Molecular Orbital Theory

Lecture 2

Last Lecture

- last lecture introduced the operations
  - existing (E), rotation (Cn), reflection(σ), improper rotation (Sn) and inversion
- introduced some concepts
  - equivalent operations
  - unique operations
  - coincident elements
- had a first look at a character table

Outline

- using a character table to determin MO symmetry labels
  - the "long way" using a representation table
  - "short cuts" using cartesian functions
- what is degeneracy
  - how can a symmetry operation have a "0" character?
- the point group of linear molecules
- practice!

Character Tables

- key part of this course is learning how to use character tables

C_{2v} character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	h=4
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 operations

number of symmetry operations

symmetry labels

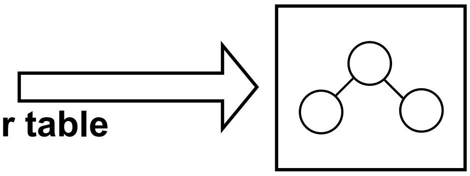
symmetry of cartesian axes

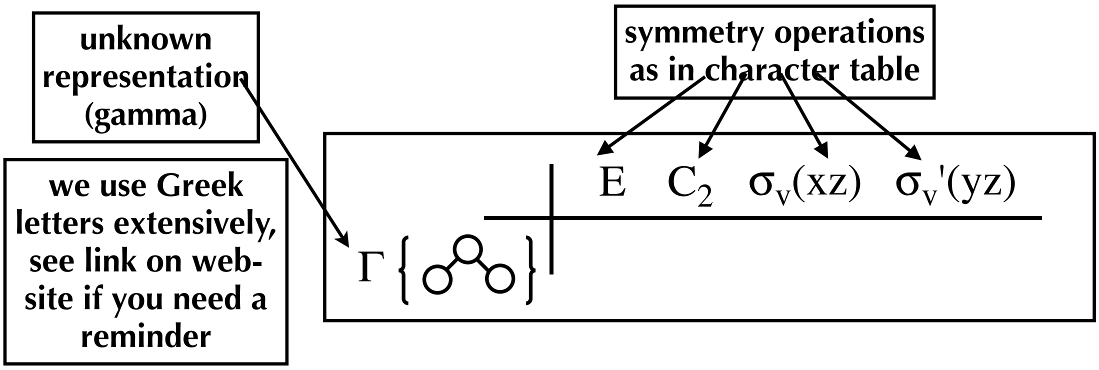
irreducible representation

1's and -1's are characters

Using Character Tables

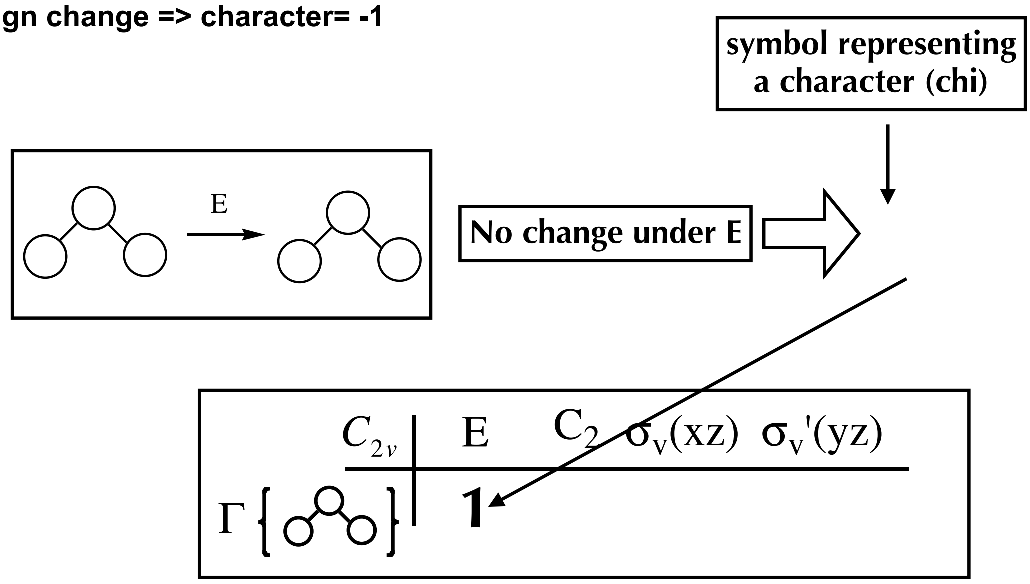
- best way to understand character table is to use it
- example: lowest energy MO of water
  - s atomic orbital on each of the H and O atoms
- H_2O has C_{2v} symmetry so use C_{2v} character table
- start by constructing a representation table:





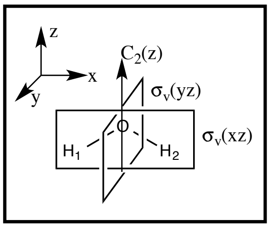
Using Character Tables

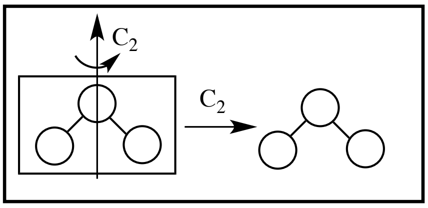
- Determine how the orbital transforms under each symmetry operation of the group
  - orbital is unchanged => character=1
  - a sign change => character= -1



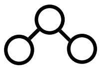
Using Character Tables

- Determine how the orbital transforms under each symmetry operation of the group
  - orbital is unchanged => character=1
  - a sign change => character= -1



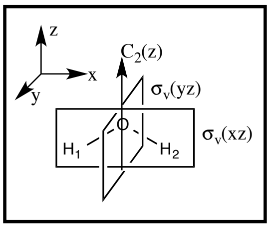


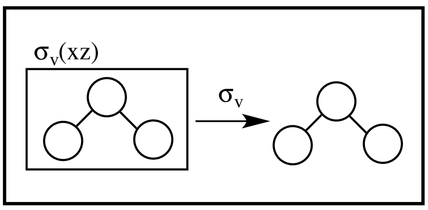
No change under C_2

C_{2v}	E	C_2	σ_v(xz)	σ_v'(yz)
Γ{}	1	1		

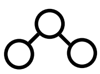
Using Character Tables

- Determine how the orbital transforms under each symmetry operation of the group
  - orbital is unchanged => character=1
  - a sign change => character= -1



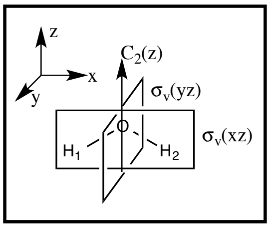


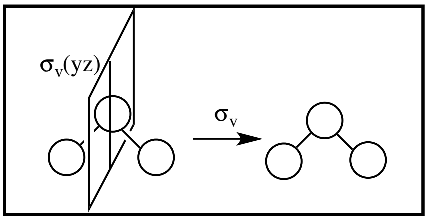
No change under σ_v

C_{2v}	E	C_2	σ_v(xz)	σ_v'(yz)
Γ{}	1	1	1	

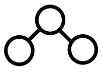
Using Character Tables

- Determine how the orbital transforms under each symmetry operation of the group
  - orbital is unchanged => character=1
  - a sign change => character= -1

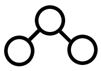




No change under σ_v

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }		**1**	**1**	**1**	**1**

Using Character Tables

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }		**1**	**1**	**1**	**1**

same set of characters as the irreducible representation (IR) a_1

- use lower case letters for symmetry labels of MOs

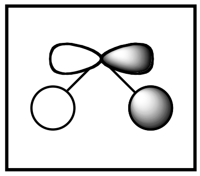
A_1 -> a_1

- upper case letters are reserved for vibrations and electronic states

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	h=4
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

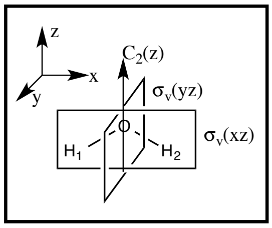
In-Class Activity P1

- **the second highest energy MO for water**
  - **out of phase s atomic orbitals on the hydrogen atoms and a p_x atomic orbital on the oxygen atom**

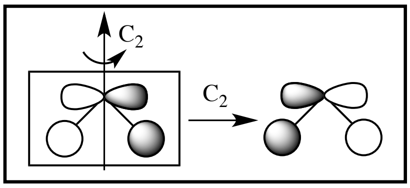


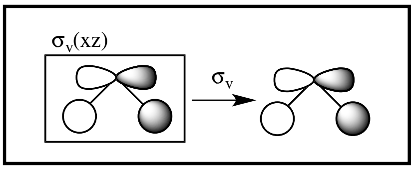
your turn:

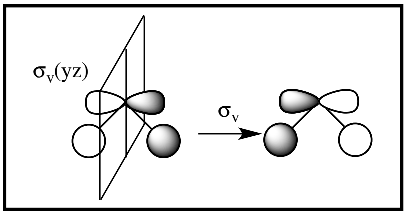
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ				



In-Class Activity P1

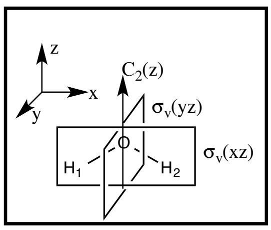






C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ	**1**	**-1**	**1**	**-1**

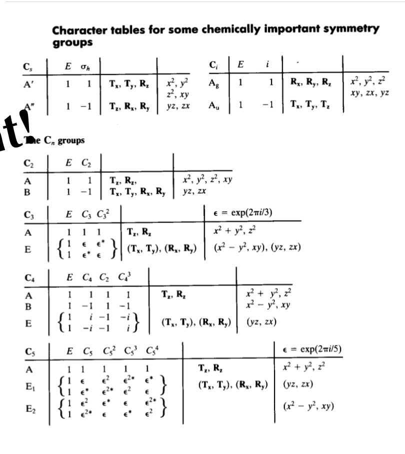
this orbital has b_1 symmetry



Character Tables

- take a couple of minutes to look through the character table file

Important!



Character tables for some chemically important symmetry groups

C_s	E	σ_h		
A′	1	1	T_x, T_y, R_z	x^2, y^2 z^2, xy
A″	1	−1	T_z, R_x, R_y	yz, zx

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2 xy, zx, yz
A_u	1	−1	T_x, T_y, T_z	

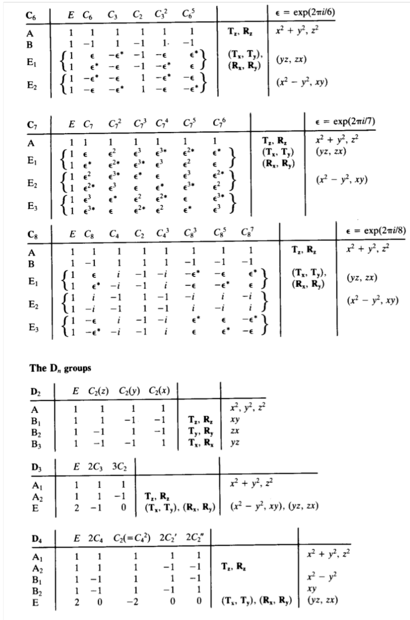
The C_n groups

C_2	E	C_2		
A	1	1	$T_z, R_z,$	x^2, y^2, z^2, xy
B	1	−1	T_x, T_y, R_x, R_y	yz, zx

C_3	E	C_3	C_3^2		$\epsilon = \exp(2\pi i/3)$
A	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
E	1	ϵ	ϵ^*	$(T_x, T_y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, zx)$
	1	ϵ^*	ϵ		

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
B	1	−1	1	−1		$x^2 - y^2, xy$
E	1	i	−1	$-i$	$(T_x, T_y), (R_x, R_y)$	(yz, zx)
	1	$-i$	−1	i		

C_5	E	C_5	C_5^2	C_5^3	C_5^4		$\epsilon = \exp(2\pi i/5)$
A	1	1	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
E_1	1	ϵ	ϵ^2	ϵ^{2*}	ϵ^*	$(T_x, T_y), (R_x, R_y)$	(yz, zx)
	1	ϵ^*	ϵ^{2*}	ϵ^2	ϵ		
E_2	1	ϵ^2	ϵ^*	ϵ	ϵ^{2*}		$(x^2 - y^2, xy)$
	1	ϵ^{2*}	ϵ	ϵ^*	ϵ^2		



C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		$\epsilon = \exp(2\pi i/6)$
A	1	1	1	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
B	1	−1	1	−1	1	−1		
E_1	1	ϵ	$-\epsilon^*$	−1	$-\epsilon$	ϵ^*	$(T_x, T_y),$ (R_x, R_y)	(yz, zx)
	1	ϵ^*	$-\epsilon$	−1	$-\epsilon^*$	ϵ		
E_2	1	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$		$(x^2 - y^2, xy)$
	1	$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$		

C_7	E	C_7	C_7^2	C_7^3	C_7^4	C_7^5	C_7^6		$\epsilon = \exp(2\pi i/7)$
A	1	1	1	1	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
E_1	1	ϵ	ϵ^2	ϵ^3	ϵ^{3*}	ϵ^{2*}	ϵ^*	(T_x, T_y) (R_x, R_y)	(yz, zx)
	1	ϵ^*	ϵ^{2*}	ϵ^{3*}	ϵ^3	ϵ^2	ϵ		
E_2	1	ϵ^2	ϵ^{3*}	ϵ^*	ϵ	ϵ^3	ϵ^{2*}		$(x^2 - y^2, xy)$
	1	ϵ^{2*}	ϵ^3	ϵ	ϵ^*	ϵ^{3*}	ϵ^2		
E_3	1	ϵ^3	ϵ^*	ϵ^2	ϵ^{2*}	ϵ	ϵ^{3*}		
	1	ϵ^{3*}	ϵ	ϵ^{2*}	ϵ^2	ϵ^*	ϵ^3		

C_8	E	C_8	C_4	C_2	C_4^3	C_8^3	C_8^5	C_8^7		$\epsilon = \exp(2\pi i/8)$
A	1	1	1	1	1	1	1	1	T_z, R_z	$x^2 + y^2, z^2$
B	1	−1	1	1	1	−1	−1	−1		
E_1	1	ϵ	i	−1	$-i$	$-\epsilon^*$	$-\epsilon$	ϵ^*	$(T_x, T_y),$ (R_x, R_y)	(yz, zx)
	1	ϵ^*	$-i$	−1	i	$-\epsilon$	$-\epsilon^*$	ϵ		
E_2	1	i	−1	1	−1	$-i$	i	$-i$		$(x^2 - y^2, xy)$
	1	$-i$	−1	1	−1	i	$-i$	i		
E_3	1	$-\epsilon$	i	−1	$-i$	ϵ^*	ϵ	$-\epsilon^*$		
	1	$-\epsilon^*$	$-i$	−1	i	ϵ	ϵ^*	$-\epsilon$		

The D_n groups

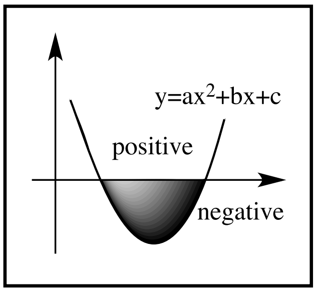
D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	−1	−1	T_z, R_z	xy
B_2	1	−1	1	−1	T_y, R_y	zx
B_3	1	−1	−1	1	T_x, R_x	yz

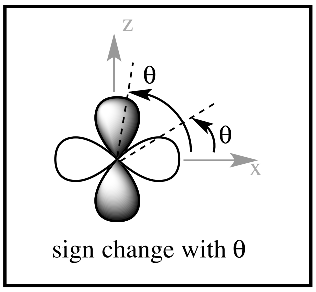
D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	−1	T_z, R_z	
E	2	−1	0	$(T_x, T_y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, zx)$

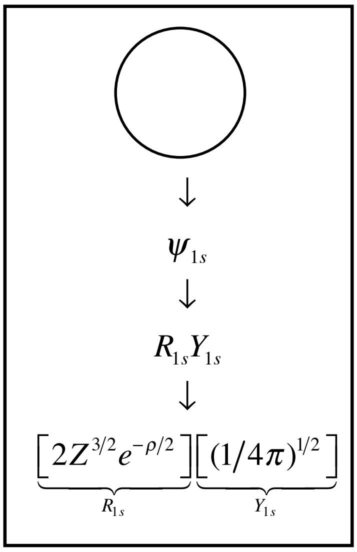
D_4	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	T_z, R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(T_x, T_y), (R_x, R_y)$	(yz, zx)

Revision: Atomic Orbitals

- wavefunction
  - have radial (R) and angular (Y) components
  - our cartoons represent outer portion
  - shaded part represents negative part of function
  - angular nature represented by the lobes



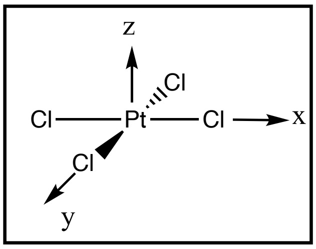


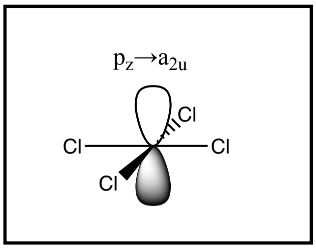


the "Orbitron" is a great web-site that plots AOs for you

Symmetry and Cartesian Functions

- 2 extra columns to character table, first contains, T_x, T_y, T_z and R_x, R_y, R_z
  - T=translation and R=rotation motions of the center of mass
  - T has same symmetry as x,y,z axes and p_x,p_y,p_z orbitals
  - R is used for vibrations, we won't consider it further here
- we can use this relationship for "short-cut"
- example: $[PtCl_4]^{2-}$ belongs to the D_{4h} point group
  - the pz AO on the Pt has same symmetry as T_z, A_{2u}

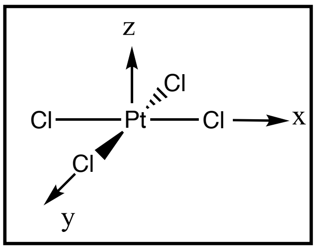


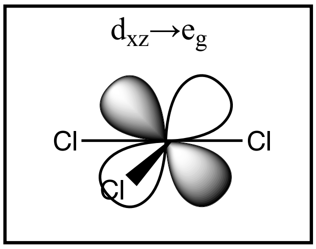


D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1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

Symmetry and Cartesian Functions

- end column contains binary functions, x^2, y^2, z^2, xz, yz and xy (sometimes we see x^2-y^2)
- relate to the dAOs, eg $z^2 \rightarrow dz^2$
- we can use this relationship for "short-cut"
- example: $[PtCl_4]^{2-}$ belongs to the D_{4h} point group
  - the dxz AO on the Pt has same symmetry as d_{xz}, E_g

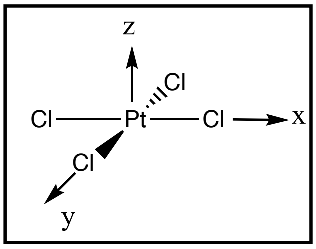




D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1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

In-Class Activity P2

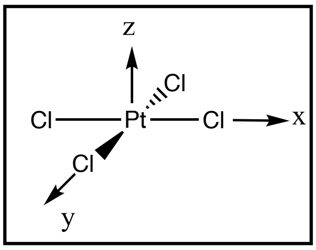
- for Pt in $[PtCl_4]^{2-}$
  - what is the symmetry of the px and py AOs?
  - what is the symmetry of the dxy AO?



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)	

In-Class Activity P2

- for Pt in $[PtCl_4]^{2-}$
  - what is the symmetry of the px and py AOs? **e_g**
  - what is the symmetry of the dxy AO?

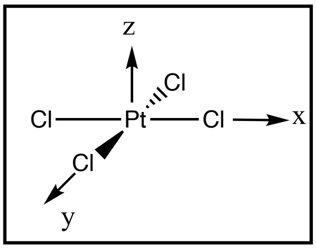


D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1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

In-Class Activity P2

- **for Pt in $[PtCl_4]^{2-}$**
  - **what is the symmetry of the px and py AOs?**
  - **what is the symmetry of the dxy AO?**

b_{2g}

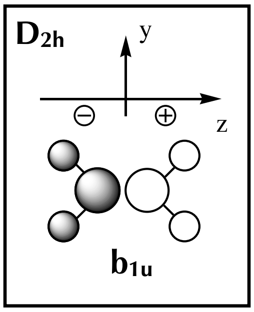


D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1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

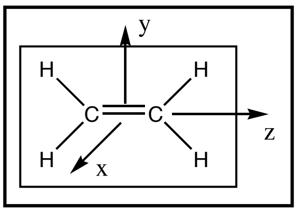
Symmetry and Cartesian Functions

- **for MOs look at the phase pattern!**
- **orbitals with the same phase pattern as an axis have the same symmetry label as the axis**

Short-cuts



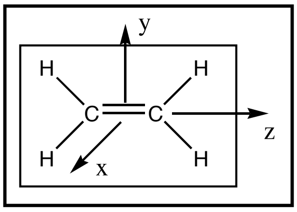
same symmetry as the z-axis



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	

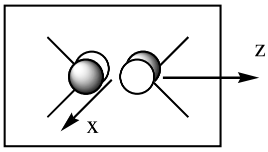
Symmetry and Cartesian Functions

- for MOs look at the phase pattern!
- orbitals with the same phase pattern as a dAO have the same symmetry as the corresponding cartesian function



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	

Short-cuts



2 p_π orbitals

↓

d_{xz} orbital

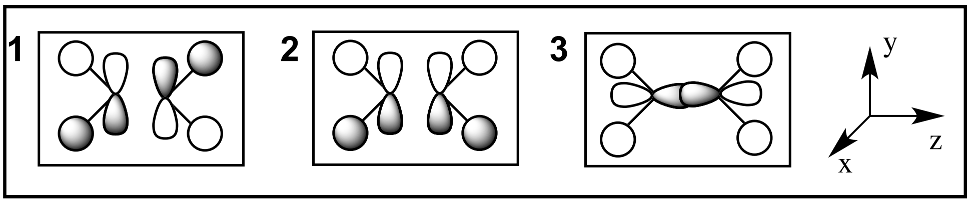
↓

b_{2g}

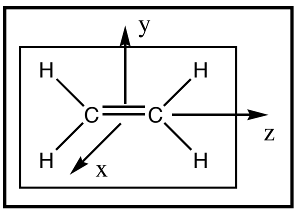
same symmetry as the dxz AO

In-Class Activity P3

- determine the symmetry of these MOs
  - from C_2H_4 which belong to the D_{2h} point group
  - explain your answer!



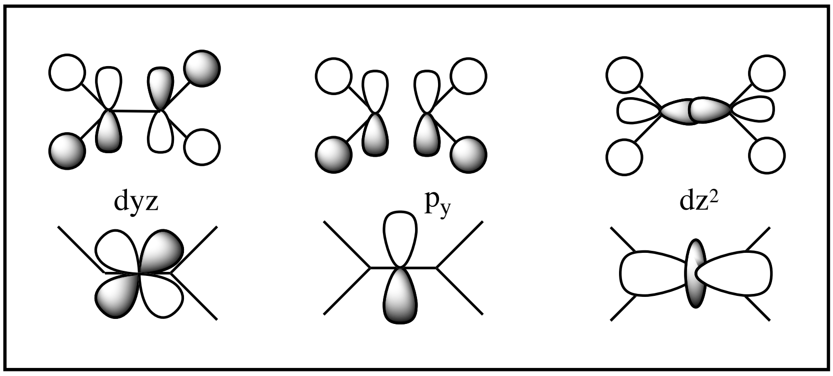
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	zx
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	T_z	
B_{2u}	1	−1	1	−1	−1	1	−1	1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



In-Class Activity P3

- **determine the symmetry of these MOs**

same symmetry as the dyz AO
b_{3g}



same symmetry as the dz² AO
a_g

same symmetry as the p_y AO
b_{2u}

Symmetry Labels

- **A and B singe representations**
  - **atoms/orbitals map onto each other**

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	(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 Labels

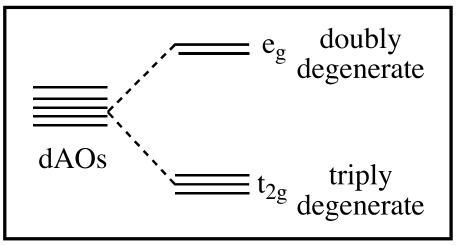
- A and B singe representations
  - atoms/orbitals map onto each other
- E doubly degenerate
  - don’t confuse with E operation!
  - orbitals as a group map onto each other
  - character =2 under E operation
- T triply degenerate
  - tetrahedral point groups (T_d)
  - character =3 under E operation

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	(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 Labels

- A and B singe representations
  - atoms/orbitals map onto each other
- E doubly degenerate
  - don’t confuse with E operation!
  - orbitals as a group map onto each other
  - character =2 under E operation
- T triply degenerate
  - tetrahedral point groups (T_d)
  - character =3 under E operation

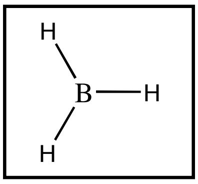
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	

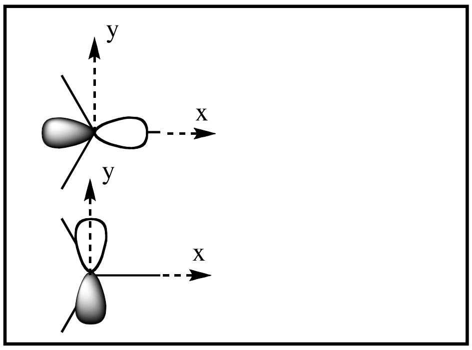


You have already seen e and t symmetry labels!

Degenerate Representations

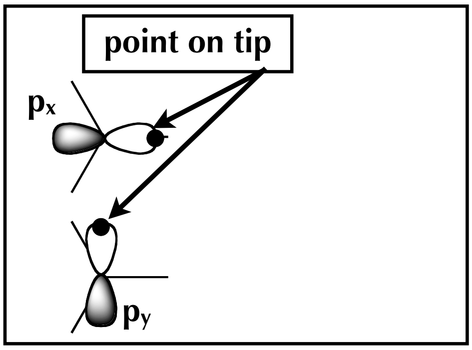
- **degenerate representations**
  - **example: (p_x,p_y) have e' symmetry in D_{3h}**





Degenerate Representations

- **degenerate representations**
  - **example: (p_x,p_y) have e' symmetry in D_{3h}**
- **character refers to BOTH components**
  - **how to work out the character?**
  - **take point on tip of each orbital**
  - **write the position in coordinates as**
  - **form matrix by combing the coordinates**

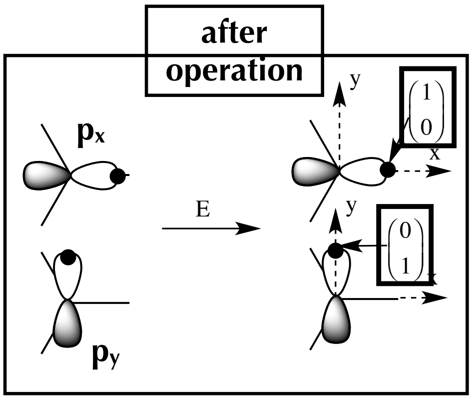


p_x p_y

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

Degenerate Representations

- **degenerate representations**
  - example: (p_x,p_y) have e' symmetry in D_{3h}
- **character refers to BOTH components**
  - how to work out the character?
  - take point on tip of each orbital
  - write the position in coordinates as
  - form matrix by combing the coordinates
  - perform the operation

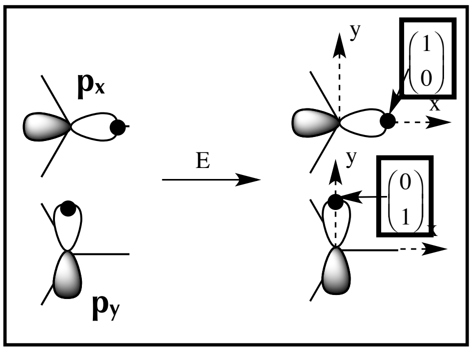


$$\begin{matrix} p_x & p_y \\ \downarrow & \downarrow \end{matrix}$$

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

Degenerate Representations

- **degenerate representations**
  - example: (p_x,p_y) have e' symmetry in D_{3h}
- **character refers to BOTH components**
  - how to work out the character?
  - take point on tip of each orbital
  - write the position in coordinates as
  - form matrix by combing the coordinates
  - perform the operation
  - the character is the TRACE of this matrix
  - trace=sum of diagonal terms
  - for this example (E) trace=1+1=2
  - character is 2

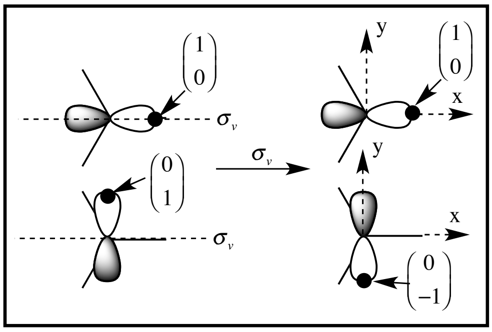


$$\begin{matrix} p_x & p_y \\ \downarrow & \downarrow \end{matrix}$$

$$E\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \boxed{1} & 0 \\ 0 & \boxed{1} \end{pmatrix}$$

Degenerate Representations

- **the character for the σ_v operation under D_{3h}**

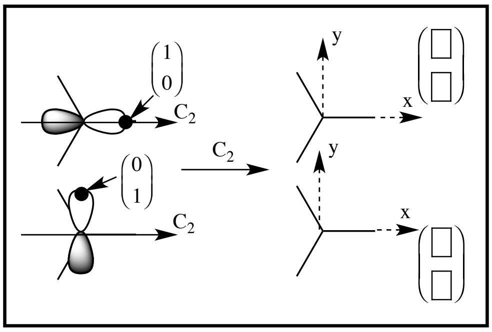


$$\sigma_v \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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	(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	

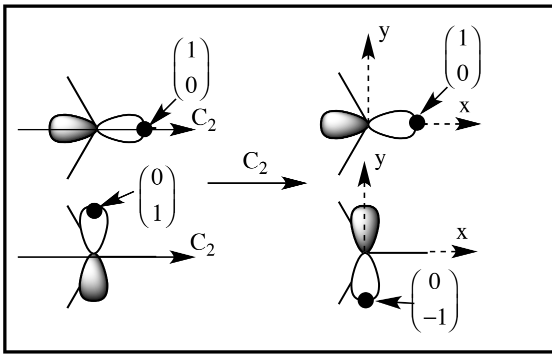
In-Class Activity P4

- **find character for the C_2 operation under D_{3h}**



In-Class Activity P4

- find character for the C_2 operation under D_{3h}



$$C_2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- trace=sum of diagonal terms
- trace=1+-1=0
- character is 0

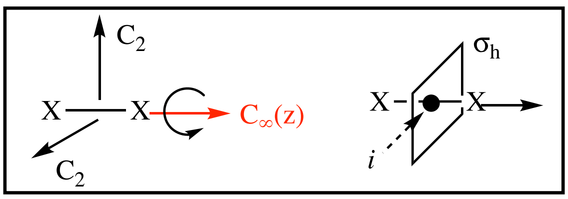
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	

Point Groups for Linear Molecules

- homonuclear X_2 diatomic molecules
  - examples: O_2, N_2, Cl_2 etc.
  - are linear
  - have a center of inversion
  - point group $D_{\infty h}$
- heteronuclear XX' diatomic molecules
  - examples: CO, HF, $[CN]^-$ etc.
  - are linear
  - have NO center of inversion
  - oint group $C_{\infty v}$

$D_{\infty h}$	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		
...	...	...	...	...	...	...	...	...		

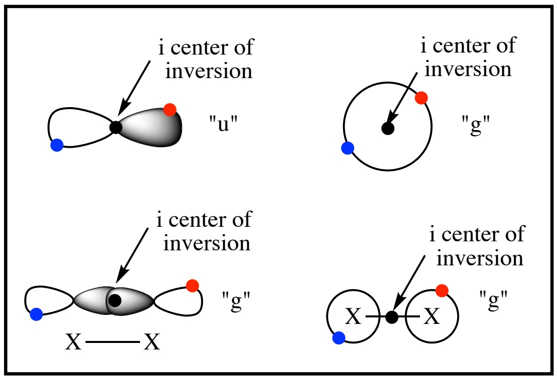
have a difficult character tables!



Point Groups for Linear Molecules

- labels are in Greek
  - familar with "little" σ, π, δ
  - but tables use the capital versions Σ, Π, Δ
  - are linear
  - have a center of inversion
  - point group $D_{\infty h}$
- center of inversion
  - leads to "gerade" g
  - no change under inversion
  - and "ungerade" u
  - phase change under inversion
- look at other point groups some have labels with u and g subscripts

$D_{\infty h}$	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		
…	…	…	…	…	…	…	…	…		



Point Groups for Linear Molecules

- ∞ number of coincident C_∞ axes
  - start with C_2, 180º rotation
  - then make the rotation angle smaller and smaller and …
  - down to an infinitesimal rotation φ
  - an infinite number of infinitesimal rotations is "continious"
  - $D_{\infty h}$ and $C_{\infty v}$ are continious groups

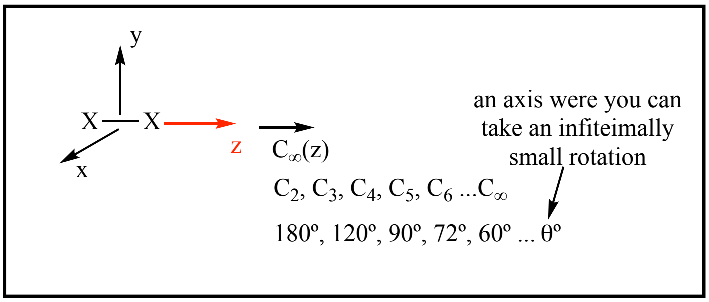
$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…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

C_{lots} rotation

Point Groups for Linear Molecules

- C_∞ axis is principle axis
- but also coincident with C_2, C_3, C_4, C_5 ….
  - means there are only 2 unique operations per axis
  - eg if φ=30° then rotation by 2φ=60° has already been counted
  - hence $2C_\infty$ in character table

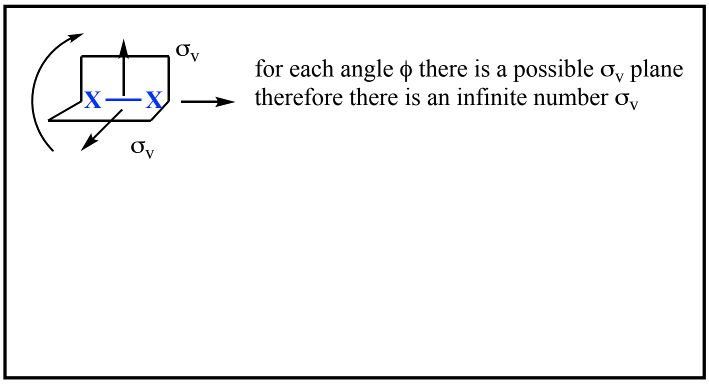
$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…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



Point Groups for Linear Molecules

- C_∞ axis is principle axis
- each rotation angle φ has an associated mirror plane σ_v
  - thus there are $\infty\sigma_v$

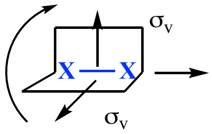
$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…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



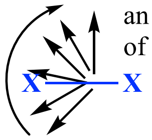
Point Groups for Linear Molecules

$D_{\infty h}$	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		
…	…	…	…	…	…	…	…	…		

- C_∞ axis is principle axis
- each rotation angle φ has an associated mirror plane σ_v
  - thus there are $\infty\sigma_v$
- perpendicular to C_∞ are an ∞C_2 axes



for each angle ϕ there is a possible σ_v plane therefore there is an infinite number σ_v



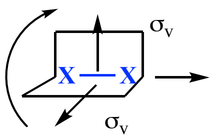
an infinite number of C_2 axes

Point Groups for Linear Molecules

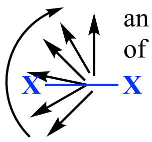
$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	−1	1	1	…	−1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…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

- C_∞ axis is principle axis
- each rotation angle φ has an associated mirror plane σ_v
  - thus there are $\infty\sigma_v$
- perpendicular to C_∞ are an ∞C_2 axes

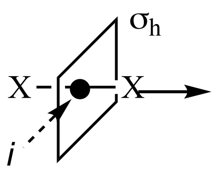
- perpendicular is σ_h plane
  - not in operations at top!
  - the ∞C_2 are equivalent
  - does appear in $2S_\infty$ axes
- $C_{\infty v}$ has no σ_h plane
  - therefore no S_∞ axes



for each angle ϕ there is a possible σ_v plane therefore there is an infinite number σ_v

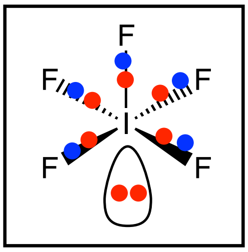


an infinite number of C_2 axes



In-Class Activity P5

- IF_5 has the following molecular shape



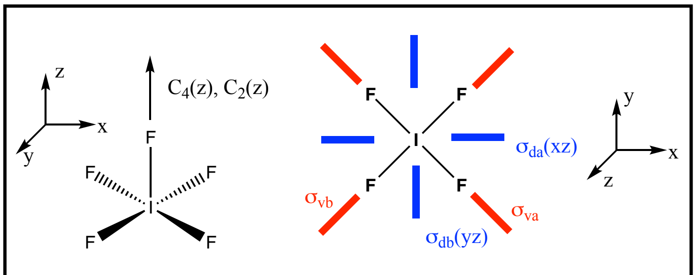
square based pyramid

- Determine the point group and draw all of the symmetry elements on a diagram of the molecule.
- Where there are multiple operations in the header of the character table (eg $2C_4$) identify if they are due to
  - multiple operations on a single element
  - or are due to multiple elements
- For the highest rotation axis (eg C_4) identify operations that have another equivalent operation, and idenitfy the equivalent operation.

In-Class Activity P5

- Determine the point group and draw all of the symmetry elements on a diagram of the molecule.
  - the F coming out of the page stops the C_2 rotations
- point group
  - linear?NO
  - T_d or O_h? NO
  - principle axis? YES C_4
  - $4C_2$ perpendicular to C_4? NO
  - σ_h? NO
  - $4(\sigma_v+\sigma_d)$? YES
  - C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(T_x, T_y), (R_x, R_y)$	(yz, zx)

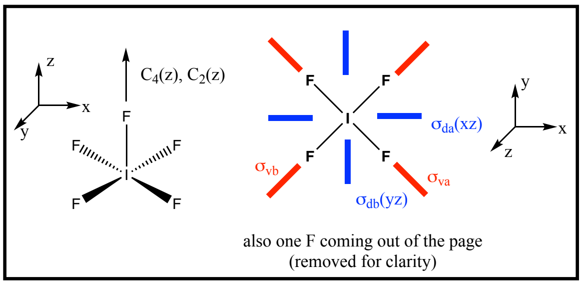


also one F coming out of the page (removed for clarity)

In-Class Activity P5

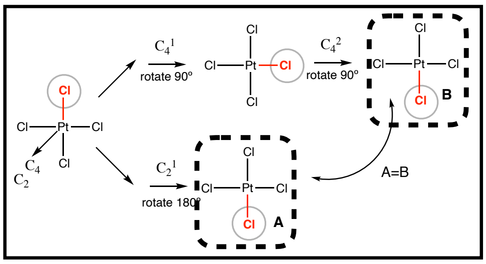
- Where there are multiple operations in the header of the character table (eg $2C_4$) identify if they are due to
  - multiple operations on a single element
  - or are due to multiple elements
- the $2C_4$ operations are around a single element the C_4 axis
- the $2\sigma_v$ and $2\sigma_d$ operations are due to the presence of different symmetry elements

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(T_x, T_y), (R_x, R_y)$	(yz, zx)

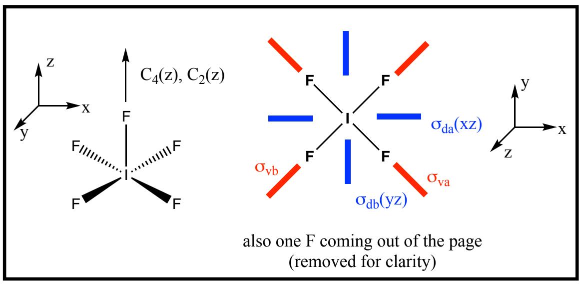


In-Class Activity P5

- For the highest rotation axis (eg C_4) identify operations that have another equivalent operation, and idenitfy the equivalent operation.
  - there are 4 possible C_4 operations C_4^1, C_4^2, C_4^3, C_4^4
  - the C_4^1 and C_4^3 are unique
  - the $C_4^1 = C_2^1$ and $C_4^4 = E$



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(T_x, T_y), (R_x, R_y)$	(yz, zx)



Key Points

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