Quantum Chemistry

Lecture 6
Group Theory

Construction of Character Tables
Orbital and Cartesian bases
Transition moments

NC State University

Construction of the character table

In most character tables, C_{2v} has the following form:

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

We will consider how the various basis functions x, y, z and others in the right hand columns map onto the basis

Vectors of the space (also known as irreducible representations). These are the A_1, A_2, B_1 and B_2.

The totally symmetric basis vector

As an example we will consider the C_{2v} point group, which corresponds to the H_2O molecule for instance. We can call the totally symmetry basis vector A_1 as shown in Table 1. A_1 is just a name like, X, Y or Z for the Cartesian space.

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
A_1	1	1	1	1

The basis vectors must be normalized and orthogonal. Normalization is like saying that these are unit vectors in the space. The dimensionality of the basis must also equal the dimensionality of the space. The C_{2v} point group is 4-dimensional (i.e. there are four symmetry elements). To determine the dimensionality of any point group we need only count the symmetry operations.

The normalization condition

Is A_1 normalized (i.e. does it have a length of 1)? We will sum over the square of the contribution for each symmetry element and then divide by the dimension of the group h. The length L is

$$|S|^2 = \frac{1}{h}\sum_{i=1}^{h} \chi_i^2$$

where S is the *basis vector name and χ is the character or value of each symmetry operation for that particular basis vector. We can see that A_1 is normalized.*

$$|A_1|^2 = \frac{1}{4}(1^2 + 1^2 + 1^2 + 1^2) = 1$$

The other basis vectors must be orthogonal to A_1 and also normalized. We could find these vectors using four equations and four unknowns.

Starting point for construction

We will call the remaining vectors A_2, B_1 and B_2. Based on the information we have up to now we can construct a table of the basis vectors that looks like this.

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

One formal way to find the remaining elements of the table is to use 9 unknown values that fill the table and then to set up nine equations based normalization, orthogonality and the sum rule that each column (except E) sums to zero. However, we will invoke an intuitive approach to find the basis vectors.

The normalization condition for A$_2$

The subscript refers to whether a basis vector changes sign upon reflection. The letter describes whether it changes sign upon rotation. A does not change upon rotation, but B does. 1 does not change sign upon reflection, but 2 does. Thus, A$_2$ does not change sign upon rotation (C$_2$ = 1), but it does change sign upon reflection, i.e $\sigma_{v(xz)} = \sigma_{v(yz)} = $ -1

C$_{2v}$	E	C$_2$	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
A$_1$	1	1	1	1
A$_2$	1	1	-1	-1
B$_1$	1			
B$_2$	1			

We can see that A$_2$ is normalized sine

$$|A_2|^2 = \frac{1}{4}(1^2 + 1^2 + (-1)^2 + (-1)^2) = 1$$

The orthonality is given by

$$|S_1||S_2| = \frac{1}{h}\sum_{i=1}^{h} \chi_{1i}\chi_{2i}$$

which is explicitly given by

$$|A_1||A_2| = \frac{1}{4}\left((1)(1) + (1)(1) + (1)(-1) + (1)(-1)\right) = 0$$

Next we consider the B basis vectors, which should change sign upon rotation.

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

The orthonormal basis in C_{2v}

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

Let's generate the C_{3v} point group.

The operations of C_{3v} are E, $2C_3$, $3\sigma_v$ (h=6, m=3)

$d_1^2 + d_2^2 + d_3^2 = 6$
$d_1 = d_2 = 1$ and $d_3 = 2$.

Since the dimensions of the irreps are the $\chi(E)$ and every group contains the totally symmetric irrep,

C_{3v}	**1**E	**2**C_3	**3**σ_v
Γ_1	1	1	1
Γ_2	1	j	k
Γ_3	2	m	n

Orthogonality of Γ_1 with Γ_2:
(**1**)(1)(1) + (**2**)(1)(j) + (**3**)(1)(k) = 0
1 + 2j + 3k = 0
j = +1 and k = -1

Normalization of Γ_3 means $(1)(2)^2 + 2(m^2) + 3(n^2) = 6$
  so, m = -1 and n =0.

C_{3v}	**1**E	**2**C_3	**3**σ_v
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

For C_{3v},

C_{3v}	**1**E	**2**C_3	**3**σ_v
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Treating rotations and binary products as before, we can represent the C_{3v} point group as

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

The x^2-y^2 and xy orbitals are also degenerate as are the xz and yz orbitals

Concept of a basis

A basis refers to a type of function that is transformed by the symmetry operations of a point group. Examples include the spherical harmonics, vectors, internal coordinates (e..g bonds, angles, torsions), translations, rotations and any other function needed to describe the electronic or nuclear properties of a molecule.

The spherical harmonics include the orbitals, s, p, d etc. and can have more than one dimension. Thus, we need to examine how those functions are changed by the operations.

Based on this treatment we can assign the basis to one of the irreducible representations of the point group.

Orbital basis

Oxygen s-orbitals in water,
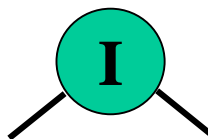
C_{2v}	E	C_2	σ_v	σ_v'
$\Gamma_{O(s)}$	+1	+1	+1	+1

$$\Gamma_{O(s)} = a_1$$

s-orbitals on central elements will always transform as the totally symmetric representation but are not included in character tables

p_z

E   **C$_2$**   **$\sigma_{v(xz)}$**   **$\sigma_{v(yz)}$**

p_z

E C_2 $\sigma_{v(xz)}$ $\sigma_{v(yz)}$

1   1   1   1

p_x

E   **C$_2$** $\boldsymbol{\sigma}_{v(xz)}$ $\boldsymbol{\sigma}_{v(yz)}$

p_x
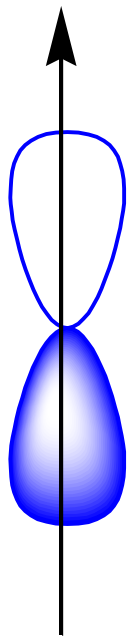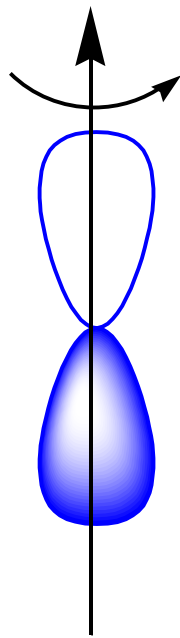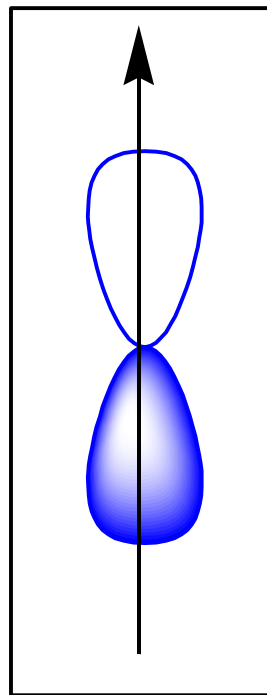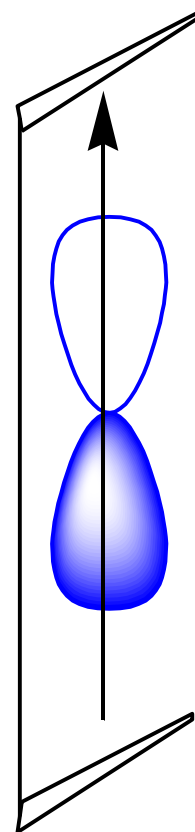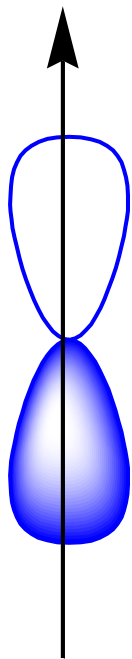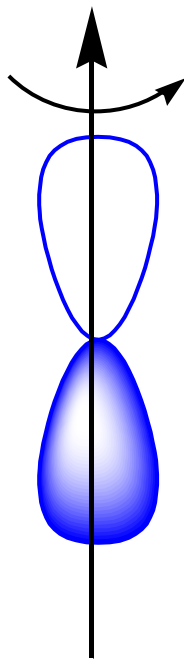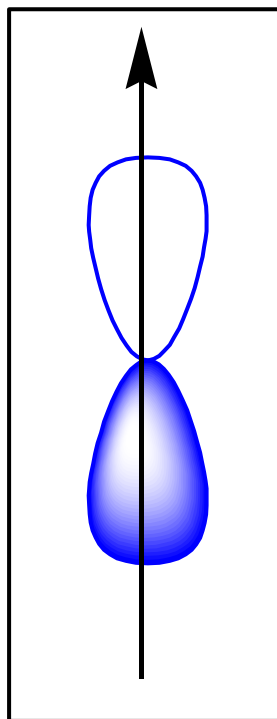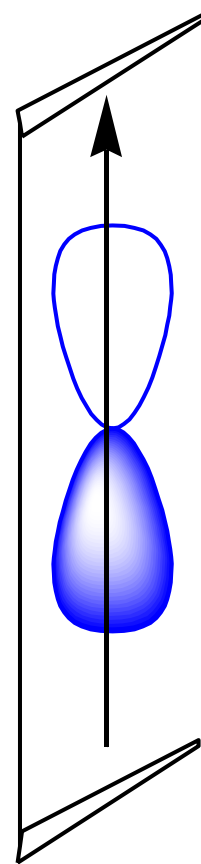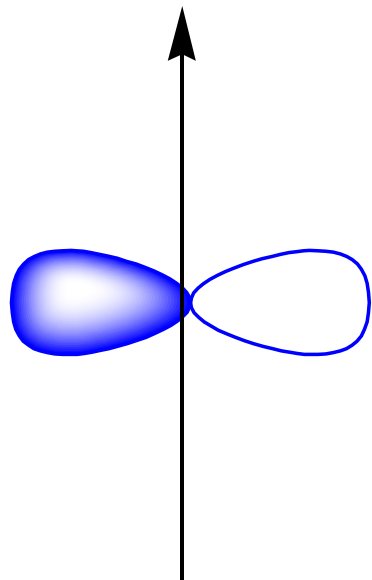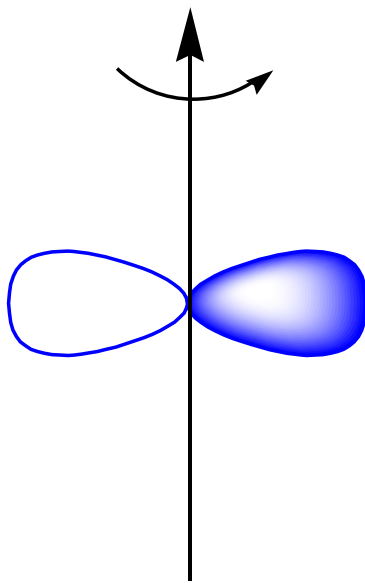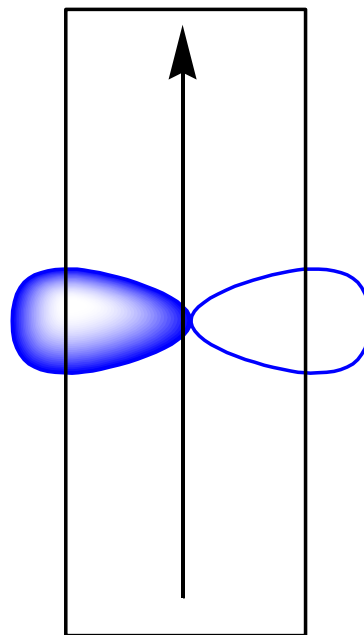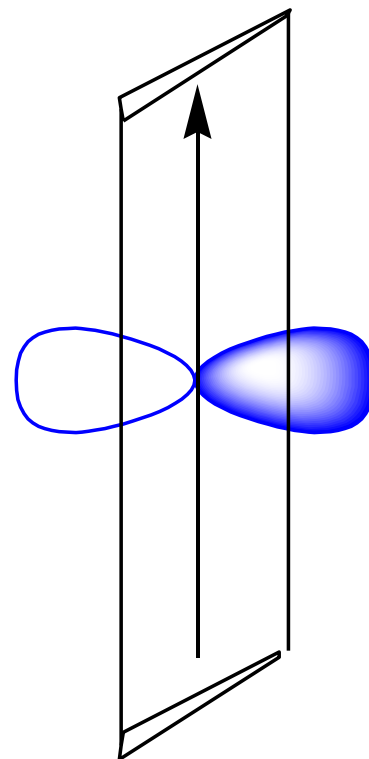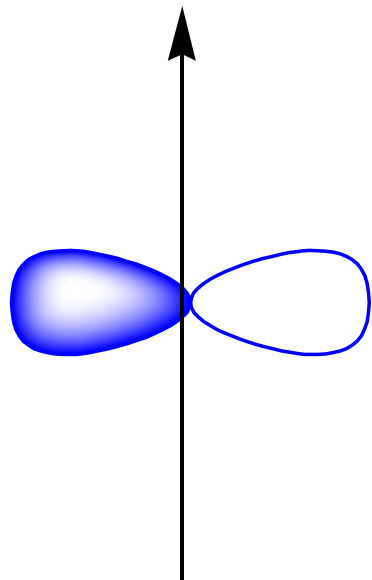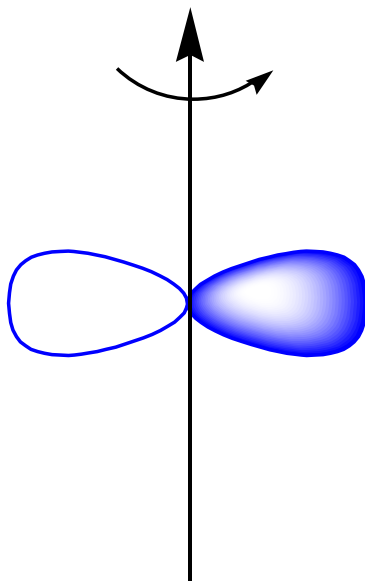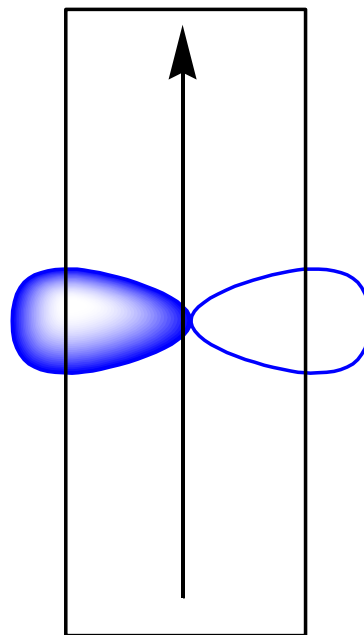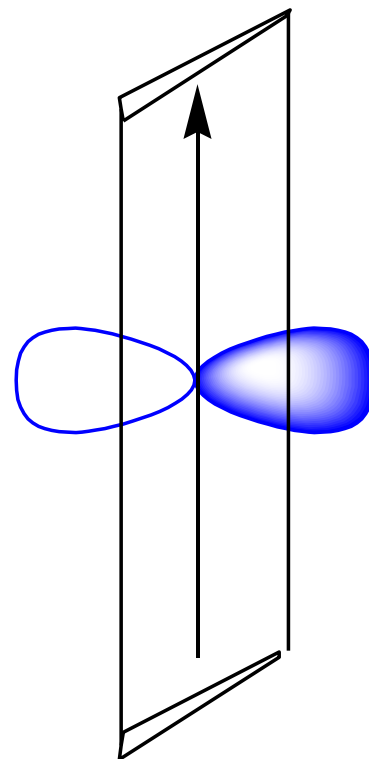
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
1	-1	1	-1

Oxygen p-orbitals in water,

p_x p_z p_y

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
p_z	+1	+1	+1	+1	a_1
p_x	+1	-1	+1	-1	b_1
p_y	+1	-1	-1	+1	b_2
Γ_p	3	-1	1	1	

Thus, $\Gamma_p = a_1 + b_1 + b_2$. The p_x orbital is said to

• form the basis for the b_1 representation,

• have b_1 symmetry, or

• transform as b_1

Translation basis
Cartesian basis

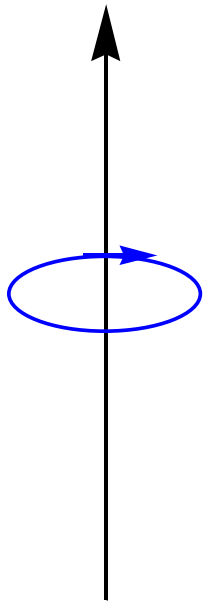Translations along the x, y and z directions (x, y, z) transform in the same way as p_x, p_y and p_z.
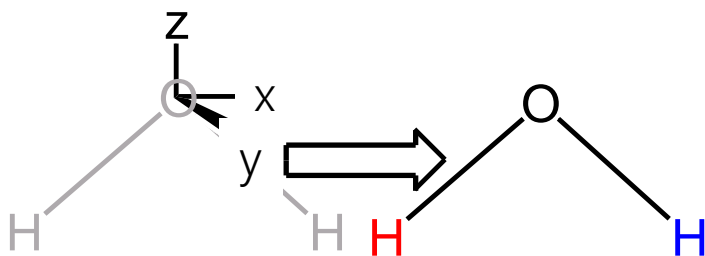
$\Gamma_{T(x)} = 1 \ -1 \ \ 1 \ -1$

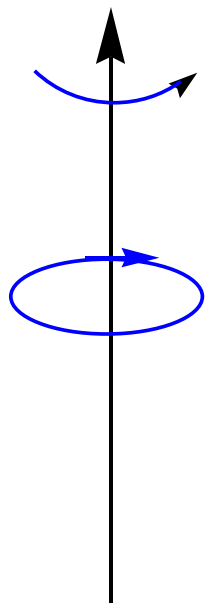| C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
T_z	+1	+1	+1	+1	a_1
T_y	+1	-1	-1	+1	b_2
T_x	+1	-1	+1	-1	b_1
Γ_{trans}	3	-1	1	1	

Thus, $\Gamma_{trans} = a_1 + b_1 + b_2$
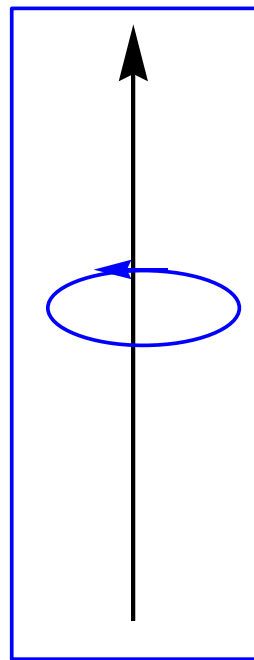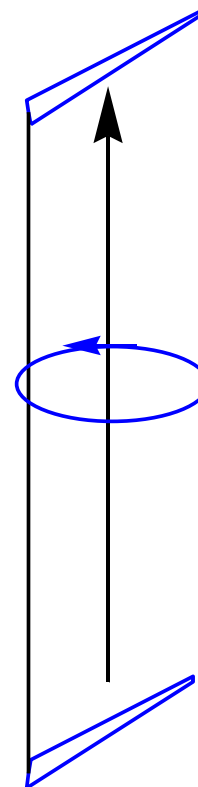
Rotation basis

R_z

E C_2 $\sigma_{v(xz)}$ $\sigma_{v(yz)}$

R_z

E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
1	**1**	**-1**	**-1**

R_y

$\mathbf{E}$ $\qquad$ $\mathbf{C_2}$ $\qquad$ $\sigma_{v(xz)}$ $\qquad$ $\sigma_{v(yz)}$

R_y
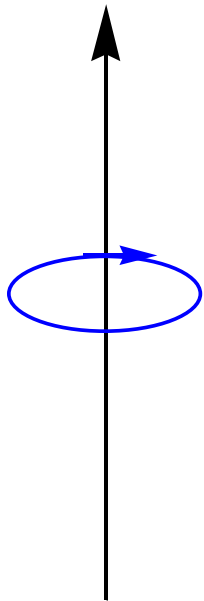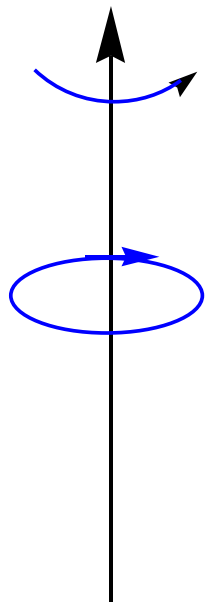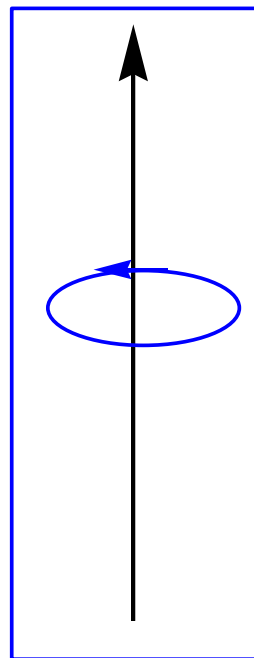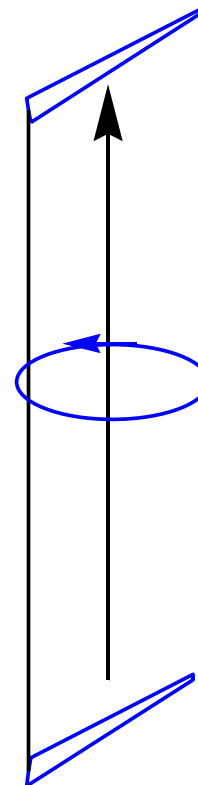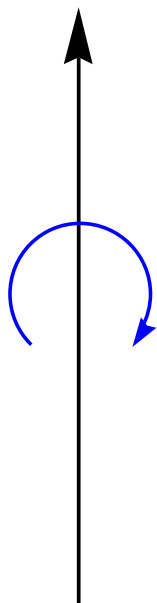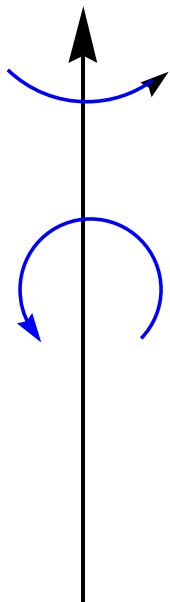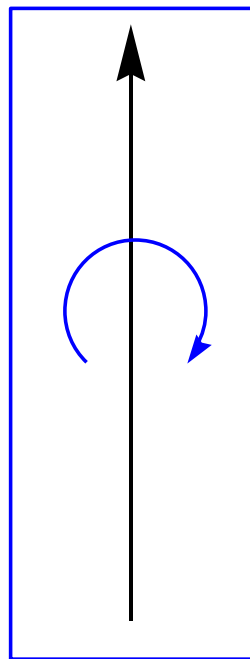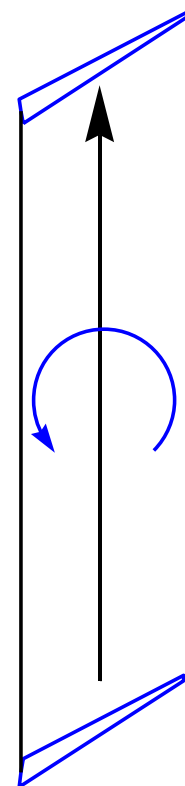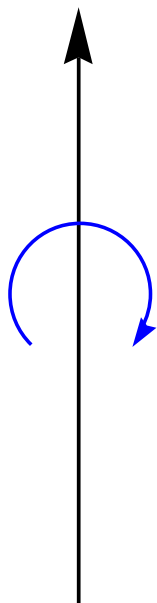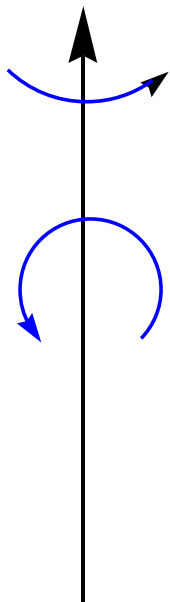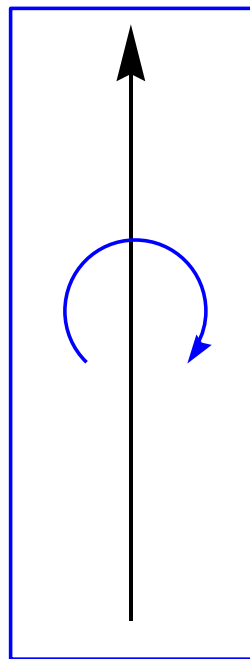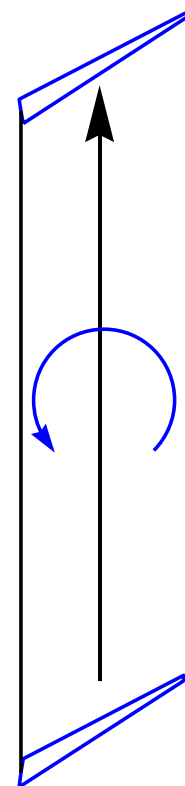
E	**C₂**	**σ**$_{v(xz)}$	**σ**$_{v(yz)}$
1	**-1**	**1**	**-1**

Rotation of the water molecule,
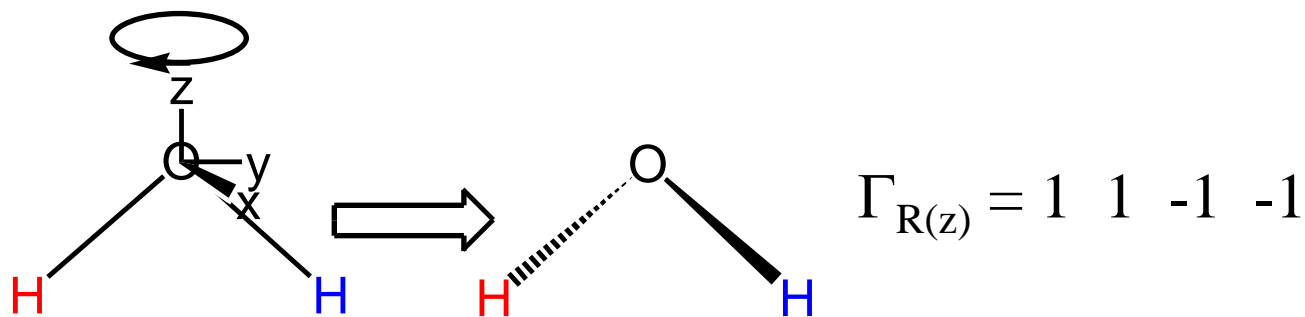
$\Gamma_{R(z)} = 1 \quad 1 \quad -1 \quad -1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
R_z	+1	+1	-1	-1	a_2
R_x	+1	-1	-1	+1	b_2
R_y	+1	-1	+1	-1	b_1
Γ_{rot}	3	-1	1	1	

Thus, $\Gamma_{rot} = a_2 + b_1 + b_2$

Internal coordinates as a basis

The internal coordinates are
- Stretch Δr
- Bend $\Delta \theta$
- Torsion $\Delta \tau$
- Wag $\Delta \omega$

The advantages of this coordinate system are:
- Translation and rotation are eliminated.
- Force constant are defined in terms of bond stretches, valence angle bends, torsions, and wags. These quantities can be related to bond strengths and barriers for internal rotation.

Example of H_2O

For example, for H_2O we have the following internal coordinates.

$$s = \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta \theta_1 \end{pmatrix}$$
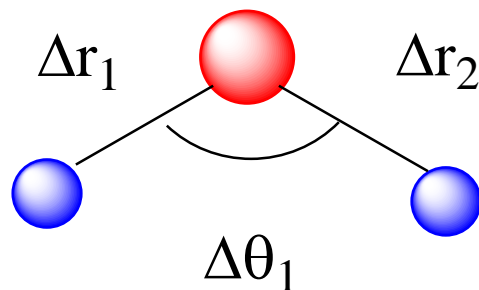
The bond coordinates Δr_1 and Δr_2 transform as:

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ	2	0	2	0

This is a reducible representation.

Mechanics of rotation about a 3-fold symmetry axis

The ammonia molecule (C_{3v} point group) and the coordinate system is shown:
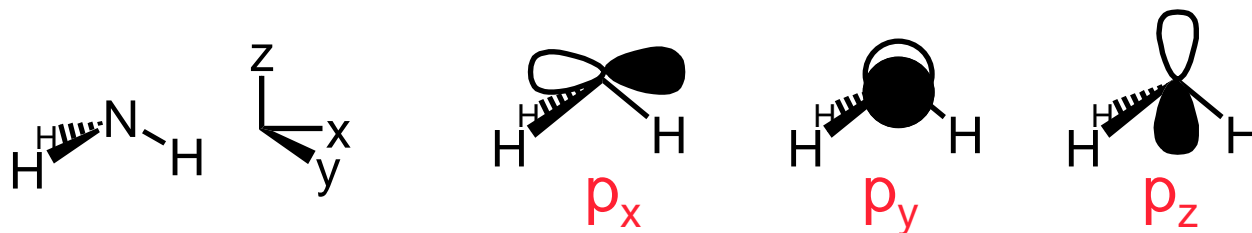
The **N-p_z orbital** is not changed by any of the operations of the group, *i.e.*, it is totally symmetric and transforms as a_1 However, **p_x and p_y** are neither symmetric nor antisymmetric with respect to the C_3 or σ_v operations, but rather go into linear combinations of one another and must therefore be considered together as components of a 2 dimensional representation.

The matrices in this irreducible representation will be 2x2 and not 1x1. The character of the identity operation will then be 2 (the trace of a 2x2 matrix with 1's on the diagonal), *i.e.*, $\chi(E)=2$.

A rotation through an angle $2\pi/n$ can be represented by the following transformation:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos(2\pi/n) & \sin(2\pi/n) \\ -\sin(2\pi/n) & \cos(2\pi/n) \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

the trace of the C_n rotation matrix is $2\cos(2\pi/n)$ which for n=3 is $2\cos(2\pi/3) = 2(-0.5) = -1$, *i.e.*,

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

The character for s_v can be determined by the effect of reflection through any one of the three s_v since they are all in the same class.
Use $s_v(xz)$ which results in $p_x \rightarrow p_x$ and $p_y \rightarrow -p_y$ or,

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

p_x p_y p_z
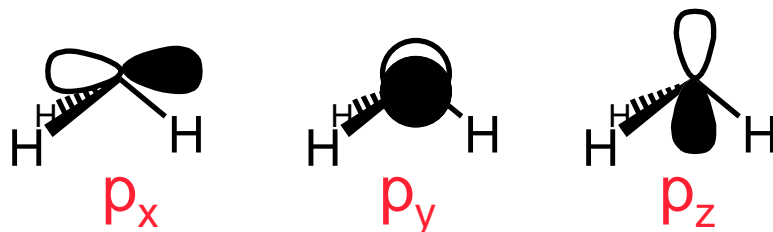
$$\chi(s_v) = 0$$

The transformation properties of the p_x and p_y orbitals are represented as,

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma_{px,py}$	2	-1	0

$$\Gamma_{px,py} = e$$

The p_x and p_y orbitals are degenerate in C_{3v} symmetry and are taken **together** to form a basis for the two-dimensional irreducible representation, **e**.

Decomposing Reducible Representations

In the determination of molecular orbital or vibrational symmetries, a reducible representation is generated from an appropriate basis set and then decomposed into its constituent irreducible representations.

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

a_i: the # of times that i^{th} irrep appears in the reducible representation

h: the order of the group

R: an operation of the group

g(R): the number of operations in the class

$\chi_i(R)$: the character of the Rth operation in the ith irrep

$\chi(R)$: the character of the Rth operation in the reducible representation

A general example of decomposition of a reducible representation

A reducible representation can also be called a vector in the space of the point group. In order to understand the application of point groups for problems in chemistry we need to have a general way to determine how the vector projects onto the space of the group. The space is defined in terms of the orthogonal basis vectors.

In the following we consider an example in the C_{3v} point group.

Γ_{red} = 7 1 1 of the C_{3v} point group, which has an order of 6.

C_{3v}	$1E$	$2C_3$	$3\sigma_v$
A_1	1	1	1
Γ_{red}	7	1	1

C_{3v}	$1E$	$2C_3$	$3\sigma_v$
A_2	1	1	-1
Γ_{red}	7	1	1

$a(a_1) = 1/6\{(1)(1)(7) + (2)(1)(1) + (3)(1)(1)\} = 1/6\{12\} = 2$

$a(a_2) = 1/6\{(1)(1)(7) + (2)(1)(1) + (3)(-1)(1)\} = 1/6\{6\} = 1$

C_{3v}	$1E$	$2C_3$	$3\sigma_v$
E	2	-1	0
Γ_{red}	7	1	1

$a(e) = 1/6\{(1)(2)(7) + (2)(-1)(1) + (3)(0)(+1)\} = 1/6\{12\} = 2$

The reducible representation is decomposed as:
$$\Gamma_{red} = 2a_1 + a_2 + 2e$$

The results can be verified by adding the characters of the irreps,

C_{3v}	$1E$	$2C_3$	$3\sigma_v$
$2a_1$	2	2	2
a_2	1	1	-1
$2e$	4	-2	0
Γ_{red}	7	1	1

Problem I.7 Decompose the following reducible representations of the C_{4v} point group.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_1	11	1	-1	5	1
Γ_2	6	0	2	0	0
Γ_3	5	1	-3	-1	-1
Γ_4	4	-4	4	0	0

C_{4v}		Symmetry elements for the group					Spectroscopy active component		
		E	$2C_4$ (z)	C_2	$2s_v$	$2s_d$	Microwave	IR	Raman
	A_1	1	1	1	1	1		z	x^2+y^2, z^2
	A_2	1	1	1	-1	-1	R_z		
Symmetry label	B_1	1	-1	1	1	-1			x^2-y^2
	B_2	1	-1	1	-1	1			xy
	E	2	0	-2	0	0	(R_x, R_y)	(x, y)	(xz, yz)

The reducible representation of the Cartesian displacement vectors for water was determined earlier and is given in the following table as Γ_{cart}

$$\Gamma_{cart}(E) = 3N$$

Here is a shortcut for generating G_{cart} for any system:
$$\Gamma_{cart} = \Gamma_{unsh}\Gamma_{xyz} = \Gamma_{unsh}[\Gamma_x + \Gamma_y + \Gamma_z]$$

C_{2v}	E	C_2	σ_v	σ'_v	
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_{cart}	9	-1	3	1	

C_{2v}	E	C_2	σ_v	σ'_v	
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_{cart}	9	-1	3	1	

Decomposition of Γ_{cart} yields,

$a(a_1) = 1/4 \{(1)(1)(9) + (1)(1)(-1) + (1)(1)(3) + (1)(1)(1)\} = 1/4 \{12\} = 3$

$a(a_2) = 1/4 \{(1)(1)(9) + (1)(1)(-1) + (1)(-1)(3) + (1)(-1)(1)\} = 1/4 \{4\} = 1$

$a(b_1) = 1/4 \{(1)(1)(9) + (1)(-1)(-1) + (1)(1)(3) + (1)(-1)(1)\} = 1/4 \{12\} = 3$

$a(a_2) = 1/4 \{(1)(1)(9) + (1)(-1)(-1) + (1)(-1)(3) + (1)(1)(1)\} = 1/4 \{8\} = 2$

$$\Gamma_{cart} = 3a_1 + a_2 + 3b_1 + 2b_2$$

Of these 3N degrees of freedom, three are translational, three are rotational and the remaining 3N-6 are the vibrational degrees of freedom.

Thus, to get the symmetries of the vibrations, the irreducible representations of translation and rotation need only be subtracted from Γ_{cart}, but the irreps of rotation and translation are available from the character table.

For the water molecule,

$$\Gamma_{vib} = \Gamma_{cart} - \Gamma_{trans} - \Gamma_{rot}$$
$$= \{3a_1 + a_2 + 3b_1 + 2b_2\} - \{a_1 + b_1 + b_2\} - \{a_2 + b_1 + b_2\}$$
$$= 2a_1 + b_1$$

Problem I.8 Determine the symmetries of the vibrations of NH_3, $PtCl_4^{2-}$ and SbF_5.

Direct Products.

Direct Products: The representation of the product of two representations is given by the product of the characters of the two representations.

Verify that under C_{2v} symmetry $A_2 \otimes B_1 = B_2$

C_{2v}	E	C_2	σ_v	σ'_v
A_2	1	1	-1	-1
B_1	1	-1	1	-1
$A_2 B_1$	1	-1	-1	1

As can be seen above, the characters of $A_2 B_1$ are those of the B_2 irrep.

Verify that $A_2 B_2 = B_1$, $B_2 B_1 = A_2$

Also verify that
  • the product of any non degenerate representation with itself is totally symmetric and
  • the product of any representation with the totally symmetric representation yields the original representation

Note that,

  • A x B = B; while A x A = B x B = A
  • "1" x "2" = "2"; while "1" x "1" = "2" x "2" = "1"
  • g x u = u; while g x g = u x u = g.

Electronic Spectroscopy Application of Group Theory

- Ψ_{Tot} assumed separable, $\Psi_{Tot} = \psi_{MO}\psi_{vib} = |n\rangle|v\rangle$

- Overall orbital wavefunction is the **product** of occupied one electron wavefunctions, ϕ_{MO}: $\psi_{MO} = \Pi\phi_{MO}$

- If transition is not allowed by symmetry then vibronic coupling can be invoked as a perturbation. We can use group theory for both Franck-Condon an vibronic spectroscopy.

Selection Rules

Transition moment integral for
ground state (gs) $\Rightarrow$ excited state (es) is,

$$\langle\mu\rangle = \langle gs|\mu|es\rangle$$

The state wavefunctions (orbital•vibrational) are:

$$|nv\rangle \quad \text{(ground state)}$$
$$|n'v'\rangle \quad \text{(excited state)}$$

The dipole operator is ($\mu = \mu_e$) is independent of spin coordinates,

$$\langle\mu\rangle = \langle nv|\mu_e| n'v'\rangle$$

The result is,

$$\langle\mu\rangle = \left\{ \langle v|v'\rangle\langle n|\mu_e|n'\rangle \right\}$$

For electronic transitions, the initial vibrational state will *usually* be v=0, and

$$\langle\mu\rangle = \langle 0|v'\rangle\langle n|\mu_e|n'\rangle$$

The intensity of the transition is proportional to $\langle\mu\rangle^2$, so,

$$I \propto \langle\mu\rangle^2 = \langle 0|v'\rangle^2\langle n|\mu_e|n'\rangle^2$$

• $\langle n'|\mu_e|n\rangle$ gives rise to the **orbital or symmetry selection rules**. If the direct product $\Gamma(n')\ \Gamma(n)$ transforms as x, y, or z the electronic transition is said to be "x-polarized", "y-polarized" or "z-polarized", respectively.

• $\langle 0|v'\rangle$ is the overlap of the vibrational wavefunctions in the ground (v=0) and excited electronic states. The $\langle v|v'\rangle^2$ terms are referred to as the **Franck-Condon factors** and can modulate the intensity of the electronic transition.

If, during the electronic transition, a quantum of an asymmetric vibration is also absorbed, the symmetry of the molecule will change and the group theoretical selection rules may be relaxed and a forbidden transition may become "vibronically allowed". Thus the electronic state interacts with the vibration through *weak vibronic coupling*. For these *vibronic* systems, electronic and vibrational components of Ψ are not separable. Thus,

$$<\mu> = <n,v|\mu_e|n',v'>$$

the symmetry of **vibronic states** given by the direct product of the orbital and vibrational irreps dictate the selection rules.

In centrosymmetric molecules, d-orbitals are always *gerade* while m is always *ungerade* so d-d transitions are orbitally or **Laporte** forbidden $\langle g| m |g\rangle = 0$.   However, these transitions can be *vibronically allowed* through *ungerade* vibrations since in the v=1 level of an *ungerade* vibration, the molecule loses its center of symmetry and thus the selection rule is relaxed!!

$\langle n'v'|m_e m_n|nv\rangle \neq 0$ means $\Gamma_{es}\Gamma_{vib}\Gamma_{xyz}\Gamma_{gs} \neq 0$

vibronically-active: $\Gamma_{es}\Gamma_{vib}\Gamma_{xyz}$ must transform as Γ_{gs}

In cases like this, the $v = 0 \rightarrow v' = 0$ band (the "origin" or 0-0 band) is not observed and the lowest energy peak maximum will be at E_{0-0} plus one quantum of excited state vibrational energy.

Such peaks are referred to as "false origins"

The lowest energy electric dipole *allowed* transition is from the v'=0 vibrational level of the ground electronic state to the v=0 vibrational level of the lowest energy excited electronic state. This transition is called the origin, or 0-0 ("zero-zero") band.

The lowest energy electric dipole *forbidden* transition is from the v'=0 vibrational level of the ground electronic state to the v=1 vibrational level of a vibronically-active mode of the lowest excited electronic state. This transition is called a false origin.

To be vibronically-active, the direct product of a mode with the with the irreps of m *and* with the excited state irrep must transform as the ground state irrep.

Types of **Electronic Transitions**
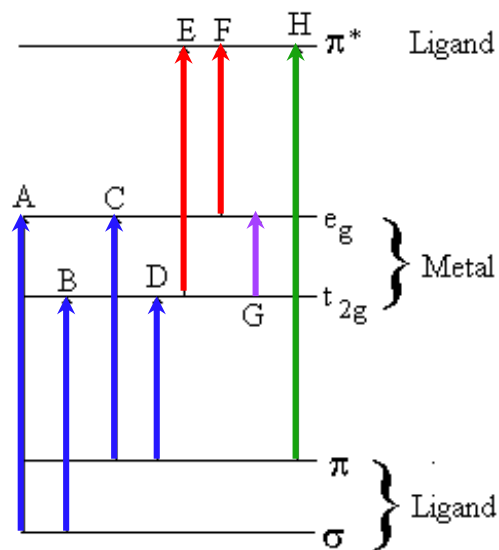
A-D: ligand to metal charge transfer bands (LMCT)

E-F: metal to ligand charge transfer bands (MLCT)

G: d-d (Ligand Field) bands

H: ligand p→p*

Electronic transitions are governed by the **Franck-Condon principle:**

Electron motion is so much faster than nuclear motion that electronic transitions involve no change in either positions or momenta of nuclei.

- FC principle: transitions are "vertical".
most originate from Q=0 of v=0

- If the excited state equilibrium geometry is different than the ground state geometry, then a vertical transition to the v=0 level may be improbable, *i.e.*, the 0-0 transition may be very weak or missing.

- The larger the value of v, however, the greater will be <0|v'>. Therefore, the strongest transitions other than 0-0 bands will occur when the transitions are to the extrema of the internuclear separations.