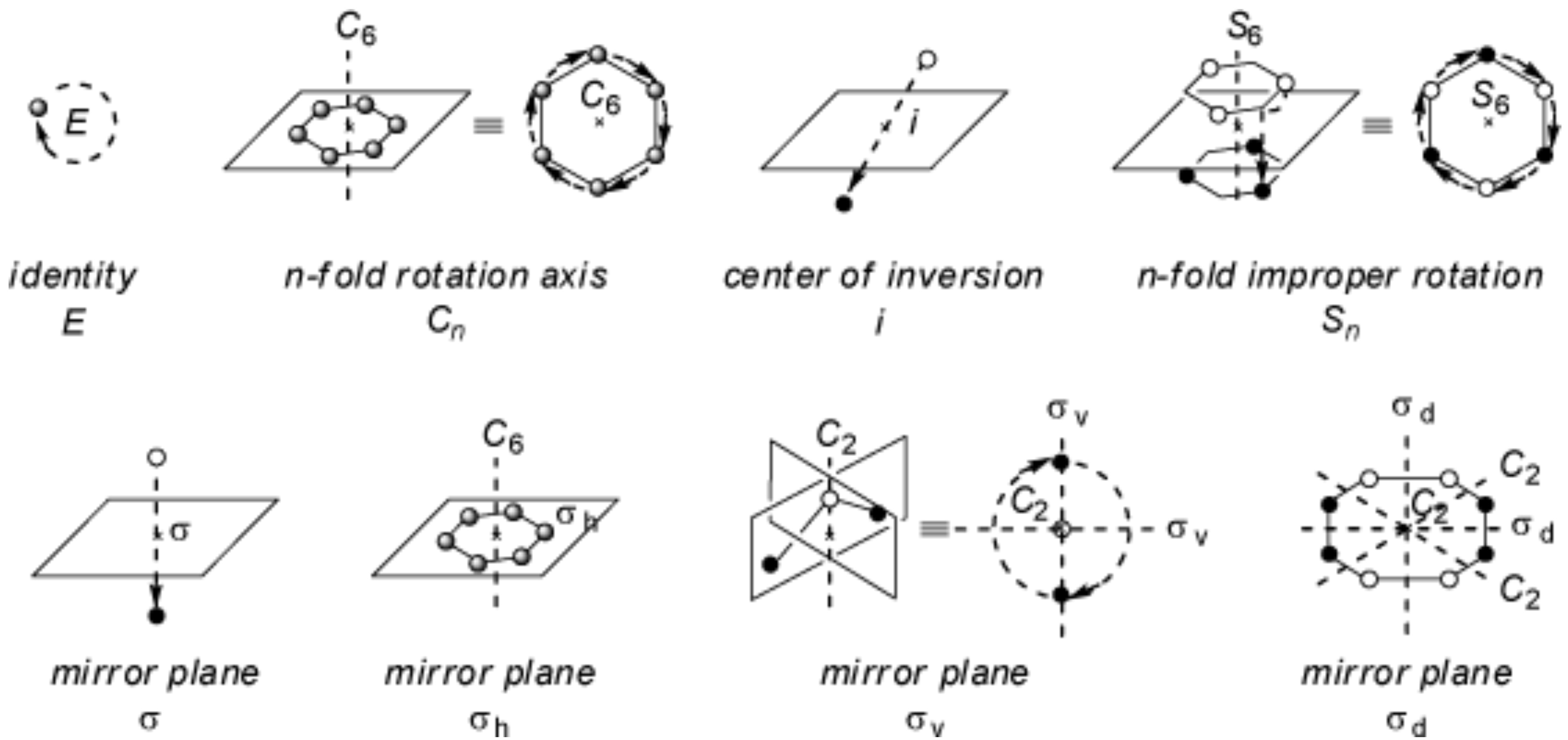
POINT GROUPS

MFT Chapter 4

Symmetry operations



Point groups

- Every molecule has a set of symmetry operations associated with it (even if it is only E!)
- The complete set of symmetry operations that describe a molecule is called a Point Group

- Within a Point group, every possible product of two operations in the set is also an operation in the set

- **A molecule's point group describes all of the symmetry the molecule contains, we can apply this information when thinking about the properties of this molecule (to be covered after first midterm)**

Steps to identify a point group

1) Does the molecule belong to special groups with very **low** (C_1, C_s, C_i) **or high** ($C_{\infty v}$, $D_{\infty h}$, T_d, O_h, I_h) **symmetry**?

2) If not, what is the principal rotation axis (**C_n** with highest n)?

3) Are there **C_2 axes perpendicular** to the principal rotation axis?

4) Is there a **σ_h** perpendicular to the principal rotation axis?

5) Are there mirror planes that contain the prinicpal rotation axis (**σ_v** or **σ_d**)?

6) Is there a collinear **S_{2n}** axis with the principal C_n axis?

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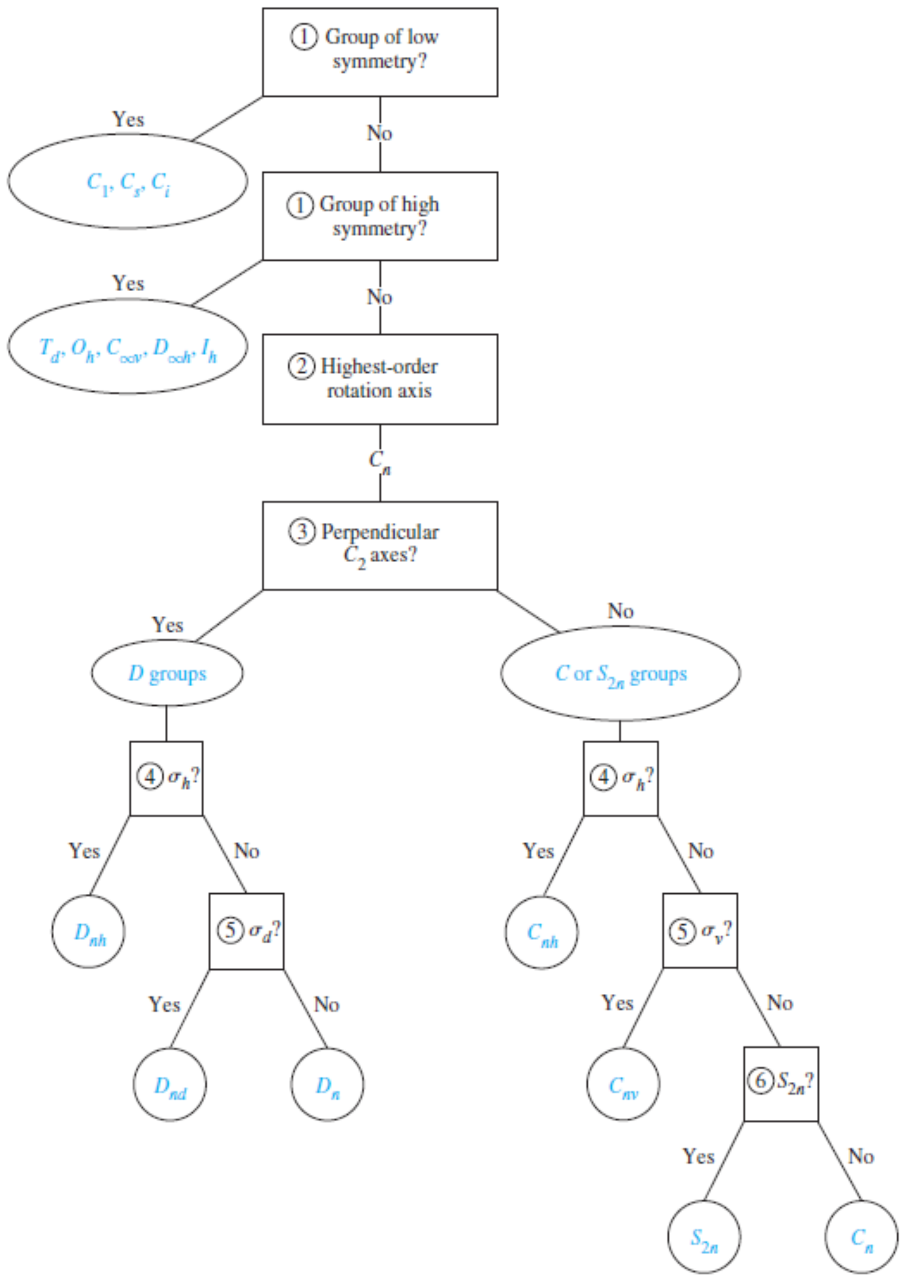
Point group flow chart



Comments on Schoenfleiss notation

- Subscript ‘n’ comes from principal rotation axis C_n
- ‘D’ indicates that there are C_2’s perpendicular to principal rotation axis. C and S do not have these
- In ‘D’ groups, can have ‘h’ and ‘d’ subscripts. ‘h; means there is a σ_h, ‘d’ means there is not a σ_h but there are mirror planes parallel to principal rotation axis
- In ‘C’ groups, can have ‘h’ and ‘v’ subscripts. ‘h; means there is a σ_h, ‘v’ means there is not a σ_h but there are mirror planes parallel to principal rotation axis

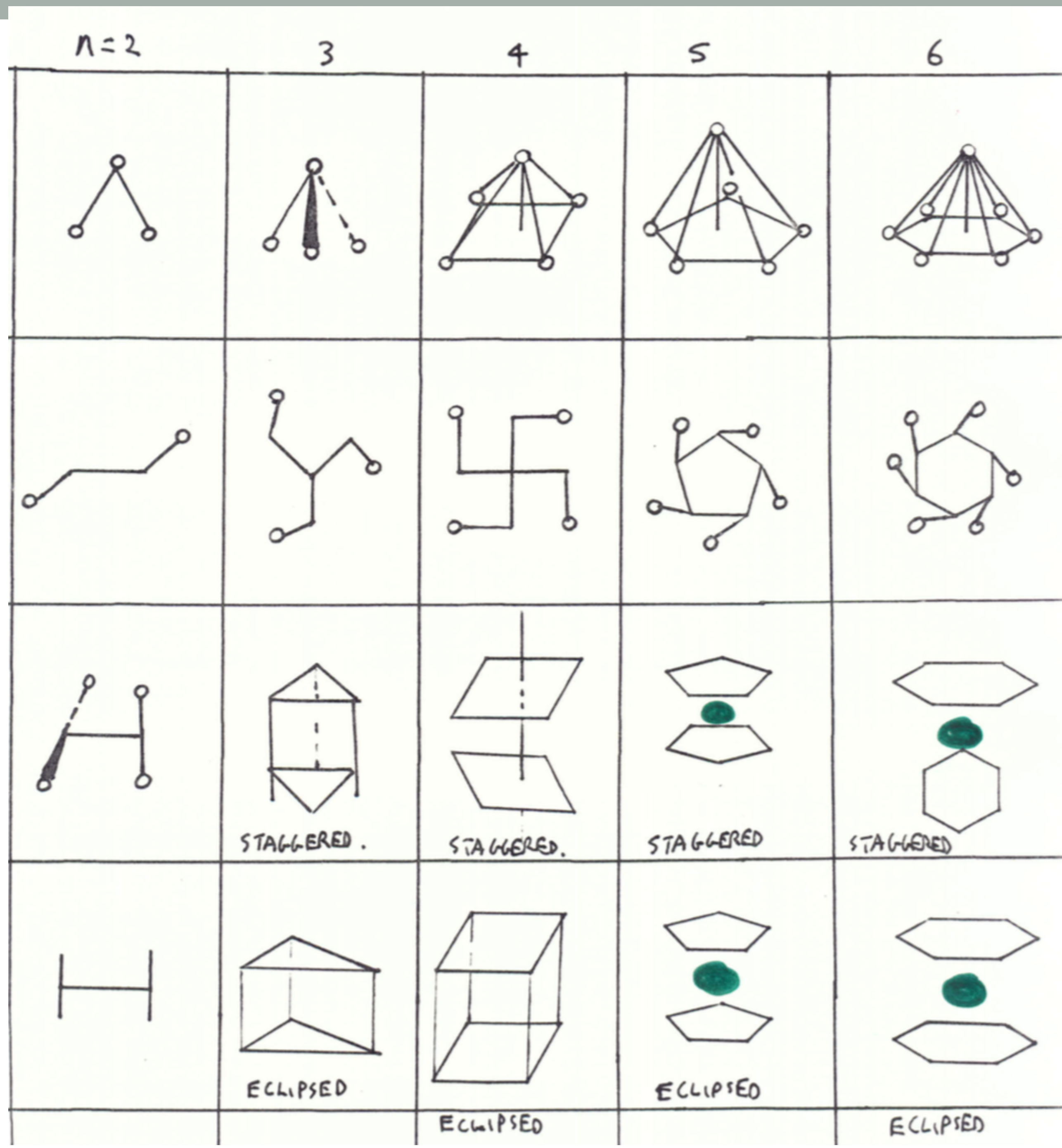
Point group short cuts

C_{nv}

C_{nh}

D_{nd}

D_{nh}



CHARACTER TABLES

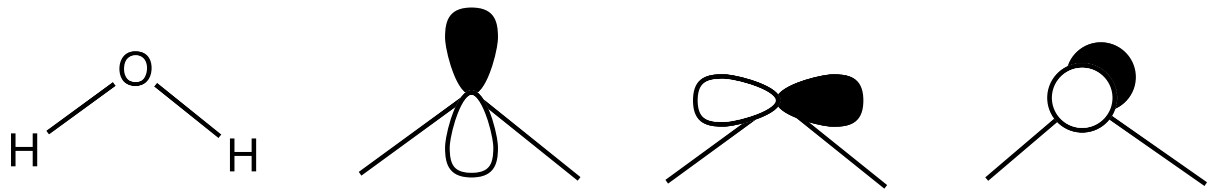
MFT Chapter 4

Character tables

- Now that we have learned how to assign point groups, we can use these point groups to help predict properties of a molecule
- Character tables are a complete list of symmetry elements and a set of “instructions” for systematically describing the symmetry properties of the molecule, and any ‘part’ of that molecule
- These tables will be our tools to understand the spectroscopy and behavior of different compounds

Character tables

- Many parts of a molecule do not possess the full symmetry of its point group
  - Examples: orbitals (mathematical functions)



p orbitals from oxygen in H_2O

  - Electronic states and vibrational states (spectroscopy)
  - Sets of ligands in a metal complex

- However, as they are part of the overall molecule, their properties follow what is described by the molecules point group and character table

Character Table

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

Point group

Symmetry operations

Symmetry operations are grouped together in classes: in this case, there are 4 classes, each containing one symmetry operation. However, in many point groups, multiple operations belong to one class

Order (h): add up coefficients of symmetry element at the top of each column

h = 1 + 1 + 1 + 1 = 4

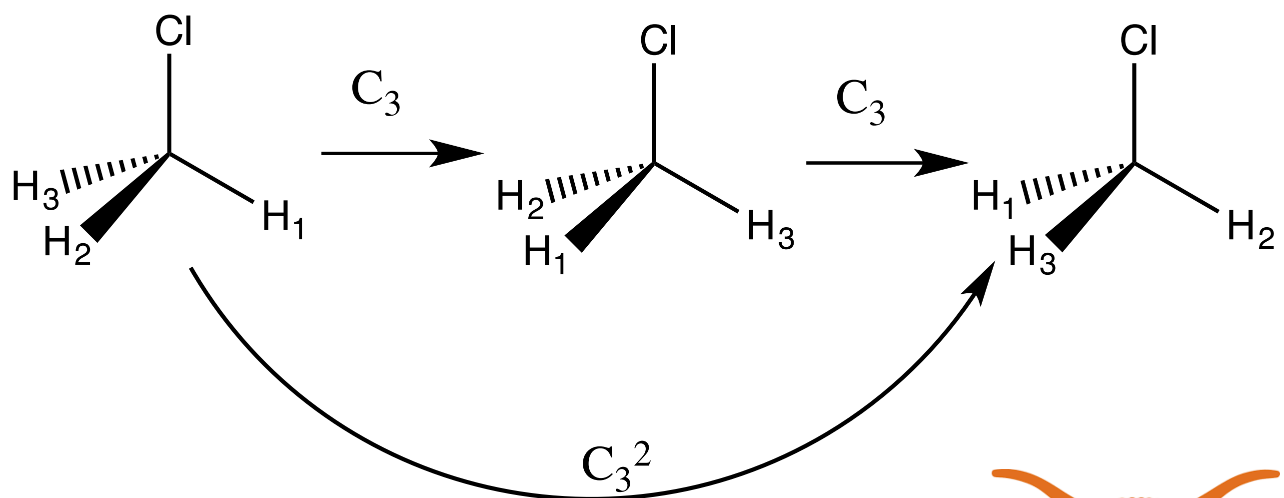
Multiple operations in one class (three different reflection planes)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Point group

Symmetry operations

Multiple operations in one class (in this case, it's C_3 and C_3^2)



h = 1 + 2 + 3 = 6

Character Table

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

Characters

Characters are the numbers in the character table.

These characters make up what are called *irreducible representations.*

The sum of the squares of the characters multiplied by the coefficient of the class they are in equal the order (h)

C_{2v}: $1^2 + 1^2 + 1^2 + 1^2 = 4$

C_{3v}: $1^2 + 2x1^2 + 3x1^2 = 6$

Character Table

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

Irreducible representation

Each row is called an irreducible representation, we'll call them $\mathrm{I_r}$ for short

Each $\mathrm{I_r}$ has a symmetry label on the left (Mulliken symbol).
In this case, A_1, A_2, B_1, B_2

The number of irreducible representations equals the number of classes

*w.r.t. = with respect to

Symmetry labels/Mulliken Symbols

C_{2v}
A_1
A_2
B_1
B_2

O_h
A_{1g}
A_{2g}
E_g
T_{1g}
T_{2g}
A_{1u}
A_{2u}
E_u
T_{1u}
T_{2u}

Each row of a character table is rigorously labeled to indicate the different irreducible representations.

All the letters, subscripts, and superscripts hold a certain meaning about the symmetry of a particular irreducible representation

C_{3v}
A_1
A_2
E

D_{3h}
A_1'
A_2'
E'
A_1''
A_2''
E''

$$X_y^z$$

*w.r.t. = with respect to

Symmetry labels/Mulliken Symbols X_y^z

- X: can be A, B, E, or T
- A: a singly degenerate irreducible representation, **symmetric** with respect to rotation about principal C_n
- B: a singly degenerate irreducible representation, **antisymmetric** with respect to rotation about principal C_n

Singly degenerate: character under E = 1

Character Table

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

Symmetry labels/Mulliken Symbols X_y^z

- X: can be A, B, E, or T
- E: a doubly degenerate irreducible representation (character under E = 2)
- T: a triply degenerate irreducible representation (character under E = 3)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	2	-1	0	0	2	2	0	1	2	0		$2z^2-x^2-y^2, x^2-y^2$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	R_x, R_y, R_z	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xz, yz, xy
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x, y, z	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Symmetry labels/Mulliken Symbols X_y^z

- y: can be nothing, a number (1 or 2), a letter (u or g), or both a number and a letter
- 1: symmetric w.r.t. σ_v or a perpendicular C_2
- 2: antisymmetric w.r.t. σ_v or a perpendicular C_2

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

*w.r.t. = with respect to

Symmetry labels/Mulliken Symbols X_y^z

- y: can be nothing, a number (1 or 2), a letter (u or g), or both a number and a letter
- g: 'gerade', symmetric w.r.t. an inversion center
- u: 'ungerade', antisymmetric w.r.t. an inversion center

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	2	-1	0	0	2	2	0	1	2	0		$2z^2-x^2-y^2, x^2-y^2$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	R_x, R_y, R_z	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xz, yz, xy
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x, y, z	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Symmetry labels/Mulliken Symbols X_y^z

- z: can be nothing, ‘, or “
- ‘ : symmetric w.r.t. σ_h
- “ : antisymmetric w.r.t. σ_h

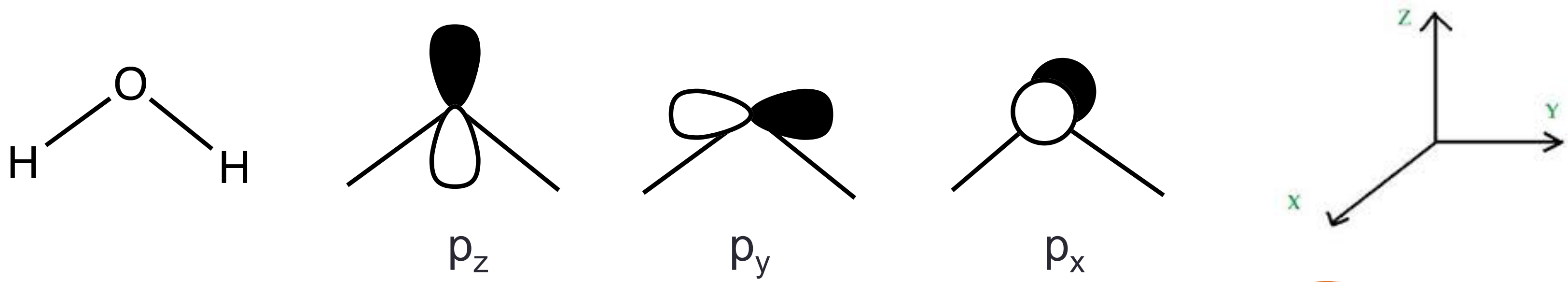
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	x,y	x^2-y^2, xy
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	xz, yz

Character Table

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

Indicates transformation properties of vectors along x, y, z and rotations around the x,y,and z axes (R_x, R_y, R_z)

We can look at these and determine, for example the symmetry of p orbitals within our molecule



Character Table

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

Indicates transformation properties of the squares and binary products of vectors.

We can look at these to determine the symmetry of the s and d orbitals within our molecule.

Note: s corresponds to the line with x^2, y^2, z^2 will always correspond to the irreducible representation that has all 1 values (think: how does s orbital change with each symmetry operation?)

d orbitals will correspond with line that matches their label

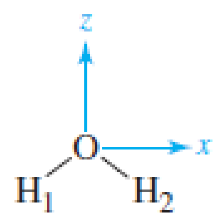
You will NOT be tested on this slide

Where do character tables come from?

- Matrix algebra (thorough description in MFT)
- Every symmetry element can be represented as a transformation matrix over the x, y, and z coordinates

Irreducible representations come from the numbers in these matrices

TABLE 4.8 Representation Flowchart: $H_2O(C_{2v})$



Symmetry Operations

Reducible Matrix Representations

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2: \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v'(yz): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character tables

- These character tables are derived from matrix representations of the different symmetry operations, however you are not explicitly expected to understand the matrix math beyond what is presented in lecture notes
  - MFT goes much more in depth to the matrix math if you are interested (Section 4.3), but most of it is beyond the scope of this course due to time constraints