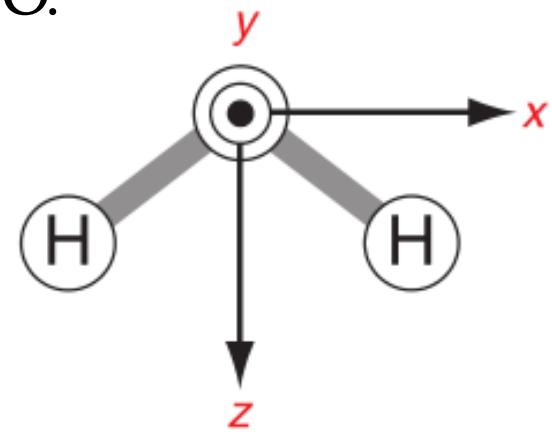
Part III Symmetry and Bonding

Chapter 2 Representations
第二章 (群)表示

Prof. Dr. Xin Lu （吕鑫）
Email: xinlu@xmu.edu.cn
http://pcoss.xmu.edu.cn/xlv/index.html
http://pcoss.xmu.edu.cn/xlv/courses/theochem/index.html

2. Representations（群的表示)

- The key thing about a symmetry operation is that it leaves the molecule in an ***indistinguishable orientation*** to the starting position, e.g., σ_{xz} over H_2O.



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

e.g, the 2*s*, $2p_z$, $2p_x$, $2p_y$ valence atomic orbitals (VAOs) of O 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*.

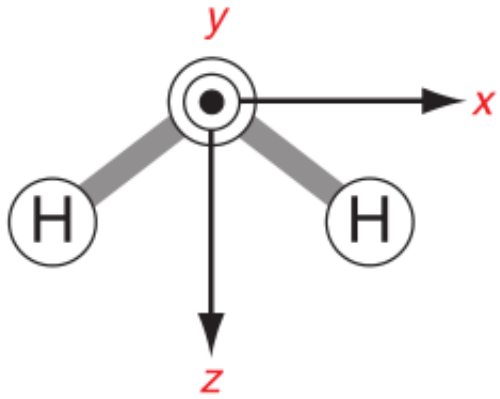
- This discussion will lead us to introduce ***representations*** (表示) and the all-important ***irreducible representations*** (不可约表示) of the point groups.

2.1 Introducing representations

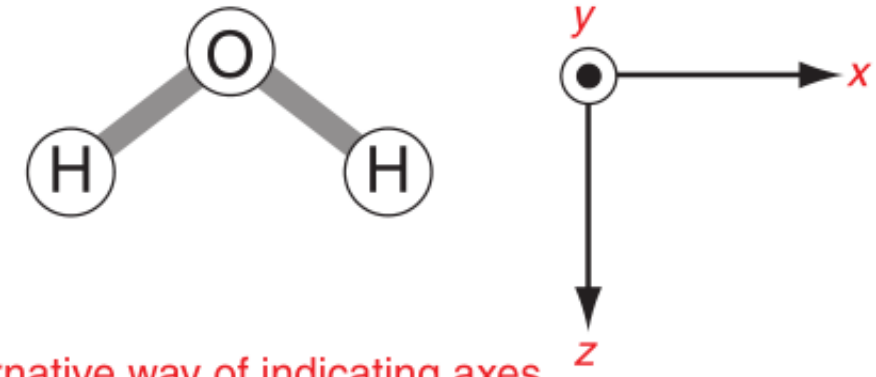
- The idea of a ***representation*** is best introduced using an example: H_2O (C_{2v})

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. (e.g., *right handed coordinates!*)



y coming out of plane of paper



alternative way of indicating axes

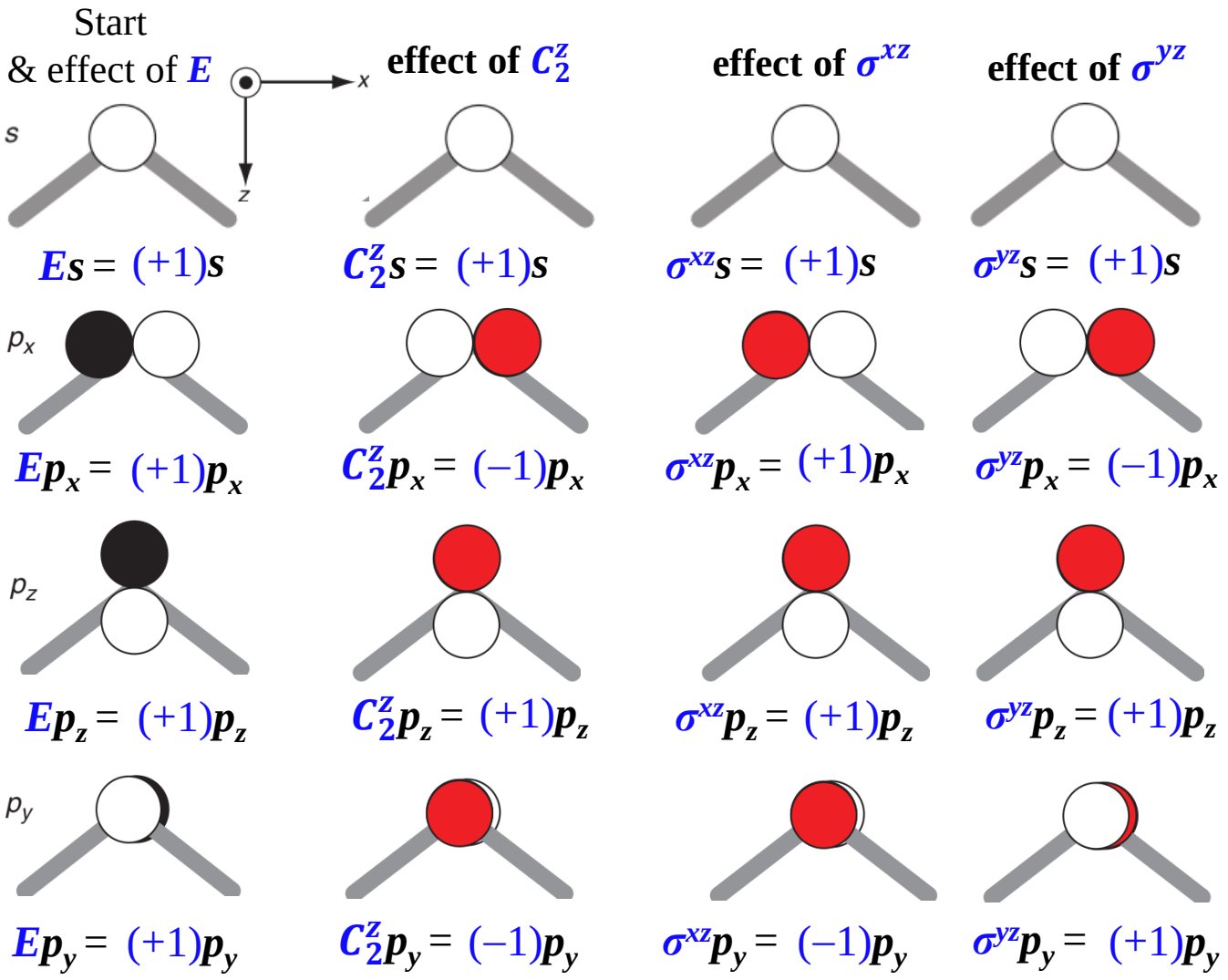
- ***Allowed symmetry operations for H_2O (C_{2v})***: E, C_2^z, σ^{xz}, σ^{yz}.

(These four operations are of course the elements of the C_{2v} point group!)

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*.
- In each case, the effect of ***a symmetry operation*** $\hat{R}$ can be expressed in the form of $\hat{R}\psi = A\psi$ (A = +1 or –1).
- 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

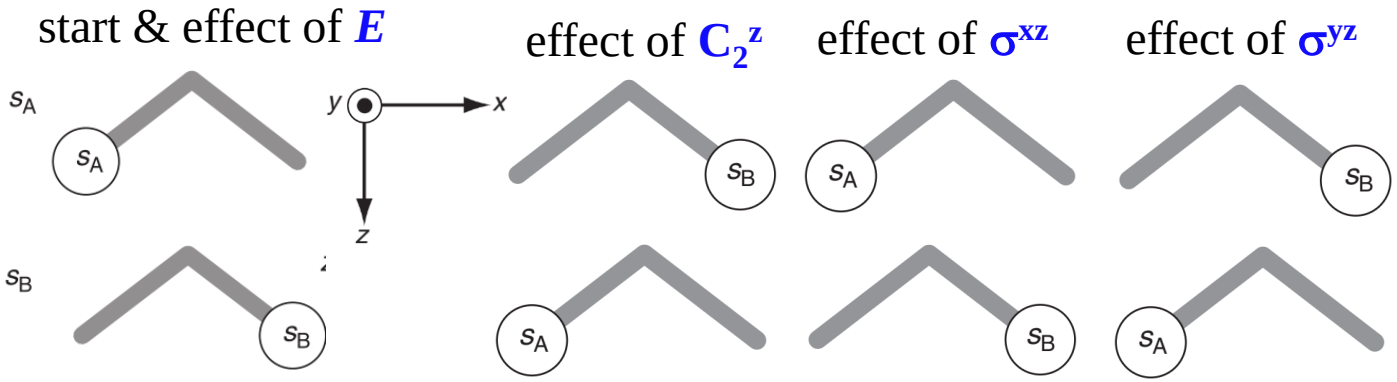
(+1,−1, −1,+1) in the basis p_y

- 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).



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

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

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

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

- The basis functions s_A and s_B are ***interconverted*** by the operations of the group. (write 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
⊕					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*** (可约的) and can be ***reduced*** to *the sum of the two* ***IRs A_1*** *and* ***B_1***, i.e., ***$A_1 \oplus B_1$***. (⊕~直和)

- 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 ***$A_1 \oplus B_1$***’.

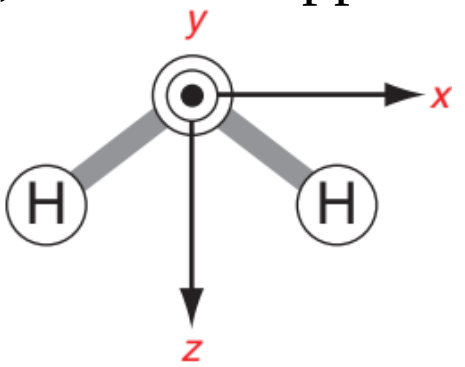
2.1.4 A quick method of finding characters

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:

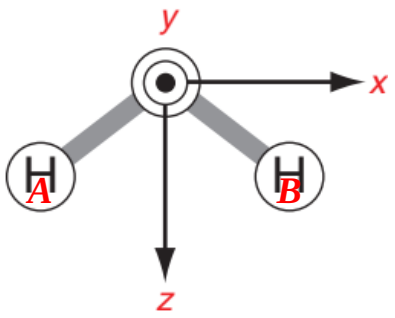
Operation E : both s_A and s_B unaffected, both count +1; character is +1 + 1 = **+2**

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**

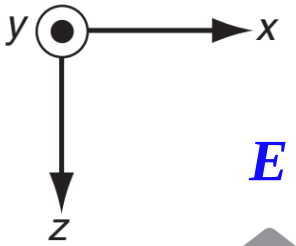
Operation σ^{yz}: both s_A and s_B moved, both count 0; character is 0+0 = **0**

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

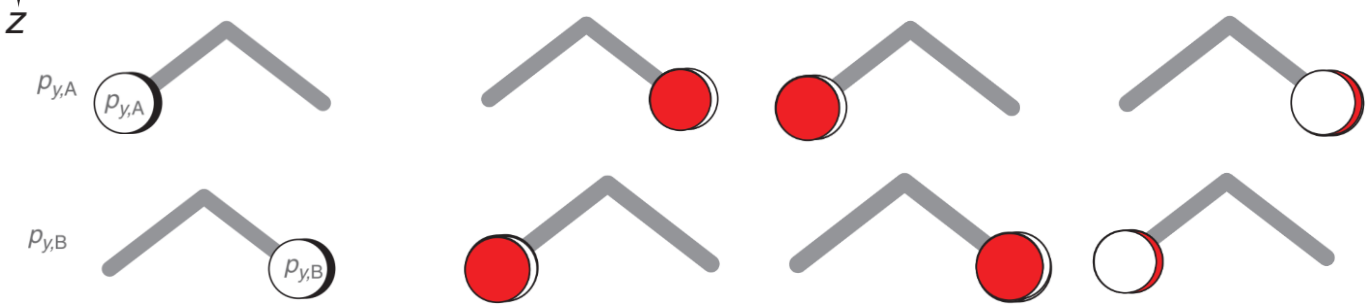


2.1.4 A quick method of finding characters

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



two functions in the basis → two -dimensional representation.



$\chi(\hat{R})$ 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 count out $\chi(\hat{R})$!

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

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

σ^{xz} : both change sign, -1-1 = -2

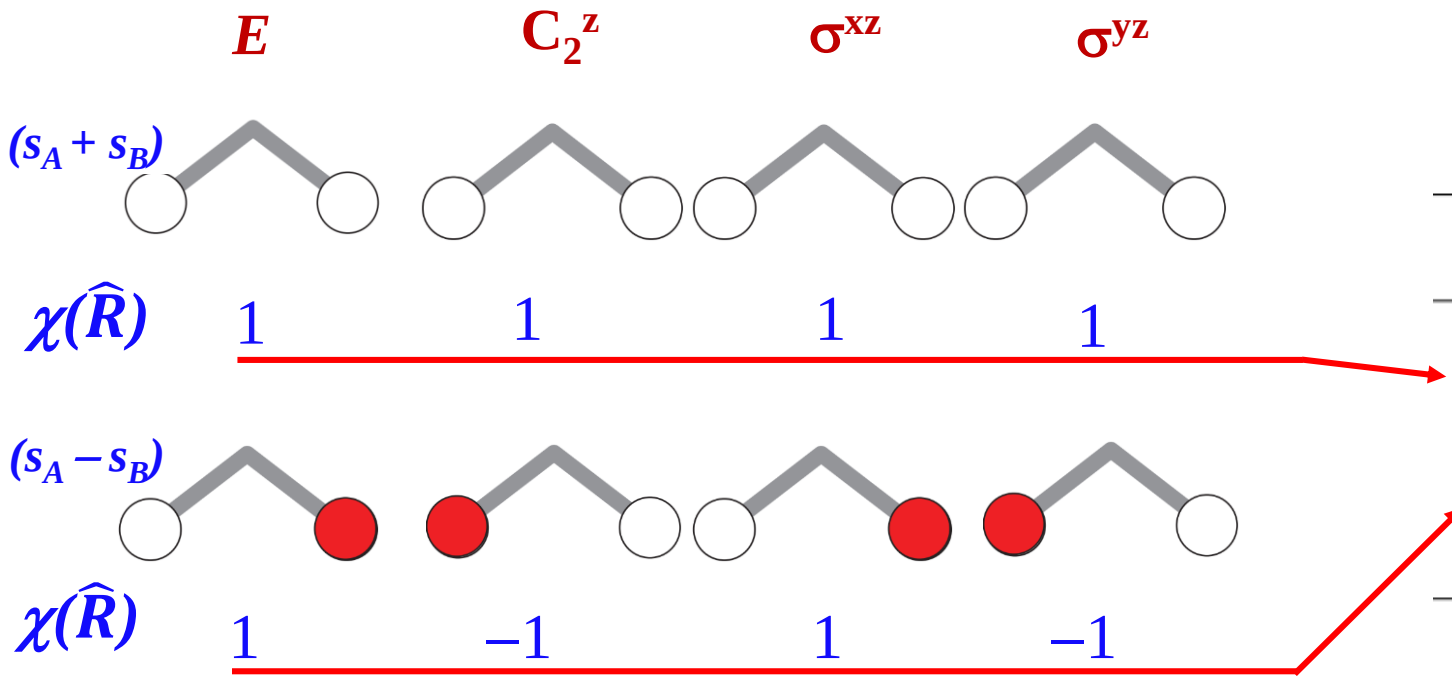
σ^{yz} : both moved, 0 + 0 = 0

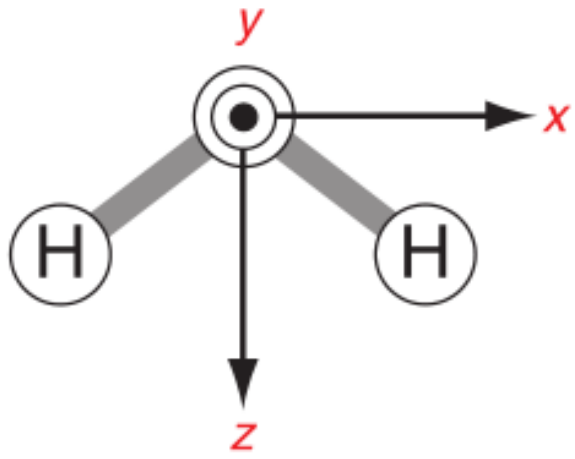
→ (2,0,-2,0) Now reduce it!?

→ $A_2 \oplus B_2$. ***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 $A_1 \oplus B_1$. We should be able to find a (linear) combination of the two AOs which transforms just as A_1 and another combination which transforms as B_1.
- Let us consider $(s_A \pm s_B)$.

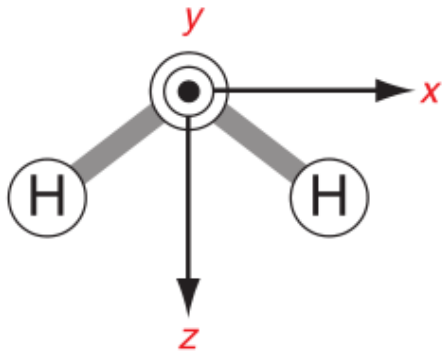




C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Ex.7

2.1.5 Introducing symmetry orbitals



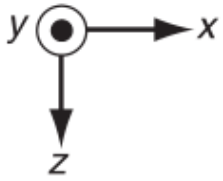
• ***(s_A+s_B)*** and ***(s_A-s_B)*** are called ***symmetry orbitals (SOs)*** or ***symmetry adapted linear combinations*** (***SALC***s) because they have the special property that they transform as a single ***irreducible representation***.

• ***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.

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	*Now look at the 3rd*
Vector z	***1***	***1***	***1***	***1***	A_1	*column of the*
Vector y	***1***	***-1***	***-1***	***1***	B_2	*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

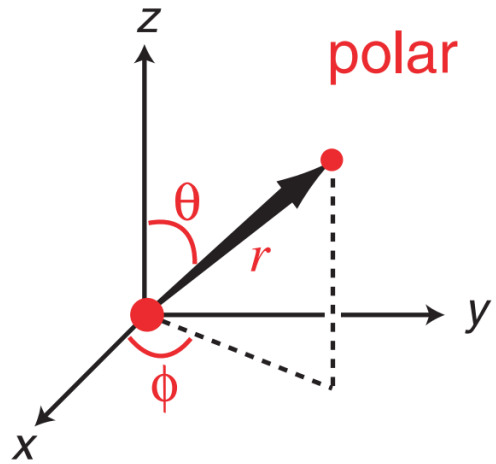
Typical basis function(s) for ***IR***s: The information about how simple functions (and the corresponding vectors) transform is usually given as part of the character table.

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 $y \cdot exp(-r/2)$ and $z \cdot exp(-r/2)$, respectively, and so transform as y and z, i.e. B_2 and A_1 from 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

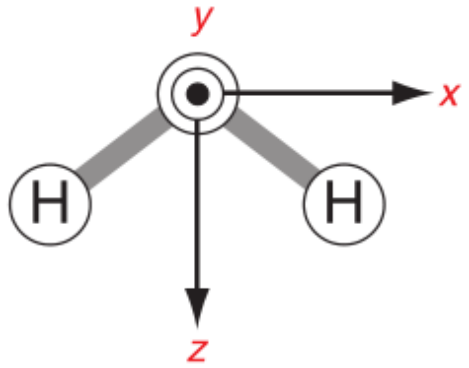
2.1.6 Using extra information from the character tables

- Again for the AOs of oxygen in H_2O,

  s AO transforms like ***?*** (of spherical symmetry!)

  d orbitals ~ their names indicate the corresponding cartesian functions.

  e.g., d_{xy} transforms 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

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

d_{xy} ?

d_{z^2} ?

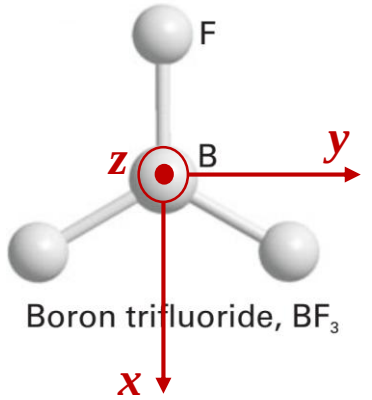
d_{yz} ?

d_{xz} ?

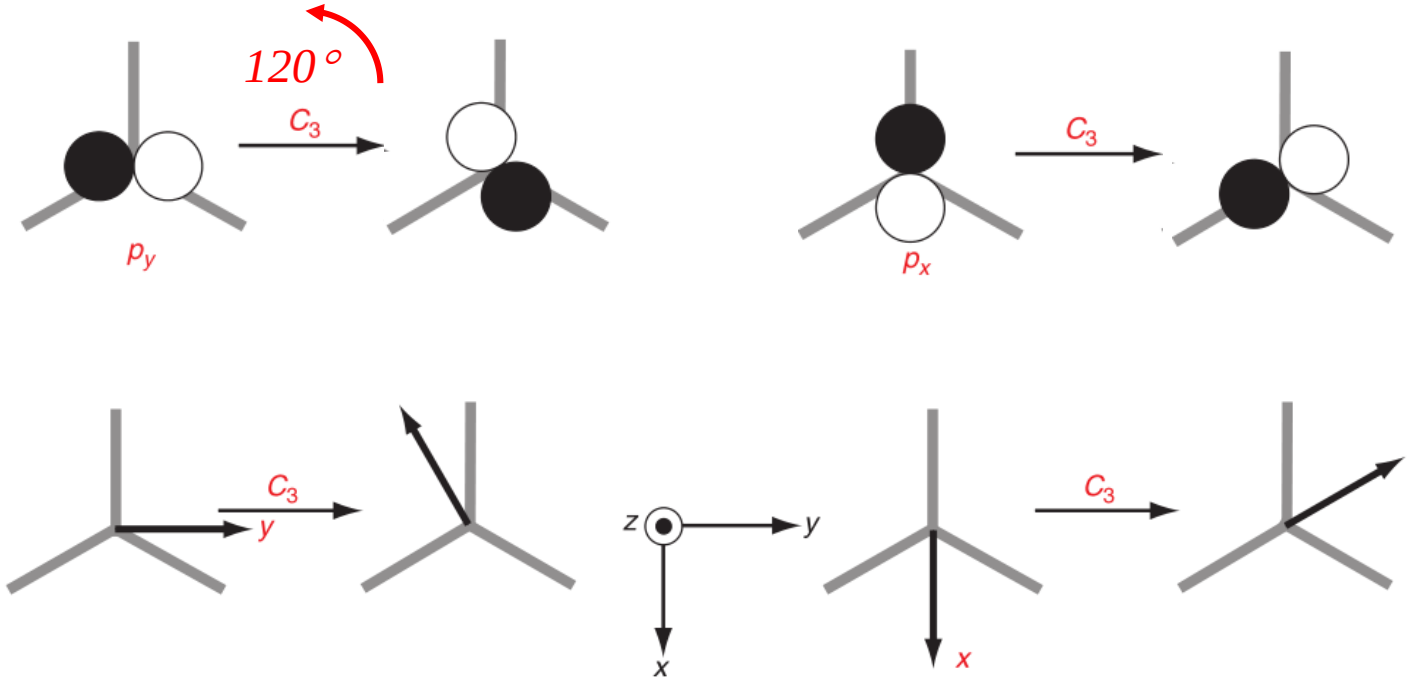
In this case, only for AOs of O can we do such reading-off!

Ex.8

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.



- neither p_x nor p_y, but seemingly to be the combination of $\boldsymbol{p_x}$ and $\boldsymbol{p_y}$.
- $\boldsymbol{p_x}$ (or $\boldsymbol{x}$) and $\boldsymbol{p_y}$ (or $\boldsymbol{y}$) are '***mixed***' by the $\boldsymbol{C_3}$ 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 of the central boron atom in BF_3, 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 irreducible representation

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

- 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

$$C_3\mathbf{j} = -\frac{\sqrt{3}}{2}\mathbf{i} - \frac{1}{2}\mathbf{j} \qquad C_3\mathbf{i} = -\frac{1}{2}\mathbf{i} + \frac{\sqrt{3}}{2}\mathbf{j}$$

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

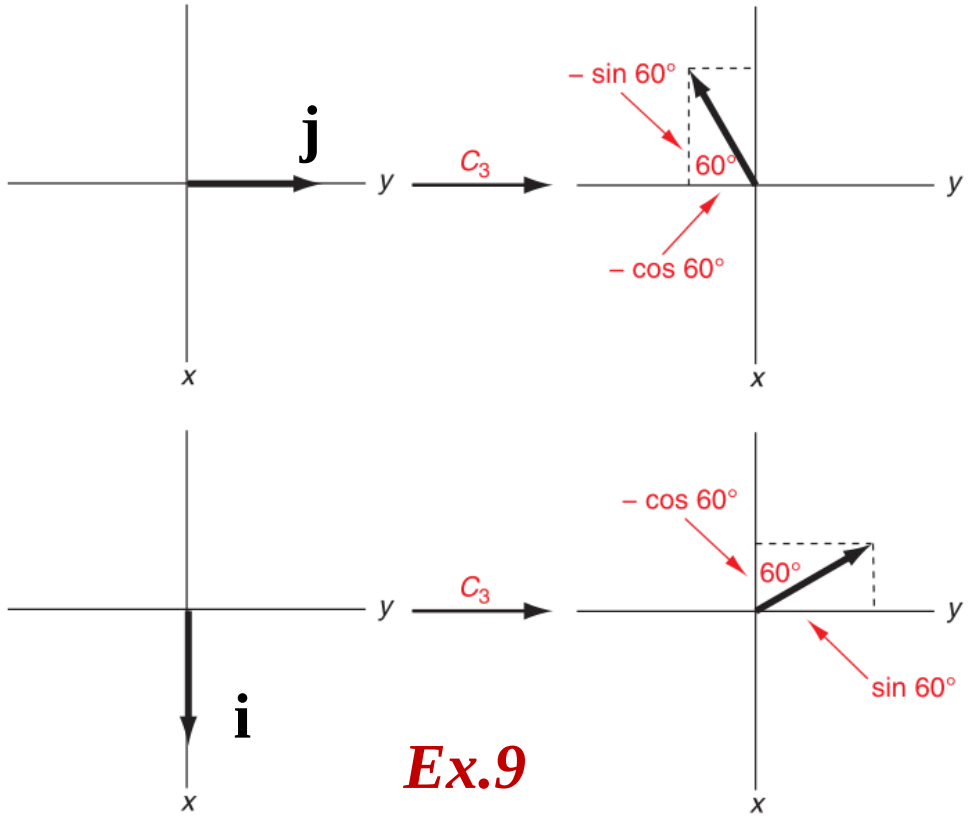
$\chi(C_3) = -1$

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

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

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

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



Ex.9

2.3 Reducing a representation (表示的约化)

- 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*** (**约化公式**).

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

- ***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 kth *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:

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

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: $\chi^{(1)}(E) = 1$, $\chi^{(1)}(C_2) = 1$, $\chi^{(1)}(\sigma^{xz}) = 1$, $\chi^{(1)}(\sigma^{yz}) = 1$

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

$$= \frac{1}{4}\left(\left[\chi^{(1)}(E)\right]^* \chi(E) + \left[\chi^{(1)}(C_2)\right]^* \chi(C_2) + \left[\chi^{(1)}(\sigma^{xz})\right]^* \chi(\sigma^{xz}) + \left[\chi^{(1)}(\sigma^{xz})\right]^* \chi(\sigma^{yz}) = 0\right.$$

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,

$$a_2 = \frac{1}{h}\sum_R [\chi^{(2)}(R)]^* \chi(R) \quad \textbf{=1}$$

- The 3rd ***IR*** is B_1,

$$a_3 = \frac{1}{h}\sum_R [\chi^{(2)}(R)]^* \chi(R) \quad \textbf{=0}$$

- 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)

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

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

cth class of operations

Number of operations within the ***c***th class

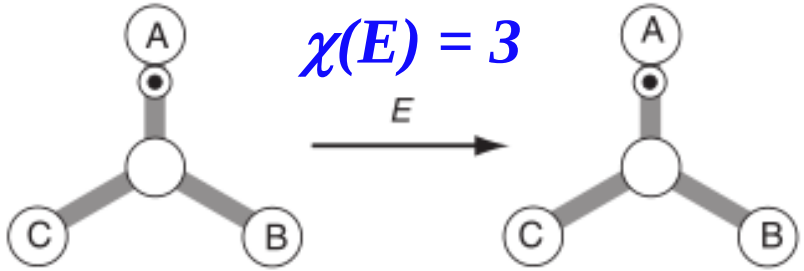
- **Example**: a basis consisting of the ***three equivalent 2s orbitals*** on the ***fluorine atoms*** in **BF_3**.

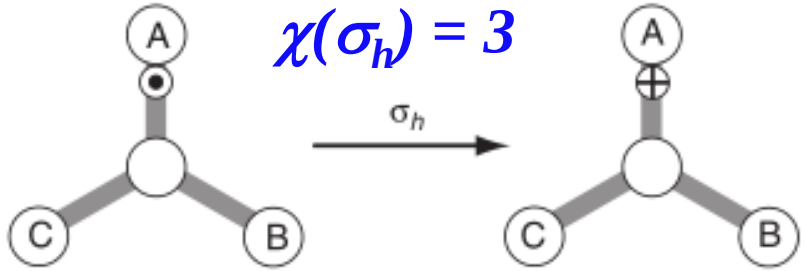
2.3.1 Reduction formula in terms of classes

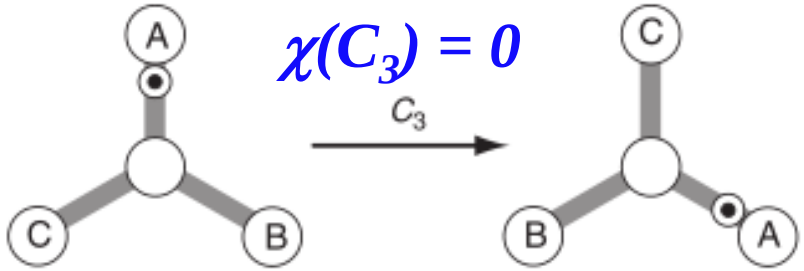
- For BF_3, we ***'count'*** the **characters** for ***each class*** of operations in the basis of **3xF 2s**.

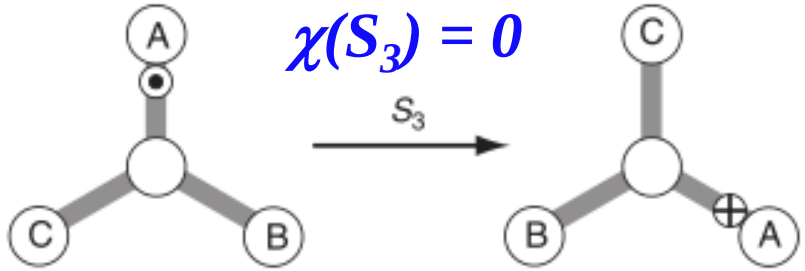
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$

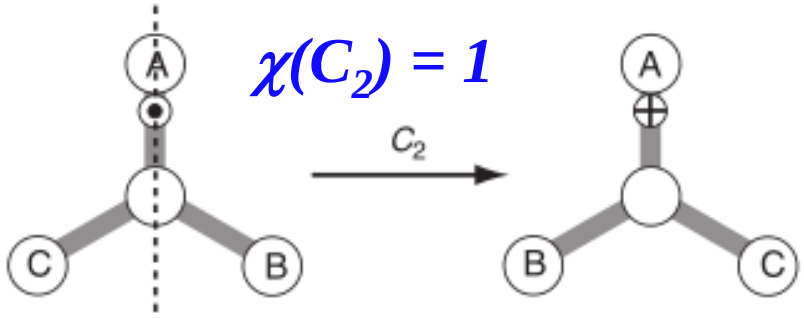
A **?** - dimension representation will be obtained.

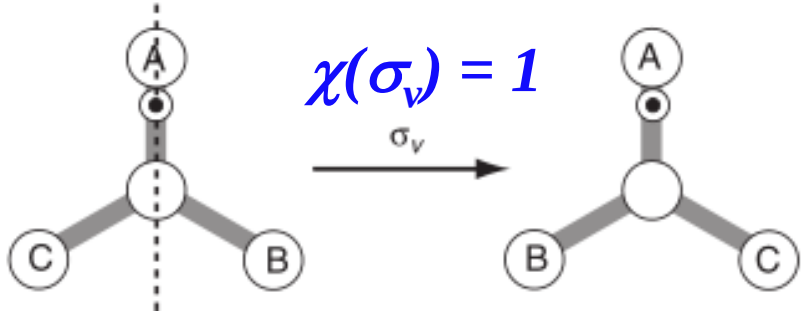












2.3.1 Reduction formula in terms of classes

- Hence, the representation generated by these three ***s*** orbitals is ***(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', $a_1 = \frac{1}{h}\sum_c g(c)\left[\chi^{(k)}(c)\right]^* \chi(c) = 1$
- For A_2', $a_2 = 0$
- For E', $a_3 = 1$
- ….. $a_{4-6} = 0$

→ Γ(3×F2s) = $A_1' \oplus E'$

→ Γ(3xF2p$_z$) = $A_2'' \oplus E''$

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.

Advantages:

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

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	$1\times3 + 1\times0 + 1\times3 + 1\times3 + 1\times0 + 1\times3 = 12$

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	$1\times3 + 1\times0 + (-1\times3) + 1\times3 + 1\times0 + (-1\times3) = 0$

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:

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

$$= 1 \times (1,1,1,1,1,1) + 1 \times (2,-1,0,2,-1,0) = (3,0,1,3,0,1) \quad \surd\text{OK}$$

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 σ_h plane:

IRs *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 representations***.

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 ***j***th IR and ***h*** is the order of a group, then

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

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

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