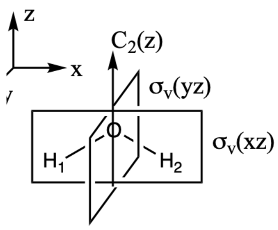
Character Tables

Introduction

- last lecture we introduced the symmetry operations and elements associated with existing (E), rotation (C_n), reflection (σ), improper rotation (S_n) and inversion(i)
- we learned about the point group of a molecule
- we expand on a number of concepts related to rotations and improper rotations including coincident elements and equivalent operations
- then I introduced a very useful resource called Character Tables
- we looked at identify when operations in the header row of the character table are due to multiple symmetry elements or operations
- today we will learn how to use the character tables for MOs through a series of examples

Introducing the Character Table

- the best way to become familiar with a character table is to use it, we will cover two examples now.
- water has C_{2v} symmetry or belongs to the C_{2v} point group, so we use the C_{2v} character table, **Figure 1**



point group — symmetry operations — characters

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

symmetry labels

identifies the symmetry label of cartesian axes

irreducible representation

Figure 1 symmetry elements and character table for the C_{2v} point group

The first MO of water

- let us consider an s atomic orbital placed on each of the atoms of water, **Figure 2**
- this is in-fact the lowest energy MO for water, it consists of a positive combination of the H 1s AOs and the O 2s AO.

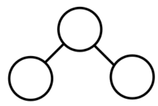
MO1 

Figure 2 first MO of H_2O

- then we ask ourselves how does this MO transform under C_{2v} symmetry?
- one way to work this out is to set up a **representation table** as shown below, **Figure 3**

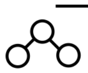
	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }				

Figure 3 Empty representation table for MO1

we will be using Greek letters extensively, if you don't know these check out the web-site

- a representation table shows the effect of each symmetry operation on an object (this can be a molecule, a molecular orbital or anything else) with the symmetry of the point group.
- capital gamma (Γ) is used when the symmetry of something is unknown
- you might notice I've used brackets in the representation table, gamma is an operator!

- now apply the symmetry operations of the group to the molecular orbital
  - if the **phase remains unchanged** under a symmetry operation enter **1**
  - if the **phase is reversed** under a symmetry operation enter **–1**
  - "under" is a strange word to use, but it is standard terminology. When we say "under C_2" we mean "what happens when we perform the C_2 operation"
- step through each of the lines of **Figure 4**
  - the orbital is unchanged under E, => we enter 1 under E in the table.
  - the orbital is unchanged under C_2, => we enter 1 under C_2 in the table.
  - the orbital is unchanged under $\sigma_v(xz)$ => we enter 1 under $\sigma_v(xz)$
  - the orbital is unchanged under $\sigma_v(yz)$ => we enter 1 under $\sigma_v(yz)$

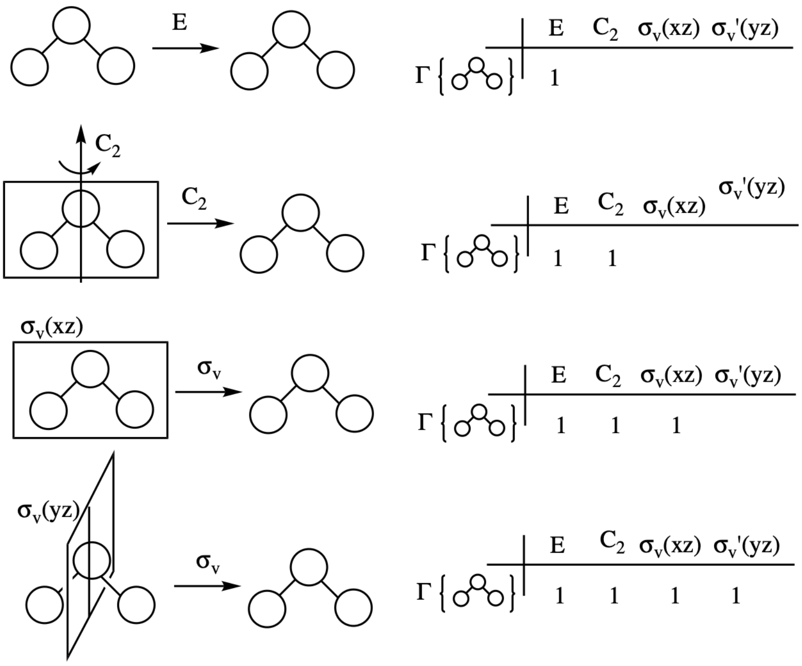
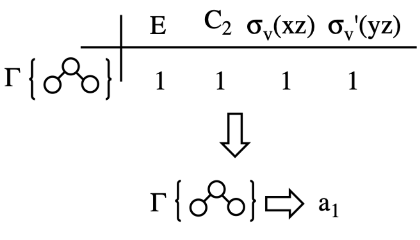


Figure 4 Filling out the representation table

- then we then compare the generated representation to the list of irreducible representations on the C_{2v} character table, and we determine which one it matches, **Figure 5**



	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	h=
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Figure 5 Matching a unknown representation to an irreducible representation

important

- this MO transforms as the irreducible representation labelled A_1
- by convention we *label orbital symmetries with small letters*, therefore the first molecular orbital water has a_1 symmetry.
- we reserve capital letters for nuclear vibrations and electronic states

In-Class Activity P1

- The second lowest energy MO of water, **Figure 2-MO2** is composed of H 1s AOs and the O $2p_x$ AO. Use a representation table to determine the symmetry label (irreducible representation) for MO2, **Figure 6**

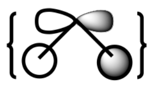
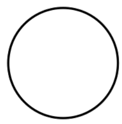
	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }				

Figure 6 Empty representation table for MO2

see the web-site for a link to the "Orbitron"

The Shaded part of Atomic Orbitals

- we need some core knowledge which you will have seen before about atomic orbitals, this is just a reminder
- atomic orbitals have a radial and angular component, **Figure 7**
- we only represent the **outer portion** in our MO diagrams
  - atomic orbital "cartoons" represent the wavefunction density (ψ^2) at a high contour (≈ 95%)
  - the radius (R) of maximum density increases with quantum shell
  - remember, there are inner nodes but these are not depicted (they are assumed)



$$\downarrow$$
$$\psi_{1s}$$
$$\downarrow$$
$$R_{1s}Y_{1s}$$
$$\downarrow$$
$$\underbrace{\left[2Z^{3/2}e^{-\rho/2}\right]}_{R_{1s}}\underbrace{\left[(1/4\pi)^{1/2}\right]}_{Y_{1s}}$$

Figure 7 Equation for the 1s atomic orbital

- the **shading** indicates the sign or **phase** of the wavefunction ψ.
  - wave-*function*, functions can be positive and negative, **Figure 8** represents the sign of a simple quadratic function
- the **angular nature** (Y) of the orbital is represented by the shaded lobes on the, s, p, and d shapes, **Figure 9**

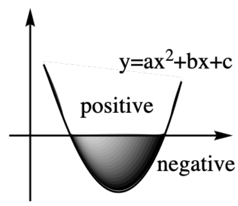


Figure 8 Negative portion of the function is shaded

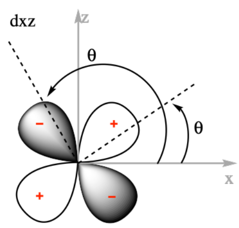
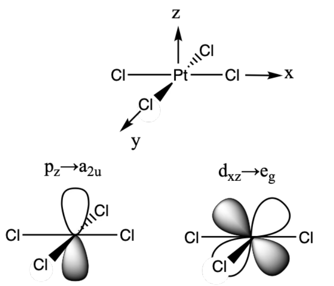


Figure 9 Angular part of the wavefunction

Orbital Symmetries that Match Cartesian Functions

- the symmetry of MOs or fragment orbitals can be determined by looking at their phase-patterns
- lets consider some the atomic orbitals for Pt in square planar $[PtCl_4]^{2-}$ which belongs to the D_{4h} point group, **Figure 10**
- consider the 2nd to last column of the character table:
  - T=translation and R=rotation,
  - T_x, has the same symmetry as the x-axis, T_y the y-axis and T_z the z-axis
  - the center-of-mass rotations also have symmetry labels, but that is only of interest when discussing molecular vibrations
  - singular p_x, p_y and p_z atomic orbitals also have the symmetry of the x, y and z-axes (when located at the origin!) so relate to T_x, T_y and T_z
  - for example the p_z AO on Pt has a_{2u} symmetry label
- consider the last column of the character table:
  - the binary cartesian functions are listed, these also have a symmetry, which is identified in the last column
  - these functions x^2, y^2, z^2, xy, xz, and yz, are related to the dAOs,
  - thus the symmetry of a dAO can be identified from the symmetry of the corresponding Cartesian functions (when located at the origin!)
  - the dx^2-y^2 orbital sometimes has the symmetry of the (x^2, y^2) pair, or sometimes the Cartesian function x^2-y^2 is explicitly given
  - for example the d_{xz} AO on Pt has the e_g symmetry label



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	T_z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(T_x, T_y)	

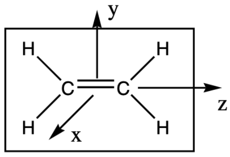
Figure 10 Symmetry of AOs of Pt in D_{4h} $[PtCl_4]^{2-}$ and the D_{4h} character table

important

- more generally molecular orbitals that have the same phase pattern as the x, y and z axes have the same symmetry as these axes
- and the molecular orbitals that have the same phase pattern as the dAOs have the same symmetry as the binary cartesian functions

In-Class Activity P2

- What is the symmetry of the p_x and p_y AOs of Pt?
- What is the symmetry of the dxy AO of Pt?



D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	zx
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	T_z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	T_y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	T_x	

Figure 11 Ethene and the D_{ch} character table

- for example the molecular orbitals in **Figure 12**
  - the top MO has a phase pattern like the z-axis (T_z) and hence this MO has a b_{1u} symmetry label
  - the bottom MO has the phase pattern of the dxz AO and hence this MO has a b_{2g} symmetry label

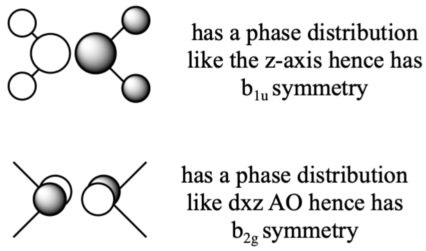


Figure 12 symmetry of FO fragments of C_2H_4

In-Class Activity P3

- Determine the symmetry of these MOs identifying appropriate "short-cut" through a relationship to cartesian functions.

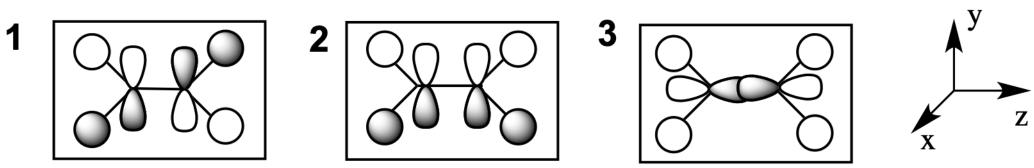


Figure 13 Determining orbital symmetry via short-cuts

Symmetry Labels

- the symmetry labels tell us something about the irreducible representation (the way that an object behaves under the symmetry operations of the group)
- A and B (or a and b for MOs) are the symmetry labels for **non-degenerate** representations, they have only have characters ±1
- E (or e) is the symbol used for a **doubly-degenerate** irreducible representations (and should not be confused with the symmetry operation E) Under the operation E, E always has a character of 2
- T (or t) is used to label **triply-degenerate** irreducible representations, under the operation E they always have a character of 3
  - T is important in the tetrahedral and octahedral point groups
  - you have already seen these labels at work, in the t_{2g} and e_g symmetry labels in your transition metal chemistry!

Degeneracy

- degenerate representations *cannot be described by a single representation they necessarily have two or more components*
  - in a degenerate representation the individual components (orbitals) do NOT always map onto themselves, however they must map onto a linear combination of each other, so they must always be considered together
  - for example if we have two items that are degenerate, say p_x and p_y (atomic orbitals) they map onto a linear combination of each other, for example: $c_1p_x+c_2p_y$ where c_1 and c_2 are coefficients
- again the best way to build up an understanding of what this means is to work through a practical example, p_x and p_y are components of the degenerate representation (E') under the D_{3h} point group, **Figure 14**

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 14 D_{3h} character table

- we start by taking a point on the tip of each orbital and define the points position in terms of the x and y axes ie the coordinates (x,y) or in our case we will use the vertical vector notation:

$$\begin{pmatrix} x \\ y \end{pmatrix}$$

  - the p_x and p_y orbital "points" have coordinates $p_x \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $p_y \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$
  - one way to think of this is as a set of unit vectors
  - then we put these side by side forming a 2 by 2 matrix, **Figure 15**, now we have our starting matrix

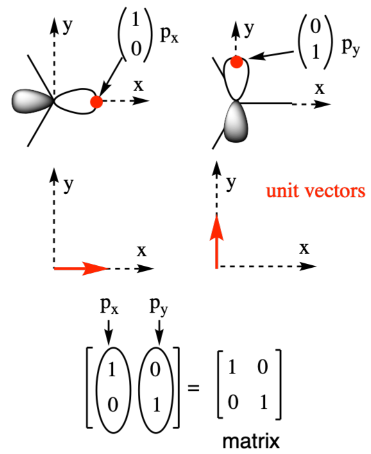


Figure 15 defining the 2*2 matrix

- now consider the transformation of each orbital under operation E
  - p_x and p_y remain the same! **Figure 16**
  - the equation for this is given below:

$$E\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- the character (in the character table) is found by taking the sum of the diagonal terms of the final matrix
  - for E this is 1+1, hence the character for E is 2
  - check this against your character table!

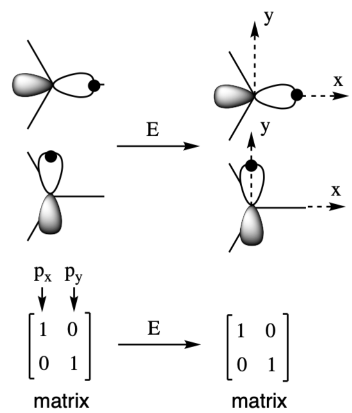


Figure 16 working out the final matrix for the E operation

- The character is the **trace** which is the sum of the diagonal elements of this matrix (this is true of all characters they are the trace of matrices that represent the symmetry operations)
- to determine the irreducible representation we have to find the character of this matrix after each symmetry operation of the point group
- now consider the transformation under σ_v, **Figure 17**
  - the character is the sum of the diagonal terms of the matrix which is just 1+(-1)=0
  - hence the character for σ_v is 0
  - check this against your character table!

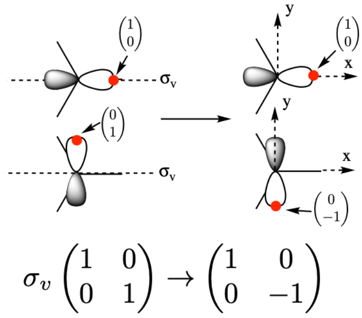


Figure 17 transformation of the p_x and p_y AOs under σ_v

In-Class Activity P4

What is the character of the degenerate B p_x and p_y AOs under the C_2 axis? Complete the diagram below and determine the transformation matrix and the hence the character.

- HINT: pick the easiest C_2 axis to work with, ie the one that is aligned with one of the orbitals
- check your answer against the character table!

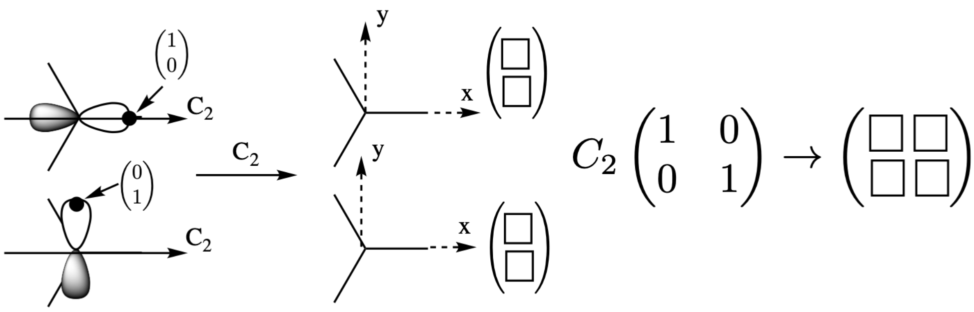


Figure 18 transformation of the p_x and p_y AOs under C_2

Point Groups for Linear Molecules

- Homonuclear diatomic molecules of the chemical formula X_2 are linear and highly symmetric, they have $D_{\infty h}$ symmetry (belong to the $D_{\infty h}$ point group)
  - examples include O_2, N_2, Cl_2
  - on the flow chart
    1. is the molecule linear? YES
    2. is there a centre of inversion? YES
  - examples include O_2, N_2, Cl_2
- Heteronuclear diatomic molecules of the chemical formula EE' are linear and less symmetric, they have $C_{\infty v}$ symmetry (belong to the $C_{\infty v}$ point group)
  - on the flow chart
    3. is the molecule linear? YES
    4. is there a center of inversion? NO
  - examples include CO, HF, $[CN]^-$, $[NO]^+$

$C_{\infty v}$	E	C_2	$2C_\infty^\phi$	…	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	1	…	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	1	…	−1	R_z	
$E_1 \equiv \Pi$	2	−2	$2\cos\phi$	…	0	(x,y) (R_x,R_y)	(xz, yz)
$E_2 \equiv \Delta$	2	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
$E_3 \equiv \Phi$	2	−2	$2\cos 3\phi$	…	0		
…	…	…	…	…	…		
…	…	…	…	…	…		

Figure 19 character table for the C∞v point group

$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…	1	−1	−1	…	−1	z	
Σ_u^-	1	1	…	−1	−1	−1	…	1		
Π_u	2	$2\cos\phi$	…	0	−2	$2\cos\phi$	…	0	(x,y)	
Δ_u	2	$2\cos 2\phi$	…	0	−2	$-2\cos 2\phi$	…	0		
…	…	…	…	… …		…	…	…		

Figure 20 character table for the D∞h point group

- Looking at the linear point groups you will notice some differences compared to the point groups we have considered so far
- you will notice is that the symmetry labels are in Greek
  - you will be already familiar with "little" sigma (σ) and pi (π) from organic chemistry, when labelling orbitals we always use the little letters.
  - when naming the irreducible representation (on the character table) we use the capital versions; sigma (Σ) and pi (Π)
  - capital delta (Δ) and little delta (δ) you may be familiar with from other contexts
  - capital phi (Φ) and little phi (φ) may be new to you (but are often used to reference an angle)
- for the $C_{\infty v}$ point group the symmetry labels are sometimes given as the letters A and E instead of the Greek symbols. In this course you should *always use the Greek symbols*.
- for $D_{\infty h}$ there is a center of inversion in the middle of the X_2 bond
  - inversion around a point is where the g (gerade) and u (underade) labels come from, **Figure 21**
  - the symmetry is gerade when there is no change on moving from one side of the inversion point to the other ie from (+x,+y,+z) to (-x, -y, -z)
  - the symmetry is ungerade when there is a change *in phase* on moving from one side of the inversion point to the other
  - if you look at the symmetry labels or irreducible representations of other point groups you will see others that have the subscript u and g

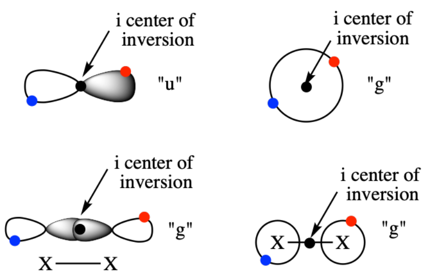


Figure 21 gerade and ungerade labels

Rotational Symmetry Operations

C_{lots} rotation

Figure 22 small angles giving rotation axis C_{lots}

- for a linear molecule there are an infinite number of coincident rotation axes, all the way up to C_∞
  - how can an axis have infinite "rotational steps"? If each step is infinitely small, imagine the rotation angle starting at 180º and getting smaller and smaller and smaller ...
  - we can relate this to the flower from lecture 1 with the petals getting smaller and smaller, **Figure 22**
  - when we have an infinite number of infinitely small steps, the system is essentially **continuous**
  - sometimes these $D_{\infty h}$ and $C_{\infty v}$ are called continuous groups

- the header row both $C_{\infty v}$ and $D_{\infty h}$ show $2C_\infty^\phi$ operations, here ϕ is the angle of rotation, , **Figure 23**

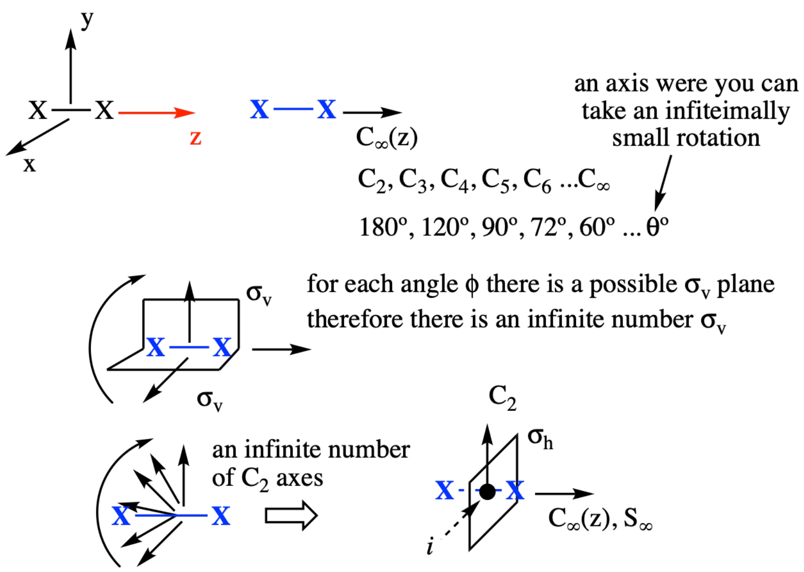


Figure 23 $D_{\infty h}$ symmetry operations

- the C_∞ axis is the highest n-axis and thus is the principle axis for any diatomic molecule, make sure you align your z-axis correctly!
  - then we can have a rotation axis of any angle ϕ coincident with the C_∞ axis, these are represented by the row of dots after the $2C_\infty^\phi$
  - for example there will be C_2, C_3, C_4, C_5 and so on coincident with the C_∞ axis
  - in the case of $C_{\infty V}$ symmetry the C_2 axis coincident with the C_∞ axis, is pulled out of the ... "list" for special attention. Note that ϕ =180º= π and cos(π)=-1, cos(2π)=+1 and so on
  - thus there are actually only 2 unique operations +ϕ and -ϕ for each angle, because all the other possible angles are counted by a higher rotation axis
  - for example if ϕ=30º around the C_∞ axis then a rotation by 2ϕ=60º has already been counted
- at each small rotation angle ϕ there is also a reflection plane σ_v which lies vertically aligned with the C_∞ (principle) axis, thus there is an infinite number of mirror planes $\infty\sigma_v$

- the perpendicular C_2 rotations
  - the XX molecule with $D_{\infty h}$ symmetry is special in that there are also an infinite number of C_2 axes perpendicular to the principle axis (C_∞)
  - in the header of the $D_{\infty h}$ character table the ∞C_2 axes come last
  - the XX' molecule with $C_{\infty v}$ symmetry has no perpendicular C_2 axes
- there the S_∞^ϕ symmetry operations
  - there is a mirror plane perpendicular to the highest axis of symmetry this is the σ_h plane
  - however σ_h does not appear in the header row of the character table because this operation has already been "counted", the same mapping is achieved by the infinite (perpendicular) C_2 axes
  - the improper rotations behave very similarly with respect to the simple rotations, just with the addition of reflection in the σ_h plane
- if you look at the $C_{\infty v}$ point group, there is no horizontal mirror plane, no inversion center and no improper rotation axis symmetry operators

In-Class Activity P5

- Draw a Lewis bonding diagram for IF5 and identify the molecular shape of IF 5 using VSEPR theory.
- Determine the point group and draw all of the symmetry elements on a diagram of the molecule.
- Identify if multiple operations in the character table are due to multiple operations on the same element or multiple elements.
- For the highest rotation axis identify, for any operations that are not-unique, the equivalent operation.

Key Points

- be able to define all the components of a character table
- be able to use character tables to find the symmetry label for a given MO
- be able to identify degenerate irreducible representations
- be able to determine the characters for degenerate irreducible representations
- be able to describe the origin of "u" and "g" in symmetry labels

Self-study Problems / Test Preparation

- **Q1** determine the symmetry label for the molecular orbitals shown for BH_3 using the "long method" of forming a representation table, for (b) check your answer using a "short-cut" method

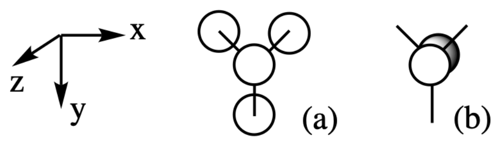


Figure 24 MOs of BH_3, (a) lies in the plane of the page and (b) is a p_zAO going into the plane of the page

- **Q2** construct a representation table for the "z-axis" and determine which irreducible representation it transforms as.

  Q3 *In your own words*, using bullet points, write out the general procedure to determine the symmetry label of a molecular orbital
- **Q4** *In your own words*, using bullet points, write out the general procedure to determine the character of a degenerate set of orbitals? This is my process however you should go through the notes and an example and write out the process for yourself in your own words!
- **Q5** Discuss and illustrate the symmetry operations of the T_d point group (*advanced!*)

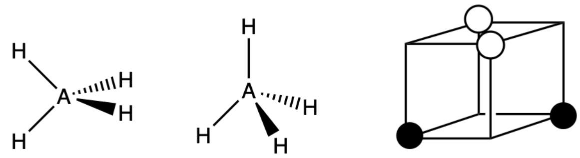


Figure 25 different ways to represent a T_d molecule

  - **hint:** there are three useful ways of thinking about a tetrahedral molecule, each one emphasises a different aspect of symmetry:
    (a) the C_2 axes
    (b) the C_3 axes
    (c) the cubic structure
- **Q6** Identify the symmetry of the following MOs of a D_{4h} molecule, use the short-cuts where possible