 2 persons to write out the characters!

$(s_A + s_B)$



$\chi(\hat{R})$ 1 1 1 1

$(s_A - s_B)$

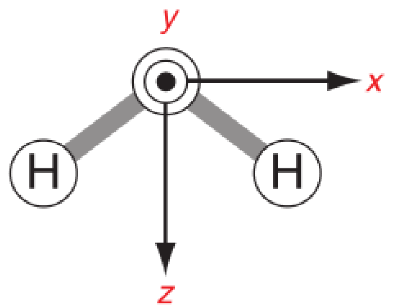


$\chi(\hat{R})$ 1 −1 1 −1

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Ex.7

2.1.5 Introducing symmetry orbitals



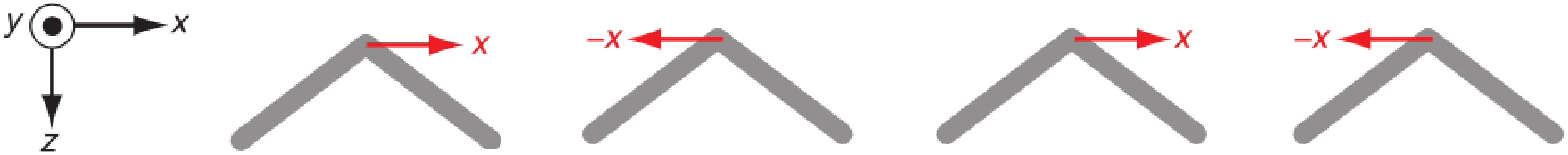
- ***(s_A+s_B)*** and ***(s_A-s_B)*** are called ***symmetry orbitals (SOs)*** or ***symmetry adapted linear combinations*** (***SALC***s) because they have the special property that they transform as a single ***irreducible representation***.

- ***Symmetry orbitals (SOs)*** play an important role in the construction of molecular orbital diagrams.

- In this simple case we were able to construct the ***symmetry orbitals*** by guess, but later on we will see that there is a more systematic way of constructing them.

2.1.6 Using extra information from the character tables

• Returning to H_2O, let us consider what happens to ***hypothetical vectors***, each attached to the oxygen and pointing along ***x***, ***y***, and ***z***, respectively. We need 1 person for ***x*** first!



Basis	start & effect of **E**	effect of **C_2^z**	effect of **σ^{xz}**	effect of **σ^{yz}**	***I.R.***
Vector x	***1***	***-1***	***1***	***-1***	***B_1***
Vector z	***1***	***1***	***1***	***1***	***A_1***
Vector y	***1***	***-1***	***-1***	***1***	***B_2***

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Typical basis function(s) for ***IR***s: The information about how simple functions (and the corresponding vectors) transform is usually given as part of the character table.

2.1.6 Using extra information from the character tables

Atomic orbitals

- The mathematical form of the orbital wavefunction for a ***$2p_x$*** AO (in hydrogen in **atomic** coordinates) is ***$r\sin\theta\cos\phi\ \exp(-r/2)$***.
- In the normal cartesian coordinate system ***$x = r\sin\theta\cos\phi$***, the orbital wavefunction can thus be written as ***$x\cdot\exp(-r/2)$***.
- Accordingly, it follows that the ***p_x*** orbital wavefunction has the same transformation properties as the function ***x***, so we can read off from the table of ***C_{2v}*** that ***p_x*** transforms as ***B_1***.
- Similarly, the ***$2p_y$*** and ***$2p_z$*** orbital wavefunctions are ***$y\ \exp(-r/2)$*** and ***$z\ \exp(-r/2)$***, respectively, and so transform as ***y*** and ***z***, i.e. ***B_2*** and ***A_1*** from the table of ***C_{2v}***.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

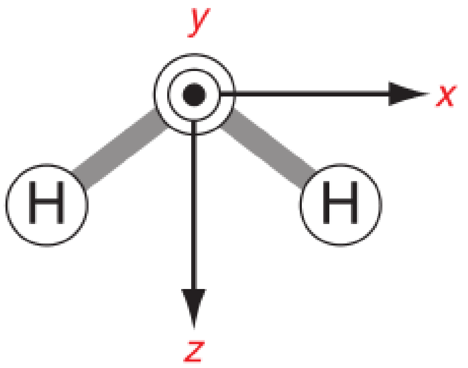
2.1.6 Using extra information from the character tables

- Again for the AOs of oxygen in H_2O,

  s AO transforms like ***?***

  d orbitals: their names indicate the corresponding cartesian functions.

  e.g., d_{xy} transforms like ***?*** .



Q1: which IR does the $d_{x^2-y^2}$ AO of O transform like?

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

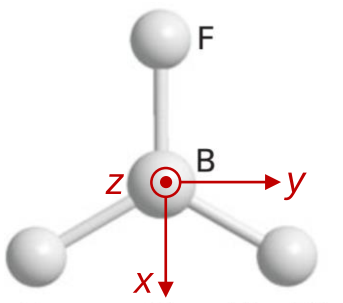
d_{xy} → xy; d_{z^2} → $x^2; y^2; z^2$; d_{yz} → yz; d_{xz} → xz

?

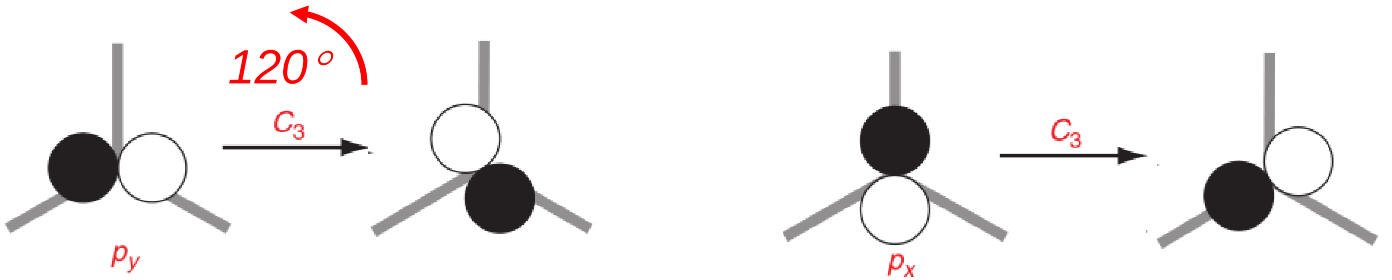
In this case, only for AOs of O can we do such reading-off!

2.2 Two-dimensional irreducible representations

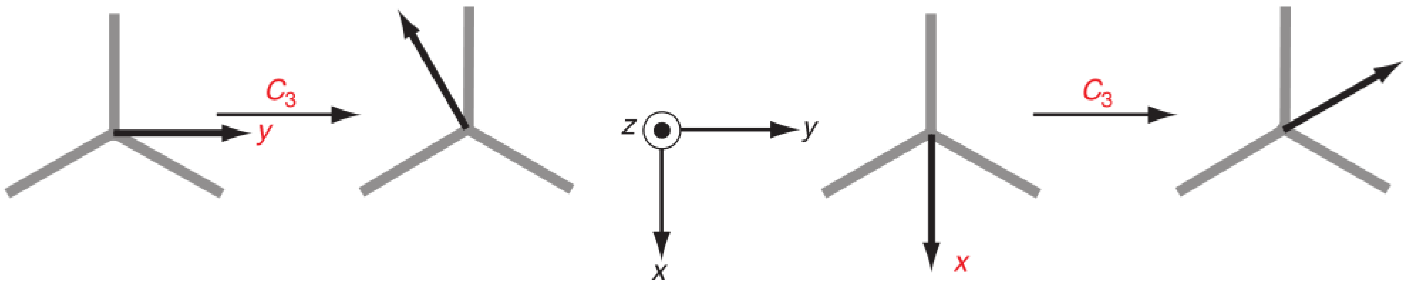
- We now switch to BF_3 and focus on the boron ***2p orbitals***.
- BF_3 belongs to D_{3h} point group.



Boron trifluoride, BF_3



- neither p_x nor p_y, but seemingly to be the combination of p_x and p_y.



- p_x (or x) and p_y (or y) are '***mixed***' by the C_3 operation!

2.2 Two-dimensional irreducible representations

- In D_{3h}, the vectors along ***x*** and ***y***, and likewise the p_x and p_y orbitals, are ***mixed*** by the operations of the group. They form ***a two-dimensional irreducible representation*** which ***CANNOT*** be broken down into ***two one-dimensional representations***.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

How do the characters of the ***E′ IR*** arise?

- ***(x,y)*** transform as ***the irreducible representation E′***, a two-dimensional ***IR***.
- In this group there is ***E″*** along with several one-dimensional ***IR***s (all labelled ***A*** with various additional annotations).

2.2.1 Forming the characters of a two-dimensional representation

- How do the characters of the *E′ IR* arise?
- To do this we will use unit vectors along *x* and *y* as our basis, denoted *i* and *j*.
- Effect of the ***C_3 operation*** on these vectors is simply a problem in geometry.
- For the vectors *y* and *x* under C_3^z operation, we have

$$C_3\begin{pmatrix}0\\ \mathrm{j}\end{pmatrix}=\begin{pmatrix}0\\ -\frac{\sqrt{3}}{2}\mathrm{i}-\frac{1}{2}\mathrm{j}\end{pmatrix}\qquad C_3\begin{pmatrix}\mathrm{i}\\ 0\end{pmatrix}=\begin{pmatrix}-\frac{1}{2}\mathrm{i}+\frac{\sqrt{3}}{2}\mathrm{j}\\ 0\end{pmatrix}$$

$$C_3\begin{pmatrix}\mathrm{i}\\ \mathrm{j}\end{pmatrix}=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}\mathrm{i}\\ \mathrm{j}\end{pmatrix}$$

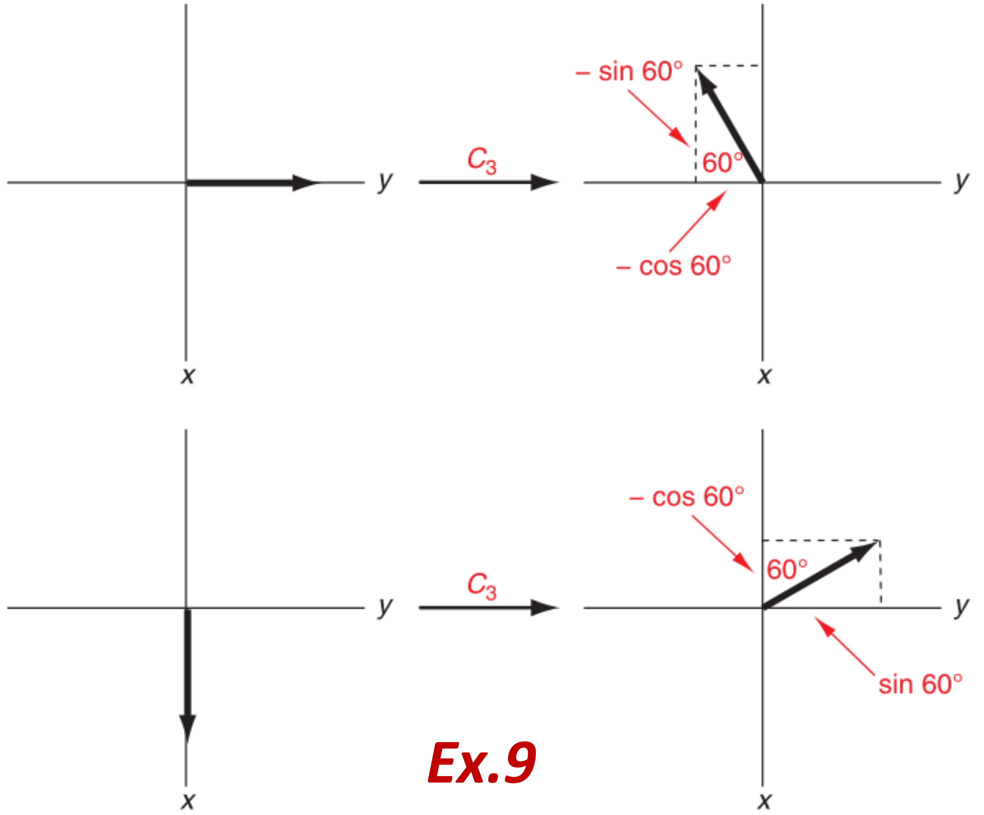
$\chi(C_3) = -1$

$\chi(S_3) = \chi(C_3) = -1$

$\chi(\sigma_h) = 1+1 = 2$

$\chi(C_2^x) = 1-1 = 0$

$\chi(\sigma_v^{xz}) = 1-1 = 0$



Ex.9

2.3 Reducing a representation

- So far we have been able to deduce by inspection the irreducible representations from which a particular representation is composed. For example, in the group C_{2v} we were able easily to spot that the representation *(2,0,-2,0)* reduces to $A_2 \oplus B_2$.
- However, for more complex examples, a more systematic method is needed, and this is provided by the ***reduction formula***.
- ***Some notations***:

i) The (arbitrary) representation of a group: $\Gamma = \{\chi(R_1), \ldots, \chi(R_h)\}$.

e.g., for the representation *(2,0,-2,0)* in C_{2v}, $\chi(E) = 2$, $\chi(C_2) = 0$, $\chi(\sigma^{xz}) = -2$ and $\chi(\sigma^{yz}) = 0$.

ii) For *k*th *IR*, $\Gamma^{(k)}$, in the group, the characters are denoted $\chi^{(k)}(R)$.

e.g., for the 4th *IR* (B_2) *(1,-1,-1,1)* in C_{2v}, $\chi^{(4)}(E) = 1$, $\chi^{(4)}(C_2) = -1$, $\chi^{(4)}(\sigma^{xz}) = -1$ and $\chi^{(4)}(\sigma^{yz}) = 1$.

2.3 Reducing a representation

- A particular representation Γ can be expressed as a sum of irreducible representations $\Gamma^{(k)}$:

$$\Gamma = a_1\Gamma^{(1)} \oplus a_2\Gamma^{(2)} \oplus a_3\Gamma^{(3)} \oplus \ldots$$

$$= \sum a_k\Gamma^{(k)}$$ (a_k: the number of times that the ***IR*** $\Gamma^{(k)}$ appears in the representation.)

- The ***reduction formula*** give us a way of finding the coefficients a_k:

$$a_k = \frac{1}{h}\sum_R [\chi^{(k)}(R)]^* \chi(R)$$

h is the total number of operations in the group, and the * indicates the complex conjugate.

- This formula is simply the **scalar product** between the ***two vectors*** formed by the characters of the ***irreducible representation*** and those of the ***representation being reduced***.

2.3 Reducing a representation

- *Example*: reducing a representation *(2,0,-2,0)* in the group C_{2v}

k	C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
1	A_1	1	1	1	1	z		$x^2; y^2; z^2$
2	A_2	1	1	−1	−1		R_z	xy
3	B_1	1	−1	1	−1	x	R_y	xz
4	B_2	1	−1	−1	1	y	R_x	yz
	Γ	2	0	-2	0			

- $\chi(E) = 2$, $\chi(C_2) = 0$, $\chi(\sigma^{xz}) = -2$, $\chi(\sigma^{yz}) = 0$;
- $h = 4$;

- Now use the reduction formula to determine the coefficient a_1 of the first *IR* A_1 with the characters: $\chi^{(1)}(E) = 1$, $\chi^{(1)}(C_2) = 1$, $\chi^{(1)}(\sigma^{xz}) = 1$, $\chi^{(1)}(\sigma^{yz}) = 1$ ⇒

$$a_1 = \sum_R \frac{1}{h}\left[\chi^{(1)}(R)\right]^* \chi(R)$$

$$= \frac{1}{4}\left(\left[\chi^{(1)}(E)\right]^* \chi(E) + \left[\chi^{(1)}(C_2)\right]^* \chi(C_2) + \left[\chi^{(1)}(\sigma^{xz})\right]^* \chi(\sigma^{xz}) + \left[\chi^{(1)}(\sigma^{xz})\right]^* \chi(\sigma^{yz})\right) = ?$$

2.3 *Reducing a representation*

k	C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
1	A_1	1	1	1	1	z		$x^2; y^2; z^2$
2	A_2	1	1	−1	−1		R_z	xy
3	B_1	1	−1	1	−1	x	R_y	xz
4	B_2	1	−1	−1	1	y	R_x	yz
	Γ	**2**	**0**	**-2**	**0**			

- The next ***IR*** is ***A*$_2$**,

$$a_2 = \frac{1}{h}\sum_R \left[\chi^{(2)}(R)\right]^* \chi(R) \qquad \mathbf{=1}$$

- The 3rd ***IR*** is ***B*$_1$**,

$$a_3 = \frac{1}{h}\sum_R \left[\chi^{(2)}(R)\right]^* \chi(R) \qquad \mathbf{=0}$$

- Likewise, for the *4*th ***IR B*$_2$**, we have ***a_4= 1***.
- The representation ***(2,0,-2,0)*** thus reduces to $\Gamma^{(2)} \oplus \Gamma^{(4)}$, i.e., $A_2 \oplus B_2$.

2.3.1 Reduction formula in terms of classes

- Operations in the ***same class*** have the ***same character*** for a given ***IR***. Similar trend holds for an arbitrary representation *Γ*.

- Accordingly, the use of the reduction formula can be somewhat simplified!

g(c)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

$$a_k = \sum_R \frac{1}{h}[\chi^{(k)}(R)]^* \chi(R)$$

$$= \frac{1}{h}\sum_c g(c)[\chi^{(k)}(c)]^* \chi(c)$$

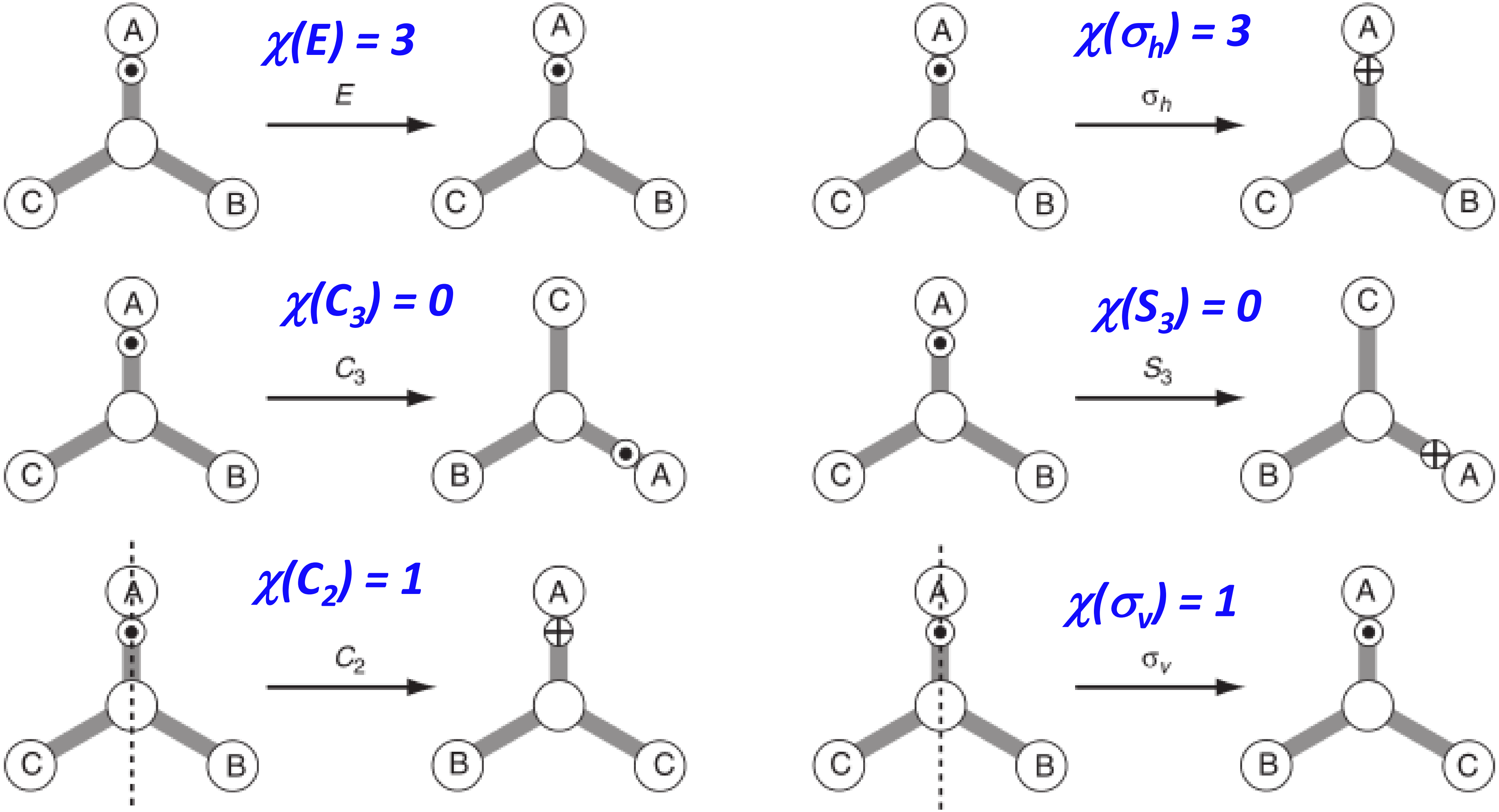
Class of operations

Number of operations within a class

- **Example**: a basis consisting of the ***three equivalent 2s orbitals*** on the ***fluorine atoms*** in $\mathbf{BF_3}$.

2.3.1 Reduction formula in terms of classes

- Now we ***'count'*** the characters for ***each class*** of operations.



2.3.1 Reduction formula in terms of classes

- Hence, the representation generated by these three ***s*** orbitals is thus ***(3,0,1,3,0,1)***, with operations in the ***same class*** being grouped together.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0
Γ(3xF2s)	***3***	***0***	***1***	***3***	***0***	***1***
Γ(3xF2p_z)	**3**	**0**	**-1**	**-3**	**0**	**1**

- For A_1', $a_1 = \frac{1}{h}\sum_c g(c)[\chi^{(k)}(c)]^*\chi(c)$ **= *1***
- For A_2', $a_2 = 0$
- For E', $a_3 = 1$
- ….. $a_{4-6} = 0$

→ $\Gamma = A_1' \oplus E'$

→ $\Gamma = A_2'' \oplus E''$

2.3.2 A possible quick method for reducing representations

- A helpful method to reduce the labour:

1. Multiply the characters of the representation to be reduced by the number of operations in each class. For the example here (3,0,1,3,0,1) becomes (1×3, 2×0,3×1,1×3,2×0,3×1) i.e. (3,0,3,3,0,3).

2. Take a piece of paper and line up its edge beneath the top row of the character table (where the operations are listed); write in the numbers you have determined in ***step 1*** in the correct columns.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
	3	0	3	3	0	3

2.3.2 A possible quick method for reducing representations

3. Move the paper down until the characters for the first ***IR*** are revealed; multiply these by the numbers written on the paper (you can usually do this in your head), and divide by ***h***. This gives you the number of times the first ***IR*** is present.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
	3	0	3	3	0	3	1×3 + 1×0 + 1×3 + 1×3 + 1×0 + 1×3 = 12

4. Move the paper down until the next ***IR*** is revealed and repeat the process.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	−1	1	1	−1	
	3	0	3	3	0	3	1×3 + 1×0 + (−1×3) + 1×3 + 1×0 + (−1×3) = 0

Advantages:

- reducing the number of calculations at each step.
- focusing on one IR at a time.

2.3.3 Checking that you have reduced a representation correctly

Two easy checks to ***ensure*** that a representation has been reduced correctly.

1. The number of times a representation is present can be ***zero*** or ***a positive integer***.

2. The sum of the irreducible representations, each multiplied by the number of times they are present, must be equal to the representation you reduced.

e.g., in D_{3h} we found that the representation (3,0,1,3,0,1) reduced to $A_1' \oplus E'$.

To check we simply add up the characters of the ***IR***s:

$$1 \times A_1' + 1 \times E'$$

$$= 1 \times (1,1,1,1,1,1) + 1 \times (2,-1,0,2,-1,0) = (3,0,1,3,0,1)$$ √OK

Ex.10-12

2.4 The names of irreducible representations

1. One-dimensional ***IR***s： ***A or B***,

   two-dimensional ***IR***s: ***E***;

   three-dimensional ***IR***s: ***T***.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

2. 1-D ***IR***s are ***labelled A*** if the character under ***the rotation about the principal axis is +1*** and ***B*** if it ***is -1***. (***A*** ~ symmetric upon the rotation about the principal axis; ***B*** ~ antisymmetry upon the rotation about the principal axis)

3. In presence of a centre of symmetry, ***a subscript g*** is added if the character under the inversion operation is **+1** (i.e. '***gerade***' or even) whereas if the character is **-1** ***a subscript u*** is added (i.e. '***ungerade***' or odd).

2.4 The names of irreducible representations

4. Reflection upon $\boldsymbol{\sigma_h}$ plane：

***IR*s** *symmetric* added a prime ($'$), *anti-symmetric* added a double prime ($''$).

5. Subscript numerals **1, 2 . . .** are added to further distinguish the ***IR*s** which would otherwise have the same label.

	D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
1	A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
2	A_2'	1	1	−1	1	1	−1		R_z	
3	E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
4	A_1''	1	1	1	−1	−1	−1			
5	A_2''	1	1	−1	−1	−1	1	z		
6	E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

2.5 Summary

A basis (a set of orbitals, functions or vectors) → Operations of the point group → A ***representation*** with a set of matrices (or simply a set of characters) reducible to the sum of ***irreducible representation***s.

1. By ***choosing a basis*** (e.g. a set of orbitals, functions or vectors) we can ***form a representation*** of the operations ***of a group***.

2. If the basis consists of just one function, the representation will simply be ***a set of numbers*** (a one-dimensional representation). If the basis consists of N functions, the representation will be a set of ***N × N matrices*** (i.e., ***N-dimensional***).

3. The ***traces*** (sum of diagonal elements) of these matrices are called the ***characters***; ***the characters*** are far ***more important*** than the matrices themselves.

2.5 Summary

4. A given representation (i.e. set of characters) can always be reduced *to a sum of irreducible representations*. These ***IR***s are listed in *the character table*.

5. The *IR*s ***corresponding to simple functions*** are indicated in the *character table*.

6. The irreducible representations which comprise a particular representation can be found either ***by inspection*** or ***by systematic*** application of the *reduction formula*.

7. For a set of orbitals (or other objects), the *characters* can be found by using the *'counting method'* in which we count ***+1*** for an ***orbital which does not move***, ***0*** for an orbital which ***moves***, and ***-1*** for an orbital which ***does not move but simply changes sign***.

8. Operations in the ***same class*** have the ***same character***.

More about irreducible representations

- For a given point group of h-order, the h-dimensional vectors whose components are the characters of two irreducible representations are orthogonal.

$$\sum_{R} \chi_{i}(R)\chi_{j}(R) = h\delta_{ij}$$

- If d_j is the dimension of jth IR and h is the order of a group, then

$$\sum_{j} d_j^2 = h$$

As $\chi_j(E) = d_j$, then

$$\sum_{j} [\chi_j(E)]^2 = h$$