Symmetry point group

Reference:

1. Chemical Applications of Group Theory, F. A. Cotton
2. Molecular Symmetry and Group Theory, R. L. Carter; John Wiley & Sons, Inc
3. Group Theory and its Applications to Chemistry, K. V. Raman; Tata McGraw-Hill Pub. Comp. Ltd.
4. Group Theory and Chemistry, David M. Bishop, Clarendon Press.
5. Symmetry and Spectroscopy of Molecules, K Veera Reddy, New Age Int. (P) Ltd.

Matrix Representations of Symmetry operations:

[4-p72]

The best way to understand how the symmetry operations of a molecule influence its properties is to study the sets of matrices which mirror those same operations. Using matrix representation we replace the geometry of symmetry operations with the algebra of matrices.

One way is to consider the effect that a symmetry operation has on the Cartesian coordinates of some point (or equivalently, on some position vector) in the molecule.

Symmetry operation on a position vector:

The Identity: A point (x,y,z) does not change under this operation. Therefore, the identity operation is represented by a unit matrix.

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

Inversion:

This operation results simply the change of signs of all the coordinates. Clearly we need a negative unit matrix to represent inversion operation.

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

Reflections:

$$\sigma(xy): \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix} \text{ etc.}$$

Proper rotation:

Defining the rotation axis as the z axis, one should note that z coordinate will be remaining unchanged by any rotation about x axis. Thus the matrix we seek must be, in part,

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

Other four elements can be obtained as follows.

Bishop [Ref. 4]

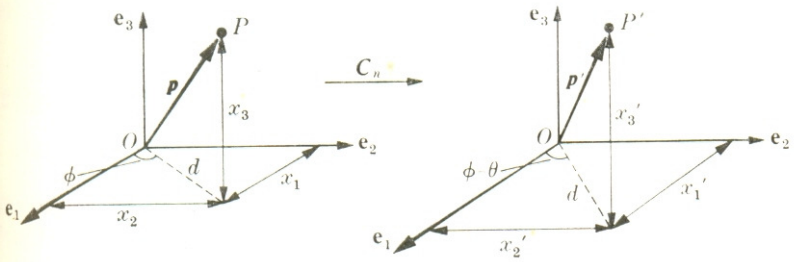


FIG. 5-2.3. Effect of C_n on $\mathbf{p}$.

and those of the final vector $\mathbf{p}'$ (point P') x_1', x_2', and x_3':

$$\begin{aligned} x_1' &= d\cos(\phi-\theta) \\ &= d\cos\phi\cos\theta + d\sin\phi\sin\theta \\ &= d(x_1/d)\cos\theta + d(x_2/d)\sin\theta \\ &= x_1\cos\theta + x_2\sin\theta \end{aligned} \tag{5-2.2}$$

$$\begin{aligned} x_2' &= d\sin(\phi-\theta) \\ &= d\sin\phi\cos\theta - d\cos\phi\sin\theta \\ &= d(x_2/d)\cos\theta - d(x_1/d)\sin\theta \\ &= -x_1\sin\theta + x_2\cos\theta \end{aligned} \tag{5-2.3}$$

$$x_3' = x_3. \tag{5-2.4}$$

Eqns (5-2.2) to (5-2.4) can be combined together (see eqn (4-3.8)) to give:

$$\begin{Vmatrix} x_1' \\ x_2' \\ x_3' \end{Vmatrix} = \begin{Vmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{Vmatrix} \begin{Vmatrix} x_1 \\ x_2 \\ x_3 \end{Vmatrix}. \tag{5-2.5}$$

[5-p158]

$C_n(z)$:

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

for clockwise rotation,

$C_n(z)$:

$$\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

for counterclockwise rotation.

Improper rotation:

$S_n(z) = \sigma(xy)\,C_n(z)$, i.e., an improper rotation equivalent to proper rotation followed by mirror image in the horizontal plane. So, one can think of just changing sign of z

coordinate in addition to proper rotation. The matrix corresponding to an improper rotation has the form

$S_n(z): \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$ for clockwise rotation.

One could however, have obtained this matrix by explicitly multiplying the matrices for rotation around z axis and reflection in the xy plane.

$$\underset{\sigma(xy)}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}} \times \underset{C_n(z)}{\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}} = \underset{S_n(z)}{\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}}$$

Character of matrices corresponding to operations: trace of the matrices; sum of the diagonal elements.

Symmetry operation	Character of matrix
Identity	3
Rotation	$2\cos\theta+1$
Reflection	1
Inversion	-3
Improper rotation	$2\cos\theta$-1

Matrix representation of C_{2h} point group: (Bishop, p-78)

Take planner trans-$C_2H_2Cl_2$ as an example. Symmetry operations: E, C_2, i, σ_h. Considering three base vectors (e_1,e_2,e_3) inside the molecule such that e_3 coincides with $C_2(z)$ one can have:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad C_2(z) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \sigma_h = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

Using matrix multiplication as the combining operation, we can construct a group multiplication table: $C_2 i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \sigma_h$

This is using the fact that if operations R, S and T obey the relation RS=T, then their corresponding matrices follow the same relation.

Representation of groups:

[1-p78]

The set of matrices for the various symmetry operations of a point group forms a representation. For C_{2v} group multiplication table:

	E	C_2 (z)	σ_v (xz)	σ_v' (yz)
E	E	C_2	σ_v,	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v,	σ_v,	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

By transformation (say, similarity transformation) we can generate a new set of matrices which also follow the rules of the group and hence will form a new representation for the same group C_{2v}.

[2-p40]
For our purpose, we define a representation of a group as a set of symbols that will satisfy the multiplication table for the group. The symbols are called character of the representation. Let's first consider the representations whose characters are simply positive and negative integers. For example we make a set of substitutions for the four operations of the C_{2v} point group such that the substituted characters also obey the general relationships of the above multiplication table, then the set of characters will be a representation of C_{2v}.

[1-p79]
Q. A natural question is then how many representations can be obtained for any particular group?

Answer is a very large number. Very simple ones(considering only vector z, or x or y individually):

E	C_2 (z)	σ_v (xz)	σ_v' (yz)			
1	1	1	1		A_1	z
1	-1	1	-1		B_1	x
1	-1	-1	1		B_2	y
1	1	-1	-1	etc.	A_2	R_z

These representations can be generated by considering unit vector transformation as follows:
[2-p43]

For C_{2v} point group,

Operations	z unit vector becomes	In matrix notation
E	z	[+1]z

C_2	z	[+1]z
σ_v	z	[+1]z
$\sigma_v^{/}$	z	[+1]z

We say then that z unit vector transform as A_1 in C_{2v}.
Similarly, look at the operations for x and y unit vectors, which transform as B_1 and B_2, respectively.

Now consider a curved unit vector, R_z, representing rotation about the z axis.

Carter p-45

Operation	$\mathbf{R}_z$ becomes	In matrix notation
E	$\mathbf{R}_z$	$[+1]\mathbf{R}_z$
C_2	$\mathbf{R}_z$	$[+1]\mathbf{R}_z$
σ_v	$-\mathbf{R}_z$	$[-1]\mathbf{R}_z$
σ_v'	$-\mathbf{R}_z$	$[-1]\mathbf{R}_z$

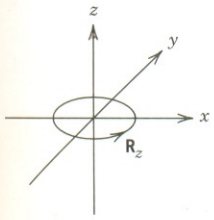


Figure 2.2 A rotational vector, $\mathbf{R}_z$.

Thus we can say that $\mathbf{R_z}$ transforms as A_2 in C_{2v} or $\mathbf{R_z}$ belongs to the A_2 species in C_{2v}.

Some higher order representation can also be obtained by considering 3 unit vectors at each atom along x,y and z, leading to a set of four 9x9 matrices.

Reducible and irreducible representations:
The simplest and fundamental representations those can not be represented by combination of other representations are called irreducible representations.

However, there are some representations for those after similarity transformations of the corresponding matrices can be block-factored and hence the representation can be represented by the combination of irreducible representation. These are reducible representation. E.g, for C_{2v} point group a representation obtained by the character of the transformation matrices of a vector in 3D (x,y & z) is :

[2-p50]

E C_2 (z) σ_v (xz) $\sigma_v^{'}$(yz)

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

Γ_v 3 -1 1 1 $= A_1 + B_1 + B_2$

The above reduction can be done using block diagonalization method, where we mark off a series of matrices along the diagonals of all the matrices as follows:

C_{2v}	E	C_2	σ_v	σ_v'
F_m	1 0 0 0 1 0 0 0 1	−1 0 0 0 −1 0 0 0 1	1 0 0 0 −1 0 0 0 1	−1 0 0 0 1 0 0 0 1

C_3v group:

[1-p13]

If B and P are two elements of a group, then P^{-1} B P will be equal to some element of the group, say A. We have A = P B P^{-1}.

We express this relation is words by saying that A is a similarity transform of B by P. We also say that B and A are conjugate.

Symmetry operations we have in this group are:

E, $\{C_3, C_3^2\}, \{\sigma_v', \sigma_v'', \sigma_v'''\}$ and these operations form a group. Again, each set of operations in a {…..} is a different class. A complete set of operations that are conjugate to one another is called a class of the group.

We know that operations under a class are related to each other by 'similarity transformation', namely with the following relation:

A = P B P^{-1}. In other words if any two operations (A,B) are related to each other by similarity transformation then they are in the same class.

In case of matrix representation, the matrices are said to be conjugate matrix of each other.

Conjugate matrices have identical characters.

[1-p69]

Character is simply the sum of the diagonal elements of a square matrix, $\chi_A = \sum_i a_{ii}$.

Theorem: If C=AB and D=BA then the characters of C and D are equal.

Proof:

[1-p70]

Since the associative law holds for matrix multiplication, we can write

$\chi_A = \chi$ of (P B P^{-1}) = χ of (P B)P^{-1} = χ of P^{-1}(PB) = χ_B

[2-p55]

Therefore, one can say that for any representation the character of the transformation matrix for a given operation is the same as that for any other operation in the same class.

This permits listing one character for each class of operations for each irreducible representation in the character table. Using counterclockwise rotation we have,

C_{3v}	E	C_3	σ_v
Γ_m	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

We can reduce this into its component irreducible representations by taking block diagonals of each matrix. The blocks we take must be the same size across all three matrices. The presence of nonzero, off-diagonal elements in the transformation matrix for C_3 restricts us to diagonalization into a 2×2 block and a 1×1 block. As a result, for all three matrices we must adopt a scheme of block diagonalization that yields one set of 2×2 matrices and another set of 1×1 matrices, as follows:

C_{3v}	E	C_3	σ_v
Γ_m	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Our inability to reduce this matrix representation into three irreducible representations of 1x1 matrices, equivalent to characters, is a consequence of the mixing of x and y by the C_3 operation.

We can still obtain irreducible representation of characters by summing along the trace of the block matrices. This gives the following representations:

C_{3v}	E	$2C_3$	$3\sigma_v$	
$\Gamma_{x,y}$	2	-1	0	Doubly degenerate Irr. Rep.
Γ_z	1	1	1	

Does the first representation follow the group multiplication table?

Properties of irreducible representation:

An irreducible representation is going to be accepted if it follows the "Great Orthogonality Theorem". In other words, Great orthogonality theorem (GOT) leads us to generate the limited set of irreducible representations that are allowed for each group.

It has similarity with the acceptable basis functions must be orthonormal. Or with the concept of unit vectors representations, where each unit vectors are orthonormal. Each basis function or each unit vector are unique, so also the irreducible representations.

Some of the general relationships arising from the GOT:

1. The sum of the squares of the dimensions of all the irreducible representations is equal to the order (total number of nonredundant symmetry operations) of the group: $\sum_i d_i^2 = h$.

   Since the character of the operation E in the i-th irreducible representation, $\chi_i(E)$, is equal to the dimension (order) of the representation, we can write $\sum_i [\chi_i(E)]^2 = h$.

2. Also note that, the sum of the squares of the characters in any irreducible representation is equal to order of the group: $\sum_R [\chi_i(R)]^2 = h$

   Example: Take C_{2v} and C_{3v} character table and explain.

3. The number of irreducible representations of a group is equal to the number of classes.
4. Any two different (nonequivalent, i.e., they are not related by similarity transformation [AK Chandra, p310]) irreducible representations are orthogonal, which means that $\sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = 0.$

   Physically this means two vectors that transform by different irreducible representations are orthogonal.
   Explain: using C_{3v} character table.

Construction of character tables:

C_{2v}: Four nonredundant symmetry operations and each is in a separate class. Hence, the order = 4 and there are four irreducible representations.

Step 1:
Rule 1: $d_1^2 + d_2^2 + d_3^2 + d_4^2 = 4$, only one solution: $d_1 = d_2 = d_3 = d_4 = 1$
Thus the group C_{2v} has four one dimensional irreducible representations.

Step 2:

Rule 2: Using $\sum_R [\chi_i(R)]^2 = h = 4$, with $\chi(E) = 1$, vector in 4-space will obviously be

C_{2v}	E	C_2	σ_v	σ_v'

Γ_1	1	1	1	1

Step 3: All other representations will have to be such that $\sum_R [\chi_i(R)]^2 = h = 4$, which us only possible if each $\chi_i(R) = \pm 1$. Moreover, each of the other representations to be orthogonal to Γ_1. As a matter of fact there will have to be two +1's and two -1's. Therefore, we will have

C_{2v} Mulliken	E	C_2	σ_v	σ_v'
Γ_1 A_1	1	1	1	1
Γ_2 B_1	1	-1	1	-1
Γ_3 B_2	1	-1	-1	1
Γ_4 A_2	1	1	-1	-1

C_{3v} Character table:
Consists of the following elements, listed by classes
E $2C_3$ $3\sigma_v$
Order of the group = 6. Number of possible irreducible representation = 3.

Step 1:
Rule 1: $d_1^2 + d_2^2 + d_3^2 = 6$, the only values of the d_i that will satisfy this requirement are 1, 1 and 2, as one can only assume positive integer values other than zero for dimension of any representation.

Step 2: Every point group possesses one representation which is totally symmetric in which all the operations have the character value +1.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	a	b
Γ_3	2	c	d

Step 3: We now look for a second vector Γ_2 in 6-space, with $\chi(E) = 1$ and orthogonal to Γ_1. We have using $\sum_R [\chi_i(R)]^2 = h$,

$1 + 2a^2 + 3b^2 = 6$ ……..(1)
and using $\sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = 0$,
$1 + 2.1.a + 3.1.b = 0$……..(2)

From eqn. 2, $a = -\frac{3b+1}{2}$. Inserting this in equation 1, we have

$$1 + 2\left(-\frac{3b+1}{2}\right)^2 + 3b^2 = 6$$

$$9b^2 + 6b + 1 + 6b^2 = 10$$

$$15b^2 + 6b - 9 = 0$$

$$5b^2 + 2b - 3 = 0$$

$$5b^2 + 5b - 3b - 3 = 0$$

$$(5b - 3)(b + 1) = 0$$

The acceptable solution b = -1 (as characters are not a fractional numbers), therefore, a = 1.

Similarly, for Γ_3 , we have d = 0, c = -1.

Description of character tables: Cotton- p90-92.

Character table for C_{2v} point group

	E	**C_2 (z)**	**σ_v(xz)**	**σ_v(yz)**	**linear, rotations**	**quadratic**
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

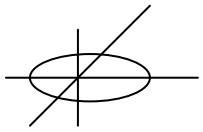
Character table for C_{3v} point group

	E	**$2C_3$ (z)**	**$3\sigma_v$**	**linear, rotations**	**quadratic**
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)

1. One dimension: A (if $\chi(C_n) = +1$); B (if $\chi(C_n) = -1$)
2. Subscript 1 (if symmetric wrt perpendicular C_2 or vertical plane of symmetry), 2 otherwise.

3. Primes (symmetric wrt σ_h), else double primes.
4. g (gerade) if inversion symmetry is there, else u

Linear, rotation:
X,y and z vector transformation. According to these vectors, a p-orbital will change. $R_{x,y,z}$ rotation about x,y,z. Consider a curved vector R_z, rotation about z axis (Carter, p-45).



Quadratic terms: in the last column are important as transformation properties of a d orbital will follow that. (Carter, p-59)
Xz,yz transform as x & y as z does not mix with x & y. (Raman, p-86)

Character $\varepsilon = \exp(2\pi i/n)$, n being order of the principal axis.

Systematic Reduction of Reducible Representation:

We may express $\chi(R)$, the character of the matrix corresponding to operation R in a reducible representation $\chi(R) = \sum_j n_j \chi_j(R)$

Where n_j represents the number of times the j-th irreducible representation occurs in the reducible representation.
Multiplying each side by $\chi_i(R)$ and summing each side over all the operations R one obtains

$$\sum_R \chi(R)\chi_i(R) = \sum_R \sum_j n_j \chi_j(R)\chi_i(R) = \sum_j n_j \sum_R \chi_j(R)\chi_i(R) \quad \text{as } n_j \text{ same for all R.}$$

$$= \sum_j n_j h \delta_{ji}$$

The terms in right hand side are going to survive only when $j=i$, $\delta_{ji} = 0$ otherwise.

Therefore, we have $\sum_R \chi(R)\chi_i(R) = n_i h$ or $n_i = \frac{1}{h}\sum_R \chi(R)\chi_i(R)$.

Or $n_i = \frac{1}{h}\sum_{R_c} g_c \chi(R)\chi_i(R)$

Examples:

Character table for C_{2v} point group

	E	**C_2 (z)**	**σ_v(xz)**	**σ_v(yz)**	**linear, rotations**	**quadratic**
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
Γ_R	**9**	**-1**	**1**	**3**	**$= 3A_1+A_2+2B_1+3B_2$**	

Character table for C_{3v} point group

	E	**$2C_3$ (z)**	**$3\sigma_v$**	**linear, rotations**	**quadratic**
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_R	**7**	**1**	**-3**	**$= 3A_2+2E$**	

Symmetry adapted atomic basis sets:
[1-p114]
For constructing MOs, we take sets of orthonormal function, which are generally atomic orbitals (AOs) or internal coordinates of a molecule and make orthonormal linear combinations of them in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule. These combinations may be called symmetry adapted linear combinations (SALCs).

[1-p119]
The fundamental, universally applicable tool for constructing SALCs is the projection operator. The most important and frequent use for projection operators is to determine the proper way to combine atomic wave functions on individual atoms in a molecule into MOs that correspond to the molecular symmetry.

Projection operator by name itself implies that if we project an MO into the atomic orbital bases gives the corresponding components. Like a vector, if we need to know the components along x,y and z we take projection along three axes. We define symmetry adapted function

$$\psi_i = \sum_R \chi_i(R)(R\phi)$$

Bonding in water: (Thakur, p-260)
1. Take a linear combination of the two hydrogen 1s atomic orbitals which transform like the irreducible representations of the C_{2v} point group. Considering the two hydrogen 1s-orbitals as the basis for new representation (to obtain SALCs) we get the new representation as

	E	C_2	σ_v	σ_v'
Γ	2	0	0	2

This can be obtained by the characters of the transformed matrices.

$$C_2\begin{bmatrix}1s_a\\1s_b\end{bmatrix}=\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}1s_a\\1s_b\end{bmatrix}$$

Or by considering the method of unshifted vector method.

2. Now we need to find out the component irreducible representations in this representation $\Gamma = A_1 + B_2$.
So there will be two SALCs.
3. To generate these we apply the projection operator method: (Cotton, p-106) take a function of the basis set and operate on it with each of the operations of the point group; multiply the result with the appropriate character of the irreducible representation and sum them up: $\psi = \left(\sum_R \chi(R)R\right)\varphi = \tilde{p}\phi$ (Chandra, p-318).

For the present case $\psi(A_1) = \frac{1}{\sqrt{2}}(1s_a + 1s_b)$, $\psi(B_2) = \frac{1}{\sqrt{2}}(1s_a - 1s_b)$

4. To obtain MOs we now combine these SALCs with atomic orbitals of O atom that transform similarly according to same irreducible representation as follows:

Symmetry species	SALC	Orbitals of atomic O
A_1	$\psi(A_1) = \frac{1}{\sqrt{2}}(1s_a + 1s_b)$	2s, $2p_z$
B_1	None	$2p_x$
B_2	$\psi(B_2) = \frac{1}{\sqrt{2}}(1s_a - 1s_b)$	$2p_y$

So the MOs are going to be:

Of A_1 symmetry: $a_1 = C_1(2s) + C_2(2p_z) + C_3\psi(A_1)\left[= \frac{1}{\sqrt{2}}(1s_a + 1s_b)\right]$

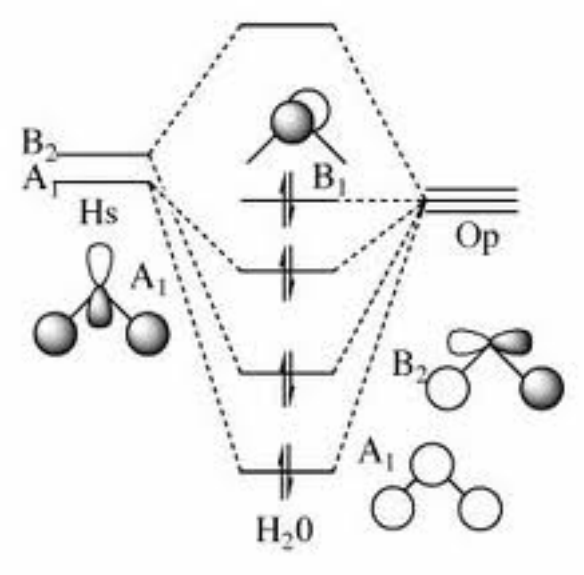
Coefficients are obtained from a 3x3 determinant (see Cotton, p-124,125), secular equation.

Of B_1 symmetry $b_1 = 2p_x$ (non bonding)

Of B_2 symmetry $b_2 = C_4(2p_y) + C_5\psi(B_2)\left[= \frac{1}{\sqrt{2}}(1s_a - 1s_b)\right]$; coefficients are obtained from 2x2 determinant.

What about another non-bonding MO: it is basically non-bonding MO at O formed by $2p_z + 2s$, $a_1(n) = C_6(2s) + C_7(2p_z)$

Schematic MO diagram for H_2O:



Bonding in NH_3:
AK Chandra, p-317

1. We take a linear combination of the hydrogen atomic orbitals which transform like the irreducible representation of the C_{3v} group. We lebel the three hydrogen 1s-orbitals as $1s_a$, $1s_b$, and $1s_c$, which form bases for a new representation.
2. The character of the new representation is given as (using unshifted basis rule)

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	3	0	1	$= A_1+E$

Component irreducible representations in this reducible representation are $A_1 + E$.

3. We need to generate symmetry-adapted functions which transform as A_1 and E. Take one function, say $1s_a$ of the basis set and operate on it with each of the operations of the group; multiply the result of each operation by the

corresponding character of the operations in the particular irreducible representation and sum the result. Systematically we do this as follows:

C_{3v}	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
Operating on $1s_a$	$1s_a$	$1s_b$	$1s_c$	$1s_a$	$1s_c$	$1s_b$
Multiplying with character of A_1	$1x1s_a$	$1x\ 1s_b$	$1x1s_c$	$1x1s_a$	$1x1s_c$	$1x1s_b$

Therefore, the symmetry adapted SALC wavefunction which transform as A_1 can be written as $\psi(A_1) = 2(1s_a + 1s_b + 1s_c)$. After normalization we have $\psi(A_1) = \frac{1}{\sqrt{3}}(1s_a + 1s_b + 1s_c)$.

Note that same result is obtained if one works with $1s_b$ or $1s_c$.

For SALCs of E symmetry:

C_{3v}	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
Operating on $1s_a$	$1s_a$	$1s_b$	$1s_c$	$1s_a$	$1s_c$	$1s_b$
Multiplying with character of E	$2x1s_a$	$-1x\ 1s_b$	$-1x1s_c$	$0x1s_a$	$0x1s_c$	$0x1s_b$

$$\psi_1(E) = \frac{1}{\sqrt{6}}(2.1s_a - 1s_b - 1s_c)$$

C_{3v}	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
Operating on $1s_b$	$1s_b$	$1s_c$	$1s_a$	$1s_c$	$1s_b$	$1s_a$
Multiplying with character of E	$2x1s_b$	$-1x\ 1s_c$	$-1x1s_a$	$0x1s_c$	$0x1s_b$	$0x1s_a$

$$\psi_2(E) = \frac{1}{\sqrt{6}}(2.1s_b - 1s_c - 1s_a)$$

But ψ_1 and ψ_2 are not orthogonal. One can generate orthogonal functions using these functions using Schmidt orthogonalization procedure.

The theorem reads as, even two degenerate functions are not orthogonal but their linear combinations may be orthogonal.

Consider the functions ψ_1 and $\psi_1' = \psi_2 + c\psi_1$ which are orthogonal. Hence

$$\int \psi_1(\psi_2 + c\psi_1)d\tau = 0$$

$$c = -\int \psi_1\psi_2 d\tau = \frac{1}{2}$$

This leads to after normalization $\psi_1'(E) = \frac{1}{\sqrt{2}}(1s_b - 1s_c)$

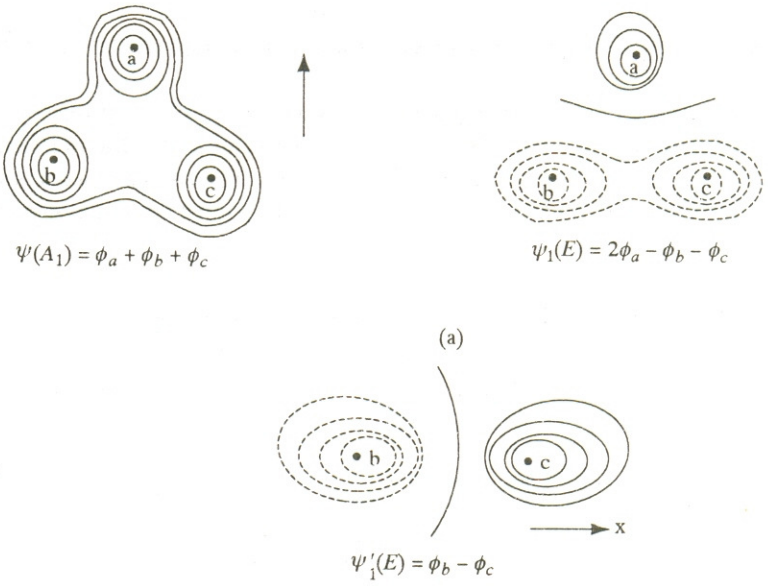
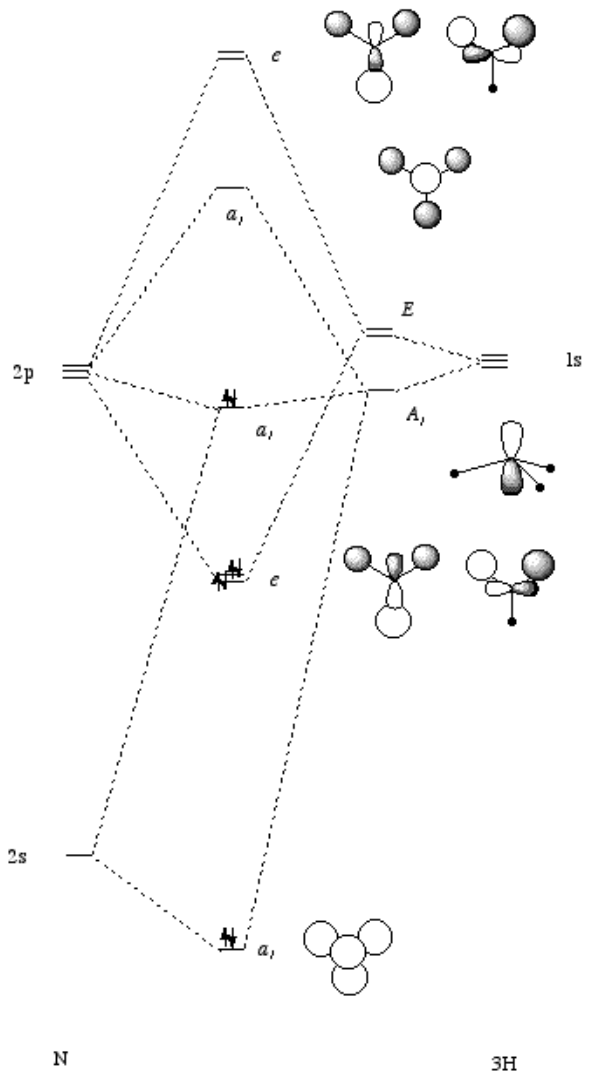


Fig. 9.24 *The schematic diagram of the contours of the orbitals $\psi(A_1)$, $\psi_1(E)$ and $\psi_1'(E)$ of Eq. (9.71)*

Symmetry species	SALC	Orbitals of atomic N
A_1	$\psi(A_1) = \frac{1}{\sqrt{3}}(1s_a + 1s_b + 1s_c)$	2s, $2p_z$
E	$\psi_1'(E) = \frac{1}{\sqrt{2}}(1s_b - 1s_c)$	$2p_x$
	$\psi_1(E) = \frac{1}{\sqrt{6}}(2.1s_a - 1s_b - 1s_c)$	$2p_y$



Direct product and its importance: (Cotton, p-93,98; Chandra, p-324)

$H\psi_i = E\psi_i$; for degenerate eigen functions.
Q. Would H change after carrying out a symmetry operation?

A. NO. Because any symmetry operation on a molecule results in an indistinguishable configuration from its original configuration, and hence energy does not change.

Therefore, R H = H R.
Hence, H $R\psi_i$ = E $R\psi_i$; indicates that $R\psi_i$ is also an eigen function of H.
Now as ψ_i is normalized, in order to $R\psi_i$ to be normalized $R\psi_i = \pm 1\psi_i$.
$\psi_{i\,;\ i=1,2,\ldots..}$ $\varphi_{k;\ k=1,2,3\ldots\ldots..}$ are two sets of functions(perhaps eigen functions) of a molecule which are bases for representations of the group and R is an operation in the symmetry group of the molecule.

$$R\,\psi_i = \sum_j a_{ji}\psi_j \;; \qquad R\,\varphi_k = \sum_l b_{lk}\varphi_l \;; \qquad R\,\psi_i\varphi_k = \sum_j \sum_l a_{ji}b_{lk}\psi_j\varphi_l$$

Example (see Chandra, p-324), taking two doubly degenerate functions f and g, find fg.

The set of functions $\psi_i\varphi_k$; $\{\psi_i\varphi_k\}$, called the direct product of $\psi_{i\,;\ i=1,2,\ldots..}$ and $\varphi_{k;\ k=1,2,3\ldots\ldots..}$, also forms a basis for a representation of the group.

Theorem:

1. The characters of the representation of a direct product are equal to the product of the characters of the representations based on the individual sets of functions. i.e., $\chi(R) = \chi_1(R)\chi_2(R)$
2. The representation of a direct product, Γ_{AB}, will contain the totally symmetric representation (A_1) only if the irreducible representation Γ_A = the irreducible Γ_B.

Usefulness:

Integrals of the type $\int \psi_i \hat{O} \psi_j d\tau$, where $\hat{O}$ is an operator, are non vanishing if it invariant under all the operations of the group, or some term in it, if it can be expressed as a sum of terms, remains invariant. In other words, for the nonzero value of the integral, the direct product of the representations (i.e., $\Gamma(\psi_i)\times\Gamma(\psi_j) = \Gamma(O)$), must contain an irreducible component having the same properties as the operator $\hat{O}$.

1. Energy elements: (Cotton, p-101) $\int \psi_i \hat{H} \psi_j d\tau \neq 0$, only if ψ_i and ψ_j belong to the same irreducible representation of the molecular point group. This is because the Hamiltonian is totally symmetric and therefore, invariant under any operation of the group. It will save the computational time wastage.
2. Spectral transition probabilities: (Cotton, p-102)

   Intensity of a transition, I, from a state ψ_i to ψ_j is given by $I \;\; \alpha \;\; \int \psi_i \hat{\mu} \psi_j d\tau$,

   where $\hat{\mu}$ is a transition moment operator, those corresponding to changes in electric or magnetic dipoles, multipoles, or polarizability tensors.

Considering electrical dipole operator $\hat{\mu} = \sum_i e_i \hat{x}_i + \sum_i e_i \hat{y}_i + \sum_i e_i \hat{z}_i$, where e_i represents the charge of the i-th particle, we can have

$$I_x \quad \alpha \quad \int \psi_i \hat{x} \psi_j d\tau ; \quad I_y \quad \alpha \quad \int \psi_i \hat{y} \psi_j \partial\tau ; \quad I_z \quad \alpha \quad \int \psi_i \hat{z} \psi_j \partial\tau$$

These equations mean that the transition from the i-th to the j-th state(or the reverse) may acquire its intensity in any of the three ways by interacting with an electric vector oscillating in the x, y or z direction.

An electric dipole transition will be allowed if the direct product representation of the two concerned states is or contains the irreducible representation to which x, y or z belongs, respectively.

Symmetry and its applications
Home work
Due date: May 4, 2020

Q1. Find out the symmetry operations and hence the point group of the following molecules:

(a) H_2O_2 (b) Allene (c) staggered ethane (d) pencil (e) a tennis ball
(f) Cyclohexane (g) Methane (h) Chloroform (i) Phenol (j) a cricket ball (k) SF_6
(l) Ethylene

Q2. Obtain group multiplication table for chloroform using matrix representation of the symmetry operations.

Q3. Construct character table for N_2F_2 molecule.

Q4. Form SALC's for π-Orbitals for the Cyclopropenyl group, C_3H_3, using the three p-orbital of three carbon atom as the basis.