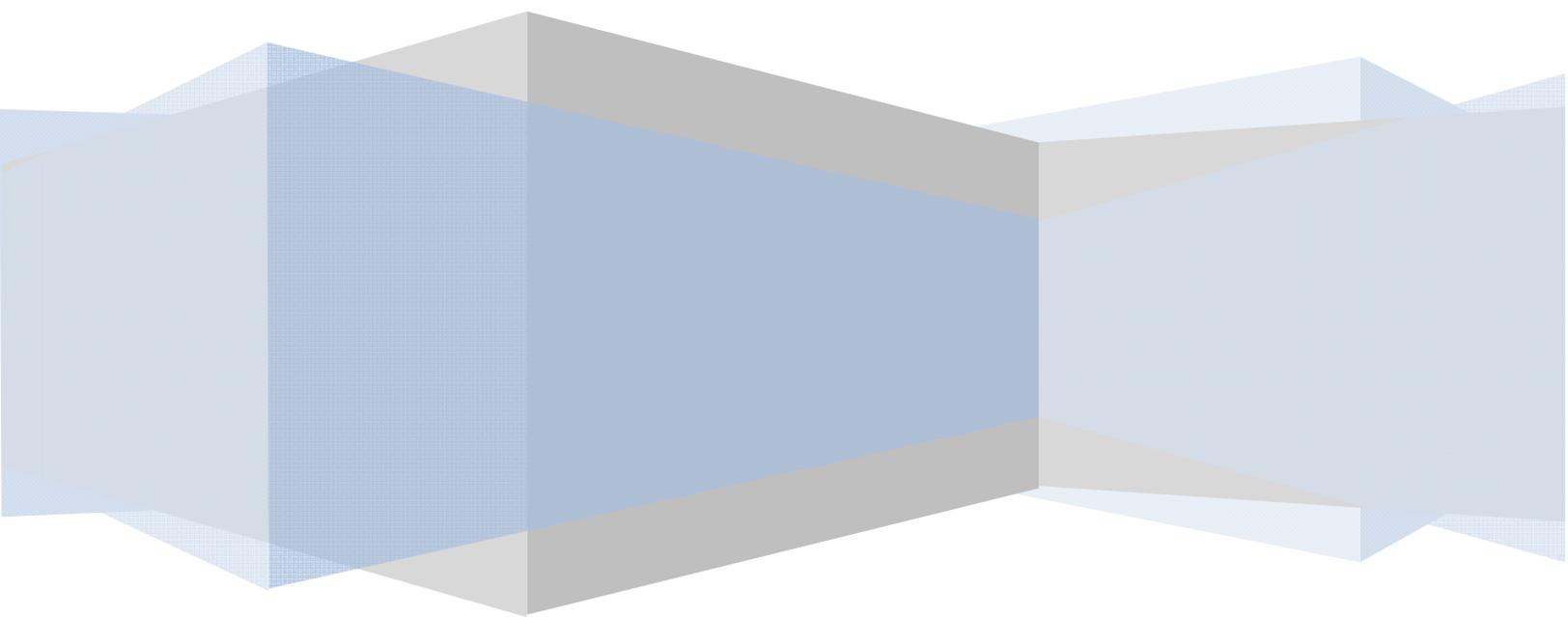


Introduction to the Chemical Applications of Group Theory

Course Lecture Notes



L.E. Laverman

Acknowledgments and Web Resources

These lecture notes have been derived from several sources including “Group Theory and Chemistry” by David M. Bishop (ISBN-13: 978-0-486-67355-4) and Chemical Applications of Group Theory by F. Albert Cotton (ISBN-10: 0-471-17570-6).

Pictures of Molecular orbitals were obtained from internet sources as follows:

Carbonate π orbitals

University of Lethbridge

http://classes.uleth.ca/200803/chem2000a/chem2000_problems_02_answers.pdf

Benzene π orbitals

Technical University of Darmstadt

<http://csi.chemie.tu-darmstadt.de/ak/immel/script/redirect.cgi?filename=http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/molecular/benzene.html>

See also for organic MO's and hybrid orbital systems.

<http://csi.chemie.tu-darmstadt.de/ak/immel/index.html> (click the “tutorials” link)

There are many 3D VRML models that can be rotated in real time on your web browser.

For help with symmetry operations and symmetry elements see:

<http://www.molwave.com/software/3dmolsym/3dmolsym.htm>

Animations of molecular vibrations can be seen here:

<http://www.molwave.com/software/3dnormalmodes/3dnormalmodes.htm>

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Introduction

Symmetry: Relationship between parts of an object with respect to size, shape and position.

Easy to recognize symmetry in nature: Flowers, leaves, animals etc....

Group Theory developed in the late 1700's. Early 1800's Évariste Galois (1811-1832) invented much of the fundamentals of group theory. This coincided with developments in matrix mathematics.

Chemists use a subset of group theory called **representation theory**.

Group characters were primarily the work of George Frobenius (1849-1917)

Early chemical applications to quantum mechanics came from the work of Hermann Weyl (1885-1955) and Eugene Wigner (1902-1995)

Symmetry Elements and Symmetry Operations

A symmetry element is a geometric entity (point, line or plane)

A symmetry operator performs an action on a three dimensional object

Symmetry operators are similar to other mathematical operators (\times , \div , $+$, \log , \cos , etc...)

We will be use only five types of operators in this subject

Operator	Symbol
Identity	E
Rotation	C
Mirror plane	σ
Inversion	i
Improper rotation	S

All symmetry operators leave the shape (molecule) in an equivalent position, i.e. it is indistinguishable before and after the operator has performed its action.

Identity (*E*)

This operator does nothing and is required for completeness. Equivalent to multiplying by 1 or adding 0 in algebra.

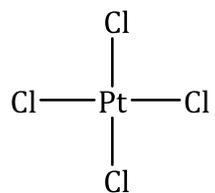
Rotation (*C*)

Rotate clockwise around an axis by $2\pi/n$ if the rotation brings the shape (molecule) into an equivalent position.

The symmetry element is called the **axis of symmetry**. For a $2\pi/n$ rotation there is an n-fold axis of symmetry. This is denoted as C_n .

Many molecules have more than one symmetry axis. The axis with the largest n is called the **principal axis**.

Consider a square planar molecule like PtCl_4 .



C_4 C_4^2 C_4^3 C_4^4 possible rotations. $C_4^2 \rightarrow C_2$ and $C_4^4 \rightarrow E$

We classify this as E , $2C_4$, C_2 . There are also two other C_2 axes (along the bonds and between the bonds)

Reflection (σ)

The shape (molecule) is reflected through a plane. (spiegel is German for “mirror”)

If a plane is \perp to the principal rotation axis then it is called σ_h (horizontal). If it is along the principal axis then it is called σ_v (vertical). There may be more than one σ_v . If the plane bisects an angle between 3 atoms then it is called σ_d (dihedral).

The reflection plane is the symmetry element.

Inversion (i)

All points in the shape (molecule) are reflected through a single point. The point is the symmetry element for inversion. This turns the molecule inside out in a sense. The symmetry element is the point through which the shape is inverted.

Improper Rotation (S)

Rotation by $2\pi/n$ followed by reflection, $\sigma \perp$ to the rotation axis. Since performing σ two times is the same as doing nothing (E), S can only be performed an odd number of times.

$$S_n^k = \sigma_h C_n^k \quad \text{if } k \text{ is odd}$$

$$S_n^k = C_n^k \quad \text{if } k \text{ is even}$$

k must be an odd value

$$\text{e.g. } S_3^2 = C_3^2 \text{ and } S_3^5 = \sigma_h C_3^5$$

Additionally...

$$S_1 = \sigma_h$$

$$S_n^n = \sigma_h \quad \text{if } n \text{ is odd}$$

$$S_n^n = E \quad \text{if } n \text{ is even}$$

The symmetry element for S is the rotation axis.

Immediate Applications of Symmetry

Dipole Moments

If a molecule has a dipole moment then the dipole must lie along the symmetry elements (lines, planes).

- If a molecule has \perp axis of rotation, then no dipole exists.
- If there is a σ , then the dipole must lie within the plane. If there are multiple σ the dipole must lie at the intersection of the planes.
- If a molecule has an inversion center (i) then no dipole exists.

Examples with H_2O , NH_3 , PtCl_4 .

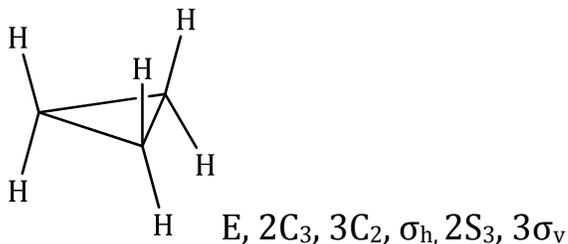
Optical Activity

In general, if a molecule has an improper rotation (S_n), then it is optically inactive. This is because, a molecule with an S_n is always superimposable on its mirror image.

Symmetry Operations

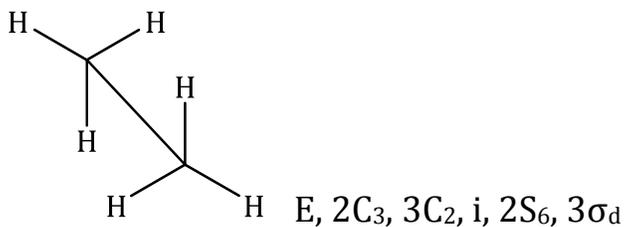
Identifying all symmetry elements and operations in molecules.

Cyclopropane – D_{3h}

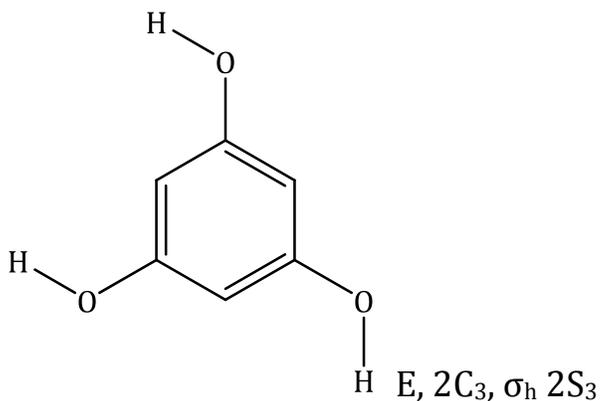


There is an S_3^1 and an S_3^5 (also called S_3^{-1})

Ethane (staggered) – D_{3d}



1,3,5-trihydroxybenzene (planar) – C_{3h}



There is an S_3^1 and an S_3^5 (also called S_3^{-1})

Algebra of Operators

An operator is a symbol for the operation (rotation, reflection, etc...)

e.g. C_3 is the operator for the operation of clockwise rotation by $2\pi/3$

Operators can operate on functions $f(x)$ to generate new functions

e.g. $O \equiv$ multiply by 3

$$f(x) = 2 + 3x^2 \text{ Then } Of(x) = 6 + 9x^2$$

O can be defined any way we like, d/dx , $()^2$, etc...

Special case of linear operators

Linear operators have the following property

$$O(f_1 + f_2) = Of_1 + Of_2$$

And $O(kf_1) = kOf_1$ where k is a constant

Differentiation clearly is a linear operator

$$\frac{d}{dx}(x^2 + x) = 2x + 1 \text{ or } \frac{d}{dx}x^2 + \frac{d}{dx}x = 2x + 1$$

and

$$\frac{d}{dx}3x^2 = 3\frac{d}{dx}x^2 = 6x$$

Algebra of linear operators

1. Sum Law
2. Product Law
3. Associative Law
4. Distributive Law

Sum Law

$$(O_1 + O_2)f(x) = O_1f(x) + O_2f(x)$$

Product Law

$$O_1O_2f(x) = O_1(O_2f(x))$$

O_2 operates first to produce a new function, then O_1 operates to produce another new function.

Note: the order of operations is important here. O_1O_2 may not be the same as O_2O_1 , i.e. operators do not necessarily commute with each other.

Associative Law

$$O_1(O_2O_3) = (O_1O_2)O_3$$

2nd 1st 2nd 1st

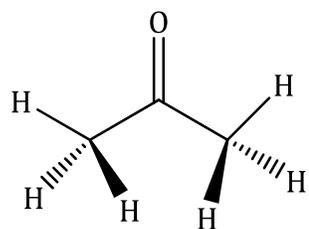
Distributive Law

$$O_1(O_2 + O_3) = O_1O_2 + O_1O_3$$

and

$$(O_2 + O_3)O_1 = O_2O_1 + O_3O_1$$

Do symmetry operators obey these laws? (they do)



consider acetone $E, C_2, \sigma_{v1}, \sigma_{v2}$

Sum Law: there is no process to “add” symmetry operators

Algebra of Symmetry Operators

Product Law:

We define the product of symmetry operators as: do one operation followed by another:

e.g. PQf means apply Q to f and then apply P to the result where P and Q are some symmetry operation. Or, alternatively $PQ = R$ where R is also a symmetry operation.

$$(C_2\sigma_{v1})f = C_2(\sigma_{v1})f$$

$C_2\sigma_{v1} \rightarrow \sigma_{v2}$ and $C_2(\sigma_{v1})f$ results in the same configuration as $\sigma_{v2}f$

Associative Law:

$$C_2(\sigma_{v1} \sigma_{v2})f = (C_2\sigma_{v1}) \sigma_{v2}f$$

$$\sigma_{v1} \sigma_{v2} \rightarrow C_2 \quad C_2\sigma_{v1} \rightarrow \sigma_{v2}$$

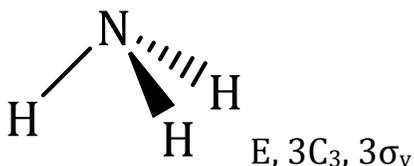
$$C_2C_2 \rightarrow E \quad \sigma_{v2} \sigma_{v2} \rightarrow E$$

Generically $(PQ)R = P(QR)$

Distributive Law:

There is no process to “add” symmetry operators

Consider the ammonia molecule (C_{3v})



Note here that $C_3^1 C_3^2 = E$

If two operators combine to give the identity, we say that they are inverse to each other.

$$C_3^2 = C_3^{-1} \text{ and } C_3 C_3^{-1} = E = C_3 C_3^2$$

It is also true that $C_3 C_3^{-1} = C_3^{-1} C_3 = E$ or generically $PQ = QP = E$

i.e. symmetry operators that are inverse to one another commute.

$$\sigma_h \sigma_h = E$$

$$i i = E$$

mirror planes are always inverse to themselves, likewise inversion is always inverse to itself.

Generically we write $(PQ)^{-1} = P^{-1}Q^{-1}$

Definition of a Group

There are four defining rules for groups.

1. The combination of any two elements as well as the square of each element must be in the group.

Combining rule can be defined as anything (multiplication, differentiation, one followed by another, etc...)

$$PQ = R; R \text{ must be in the group}$$

The commutative law may not hold $AB \neq BA$

2. One element must commute with all other elements and leave them unchanged. That is, an identity element must be present.

$$ER = RE = R; E \text{ must be in the group}$$

3. The associative law must hold.

$$P(QR) = (PQ)R; \text{ for all elements}$$

4. Every element must have an inverse which is also in the group.

$$RR^{-1} = R^{-1}R = E; R^{-1} \text{ must be in the group}$$

Summary

Definition of a group

$$PQ = R \quad R \text{ must be in the group}$$

$$ER = RE = R \quad E \text{ must be in the group}$$

$$P(QR) = (PQ)R \quad \text{for all elements}$$

$$RR^{-1} = R^{-1}R = E \quad R^{-1} \text{ must be in the group}$$

Example Groups

With a combining rule of addition, *all integers* form a group.

The identity element is 0, and the inverse of each element is the negative value.

This is an example of an *infinite group*.

=====

With a combining rule of multiplication, we can form a finite group with the following set {i, -i, 1, -1}

The identity element is 1 in this case.

=====

A set of matrices can also form a finite group with the combining rule of matrix multiplication.

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

The identity matrix is $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$

e.g.

$$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$\sum_k^n A_{ik} \times B_{kj} = (AB)_{ij}$$

A_{ik} = element in the i^{th} row and k^{th} column

Lastly, the set of symmetry operators (not symmetry elements) present for a given molecular shape forms a group with the combining rule of one followed by another.

These types of groups are called *point groups*.

Group Multiplication Tables

The number of elements in the group is called the order of the group (h)

Rearrangement Theorem:

In a group multiplication table, each row and column lists each element in the group once and only once. No two rows or two columns may be identical.

Consider a group of order 3

G_3	E	A	B
E	E	A	B
A	A	?	?
B	B	?	?

There are two options for filling out the table $AA = B$ or $AA = E$

If $AA = E$ then the table becomes...

G_3	E	A	B
E	E	A	B
A	A	E	B
B	B	A	E

This violates the rearrangement theorem as the last two columns have elements that appear more than once.

The only solution for group G_3 is

G_3	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

Note: The group G_3 is a member of a set of groups called **cyclic groups**. Cyclic groups have the property of being Abelian, that is all elements commute with each other.

A cyclic group is one which every element can be generated by a single element and its powers. In this case $A = A$ and $AA = A^2 = B$ and $AAA = A^3 = E$.

There are two possible groups of order 4

G_4	E	A	B	C
E	E	A	B	C
A	A	B	C	E
B	B	C	E	A
C	C	E	A	B

G_4	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

In the second case of G_4 there is a subgroup of order 2 present.

G_2	E	A
E	E	A
A	A	E

The order of a subgroup (g) must be a divisor of the order of the main group (h), that is $h/g = k$, where k is an integer.

Classes

Groups can further be divided into smaller sets called **classes**.

Similarity Transforms

If A , B and X are in a group and $X^{-1}AX = B$ we say that B is similarity transform of A by X . We also can say that A and B are **conjugate** of each other.

Conjugate elements have the following properties

- 1) All elements are conjugate with themselves
 $A = X^{-1}AX$ for some X
- 2) If A is conjugate to B , then B is conjugate to A
 $A = X^{-1}BX$ and $B = Y^{-1}AY$ with X, Y in the group
- 3) If A is conjugate to B and C then B and C are also conjugates of each other.

The complete set of elements (operations) that are conjugate to each other is called a class.

Find the classes in G_6

G_6	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

E is in a class by itself of order 1

$A^{-1}EA = E$ etc..

Other classes in G_6

$$E^{-1}AE = A$$

$$A^{-1}AA = A$$

$$B^{-1}AB = C$$

$$C^{-1}AC = B$$

$$D^{-1}AD = B$$

$$F^{-1}AF = C$$

We see here that the elements A,B and C are all conjugate to each other and form a class of order 3.

$$E^{-1}DE = D$$

$$A^{-1}DA = F$$

$$B^{-1}DB = F$$

$$C^{-1}DC = F$$

$$D^{-1}DD = D$$

$$F^{-1}DF = D$$

We see here that the elements D and F are conjugate to each other and form a class of order 2.

Homework Set 1

NAME :

(1) Below is one of the two possible group multiplication tables of order 6, $G_6^{(1)}$. Write the group multiplication table for $G_6^{(2)}$.

Keep in mind the rearrangement theorem when building the new table.

The result of "multiplication" of XY is the intersection of the X column and they Y row so that BC = F and CB = D in the given table below. Hint, the group $G_6^{(2)}$ is a cyclic group.

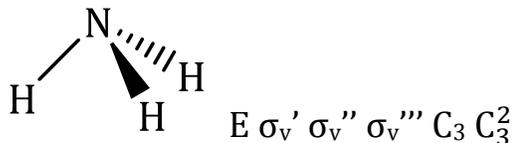
$G_6^{(1)}$	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

$G_6^{(2)}$	E	A	B	C	D	F
E						
A						
B						
C						
D						
F						

(2) Identify all of the subgroups within $G_6^{(2)}$ and write their group multiplication tables.

Point Groups

Consider all of the symmetry operations in NH_3



NH_3	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
E	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
σ_v'	σ_v'	E	C_3	C_3^2	σ_v''	σ_v'''
σ_v''	σ_v''	C_3^2	E	C_3	σ_v'''	σ_v'
C_3	σ_v'''	C_3	C_3^2	E	σ_v'	σ_v''
C_3^2	C_3	σ_v'''	σ_v'	σ_v''	C_3^2	E
C_3^2	C_3^2	σ_v''	σ_v'''	σ_v'	E	C_3

Note that all of the rules of a group are obeyed for the set of allowed symmetry operations in NH_3 .

G_6	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Compare the multiplication table of NH_3 to that of G_6 .

There is a 1:1 correspondence between the elements in each group

$$E \rightarrow E$$

$$\sigma_v' \rightarrow A$$

$$\sigma_v'' \rightarrow B$$

$$\sigma_v''' \rightarrow C$$

$$C_3 \rightarrow D$$

$$C_3^2 \rightarrow F$$

Groups that have a 1:1 correspondence are said to be **isomorphic** to each other.

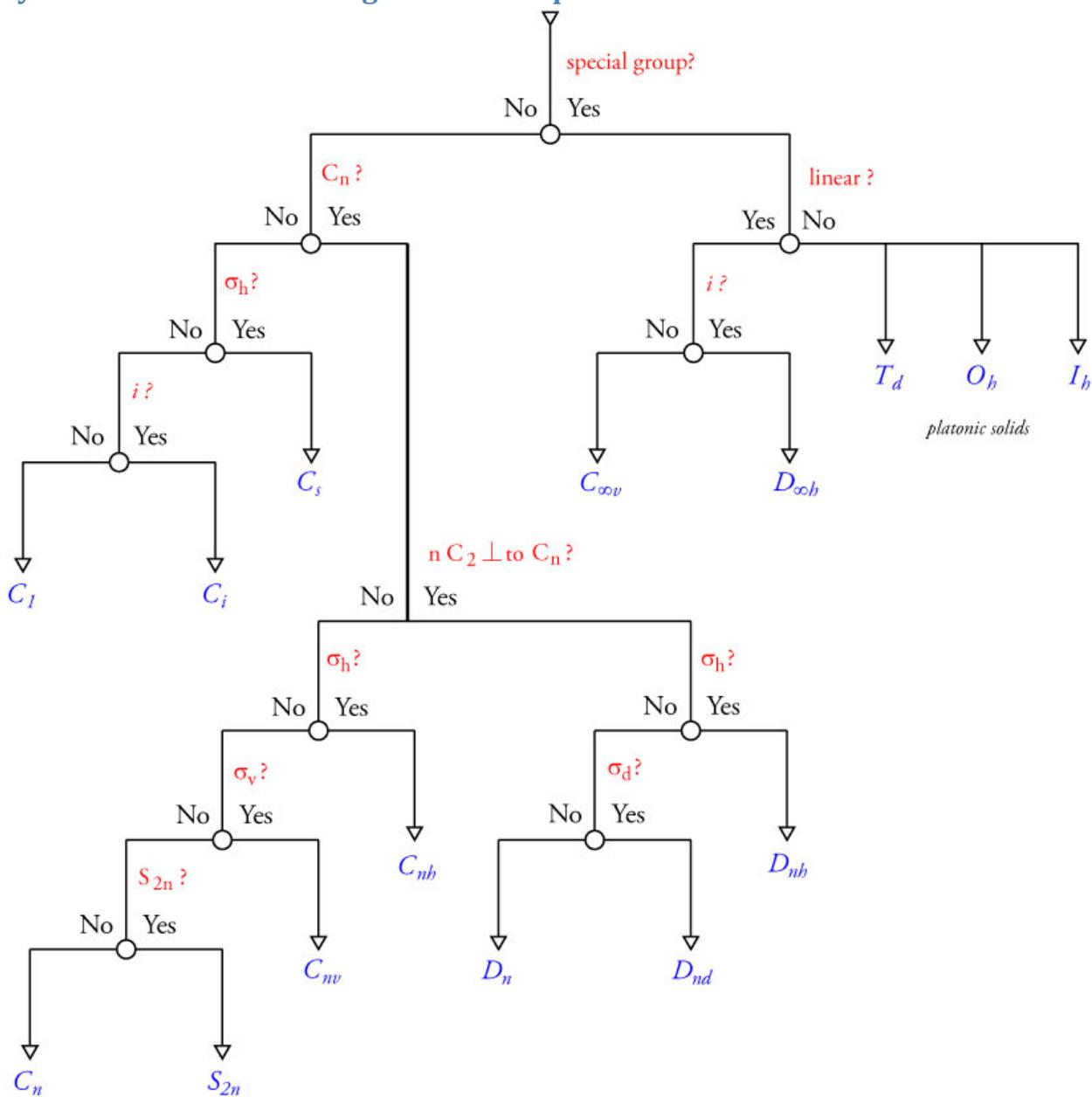
If there is a more than 1:1 correspondence between two groups, they are said to be homomorphic to each other. All groups are homomorphic with the group E. i.e. $A \rightarrow E$, $B \rightarrow E$, $C \rightarrow E$ etc...

Classification of Point Groups

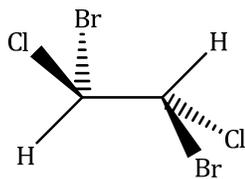
Shoenflies Notation

Group Name	Essential Symmetry Elements*	
C_s	one σ	
C_i	one i	
C_n	one C_n	
D_n	one C_n plus $nC_2 \perp$ to C_n	
C_{nv}	one C_n plus $n\sigma_v$	
C_{nh}	one C_n plus σ_h	
D_{nh}	those of D_n plus σ_h	
D_{nd}	those of D_n plus σ_d	
S_n (even n)	one S_n	
T_d	tetrahedron] Special Groups
O_h	octahedron	
I_h	icosahedrons	
H_h	sphere	

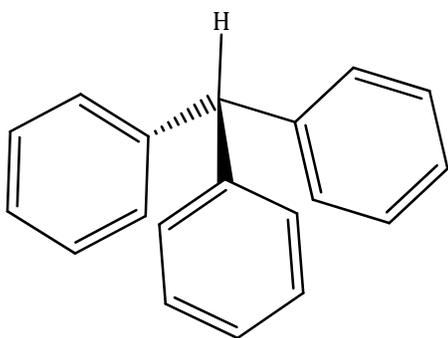
Systematic Method to Assign Point Groups



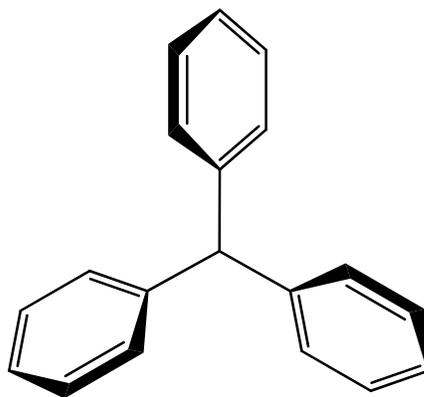
Assign the point groups to the following molecules



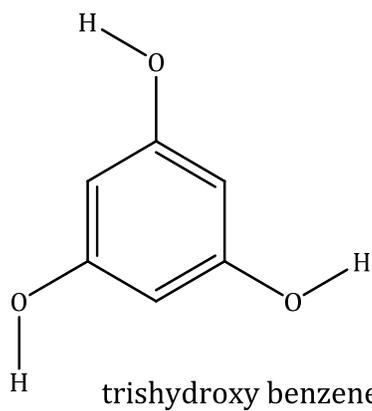
dichlorodibromo ethane i only $\rightarrow C_i$



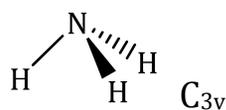
triphenyl methane



$C_n \rightarrow C_3$



trishydroxy benzene C_{3h}



C_{3v}

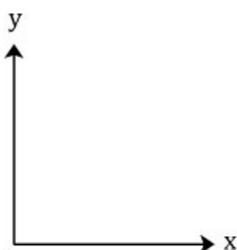
Classes in Symmetry Point Groups

You can test all possible similarity transforms to find the conjugate elements.

$X^{-1}AX = B$, however this is tedious and with symmetry elements it is much easier to sort classes.

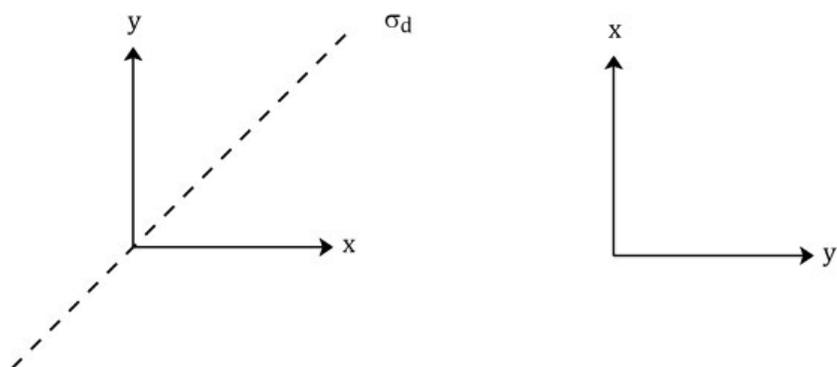
Two operations belong to the same class if one may be replaced by another in a new coordinate system which is accessible by an allowed symmetry operation in the group.

Consider the following for a D_{4h} group



$$C_4 [x,y] \rightarrow [-y, x] \text{ and } C_4^3 [x,y] \rightarrow [y,-x]$$

Reflect the coordinate system by σ_d



$$C_4' [x,y] \rightarrow [y, -x] \text{ and } C_4^{3'} [x,y] \rightarrow [-y,x]$$

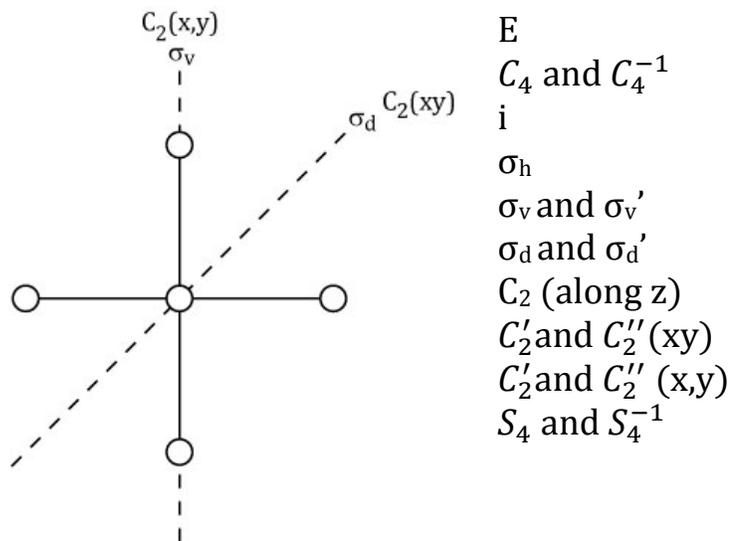
By changing the coordinate system we have simply replace the roles that C_4 and C_4^3 play. That is $C_4' \rightarrow C_4^3$ and $C_4^{3'} \rightarrow C_4$

More generally we can state the following

1. E , i and σ_h are always in a class by themselves.
2. C_n^k and C_n^{-k} are in the same class for each value of k as long as there is a plane of symmetry along the C_n^k axis or a $C_2 \perp$ to C_n^k . If not then C_n^k and C_n^{-k} are in classes by themselves. Likewise for S_n^k and S_n^{-k} .
3. σ' and σ'' are in the same class if there is an operation which moves one plane into the other. Likewise for C_n^k and $C_n^{k'}$ that are along different axes.

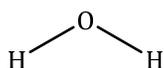
Consider the elements of D_{4h} (square plane)

There are 10 classes in this group with order 14

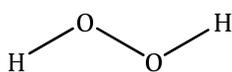


Homework Set 2

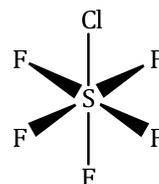
- List all of the symmetry **operations** and symmetry **elements** for the following molecules. List the operations that commute with each other. Exclude E which always commutes with every element - For example in water you could write $C_2\sigma_v(xy) = \sigma_v(xy)C_2$, where $\sigma_v(xy)$ is the mirror plane containing the H-O-H atoms. $\sigma_v(xz)$ is the mirror plane containing only the O atom.



water

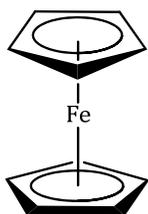


hydrogen peroxide
(planar)

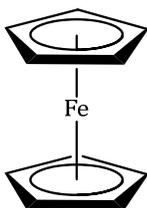


sulfur chloropentafluoride

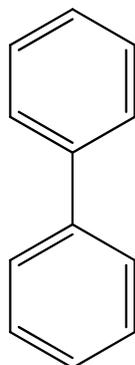
- Construct the group multiplication table for the symmetry operations of water.
- Assign the following sets of geometric isomers to their respective point groups (ignore any hydrogen atoms when assigning the group).



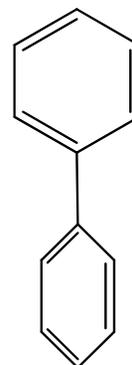
ferrocene
(staggered)



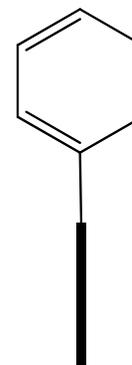
ferrocene
(eclipsed)



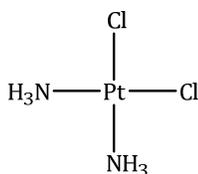
biphenyl
(planar)



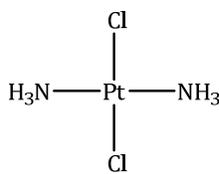
biphenyl
(twisted)



biphenyl
(perpendicular)



cis-platin



trans-platin

- How many classes are in the point group assigned to sulfur chloropentafluoride?

Properties of Matrices

Matrix: rectangular array of numbers or elements

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad a_{ij} \text{ } i^{\text{th}} \text{ row and } j^{\text{th}} \text{ column}$$

A vector is a one dimensional matrix

$$\begin{bmatrix} a_{11} \\ a_{21} \\ a_{31} \end{bmatrix} \quad \text{This could be a set of Cartesian coordinates (x,y,z)}$$

Matrix math basics

Addition and Subtraction

Matrices must be the same size

$$c_{ij} = a_{ij} \pm b_{ij} \quad \text{add or subtract the corresponding elements in each matrix}$$

Multiplication by a scalar (k)

$$k[a_{ij}] = [ka_{ij}] \quad \text{every element is multiplied by the constant } k$$

Matrix multiplication

$$\sum_k^n a_{ik} \times b_{kj} = c_{ij}$$

a_{ik} = element in the i^{th} row and k^{th} column

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \times \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

Where $c_{11} = (a_{11}b_{11} + a_{12}b_{21})$

$c_{12} = (a_{11}b_{12} + a_{12}b_{22})$

etc...

matrix multiplication is not commutative ($ab \neq ba$)

Matrix Division

Division is defined as multiplying by the inverse of a matrix. Only square matrices may have an inverse.

The inverse of a matrix is defined as

$a \cdot a^{-1} = \delta_{ij}$ $\delta_{ij} \rightarrow$ Kronecker delta

$\delta_{ij} = 1$ if $i=j$ otherwise $\delta_{ij} = 0$

$$\delta_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Special Matrices

Block diagonal matrix multiplication

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 3 & 2 \\ 0 & 0 & 0 & 1 & 2 & 2 \\ 0 & 0 & 0 & 4 & 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 2 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 2 \\ 0 & 0 & 0 & 3 & 0 & 2 \\ 0 & 0 & 0 & 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 8 & 7 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 13 & 3 & 10 \\ 0 & 0 & 0 & 10 & 3 & 8 \\ 0 & 0 & 0 & 2 & 5 & 9 \end{bmatrix}$$

Each block is multiplied independently

i.e.

$$\begin{bmatrix} 1 & 0 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix} = \begin{bmatrix} 4 & 1 \\ 8 & 7 \end{bmatrix}$$

$$[3][1] = [3]$$

$$\begin{bmatrix} 1 & 3 & 2 \\ 1 & 2 & 2 \\ 4 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 2 \\ 3 & 0 & 2 \\ 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 13 & 3 & 10 \\ 10 & 3 & 8 \\ 2 & 5 & 9 \end{bmatrix}$$

Square Matrices

$\chi_a = \sum_j a_{jj}$ This is the sum of the diagonal elements of a matrix (trace).

χ_a is call the character of a matrix

properties of χ

if $c = ab$ and $d = ba$ then $\chi_c = \chi_d$

conjugate matrices have identical χ

$r = b^{-1}pb$ then $\chi_r = \chi_b$

Operations that are in the same class have the same character.

Matrix Representations of Symmetry Operations

We will now use matrices to represent symmetry operations.

Consider how an $\{x,y,z\}$ vector is transformed in space

Identity

E

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Reflection

σ_{xy}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

σ_{xz}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

Inversion

i

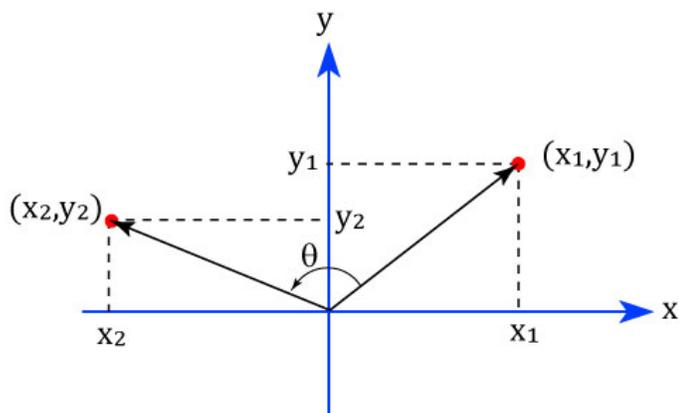
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

Rotation

C_n about the z axis

$$\begin{bmatrix} ? & ? & 0 \\ ? & ? & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z \end{bmatrix} \quad \text{The z coordinate remains unchanged.}$$

Consider a counter clockwise rotation by θ about the z axis



From trigonometry we know that

$$x_2 = x_1 \cos \theta - y_1 \sin \theta \quad \text{and} \quad y_2 = x_1 \sin \theta + y_1 \cos \theta$$

Represented in matrix form this gives:

$$\begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$

For a clockwise rotation we find

$$\begin{bmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix} \quad \text{recall } \cos \phi = \cos(-\phi) \quad \text{and} \quad \sin \phi = -\sin(-\phi)$$

The transformation matrix for a clockwise rotation by ϕ is:

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z \end{bmatrix}$$

Improper Rotations

S_n

Because an improper rotation may be expressed as $\sigma_{xy}C_n$ we can write the following since matrices also follow the associative law.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

The set of matrices that we have generated that transform a set of $\{x,y,z\}$ orthogonal coordinates are called orthogonal matrices. The inverse of these matrices is found by exchanging rows into columns (taking the transpose of the matrix).

Consider a C_3 rotation about the z-axis.

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_3$$

exchanging rows into columns gives

$$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = (C_3)^T = C_3^2$$

Multiplying these two matrices gives the identity matrix

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We know from symmetry that $C_3 C_3^2 = C_3^2 C_3 = E$

Here we see that C_3 and C_3^2 are inverse and orthogonal to each other.

In general we can write a set of homomorphic matrices that form a **representation** of a given point group

For example, consider the water molecule which belongs to the C_{2v} group.

C_{2v} contains E, C_2 , σ_{xz} , σ_{yz}

The set of four matrices below transform and multiply exactly like the symmetry operations in C_{2v} . That is, they are homomorphic to the symmetry operations.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

E C_2 σ_{xz} σ_{yz}

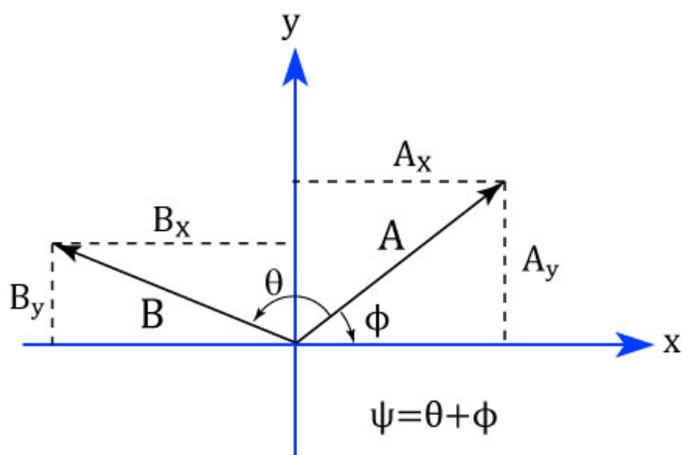
Show that $C_2 \sigma_{xz} = \sigma_{yz}$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The algebra of matrix multiplication has been substituted for the geometry of applying symmetry operations.

Vectors and Scalar Products

Consider two vectors in 2D space



The scalar or “dot” product results in a scalar or number

Defined as the length of each vector times each other times the cos of the angle between them: $A \cdot B = AB \cos \theta$

$$\text{If } \theta = 90^\circ \text{ then } A \cdot B = 0$$

$$\text{If } \theta = 0^\circ \text{ then } A \cdot B = AB$$

We can write the following:

$$\phi = \text{angle to the x axis for A}$$

$$\psi = \text{greater angle to the x axis for B } (\psi = \theta + \phi)$$

Projections

$$A_x = A \cos \phi$$

$$A_y = A \sin \phi$$

$$B_x = B \cos \psi$$

$$B_y = B \sin \psi$$

Using a trig identity we can write

$$A \cdot B = AB(\cos \phi \cos \psi + \sin \phi \sin \psi)$$

Rearrange to $A \cos \phi B \cos \psi + A \sin \phi B \sin \psi$

Substitute from above

$$A \cdot B = A_x B_x + A_y B_y$$

More generally

$$A \cdot B = \sum_{i=1}^n A_i B_i \quad \text{for n-dimensional space}$$

Orthogonal vectors are defined as those in which the following is true

$$A \cdot B = \sum_{i=1}^n A_i B_i = 0$$

Representations of Groups

The following matrices form a representation of the C_{2v} point group

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

E

C_2

σ_{xz}

σ_{yz}

Group Multiplication Table for C_{2v}

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

How many other representations exist for the C_{2v} point group?

A: As many as we can think up

The set of numbers $\{1,1,1,1\}$ transform like C_{2v} etc...

However, there are only a few representations that are of fundamental importance.

Consider the matrices E, A, B, C, \dots and we perform a similarity transform with Q

$$E' = Q^{-1}EQ$$

$$A' = Q^{-1}AQ$$

$$B' = Q^{-1}BQ$$

Etc...

For example $A' = Q^{-1}AQ$

$$A' = Q^{-1}AQ = \begin{array}{|c|c|c|c|} \hline & A'_1 & & \\ \hline & & A'_2 & \\ \hline & & & A'_3 \\ \hline & & & & A'_4 \\ \hline \end{array}$$

The similarity transform of A by Q will block diagonalize all of the matrices

All of the resulting subsets form representations of the group as well

e.g. $E'_1, A'_1, B'_1 \dots etc \dots$

We say that $E, A, B, C \dots$ are **reducible matrices** that form a set of **reducible representations**.

If Q does not exist which will block diagonalize all of the matrix representations then we have an **irreducible representation**.

The Great Orthogonality Theorem

The theorem states

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

Terms

h = order of the group (# of symmetry operators)

Γ_i = i^{th} representation

l_i = dimension of Γ_i (e.g. 3×3 , $l_i = 3$)

R = generic symbol for an operator

$[\Gamma_i(R)_{mn}]$ = the element in the m^{th} row and n^{th} column of an operator R in representation Γ_i

$[\Gamma_j(R)_{m'n'}]^*$ = complex conjugate of the element in the m'^{th} row and n'^{th} column of an operator R in representation Γ_j

What does this all mean?

For any two irreducible representations Γ_i, Γ_j

Any corresponding matrix elements (one from each matrix) behave as components of a vector in h -dimensional space, such that all vectors are **orthonormal**. That is, orthogonal and of unit length.

Examine the theorem under various conditions...

If vectors are from different representations then they are orthogonal

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = 0 \text{ if } i \neq j$$

If vectors are from the same representation but are different sets of elements then they are orthogonal

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{m'n'}]^* = 0 \text{ if } m \neq m' \text{ or } n \neq n'$$

The square of the length of any vector is h/l_i

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{mn}]^* = \frac{h}{l_i}$$

Irreducible Representations

There are five important rules concerning irreducible representations

- 1) The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group

$$\sum_i l_i^2 = h$$

- 2) The sum of the squares of the characters in an irreducible representation is equal to the order of the group

$$\sum_i [\chi_i(R)]^2 = h$$

- 3) Vectors whose components are the characters of two irreducible representations are orthogonal

$$\sum_i [\chi_i(R)][\chi_j(R)] = 0 \text{ when } i \neq j$$

- 4) In a given representation (reducible or irreducible) the characters of all matrices belonging to the same class are identical
- 5) The number of irreducible representations of a group is equal to the number of classes in the group.

Let's look at a simple group, C_{2v} (E, C_2 , σ_v , σ_v')

There are four elements each in a separate class. By rule 5, there must be 4 irreducible representations. By rule 1, the sum of the squares of the dimensions must be equal to h (4).

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 = 4$$

The only solution is $l_1 = l_2 = l_3 = l_4 = 1$

Therefore the C_{2v} point group must have four one dimensional irreducible representations.

C_{2v}	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1

All other representations must satisfy $\sum_i [\chi_i(R)]^2 = 4$

This can only work for $\chi_i = \pm 1$. And for each of the remaining Γ to be orthogonal to Γ_1 there must be two +1 and two -1.

Therefore, the remaining Γ must be (E is always +1)

C_{2v}	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

Take any two and verify that they are orthogonal

$$\Gamma_1 \Gamma_2 = (1 \times 1) + (1 \times -1) + (1 \times -1) + (1 \times 1) = 0$$

These are the four irreducible representation of the point group C_{2v}

Consider the C_{3v} group (E, $2C_3$, $3\sigma_v$)

There are three classes so there must be three irreducible representations

$$l_1^2 + l_2^2 + l_3^2 = 6$$

The only values which work are $l_1 = 1, l_2 = 1, l_3 = 2$

That is, two one dimensional representations and one two dimensional representation.

So for Γ_1 we can choose

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1

For Γ_2 we need to choose ± 1 to keep orthogonality

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1

$$\Gamma_1\Gamma_2 = (1 \times 1) + 2(1 \times -1) + 3(1 \times -1) = 0$$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2		

To find Γ_3 we must solve the following

$$\sum_i [\chi_1(R)][\chi_3(R)] = (1)(2) + 2(1)[\chi_3(C_3)] + 3(1)[\chi_3(\sigma_v)] = 0$$

$$\sum_i [\chi_2(R)][\chi_3(R)] = (1)(2) + 2(1)[\chi_3(C_3)] + 3(-1)[\chi_3(\sigma_v)] = 0$$

Solving this set of two equations and two unknowns gives

$$[\chi_3(C_3)] = -1 \text{ and } [\chi_3(\sigma_v)] = 0$$

Therefore the complete set of irreducible representations is

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

We have derived the character tables for C_{2v} and C_{3v} (check the book appendix)

C_{2v}	E	C_2	σ_v	σ_v'	C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1	1	A_1	1	1	1
A_2	1	-1	-1	1	A_2	1	1	-1

$$\begin{array}{l|cccc} B_1 & 1 & -1 & 1 & -1 \\ B_2 & 1 & 1 & -1 & -1 \end{array} \quad \begin{array}{l|ccc} E & 2 & -1 & 0 \end{array}$$

We now know that there is a similarity transform that may block diagonalize a reducible representation. During a similarity transform the character of a representation is left unchanged.

$$\chi(R) = \sum_j a_j \chi_j(R)$$

Where $\chi(R)$ is the character of the matrix for operation R and a_j is the number of times that the j^{th} irreducible representation appears along the diagonal.

The good news is that we do not need to find the matrix Q to perform the similarity transform and block diagonalize the matrix representations. Because the characters are left intact, we can work with the characters alone.

We will multiply the above by $\chi_i(R)$ and sum over all operations.

$$\sum_R \chi(R) \chi_i(R) = \sum_R \sum_j a_j \chi_j(R) \chi_i(R) = \sum_j \sum_R a_j \chi_j(R) \chi_i(R)$$

and

$$\sum_R \chi_i(R) \chi_j(R) = h \delta_{ij}$$

For each sum over j we have

$$\sum_R a_j \chi_j(R) \chi_i(R) = a_j \sum_R \chi_j(R) \chi_i(R) = a_j h \delta_{ij}$$

The characters for χ_i and χ_j form orthogonal vectors we can only have non-zero values when $i \neq j$

The Reduction Formula

The above leads to the important result called “The Reduction Formula”

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

Where a_i is the number of times the i^{th} irreducible representation appears in the reducible representation.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_a	5	2	-1
Γ_b	7	1	-3

Apply the reduction formula to Γ_a and Γ_b

For Γ_a

$$a_1 = \frac{1}{6} [(1)(1)(5) + (2)(1)(2) + (3)(1)(-1)] = 1$$

$$a_2 = \frac{1}{6} [(1)(1)(5) + (2)(1)(2) + (3)(-1)(-1)] = 2$$

$$a_3 = \frac{1}{6} [(1)(2)(5) + (2)(-1)(2) + (3)(0)(-1)] = 1$$

For Γ_b

$$a_1 = \frac{1}{6} [(1)(1)(7) + (2)(1)(1) + (3)(1)(-3)] = 0$$

$$a_2 = \frac{1}{6} [(1)(1)(7) + (2)(1)(1) + (3)(-1)(-3)] = 3$$

$$a_3 = \frac{1}{6} [(1)(2)(7) + (2)(-1)(1) + (3)(0)(-3)] = 2$$

Sum the columns...

For Γ_a

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_a	5	2	-1

For Γ_b

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_3	2	-1	0
Γ_b	7	1	-3

Character Tables

For C_{3v} we find the following character table with four regions.

C_{3v}	E	2 C_3	3 σ_v		
A ₁	1	1	1	z	x^2+y^2, z^2
A ₂	1	1	-1	Rz	
E	2	-1	0	(x,y)(Rx,Ry)	$(x^2-y^2, xy)(xz,yz)$
I		II		III	IV

Region I – Mulliken Symbols for Irreducible Representations

- 1) All 1×1 representations are “A” or “B”, 2×2 are “E” and 3×3 are “T”
- 2) 1×1 which are symmetric with respect to rotation by $2\pi/n$ about the principle C_n axis are “A” (i.e. the character is +1 under C_n). Those that are anti-symmetric are labeled “B” (the character is -1 under C_n).
- 3) Subscripts 1 or 2 are added to A and B to designate those that are symmetric (1) or anti-symmetric (2) to a $C_2 \perp$ to C_n or if no C_2 is present then to a σ_v .
- 4) ' and '' are attached to those that are symmetric (') or anti-symmetric (') relative to a σ_h .
- 5) In groups with an inversion center (i), subscript g (German for gerade or even) is added for those that are symmetric with respect to i or a subscript u (German for ungerade or uneven) is added for those anti-symmetric with respect to i.
- 6) Labels for E and T representations are more complicated but follow the same general rules.

Region II - Characters

This region list the characters of the irreducible representations for all symmetry operations in each group.

Region III - Translations and Rotations

The region assigns translations in x,y and z and rotations Rx, Ry, Rz to irreducible representations. E.g., in the group above (x,y) is listed in the same row as the E irreducible representation. This means that if one formed a matrix representation based on x and y coordinates, it would transform (that is have the same characters as) identically as E.

Recall that previously we looked at a C_3 transformation matrix for a set of Cartesian coordinates

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = C_3$$

Notice that this matrix is block diagonalized. If we break this into blocks we are left with

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x' \\ y' \end{bmatrix} = C_3 \quad \text{and} \quad [1][z] = [z'] = C_3$$

Compare the characters of these matrices to the characters under C_3 in the table above. Notice that for (x,y) $\chi = -1$ and for (z) $\chi = 1$. If you compared the characters for all of the other transformation matrices you will see that (x,y) $\rightarrow E$ and (z) $\rightarrow A_1$ as shown in region III of the table. Similar analysis can be made with respect to rotations about x, y and z.

Region IV- Binary Products

This region list various binary products and to which irreducible representation that they belong. The d-orbitals have the same symmetry as the binary products. For example the d_{xy} orbital transforms the same as the xy binary product.

Writing Chemically Meaningful Representations

We will begin by considering the symmetry of molecular vibrations. To a good approximation, molecular motion can be separated into translational, rotational and vibrational components.

Each atom in a molecule has three degrees of freedom (motion) possible. An entire molecule therefore has $3N$ degrees of freedom for N atoms.

3 DOF are for translation in x , y and z .

3 DOF are for rotation in x , y and z (note: linear molecules can only rotate in 2 dimensions)

The remain DOF are vibrational in nature

A molecule will have $3N - 6$ possible vibrations

$3N - 5$ for linear molecules

Using the tools of classical mechanics it is possible to solve for the energies of all vibrations (think balls and springs model for a molecule). The calculations are tedious and complicated and as early as the 1960's computers have been used to do the calculations.¹

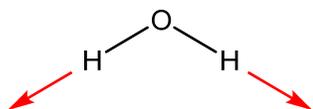
Vibrations

We can use the tools of group theory to deduce the qualitative appearance of the normal modes of vibration.

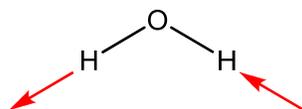
We'll start with a simple molecule like H_2O .

¹ For more information on these calculations, look up F and G matrices in a group theory or physical chemistry text. In summary this method sums up and solves all of the potential energies based on the force constants (bond strength) and displacement vectors (vibrations). $V = \frac{1}{2} \sum_{i,k} f_{ik} s_i s_k$ where, f_{ik} is the force constant and s_i and s_k are displacements (stretching or bending). The term $f_{ii} s_i^2$ represents the potential energy of a pure stretch or bend while the cross terms represent interactions between the vibrational modes.

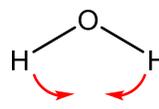
For water we expect $3N-6 = 3$ normal modes of vibration. Water is simple enough that we can guess the modes.



symmetric stretching



anti-symmetric stretching



bending

Assign these three vibrations to irreducible representations in the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

Consider the displacement vectors (red arrows) for each mode and write what happens under each symmetry operation.

Symmetric stretching (Γ^{v1})

$$E \rightarrow 1, C_2 \rightarrow 1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow 1$$

Anti - Symmetric stretching (Γ^{v2})

$$E \rightarrow 1, C_2 \rightarrow -1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow -1$$

Bending (Γ^{v3})

$$E \rightarrow 1, C_2 \rightarrow -1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow -1$$

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x
Γ^{v1}	1	1	1	1	
Γ^{v2}	1	-1	1	-1	
Γ^{v3}	1	1	1	1	

In a more complicated case we would apply the reduction formula to find the Γ^{irr} which comprise Γ^v . However, in this case we see by inspection that

$$\Gamma^{v1} \rightarrow A_1$$

$$\Gamma^{v2} \rightarrow B_1$$

$$\Gamma^{v3} \rightarrow A_1$$

A more generalized approach to finding Γ^v will be discussed later.

Selection Rules for Vibrations

Born-Oppenheimer approximation: electrons move fast relative to nuclear motion.

$$\psi = \psi_{el}\psi_N$$
$$\iint \psi_{el}^* \psi_N^* \hat{d} \psi_{el} \psi_N' d\tau_{el} d\tau_N$$

Where:

ψ_{el} is the electronic wavefunction and ψ_N is the nuclear wavefunction

\hat{d} is the dipole moment operator

$$\hat{d} = \sum_i (-e)r_i + \sum_\alpha Z_\alpha e r_\alpha$$

Where:

r_i is the radius vector from the origin to a charge q_i (an electron in this case)

$-e$ is the electron charge

Z_α is the nuclear charge

r_α is the radius vector for a nucleus

Integrals of this type define the overlap of wavefunctions. When the above integral is not equal to 0, a vibrational transition is said to be allowed. That is, there exists some degree of overlap of the two wavefunctions allowing the transition from one to the other.

In 1800 Sir William Herschel put a thermometer in a dispersed beam of light. When he put the thermometer into the region beyond the red light he noted the temperature increased even more than when placed in the visible light. He had discovered infrared (IR) light.

Similar to electronic transitions with visible and UV light, IR can stimulate transitions from $v_1 \rightarrow v_2$. A simplified integral describing this transition is

$$\int \psi_0^{vib*} \hat{d} \psi_m^\rho d\tau$$

which is allowed when the integral does not equal zero.

In this integral ψ_0^{vib*} = vibrational ground state wavefunction and ψ_m^ρ is the ρ^{th} fundamental vibrational level wavefunction.

What this all means is that a vibrational transition in the infrared region is only allowed if the vibration causes a change in the dipole moment of the molecule.

Dipole moments translate just like the Cartesian coordinate vectors x, y and z. Therefore only vibrations that have the same symmetry as x, y or z are allowed transitions in the infrared.

Selection Rules for Raman Spectroscopy

In Raman spectroscopy, incident radiation with an electric field vector \vec{E} may induce a dipole in a molecule. The extent of which depends on the polarizability of the molecule (α_{ij} polarizability operator).

$$\int \psi_0^{vib*} \alpha_{ij} \psi_m^\rho d\tau$$

Transitions in Raman spectroscopy are only allowed if the vibration causes a change in polarizability.

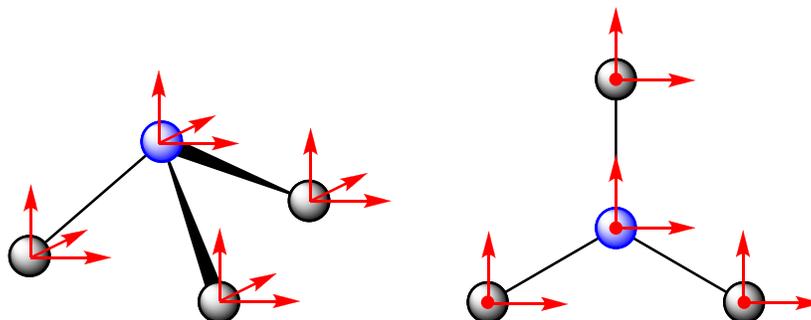
Polarizability transforms like the binary product terms (xy, z^2 etc...) and therefore vibrations that have the same symmetry as the binary products are allowed transitions in Raman spectroscopy.

For water, all three vibrations are IR and Raman active.

Normal Coordinate Analysis

Let's find all of the vibrational modes for NH_3 . We expect $3N - 6 = 6$ vibrations.

A simple way to describe all possible motions of a molecule is to consider a set of three orthonormal coordinates centered on each atom. For NH_3 , this results in a set of 12 vectors. Any motion will be the sum of all twelve components.



As performed previously for a set of three x , y and z vectors we can write a transformation matrix that describes what happens to each of the vectors for each symmetry operation in the group.

We now need to find the characters of Γ^{3N}

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

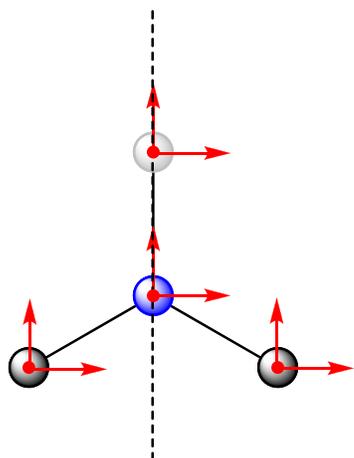
The transformation matrices will be 12×12 . However, we are only interested in the characters (χ) of each matrix. For E the character will be 12 since all elements remain unchanged.

Consider a C_3 rotation:

Only vectors on the N atom will go into \pm themselves. From our previous results we know that x, y and z transform like...

$-\frac{1}{2}$	$\frac{\sqrt{3}}{2}$	0	0	0	0	0	0	0	0	0	0
$-\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0	0	0	0	0
0	0	1	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	-1	0	0	0	0	0
0	0	0	0	0	0	0	0	1	0	0	0
0	0	0	0	0	0	0	0	0	0	1	0
0	0	0	0	0	0	0	0	0	-1	0	0
0	0	0	0	0	0	0	0	0	0	0	1
0	0	0	0	-1	0	0	0	0	0	0	0
0	0	0	1	0	0	0	0	0	0	0	0
0	0	0	0	0	1	0	0	0	0	0	0

All other components are off diagonal and do not contribute to the character of the matrix. Here, $\chi = 0$ for C_3 .



For the vertical mirror plane, σ_v

Four vectors remain unchanged (on **N** and **H**) and two go into -1 of themselves (on **N** and **H**). The other 6 on the out of plane **H** atoms all become off diagonal elements.

$$\chi = 2 \quad (1+1-1+1+1-1+0+0+0+0+0+0)$$

Now we can write Γ^{3N}

C_{3v}	E	2 C_3	3 σ_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)	$(x^2-y^2, xy)(xz,yz)$
Γ^{3N}	12	0	2		

Apply the reduction formula to find what Γ^{irr} comprise Γ^{3N}

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

$$a_{\Gamma^{A_1}} = \frac{1}{6} [(1)(1)(12) + (2)(1)(0) + (3)(1)(2)] = 3$$

$$a_{\Gamma^{A_2}} = \frac{1}{6} [(1)(1)(12) + (2)(1)(0) + (3)(-1)(2)] = 1$$

$$a_{\Gamma^E} = \frac{1}{6} [(1)(2)(12) + (2)(-1)(0) + (3)(0)(2)] = 4$$

We write the following

$$\Gamma^{3N} = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 4\Gamma^E$$

However, Γ^{3N} describes all possible motion, including translation and rotation. Inspection of the character table reveals that

$$\Gamma^{trans} = \Gamma^{A_1} \oplus \Gamma^E$$

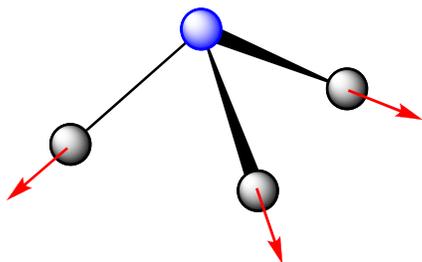
$$\Gamma^{rot} = \Gamma^{A_2} \oplus \Gamma^E$$

This leaves the vibrations as

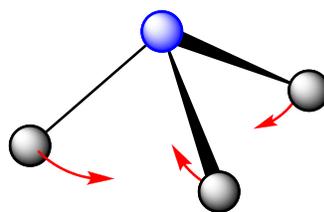
$\Gamma^{vib} = 2\Gamma^{A_1} \oplus 2\Gamma^E$ notice we predicted 6 normal modes and we have 6 dimensions represented (two 1×1 and two 2×2).

Now we will write pictures representing what the vibrations look like.

Γ^{A_1} is symmetric with respect to all operations



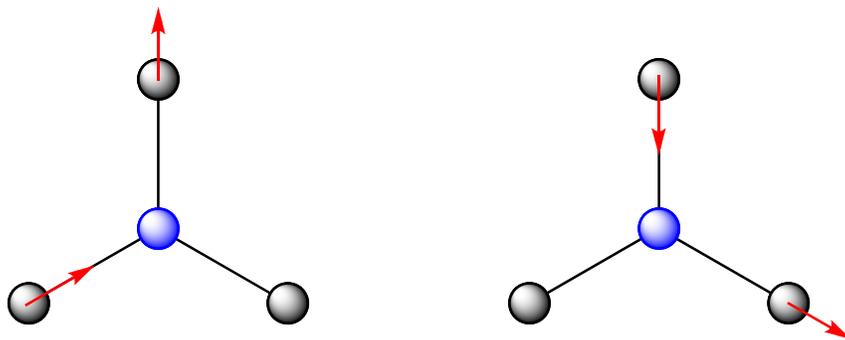
Γ^{A_1} – symmetric stretching



Γ^{A_1} – symmetric bending

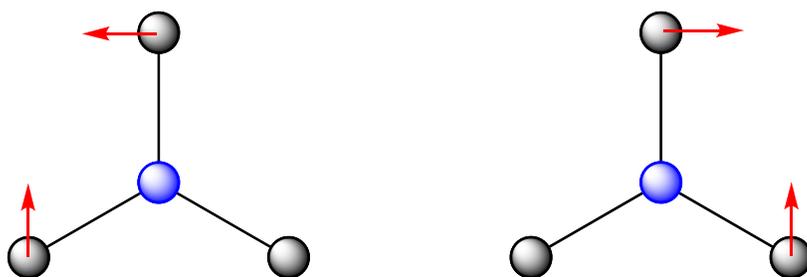
The E modes are degenerate. That is they are made up of vibrations that are of equal energy.

Γ^E – asymmetric stretching



The third possible way of drawing an asymmetric stretch is just a linear combination of the two above (add the two vibrations).

Γ^E – asymmetric bending



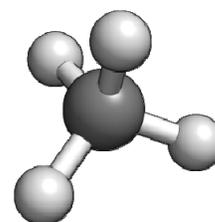
As with the stretches, the third bend is formed from a linear combination of the other two and is not unique (subtract the two bends).

IR and Raman Spectra of CH₄ and CH₃FMethane CH₄ belongs to the T_d point group

Perform the normal coordinate analysis for methane and determine the number and symmetry of all IR and Raman active bands

There will be $3(5) - 6 = 9$ normal modes of vibration in both moleculesNormal Coordinate Analysis of CH₄1st write the characters for Γ^{3N}

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d		
A ₁	1	1	1	1	1		x ² +y ² +z ²
A ₂	1	1	1	-1	-1		
E	2	-1	2	0	0		2z ² -x ² -y ²
T ₁	3	0	-1	1	-1	(R _x ,R _y ,R _z)	x ² -y ²
T ₂	3	0	-1	-1	1	(x,y,z)	(xy,xz,yz)
Γ ^{3N}	15	0	-1	-1	3		

Reduce Γ^{3N} into its irreducible representations.

$$\Gamma^{A_1} = \frac{1}{24}(15 + 0 - 3 - 6 + 18) = 1$$

$$\Gamma^{A_2} = \frac{1}{24}(15 + 0 - 3 + 6 - 18) = 0$$

$$\Gamma^E = \frac{1}{24}(30 + 0 - 6 + 0 + 0) = 1$$

$$\Gamma^{T_1} = \frac{1}{24}(45 + 0 + 3 - 6 - 18) = 1$$

$$\Gamma^{T_2} = \frac{1}{24}(45 + 0 + 3 + 6 + 18) = 3$$

$$\Gamma^{3N} = \Gamma^{A_1} \oplus \Gamma^E \oplus \Gamma^{T_1} \oplus 3\Gamma^{T_2}$$

$$\Gamma^{trans} = \Gamma^{T_2} \text{ and } \Gamma^{rot} = \Gamma^{T_1}$$

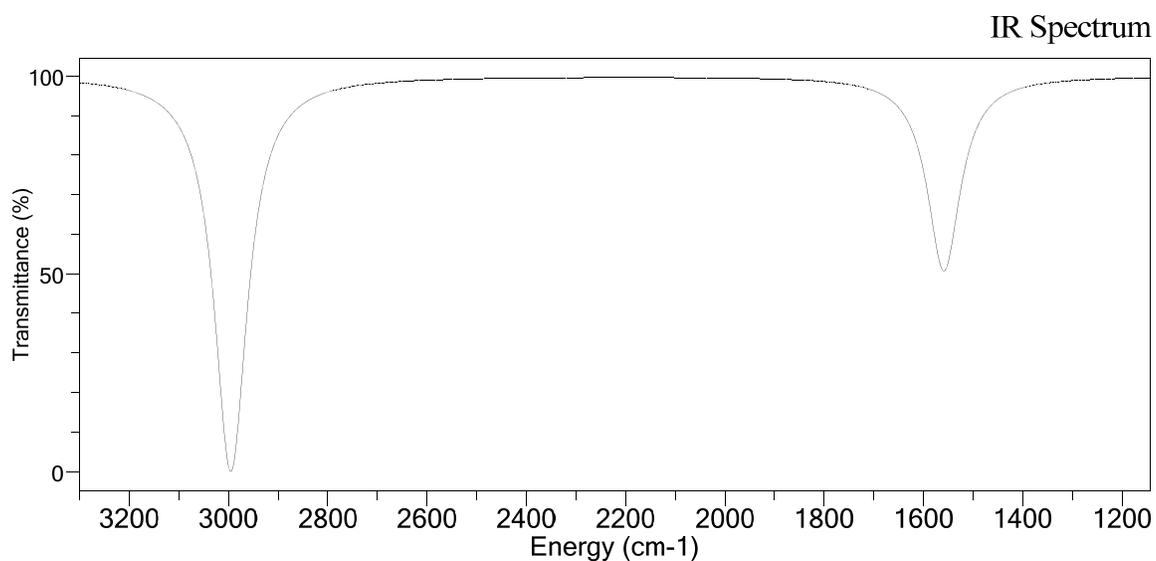
Subtracting the translational and rotational irreducible representations we are left with

$$\Gamma^{vib} = \Gamma^{A_1} \oplus \Gamma^E \oplus 2\Gamma^{T_2}$$

IR active modes are the 6 modes in $2\Gamma^{T_2}$

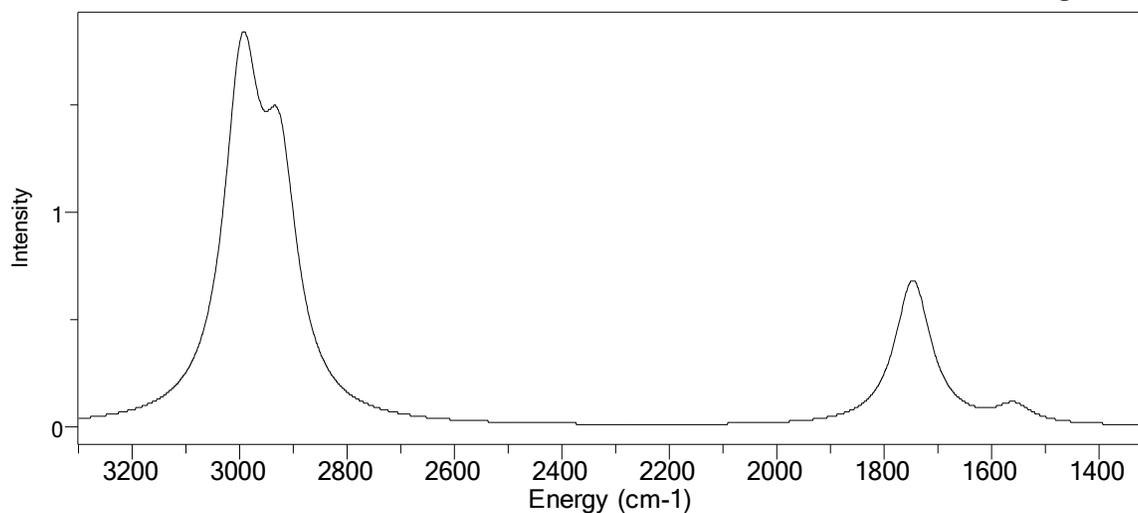
All 9 modes are Raman active

Calculated IR and Raman spectra for CH_4 are shown below²



² Spectra calculated by GAMESS using Hartree-Fock methods

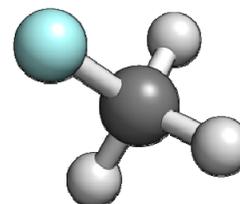
Raman Spectrum

Normal Coordinate Analysis of CH₃F

Now we perform the identical analysis for CH₃F which belongs to the C_{3v} point group.

1st write the characters for Γ^{3N}

C _{3v}	E	2C ₃	3σ _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)
Γ ^{3N}	15	0	3		



Reduce Γ^{3N} into its irreducible representations.

$$\Gamma^{A_1} = \frac{1}{6} (15 + 0 + 9) = 4$$

$$\Gamma^{A_2} = \frac{1}{6} (15 + 0 - 9) = 1$$

$$\Gamma^E = \frac{1}{6} (30 + 0 + 0) = 5$$

$$\Gamma^{3N} = 4\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 5\Gamma^E$$

$$\Gamma^{trans} = \Gamma^{A_1} \oplus \Gamma^E \quad \text{and} \quad \Gamma^{rot} = \Gamma^{A_2} \oplus \Gamma^E$$

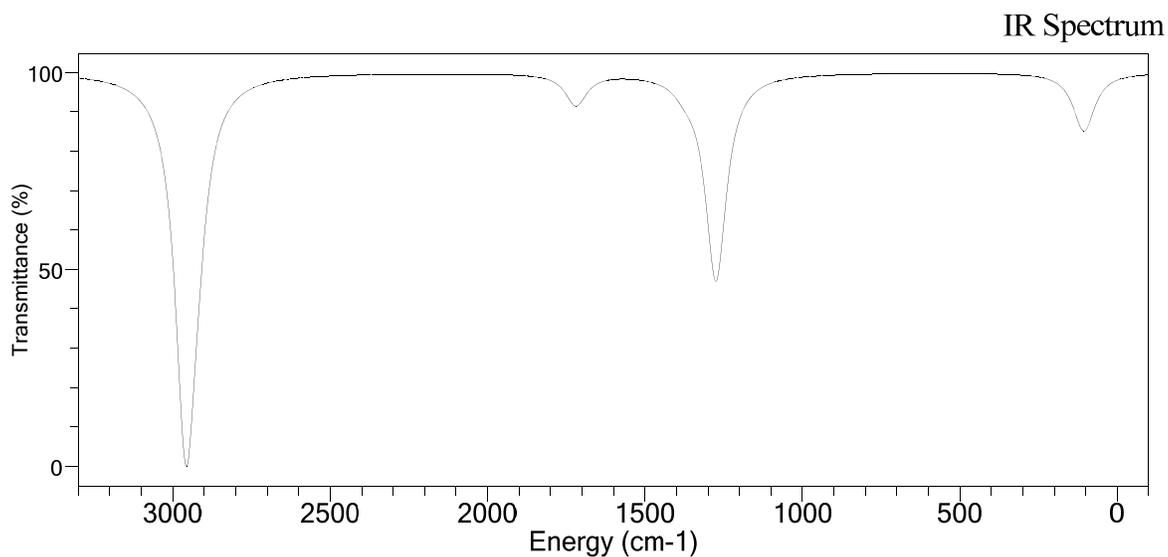
Subtracting the translational and rotational irreducible representations we are left with

$$\Gamma^{vib} = 3\Gamma^{A_1} \oplus 3\Gamma^E$$

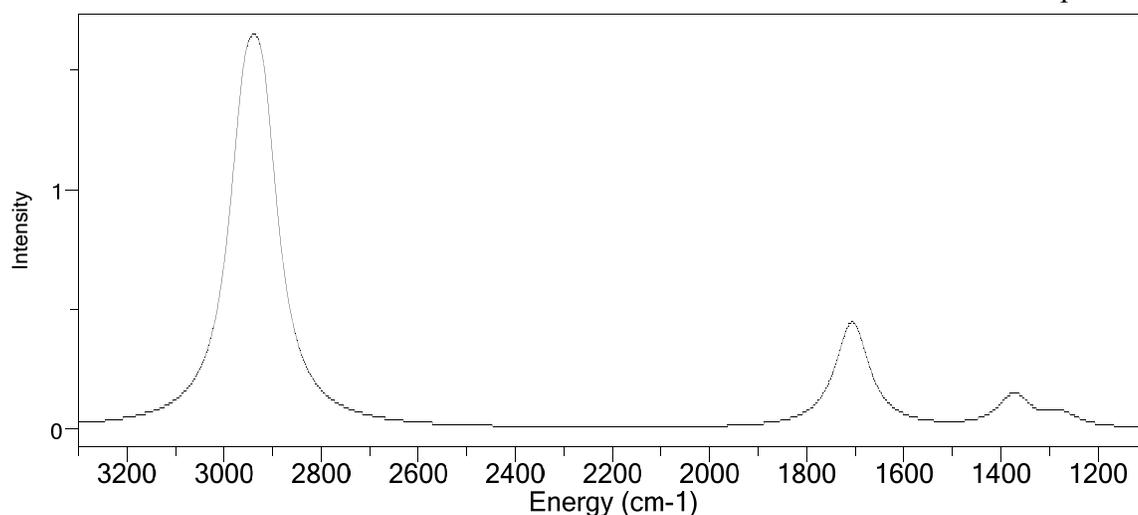
All 9 modes are IR active

All 9 modes are Raman active

Calculated IR and Raman spectra for CH₃F are shown below



Raman Spectrum



Alternate Basis Sets

To help draw pictures of the vibrational modes we can use a *basis set* that relates to vibrations. For CH_4 we can use CH bond stretches as a basis and HCH bends as a basis.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
Γ^{CH}	4	1	0	0	2	Stretches
Γ^{HCH}	6	0	2	0	2	bends

$$\Gamma^{\text{CH}} = \Gamma^{A_1} \oplus \Gamma^{T_2}$$

$$\Gamma^{\text{HCH}} = \Gamma^{A_1} \oplus \Gamma^E \oplus \Gamma^{T_2}$$

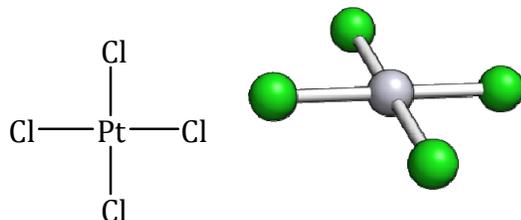
If we add this up we find that this is 10 normal modes but we expect only 9.

Looking at the bending modes we see an A_1 representation. Since there is no way to increase all the bond angles at once in CH_4 this must be discounted.

In order to visualize the vibrations we must make linear combinations of our basis set elements that are orthonormal (symmetry adapted).

Homework Set 3

1. Construct the set of 3×3 matrices that transform a set of $\{x, y, z\}$ coordinates for the following operations: E, C_2, i, σ_h . Show that these matrices form a reducible representation of the C_{2h} point group.
2. Consider the following molecule (tetrachloroplatinate)



Write the characters for Γ^{3N}

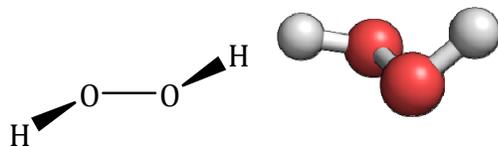
Find all of the irreducible representations that form Γ^{3N}

Indicate which irreducible representation correspond to Γ^{tran} , Γ^{rot} and Γ^{vib}

How many vibrations are infrared active and what are their symmetries?

How many vibrations are Raman active and what are their symmetries?

3. Hydrogen peroxide (H_2O_2) is non-planar with both H atoms lying above the plane.



Assign the point group and determine the symmetry of the vibrations for this molecule.

Sketch what the vibrations might look like. After you've finished, check your results using the 3DNormalModes program (link on the course website). How well do your predictions match?

Projection Operator

The projection operator allows us to find the symmetry adapted linear combinations we need to visualize the vibrational modes in CH₄ and CDH₃.

$$\hat{P}_{\Gamma_i} = \left(\frac{l_i}{h}\right) \sum_R \chi_i(R)(\hat{R})$$

Where

l_i = the dimension of the irreducible representation Γ_i

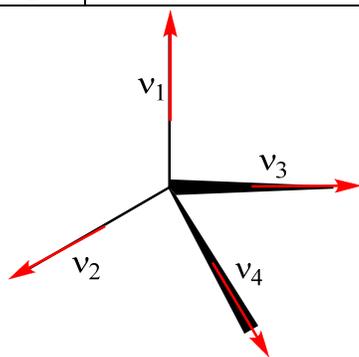
h = the order of the group

$\chi_i(R)$ = character of operation R

\hat{R} = result of the symmetry operation R on a basis function

Project out the A_1 mode for methane (recall $\Gamma^{\text{CH}} = \Gamma^{A_1} \oplus \Gamma^{T_2}$)

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d
A ₁	1	1	1	1	1

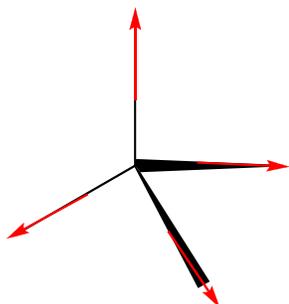


Now we must label our *basis functions* and keep track of what happens to them under each operation.

$$\hat{P}^{A_1}(v_1) = \frac{1}{24} (v_1 + v_1 + v_1 + v_2 + v_3 + v_3 + v_4 + v_2 + v_4 + v_2 + v_3 + v_4 + v_2 + v_4 + v_2 + v_3 + v_3 + v_4 + v_1 + v_1 + v_1 + v_2 + v_3 + v_4)$$

$$\hat{P}^{A_1}(v_1) = \frac{1}{24}(6v_1 + 6v_2 + 6v_3 + 6v_4) = \frac{1}{4}(v_1 + v_2 + v_3 + v_4)$$

As you would predict this is the totally symmetric stretch



A₁ stretching mode

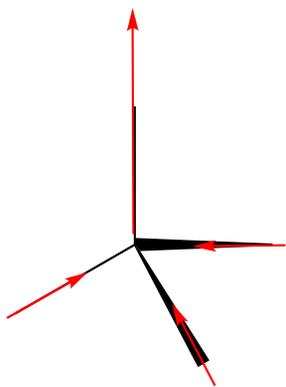
Do the same for the T₂ mode

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d
T ₂	3	0	-1	-1	1

$$\hat{P}^{T_2}(v_1) = \frac{3}{24}(3v_1 + 0(v_1 + v_1 + v_2 + v_3 + v_3 + v_4 + v_2 + v_4) - v_2 - v_3 - v_4 - v_2 - v_4 - v_2 - v_3 - v_3 - v_4 + v_1 + v_1 + v_1 + v_2 + v_3 + v_4)$$

$$\hat{P}^{T_2}(v_1) = \frac{3}{24}(6v_1 - 2v_2 - 2v_3 - 2v_4) = \frac{1}{4}(3v_1 - v_2 - v_3 - v_4)$$

This is an asymmetric stretching mode that is triply degenerate.

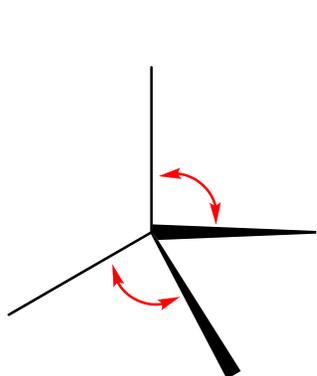


T₂ stretching modes

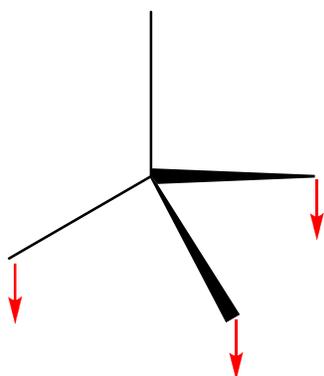
One must project out two other basis functions to find the other two modes. They will look identical but be rotated relative to the mode drawn here.

Notice the v₁ function is displaced 3 times more than the other 3 basis functions.

In an analogous manner the bending modes may be projected to reveal the following:



E bending modes



T₂ bending modes

Animations of these vibrations can be seen online here:

<http://www.molwave.com/software/3dnormalmodes/3dnormalmodes.htm>

Bonding Theories

Lewis Bonding Theory

Atoms seek to obtain an octet of electrons in the outer shell (duet for hydrogen).

A single bond is formed when two electrons are shared between two atoms

e.g. H:H

A double bond is formed when two pairs of electrons are shared

e.g. O::O

Lewis theory works well for connectivity but does not give predictions about three dimensional shape.

VSEPR – Valence Shell Electron Pair Repulsion Theory

Predicts shape by assuming that atoms and lone electron pairs seek to maximize the distance between other atoms and lone pairs.

Works well for shapes but must be combined with Lewis theory for connectivity and bond order.

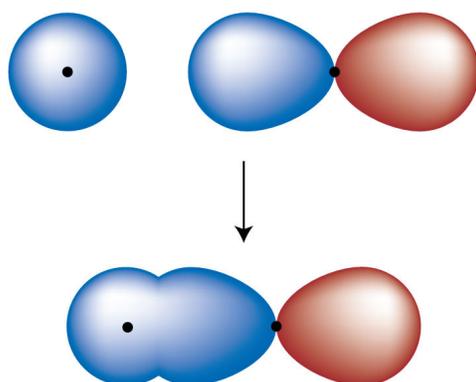
e.g. An atom with four “things” (i.e. bonds or lone pairs) would adopt a tetrahedral geometry with respect to the things. The molecular shape is described relative to the bonds only.

NH₃ has three bonds and one lone pair on the N atom, giving a tetrahedral geometry. However, the shape of NH₃ is described as trigonal pyramidal when only the bonds are considered.

Valance Bond Theory

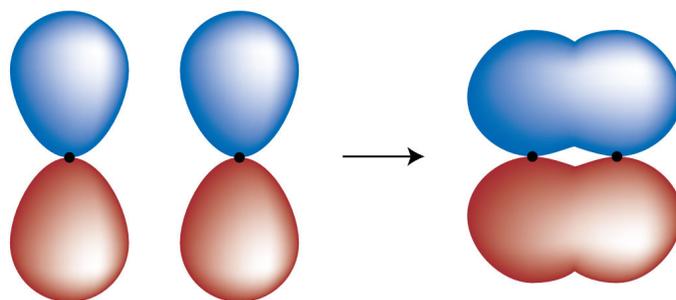
VB theory was developed in the 1920's and was the first quantum mechanical description of bonding. In VB theory bonds are formed from the overlap of atomic orbitals between adjacent atoms. This theory predicted different shapes for single (σ) and multiple (π) bonds.

Consider the overlap of an electron in hydrogen $1s^1$ orbital and an electron in a carbon $2p^1$ orbital



The resulting overlap of wavefunctions results in continuous electron density between the atoms which is classified as a bonding interaction. The resulting σ bond has cylindrical symmetry relative to the bond axis.

Double and triple bonds form from the overlap of adjacent parallel p-orbitals. The result is shown below.



A double bond consists of one σ bond and one π bond. A triple bond is a σ bond and two π bonds.

Hybrid Orbital Theory

VB theory gets us started but we know that other geometries exist in molecules. Consider carbon with a ground state electron configuration of $[\text{He}]2s^22p^2$. With the addition of a small amount of energy one 2s electron is promoted to the 2p shell and the following configuration results $[\text{He}]2s^12p_x^12p_y^12p_z^1$. This leaves four half filled orbitals that can overlap with other orbitals on adjacent atoms.

Will this result in different types of bonds? Overlap of an s-orbital and a p-orbital will not be the same. However, we know that in CH_4 all of the bonds are equivalent.

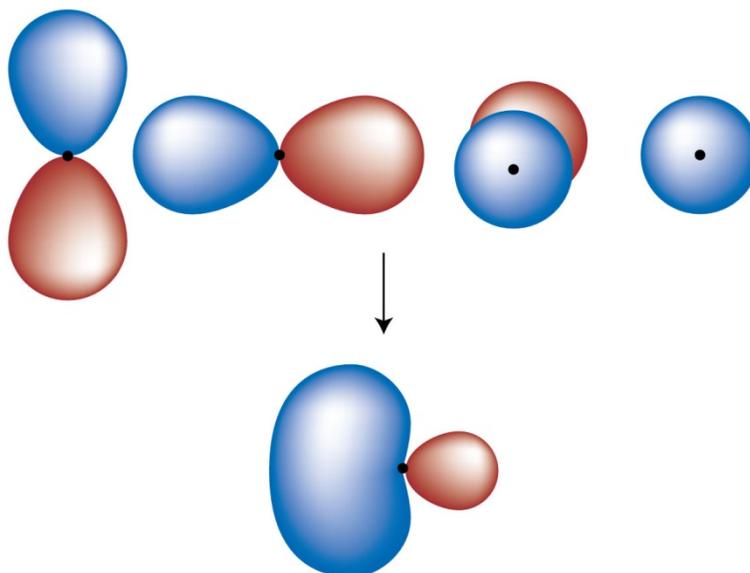
The solution is to create **hybrid orbitals** that are formed when we take linear combinations of the four available atomic orbitals.

The four unique linear combinations that can be formed are as follows

$$h_1 = s + p_x + p_y + p_z \quad h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z \quad h_4 = s + p_x - p_y - p_z$$

Graphically the results are shown below:



These linear combination give rise to four new orbitals that have electron density pointed along tetrahedral angles. The orbitals are named sp^3 hybrid orbitals.

Other hybrid orbitals are possible with differing geometry

Orbital	Shape
sp	Linear
sp^2	Trigonal planar
sp^3	Tetrahedral
sp^3d	Trigonal pyramidal
sp^3d^2	octahedral

Overlap of the hybrid orbitals with other orbital (hybrid or atomic) describe the σ bonding network in molecule. Multiple bonds are formed with unused p-orbitals overlapping to form π bonds as described in VB theory.

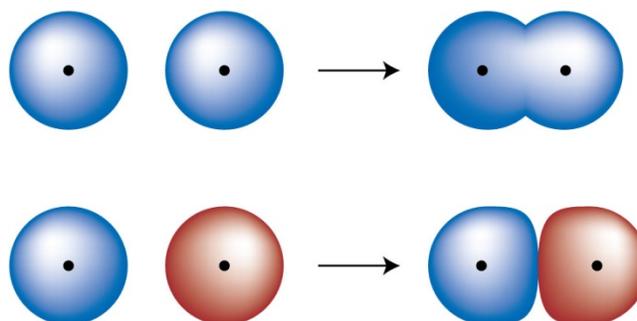
Molecular Orbital Theory

MO theory was also developed during the 1920's and is a quantum mechanical description of bonding. All of the preceding bonding models are termed localized electron bonding models because it is assumed that a bond is formed when electrons are shared between two atoms only. MO theory allows for delocalization of electrons. That is, electrons may be shared between more than two atoms over longer distances.

Similarly to VB theory, MO's are formed from the interaction of atomic orbitals. Here we form linear combinations of atomic orbitals. When we combine two AO's we must form two MO's

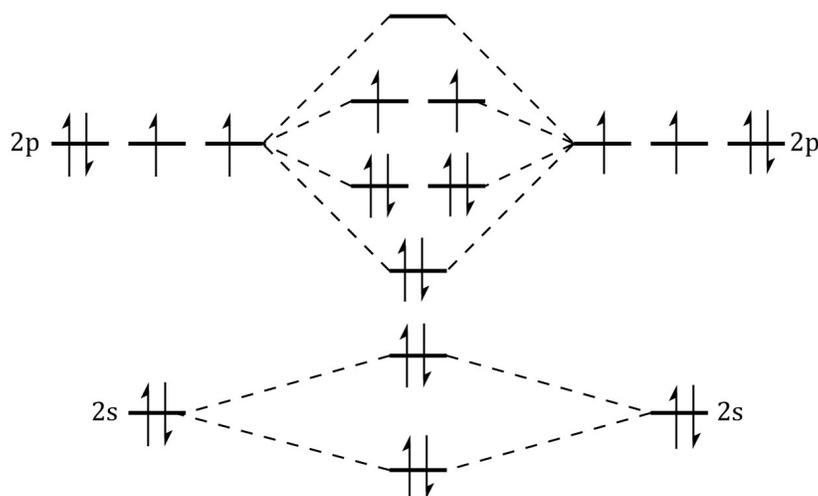
$$\psi_1 = \psi_{1s_A} + \psi_{1s_B}$$

$$\psi_1 = \psi_{1s_A} - \psi_{1s_B}$$



Constructive interference leads to the MO shown in the top example and the resulting MO is said to be bonding. Destructive interference gives the second example is termed anti-bonding.

For O_2 the MO diagram is shown below. This correctly predicts that O_2 has two unpaired electrons. None of the previous theories could accommodate for this fact.



Quantum mechanical description of orbitals

Erwin Schrödinger proposed a method to find electron wavefunctions. The time-independent Schrödinger equation in one dimension is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

where ψ is the wavefunction and

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34}$$

$V(x)\psi$ is the potential energy of the electron at position x and

and $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}$ is the kinetic energy of the electron. This equation is often simplified as

$$\hat{H}\psi = E\psi$$

where \hat{H} is called the Hamiltonian operator. Written in this form we see that this is an Eigen value equation. The total energy of the electron becomes the Eigen value of the Hamiltonian and ψ is the Eigen function.

ψ describes the dynamic information about a given electron. The probability of finding an electron in a given volume of infinitely small size is

$$P = |\psi^2|d\tau$$

$$d\tau = dxdydz$$

With regard to specifically identifying the dynamic information about an electron we are limited by the following:

$$\Delta x \cdot \Delta p \geq \frac{1}{2} \hbar$$

This is known as the Heisenberg uncertainty principle and states that we cannot know both the position and momentum of a particle with arbitrary precision. Δx is the error (uncertainty) in position and Δp is the error in momentum.

Group Theory and Quantum Mechanics

If we exchange any two particles in a system by carrying out a symmetry operation, the Hamiltonian must remain unchanged because we are in an equivalent state.

In other words, the Hamiltonian commutes with all R for a group

$$R\hat{H} = \hat{H}R$$

There are cases in which multiple Eigen functions give the same Eigen value.

$$\hat{H}\psi_{i1} = E_i\psi_{i1}$$

$$\hat{H}\psi_{i2} = E_i\psi_{i2}$$

: :

$$\hat{H}\psi_{in} = E_i\psi_{in}$$

We say that the Eigen value is degenerate or n-fold degenerate. In these cases the Eigen functions are a solution to the Schrödinger equation and also any linear combination of the degenerate Eigen functions

$$\hat{H} \sum_j a_{ij}\psi_{ij} = E_i \sum_j a_{ij}\psi_{ij}$$

We will construct the Eigen functions (and subsequently the linear combinations) so that they are all orthonormal to each other.

$$\int \psi_i^* \psi_j d\tau = \delta_{ij}$$

The set of orthonormal Eigen functions for a molecule can form the basis of an irreducible representation of the group. For a non-degenerate Eigen function we have

$$\hat{H}R\psi_i = E_iR\psi_i$$

so that $R\psi_i$ is an Eigen function of the Hamiltonian.

Because ψ_i is normalized $R\psi_i = \pm 1 \psi_i$. Therefore if we apply all R in a group to a non-degenerate ψ_i , we get a representation where each matrix element, $\Gamma_i(R)$ will be ± 1 . A one-dimensional matrix is by definition irreducible.

A similar analysis for n-fold degenerate Eigen functions will result in an n-dimensional irreducible representation.

How do we find the linear combination of wavefunctions that result in a set of orthonormal Eigen functions?

The projection operator discussed previously for vibrational analysis is useful again here.

$$\hat{P}^{\Gamma_i} = \left(\frac{l_i}{h}\right) \sum_R \chi_i(R)(\hat{R})$$

Construction of basis sets to project is the subject of theoretical chemistry and physics. Because we cannot solve the Schrödinger equation directly we must make approximations.

Hartree-Fock Approximation – write MO's for each electron independently of the others. The error that is introduced here is that the electron position depends on the position of all of the other electrons (electron-electron repulsion). A correction factor must be applied after solving the problem to account for this. This is called the “correlation energy”.

Rules for Molecular Orbitals

- 1) Wavefunctions cannot distinguish between electrons
- 2) If electrons exchange positions, the sign of the wavefunction must change.

LCAO Approximation

Molecular Orbitals are **l**inear **c**ombinations of **a**tomic **o**rbitals.

π electron Approximation

– assume that σ and π bonds are independent of each other. That is, σ bonds are localized, while π bonds may be delocalized.

Hückel π Orbital Method

We will use a redefined Hamiltonian called the effective Hamiltonian.

$$H^{eff,\pi}(\mu) = h_{\mu}^{core} + \sum_i \{2J_i(\mu) - K_i(\mu)\}$$

where J and K are the Coulomb and exchange integrals respectively. The Coulomb integral takes into account the electron-electron repulsion between two electrons in different orbitals, and the exchange integral relates to the energy when electrons in two orbitals are exchanged with each other.³

In the Hückel π orbital method we construct new MO's as follows

$$\Phi_i^{\pi}(k) = \sum_{s=1}^N C_{sj} \phi_s(k)$$

where N is the number of atoms in the π orbital system, ϕ_s is a p_z orbital on a given atom and C_{sj} is a coefficient (determined by projection).

Hückel theory makes the following approximations:

$$H_{rr}^{eff,\pi} = \alpha$$

$$H_{rs}^{eff,\pi} = \begin{cases} \beta & \text{(if r and s are nearest neighbors)} \\ 0 & \text{(otherwise)} \end{cases}$$

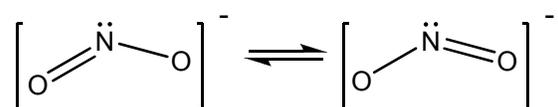
α is the Coulombic integral which raises the energy of a wavefunction (positive value) and β is the resonance integral which lowers the energy of a wavefunction (negative value). These integrals can be evaluated numerically but are beyond the scope of what we hope to accomplish here.³

³ For more information on bonding theory consult an appropriate text on quantum mechanics.

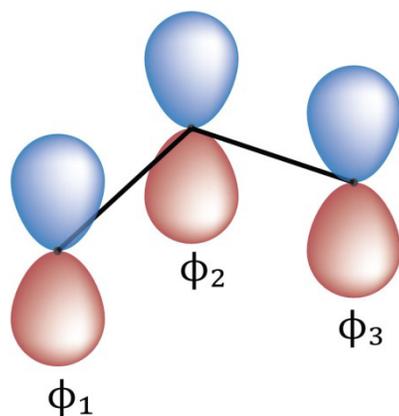
As it stands so far, we have a method for finding the energies of N π orbitals for N atoms. The result is an N -dimensional polynomial. Problems of this type can be solved but application of symmetry to the system greatly reduces the amount of work to be done.

Hückel Orbitals for Nitrite

Consider the π orbital system for the nitrite anion (NO_2^-)



This molecule belongs to the C_{2v} point group. We will use a p_z orbital on each atom to construct the π orbital system for nitrite. This forms the basis for a reducible representation, Γ^{AO}



We must write the characters for Γ^{AO} in an analogous manner as we wrote the characters for Γ^{3N} . Keep in mind the sign of the wavefunctions when performing the symmetry operations.

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma'_{(yz)}$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$$\overline{\Gamma^{A_0} \quad \left| \begin{array}{cccc} 3 & -1 & 1 & -3 \end{array} \right|}$$

Next we reduce Γ^{A_0} to find the irreducible components.

$$a_{A_1} = \frac{1}{4} [(1)(3) + (1)(-1) + (1)(1) + (1)(-3)] = 0$$

$$a_{A_2} = \frac{1}{4} [(1)(3) + (1)(-1) + (-1)(1) + (-1)(-3)] = 1$$

$$a_{B_1} = \frac{1}{4} [(1)(3) + (-1)(-1) + (1)(1) + (-1)(-3)] = 2$$

$$a_{B_2} = \frac{1}{4} [(1)(3) + (-1)(-1) + (-1)(1) + (1)(-3)] = 0$$

$$\Gamma^{A_0} = \Gamma^{A_2} \oplus 2\Gamma^{B_1}$$

Next we project the basis functions out of the irreducible representations. Because ϕ_1 and ϕ_3 are equivalent it doesn't matter which one we pick. However, ϕ_2 is unique and must also be projected each time.

$$P^{\Gamma^{A_2}}(\phi_1) = \frac{1}{4}(\phi_1 - \phi_3 - \phi_3 + \phi_1) = \frac{1}{2}(\phi_1 - \phi_3)$$

$$P^{\Gamma^{B_1}}(\phi_2) = \frac{1}{4}(\phi_2 - \phi_2 - \phi_2 + \phi_2) = 0 \text{ (i.e. no contribution)}$$

$$P^{\Gamma^{B_1}}(\phi_1) = \frac{1}{4}(\phi_1 + \phi_3 + \phi_3 + \phi_1) = \frac{1}{2}(\phi_1 + \phi_3)$$

$$P^{\Gamma^{B_1}}(\phi_2) = \frac{1}{4}(\phi_2 + \phi_2 + \phi_2 + \phi_2) = \phi_2$$

There are two orbitals with B_1 symmetry. So we will take linear combinations of the two projected orbitals to find the orthogonal results

$$\Phi_1 = \frac{1}{2}(\phi_1 - \phi_3)$$

$$\Phi_2 = \frac{1}{2}\phi_1 + \phi_2 + \frac{1}{2}\phi_3$$

$$\Phi_3 = \frac{1}{2}\phi_1 - \phi_2 + \frac{1}{2}\phi_3$$

Lastly we must normalize the orbitals since it is assumed that

$$\int \Phi_i^* \Phi_j d\tau = \delta_{ij}$$

There is a normalization factor N that is found as follows for Φ_1

$$\int N \frac{1}{2}(\phi_1 - \phi_3)^* N \frac{1}{2}(\phi_1 - \phi_3) d\tau = 1$$

$$\frac{1}{4} N^2 \int (\phi_1 - \phi_3)^* (\phi_1 - \phi_3) d\tau = 1$$

$$\frac{1}{4} N^2 \sum_{i=1}^2 \sum_{j=1}^2 \int (\phi_1 - \phi_3)^* (\phi_1 - \phi_3) d\tau = 1$$

Note that the sums here give δ_{ij} for the individual $\phi_i \phi_j$ terms. There are four integrals in this case involving overlap of $\langle \phi_1, \phi_1 \rangle$, $\langle \phi_1, -\phi_3 \rangle$, $\langle -\phi_3, \phi_1 \rangle$, $\langle -\phi_3, -\phi_3 \rangle$. These give $1 + 0 + 0 + 1$ respectively.

$$\frac{1}{4} N^2 \times 2 = 1$$

solving for N we find $N = \sqrt{2}$ our normalized Φ_1 is then

$$\Phi_1 = \frac{\sqrt{2}}{2} (\phi_1 - \phi_3) \text{ (A}_2 \text{ symmetry)}$$

Similarly we find the normalized Φ_2 and Φ_3 to be

$$\Phi_2 = \sqrt{\frac{2}{3}} \left(\frac{1}{2}\phi_1 + \phi_2 + \frac{1}{2}\phi_3 \right) \text{ (B}_1 \text{ symmetry)}$$

$$\Phi_3 = \sqrt{\frac{2}{3}} \left(\frac{1}{2} \phi_1 - \phi_2 + \frac{1}{2} \phi_3 \right) \text{ (B}_1 \text{ symmetry)}$$

If we evaluate $H^{eff,\pi}$ for each new orbital we find that

$$H_{(\Phi_1\Phi_1)}^{eff,\pi} = \int \frac{\sqrt{2}}{2} (\phi_1 - \phi_3)^* H^{eff,\pi} \frac{\sqrt{2}}{2} (\phi_1 - \phi_3) d\tau$$

Distributing the ϕ_i across the Hamiltonian and separating the integrals we are left with the following sum

$$\int \frac{\sqrt{2}}{2} (\phi_1)^* H^{eff,\pi} \frac{\sqrt{2}}{2} (\phi_1) d\tau + \int \frac{\sqrt{2}}{2} (\phi_1)^* H^{eff,\pi} \frac{\sqrt{2}}{2} (-\phi_3) d\tau + \int \frac{\sqrt{2}}{2} (-\phi_3)^* H^{eff,\pi} \frac{\sqrt{2}}{2} (\phi_1) d\tau + \int \frac{\sqrt{2}}{2} (-\phi_3)^* H^{eff,\pi} \frac{\sqrt{2}}{2} (-\phi_3) d\tau$$

These integrals evaluate according to Hückel approximations as

$$H_{(\Phi_1\Phi_1)}^{eff,\pi} = \frac{1}{2} \alpha + 0 + 0 + \frac{1}{2} \alpha$$

Simplifying leaves us with:

$$H_{(\Phi_1\Phi_1)}^{eff,\pi} = \frac{1}{2} (\alpha + \alpha) = \alpha$$

A similar analysis for Φ_2 and Φ_3 yields:

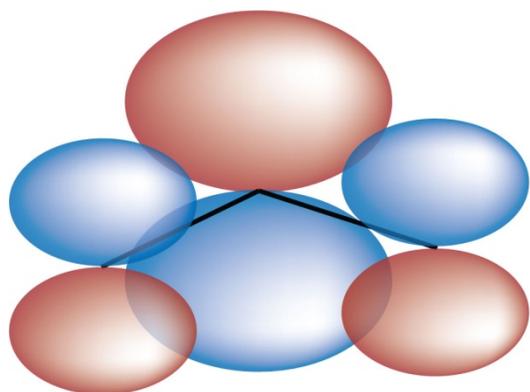
$$H_{(\Phi_2\Phi_2)}^{eff,\pi} = \frac{2}{3} \left(\frac{1}{4} \alpha + \frac{1}{2} \beta + \frac{1}{2} \beta + \alpha + \frac{1}{2} \beta + \frac{1}{2} \beta + \frac{1}{4} \alpha \right) = \alpha + \frac{4}{3} \beta$$

$$H_{(\Phi_3\Phi_3)}^{eff,\pi} = \frac{2}{3} \left(\frac{1}{4} \alpha - \frac{1}{2} \beta - \frac{1}{2} \beta + \alpha - \frac{1}{2} \beta - \frac{1}{2} \beta + \frac{1}{4} \alpha \right) = \alpha - \frac{4}{3} \beta$$

In order of increasing energy we find $\Phi_2 < \Phi_1 < \Phi_3$

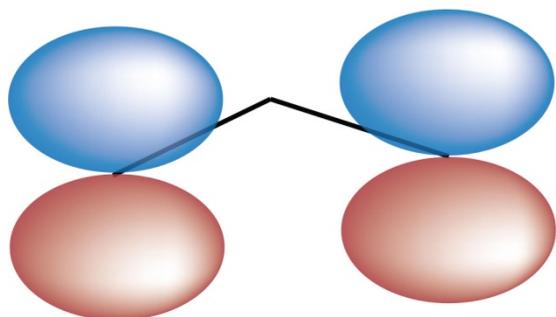
Recall that β is a negative term and lowers the energy of the orbital.

Drawing pictures of the orbitals helps to visualize the results



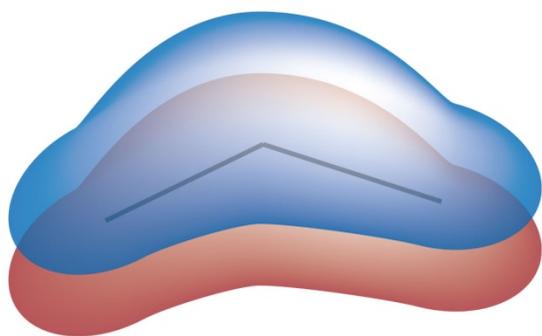
B₁ anti-bonding orbital

$$\alpha - \frac{4}{3}\beta$$



A₂ non-bonding orbital

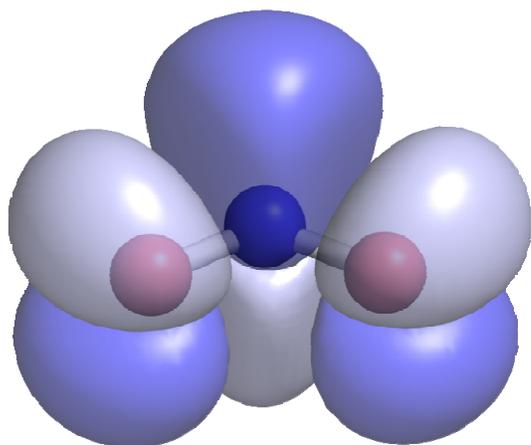
$$\alpha$$



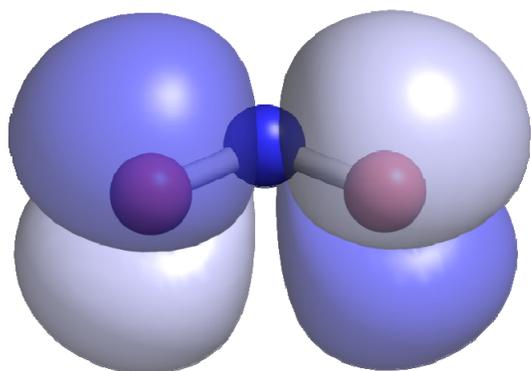
B₁ bonding orbital

$$\alpha + \frac{4}{3}\beta$$

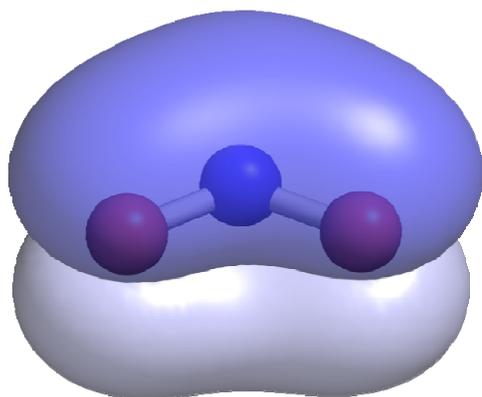
Nitrite π orbitals calculated using *ab initio* methods.



B_1 anti-bonding orbital



A_2 non-bonding orbital



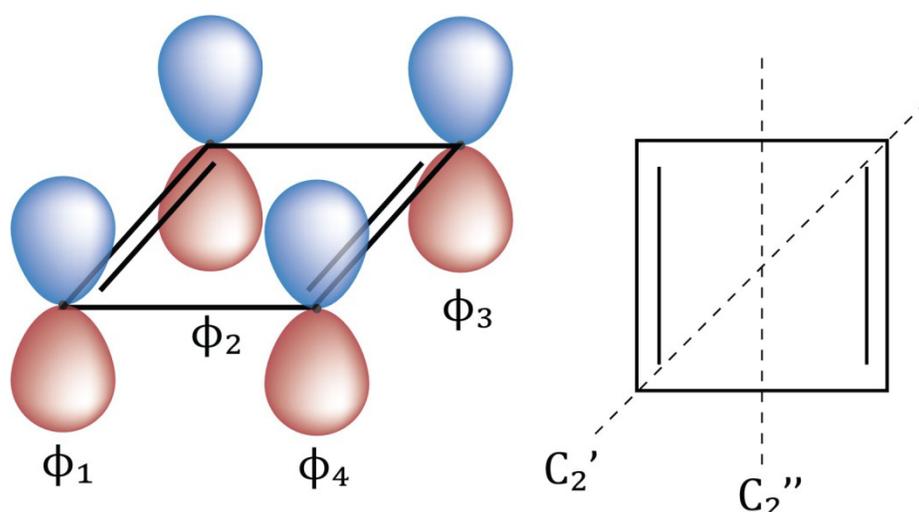
B_1 bonding orbital

Hückel MO's for Cyclobutadiene

Find the π orbitals for cyclobutadiene using the Hückel π orbital method.

Cyclobutadiene belongs to the D_{4h} point group. This group has an order of 16. To reduce the work, we can use a subgroup of D_{4h} , D_4 which has an order of 8. In doing so we lose information about the odd or even nature of the orbital (g or u). However, once the MO's are constructed we can easily determine an MO's g or u status through examination of symmetry operations on the new MO's.

The basis set will be the four p_z orbitals perpendicular to the molecular plane.



Writing Γ^{A0} for D_4 we find;

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0
Γ^{A0}	4	0	0	-2	0

Reducing Γ^{A0} results in $\Gamma^{A0} = \Gamma^{A_2} \oplus \Gamma^{B_2} \oplus \Gamma^E$

Now we must project out the symmetry adapted linear combinations and then normalize the resulting functions.

$$P^{\Gamma^{A_2}}(\phi_1) = \frac{1}{8}(\phi_1 + \phi_2 + \phi_4 + \phi_3 + \phi_1 + \phi_3 + \phi_2 + \phi_4)$$

$$\Phi_1 = \frac{1}{4}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

$$P^{\Gamma^{B_2}}(\phi_1) = \frac{1}{8}(\phi_1 - \phi_2 - \phi_4 + \phi_3 + \phi_1 + \phi_3 - \phi_2 - \phi_4)$$

$$\Phi_2 = \frac{1}{4}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

$$P^{\Gamma^E}(\phi_1) = \frac{2}{8}(2\phi_1 - 2\phi_3) = \frac{1}{2}(\phi_1 - \phi_3)$$

Because E is two-dimensional, we must project an additional orbital.

$$P^{\Gamma^E}(\phi_2) = \frac{2}{8}(2\phi_2 - 2\phi_4) = \frac{1}{2}(\phi_2 - \phi_4)$$

The two E MO's will be the linear combination (sum and difference) of the two projections we have just made.

$$\Phi_3 = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4)$$

$$\Phi_4 = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4)$$

Normalizing the MO's results in the following orthonormal set of functions

$$\Phi_1 = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \quad A_2 \text{ symmetry}$$

$$\Phi_2 = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \quad B_2 \text{ symmetry}$$

$$\Phi_3 = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \quad E \text{ symmetry}$$

$$\Phi_4 = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4) \quad E \text{ symmetry}$$

To put the orbital in the correct order energetically, we evaluate $H_{rr}^{eff,\pi}$ for each MO.

$$H_{(\Phi_1\Phi_1)}^{eff,\pi} = \alpha + 2\beta$$

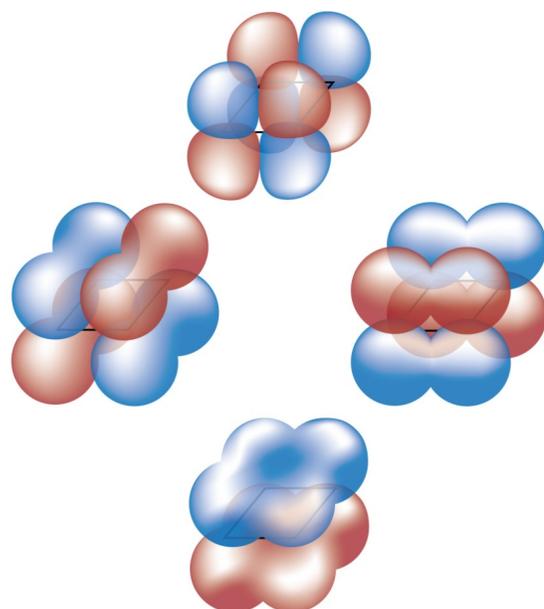
$$H_{(\Phi_2\Phi_2)}^{eff,\pi} = \alpha - 2\beta$$

$$H_{(\Phi_3\Phi_3)}^{eff,\pi} = \alpha$$

$$H_{(\Phi_4\Phi_4)}^{eff,\pi} = \alpha$$

Because the E orbital is degenerate, both orbitals must have the same energy. We find the in order of increasing energy, $\Phi_1 < \Phi_3, \Phi_4 < \Phi_2$.

Lastly we can look at how the each of these orbitals transforms in the D_{4h} point group and assign the g or u subscript. For example, the B₂ orbital could be B_{2u} or B_{2g}. Under inversion (i) the orbital goes into -1 of itself so it must be B_{2u} (the character under i for B_{2g} is +1 and -1 for B_{2u}). Analysis of the remaining orbits gives A_{2u} and E_g.



B_{2u} anti-bonding

$$\alpha - 2\beta$$

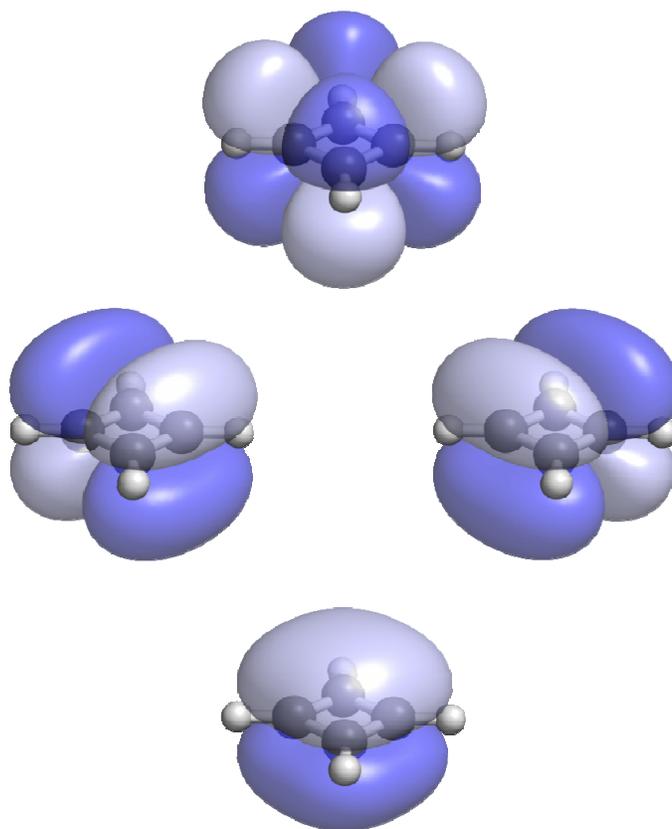
E_g bonding

$$\alpha$$

A_{2u} bonding

$$\alpha + 2\beta$$

π molecular orbitals as calculated by *ab initio* methods

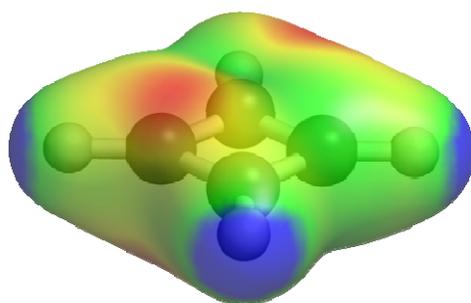


B_{2u}

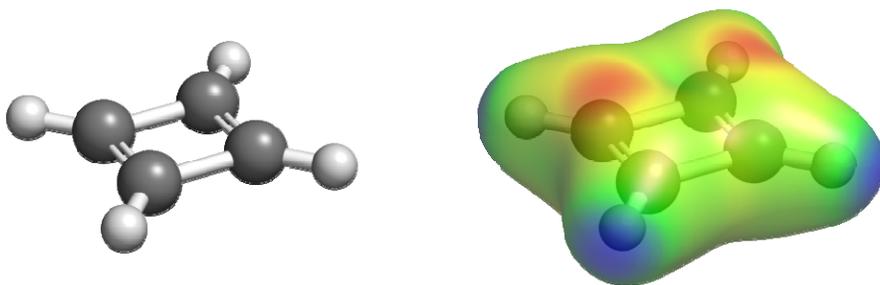
E_g

A_{2u}

A note of caution. We might be tempted to view cyclobutadiene as an aromatic ring system based upon the appearance of the A_{2u} π orbital. However, examination of the electron density color mapped with the electrostatic potential (red = negative, blue = positive) reveals a non-uniform electron density distribution. This indicates that cyclobutadiene is not aromatic but rather alternating double and single bonds.

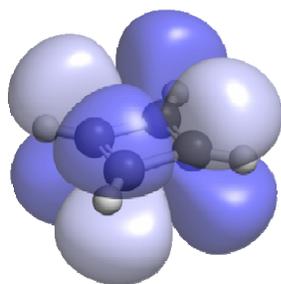


If the structure is geometry optimized, we see that the symmetry is no longer D_{4h} , but rather that of a rectangle, D_{2h} . The electrostatic potential map places extra electron density along the shorter double bonds we would predict. The Hückel rule for aromaticity requires $4n + 2$ π electrons and here we have only 4 π electrons, so the lack of aromaticity is expected.

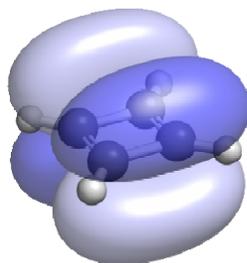


If the symmetry changes, the symmetry of the molecular orbitals also changes. Calculations of the new orbitals are shown on the following page.

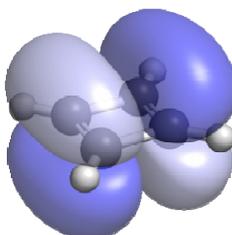
Ab initio calculations for the π orbitals in geometry optimized cyclobutadiene.



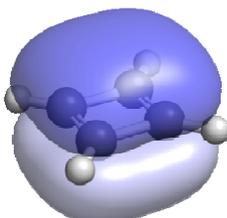
A_u



B_{3g}



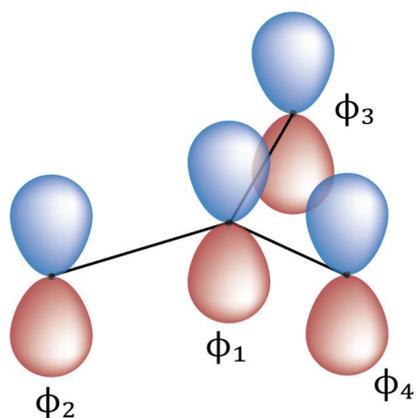
B_{2g}



B_{1u}

Notice that the general shape of the MO's is similar to what we calculated for the molecule under D_{4h} symmetry, but the E_g orbital has split into the non-degenerate B_{2g} and B_{3g} orbitals shown above.

Hückel MO's for Boron Trifluoride



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

Construct the Hückel π molecular orbitals for carbonate and compare to the results for semi-empirical calculations of all molecular orbitals for carbonate.

Step 1. Find Γ^{AO}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ^{AO}	4	1	-2	-4	-1	2

Step 2. Apply the reduction formula to find the irreducible representations.

$$a_{A_1'} = \frac{1}{12} (4 + 2 - 6 - 4 - 2 + 6) = 0$$

$$a_{A_2'} = \frac{1}{12} (4 + 2 + 6 - 4 - 2 - 6) = 0$$

$$a_{E'} = \frac{1}{12} (8 - 2 + 0 - 8 + 2 + 0) = 0$$

$$a_{A_1''} = \frac{1}{12} (4 + 2 - 6 + 4 + 2 - 6) = 0$$

$$a_{A_2''} = \frac{1}{12} (4 + 2 + 6 + 4 + 2 + 6) = 2$$

$$a_{E''} = \frac{1}{12} (8 - 2 + 0 + 8 - 2 + 0) = 1$$

$$\Gamma^{AO} = 2\Gamma^{A_2''} \oplus \Gamma^{E''}$$

Step 3. Project the new MO's

Because ϕ_1 is on the center atom we must project ϕ_1 and one of the others and make linear combinations to be sure to have complete orbitals.

$$P^{\Gamma A_2''}(\phi_1) = \frac{1}{12}(\phi_1 + \phi_1 + \phi_1) = \phi_1$$

$$\begin{aligned} P^{\Gamma A_2''}(\phi_2) &= \frac{1}{12}(\phi_2 + \phi_3 + \phi_4 + \phi_2 + \phi_3 + \phi_4 + \phi_2 + \phi_3 + \phi_4 + \phi_2 + \phi_3 + \phi_4) \\ &= \frac{1}{3}(\phi_2 + \phi_3 + \phi_4) \end{aligned}$$

Taking the linear combinations of these two we obtain the following:

$$\Phi_1 = \phi_1 + \frac{1}{3}\phi_2 + \frac{1}{3}\phi_3 + \frac{1}{3}\phi_4$$

$$\Phi_2 = \phi_1 - \frac{1}{3}\phi_2 - \frac{1}{3}\phi_3 - \frac{1}{3}\phi_4$$

Normalizing these results gives:

$$\Phi_1 = \frac{\sqrt{3}}{2} \left(\phi_1 + \frac{1}{3}\phi_2 + \frac{1}{3}\phi_3 + \frac{1}{3}\phi_4 \right)$$

$$\Phi_2 = \frac{\sqrt{3}}{2} \left(\phi_1 - \frac{1}{3}\phi_2 - \frac{1}{3}\phi_3 - \frac{1}{3}\phi_4 \right)$$

Now project the E'' orbitals...

$$P^{E''}(\phi_1) = \frac{1}{12}(2\phi_1 - \phi_1 - \phi_1 + 2\phi_1 - \phi_1 - \phi_1) = 0$$

Because ϕ_1 does not contribute to the E'' orbital we must project two other basis functions and take their linear combinations.

$$P^{E''}(\phi_2) = \frac{2}{12}(2\phi_2 - \phi_3 - \phi_4 + 2\phi_2 - \phi_3 - \phi_4) = \frac{1}{6}(2\phi_2 - \phi_3 - \phi_4)$$

$$P^{E''}(\phi_3) = \frac{2}{12}(2\phi_3 - \phi_4 - \phi_2 + 2\phi_3 - \phi_4 - \phi_2) = \frac{1}{6}(2\phi_3 - \phi_4 - \phi_2)$$

$$\Phi_3 = \frac{1}{6}(\phi_2 + \phi_3 - 2\phi_4)$$

$$\Phi_4 = \frac{1}{6}(3\phi_2 - 3\phi_3)$$

After normalization we are left with

$$\Phi_3 = \frac{1}{\sqrt{6}}(\phi_2 + \phi_3 - 2\phi_4)$$

$$\Phi_4 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Step 4. Determine the energy of each orbital by evaluating $H^{\text{eff},\pi}$.

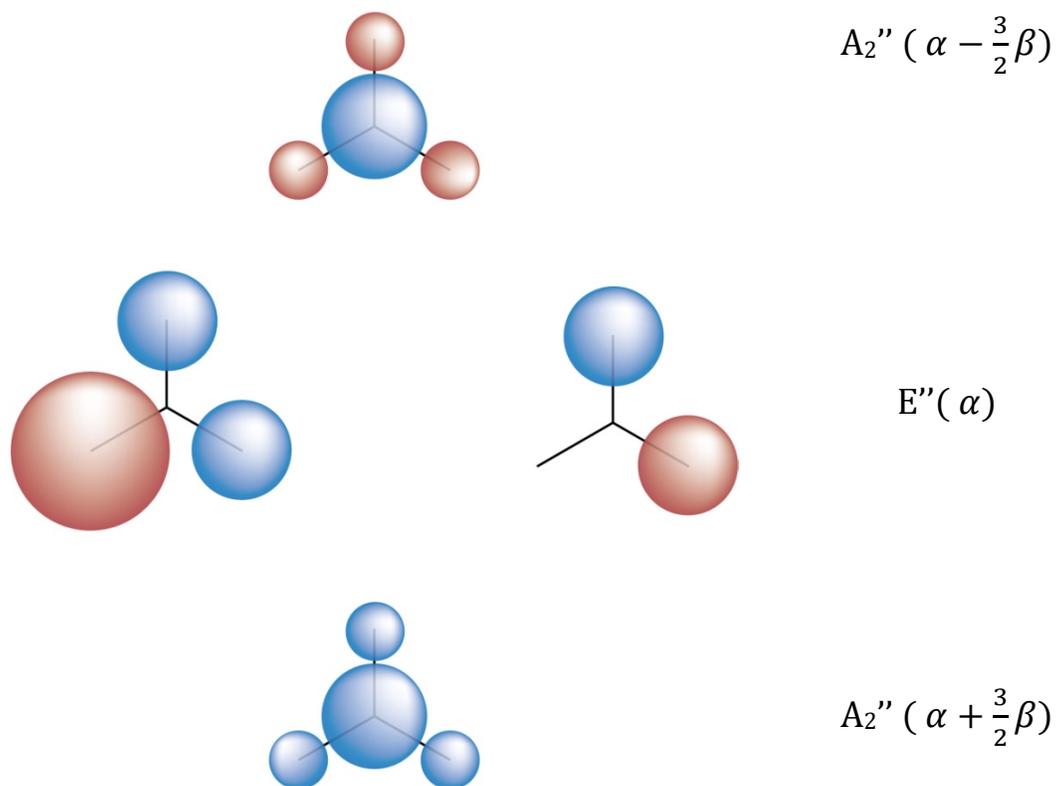
$$\begin{aligned} H_{(\Phi_1\Phi_1)}^{\text{eff},\pi} &= \frac{3}{4}\left(\alpha + \frac{1}{3}\beta + \frac{1}{3}\beta + \frac{1}{3}\beta + \frac{1}{9}\alpha + \frac{1}{3}\beta + \frac{1}{9}\alpha + \frac{1}{3}\beta + \frac{1}{9}\alpha + \frac{1}{3}\beta\right) \\ &= \alpha + \frac{3}{2}\beta \end{aligned}$$

$$\begin{aligned} H_{(\Phi_2\Phi_2)}^{\text{eff},\pi} &= \frac{3}{4}\left(\alpha - \frac{1}{3}\beta - \frac{1}{3}\beta - \frac{1}{3}\beta + \frac{1}{9}\alpha - \frac{1}{3}\beta + \frac{1}{9}\alpha - \frac{1}{3}\beta + \frac{1}{9}\alpha - \frac{1}{3}\beta\right) \\ &= \alpha - \frac{3}{2}\beta \end{aligned}$$

$$H_{(\Phi_3\Phi_3)}^{\text{eff},\pi} = \frac{1}{6}(\alpha + \alpha + 4\alpha) = \alpha$$

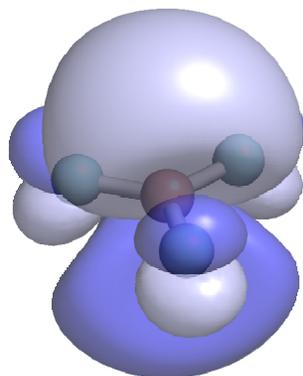
$$H_{(\Phi_4\Phi_4)}^{\text{eff},\pi} = \frac{1}{2}(\alpha + \alpha) = \alpha$$

Step 5. Construct the MO diagram and draw pictures of the MO's

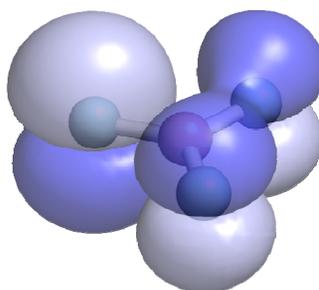
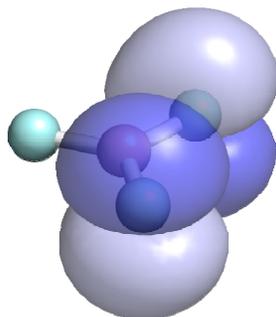


These sketches are a top-down view. The sign of the wavefunction is opposite on the bottom side.

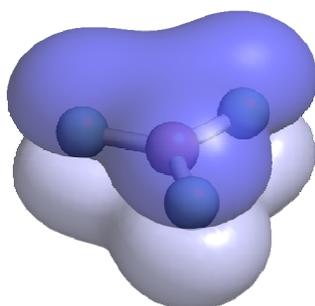
Ab initio calculations give the following MO pictures and the corresponding energy (in Hartree).



A_2''
0.0418 Ha



E''
-0.9073 Ha



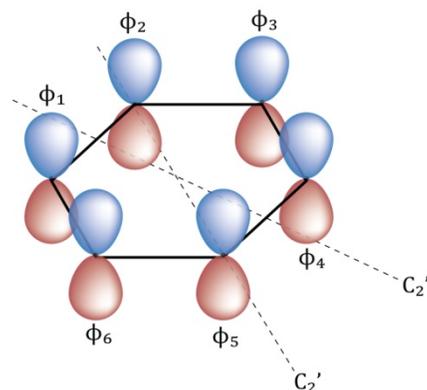
A_2''
-0.9411 Ha

Homework Set 4 – Final Exam

Take home final. You may use your book and class notes but please work on your own. Exams are due Friday before noon. Turn them in to my chemistry department mailbox. You must clearly show all of your work for full credit.

1. Construct the orthonormal Hückel π molecular orbitals for benzene using the subgroup D_6 (given below) and a basis set of the six p_z orbitals that lie perpendicular to the plane of the ring.
2. Determine the correct ordering of the MO's energetically and construct the MO diagram for the π system. Refer to the full D_{6h} point group character table to assign 'g' and 'u' designations to the orbitals.
3. Sketch each of the six orbitals.

D_6	E	2 C_6	2 C_3	C_2	3 C_2'	3 C_2''
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0
Γ_{AO}						



Ab initio calculations for the π orbitals of benzene are shown below

