4. Molecular Symmetry

4.3 Point Group Character Tables

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z, z^2; x^2+y^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) Character Table 의 주요 성질

① Symbols of irreducible represention

A : one dimensional representation, symmetric to ~~principle~~ principal axis (C_n)

B : one dimensional representation, antisymmetric to ~~principle~~ principal axis (C_n)

E : two dimensional degenerate representation

T (or F): three dimensional degenerate representation (Td, T)

1,2 : symmetric and antisymmetric to ~~to~~ C_2 or σ_v, respectively

','' : symmetric and antisymmetric to σ_h, respectively

g,u : symmetric and antisymmetric to inversion

② Great Orthogonality Theorem

ⓐ The sum of the squares of the dimensions of the irreducible represenations of ~~a~~ a group is equal to the order of the group

$$\sum_{i} l_i^2 = l_1 + l_2 + \cdots = h$$

ⓑ The sum of the squares of the characters in any irreducible representation is equal to h.

$$\sum_{R} [\chi_i(R)]^2 = h$$

ⓒ The vetors whose components are the characters of two different irreducible representations are orthogonal.

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

ⓓ In a given representation (reducible or irreducible) the characters of all matrices belonging to operations in the same class are identical.

ⓔ The number of irreducible representations of a group is equal to the number of classes in the group. square ↔ rectangle

③ Multiplication of the characters between any two representations (except between two degenerate representations) results in the character of another representation of the group.

→ Direct Product의 성질 : The characters of the representation of a direct product are equal to the products of the characters of the representation based on the individual sets of functions.

④ If the characters of two degenerate representaions are multiplied, the result is the sum of the characters of several irreducible representation.

e.g.

$$A_1 \times A_2 = A_2 \times A_1 = A_2$$

$$E^2 = A_1 + A_2 + B_1 + B_2 \quad \text{in } C_{4v}$$

$$E_1 \times E_2 = B_1 + B_2 + E_1 \quad \text{in } C_{6v}$$

$$E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_2$$

$$g \times g = u \times u = g, \qquad g \times u = u$$

$$' \times '' = '' \qquad , \qquad ' \times ' = '' \times '' = '$$

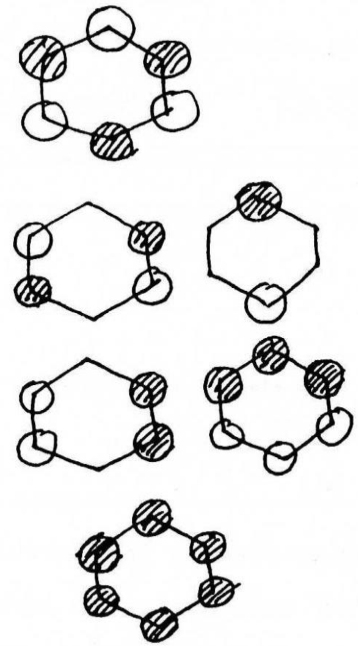
④,⑤의 적용 : Benzene의 π-orbital

a_{1g} ———

e_{2u} ——— ———

e_{1g} ——— ———

a_{2u} ———



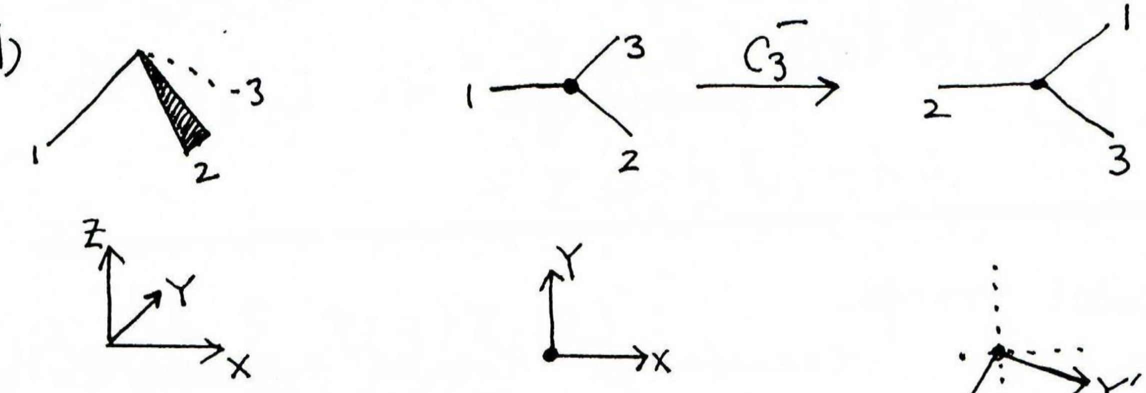
ground state : $(a_{2u})^2(e_{1g})^4 = A_{1g}$ 즉 filled orbital state는 totally symmetric.

1st excited state : $(a_{2u})^2(e_{1g})^3(e_{2u})^1$

$$= (E_{1g})(E_{2u}) = B_{1u} + B_{2u} + E_{1u}$$

2) Transformation of other bases

예)



(x, y)를 basis set로 할 때

$$\therefore \begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} \\ -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{3}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

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

같은 방법으로 $\chi(C_3^+) = -1$, $\chi(\sigma_v) = 0$, $\chi(\sigma_v') = 0$ $\chi(\sigma_v'') = 0$

$\chi(E) = 2$

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

	E	$2C_3$	$3\sigma_v$
$\Gamma_{(x,y)}$	2	-1	0

$\therefore$ (x, y) transforms as E in C_{3v}

z transforms as A_1 in C_{3v}

(T_x, T_y) transforms as E in C_{3v}

T_z " A_1 "

(antisymmetric to σ_v)

$R_z \ (\propto x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$ transforms as A_2 in C_{3v}

(R_x, R_y) transforms as E in C_{3v}

In all point groups

$s \ (= f(r))$ transforms totally symmetrically

$p_x \ (= x f(r))$ transforms as x

$p_y \ (= y f(r))$ 〃 y

$p_z \ (= z f(r))$ 〃 z

$d_{z^2} \ (= (3z^2 - r^2) f(r))$ 〃 $2z^2 - x^2 - y^2$

$d_{xy} \ (= xy f(r))$ 〃 xy

$d_{yz} \ (= yz f(r))$ 〃 yz

$d_{zx} \ (= zx f(r))$ 〃 zx

$d_{x^2-y^2} \ (= (x^2 - y^2) f(r))$ 〃 $x^2 - y^2$

---

3) Reducible representation을 irreducible representation의 합으로 나타내는 법

We write $\chi(R) = \sum_j a_j \chi_j(R)$,

where $\chi(R)$ is the character of symmetry operation R in reducible representation,

$\chi_j(R)$ is the character of R in irreducible representation

a_j : # of times that jth irreducible representation will appear.

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

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

$$= \sum_j a_j\,h\,\delta_{ij} = h\,a_i$$

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

$$\text{or} \quad a_i = \frac{1}{h} \sum_{R'} n(R')\,\chi(R')\,\chi_j(R')$$

(h : order of group

$n(R')$: # of element in the symmetry class R')

예.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ_a	5	2	-1

$$a(A_1) = \frac{1}{6}(1\cdot1\cdot5 + 2\cdot1\cdot2 + 3\cdot1\cdot-1) = 1$$

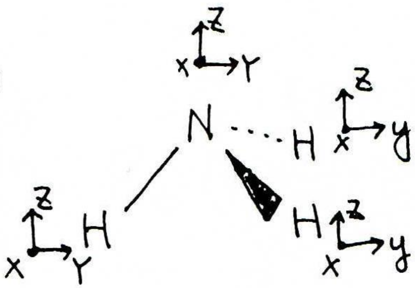
$$a(A_2) = \frac{1}{6}(1\cdot1\cdot5 + 2\cdot1\cdot2 + 3\cdot-1\cdot-1) = 2$$

$$a(E) = \frac{1}{6}(1\cdot2\cdot5 + 2\cdot-1\cdot2 + 3\cdot0\cdot-1) = 1$$

$$\therefore \quad \Gamma_a = A_1 + 2A_2 + E$$

즉. $(5,2,1) = (1,1,1) + 2(1,1,-1) + (2,1,0)$

예)



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
Γ_{12}	12	0	2

$$\chi(E) = 12$$

$$\chi(C_3^-) = 1 + \underbrace{\chi\begin{pmatrix} \cos-\frac{2}{3}\pi & \sin\frac{2}{3}\pi \\ -\sin\frac{2}{3}\pi & \cos\frac{2}{3}\pi \end{pmatrix}}_{-1} = 0$$

$$\chi(C_3^+) = 0$$

$$\chi(\sigma_v) = 1 + 1 = 2$$

$$\chi(\sigma_v') = 2$$

$$\chi(\sigma_v'') = 2$$

$$\Downarrow \; C_3^-$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos-\frac{2}{3}\pi & \sin\frac{2}{3}\pi \\ 0 & -\sin\frac{2}{3}\pi & \cos\frac{2}{3}\pi \end{pmatrix}\begin{pmatrix} z \\ x \\ y \end{pmatrix}$$

$\Downarrow$ N only 다른 세개의 H atoms 위치 바꿈

$$\sigma_v$$

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

$\Downarrow$ N과 H 다른 두개의 H atoms 은 서로 위치가 바뀜

$$(12, 0, 2) = a(1, 1, 1) + b(1, 1, -1) + c(2, -1, 0)$$

$$a = \frac{1}{6}(12 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times 1 \times 3) = 3$$

$$b = \frac{1}{6}(12 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times (-1) \times 3) = 1$$

$$c = \frac{1}{6}(12 \times 2 \times 1 + 0 \times (-1) \times 2 + 2 \times 0 \times 3) = 4$$

$$\Gamma_{12} = 3A_1 + A_2 + 4E$$

(C_{3v} character table last column 참조)

(T_x, T_y, T_z) spans as $A_1 + E$; translational Motion

(R_x, R_y, R_z) spans as $A_2 + E$; Rotational Motion

$\therefore$ Vibrational Motion spans as $2A_1 + 2E$

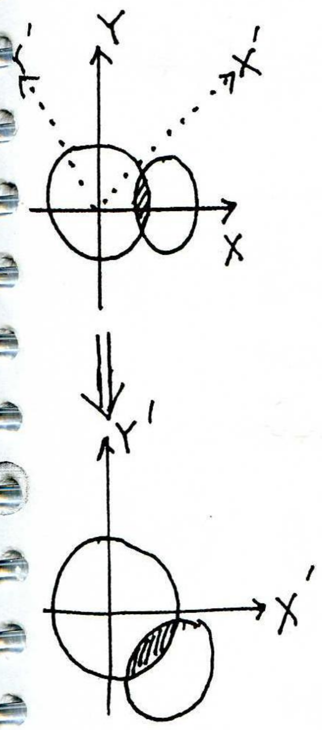
* A molecule has a permanent dipole moment if any of the translational species of the point group to which the molecule belongs is totally symmetic ; that is only the molecules belonging to C_1, C_s, C_n, C_{nv}, groups have a permanent dipole moment.

4) Using Character Tables

- Vanishing Integral
- Symmetry Adapted linear combination.

① Vanishing Integral

$$I = \int g(\vec{r})\,d\tau$$ 를 생각해 보면



Integral 은 어떤 coordinate transformation, R, 에 대해서도 불변 즉 $RI = I$

$$RI = \int R\{g(\vec{r})\,d\tau\} = \int' Rg(\vec{r}')\,d\tau'$$

$$I = \int' g(\vec{r}')\,d\tau'$$

$$\therefore \ Rg(\vec{r}') = g(\vec{r}')$$

R

만일 어떤 분자가 가지고 있는 symmetry operation R 에 대해서

$R\,g(\vec{r}) = -g(\vec{r})$ 이면 $RI = -I = I = 0$

$\therefore$ I 가 nonzero 값을 가지려면 분자가 가지고 있는 모든 symmetry operation R 에 대해서 $Rg = +1g$ 가 되어야 한다

즉 g 는 totally symmetric irreducible representation $\{A, A_1, A_{1g}, A_1', A_{1g}'$ 등$\}$ 을 가져야 한다.

< $g = f_1 f_2$ 일때 >

f_1, f_2의 symmetry representation을 분자가 속한 group의 character table을 참조하여 적는다. 그리고 $f_1 f_2$의 character를 direct product를 사용하여 적는다. 마지막으로 이 character를 reduce하여 totally symmetric representation을 갖는가 본다.

예) NH_3의 각 atom의 1s orbitals (S_N, S_1, S_2, S_3)의 linear combination인 $f_1 = S_N$, $f_2 = S_1 + S_2 + S_3$, $f_3 = 2S_1 - S_2 - S_3$, $f_4 = S_2 - S_3$ 중에서 서로 겹치는 orbitals은 어떤 것들인가?

풀이) C_{3v} 에서 S_N은 A_1, $S_1 + S_2 + S_3$은 A_1, f_3는 E, f_4는 E representation을 갖는다.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
$f_1 f_2$	1	1	1	$\rightarrow A_1$
$f_1 f_3$	2	-1	0	$\rightarrow E$
$f_1 f_4$	2	-1	0	$\rightarrow E$
$f_2 f_3$	2	-1	0	$\rightarrow E$
$f_2 f_4$	2	-1	0	$\rightarrow E$
$f_3 f_4$	4	1	0	$\rightarrow A_1 + A_2 + E$

$\therefore$ Only $(S_N, S_1+S_2+S_3)$ 와 $(2S_1-S_2-S_3, S_2-S_3)$ 만이 겹쳐진다.

※ $I = \int f_1 f_2 d\tau$ 가 nonzero가 될려면 f_1과 f_2의 symmetry representation이 같아야 된다.

⟨ $g = f_1 f_2 f_3$ 일 때 ⟩

만일 f_1이 totally symmetric 하면 (ground state는 대부분 totally symmetric하다) $f_2 f_3$가 totally symmetric 한가 아닌가를 따지면 된다. $f_2 f_3$가 totally symmetric 하려면 $f_2 f_3$의 symmetric representation이 같아야 한다.

예) 앞의 Benzene 문제에서 구한 세 first excited electronic state, B_{1u}, B_{2u}, E_{1u} 중에서 ground electronic state로 부터 dipole allowed transition이 가능한 state는 어느것인가?

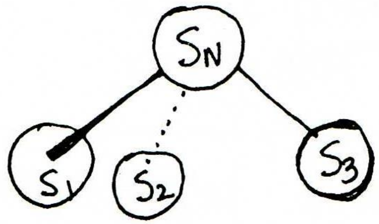
풀이) ground state는 A_{1g} ∴ x, y, z 의 symmetry가 B_{1u}, B_{2u}, E_{1u}를 갖는가 보면된다. D_{6h} Character Table 에서, (x,y) spans as E_{1u}, z spans as A_{2u}.
∴ E_{1u}가 transition 가능한 state이다.

② Symmetry Adapted Linear Combination (SALC)

Projection Operator

$$P_i = \frac{l_i}{h} \sum_R \chi_i(R) R$$

예) NH_3 의 S_N, S_1, S_2, S_3 orbital을 linear combination 하여 각각 A_1, A_2, E symmetry를 갖는 orbital 만들기



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$P_{A_1}(S_N) = \frac{1}{6}(1E + 1C_3^+ + 1C_3^- + 1\sigma_v + 1\sigma_v' + 1\sigma_v'')(S_N)$$

$$= \frac{1}{6}(S_N + S_N + S_N + S_N + S_N + S_N) = S_N \Rightarrow \underset{S_N}{\text{Normalization}}$$

$$P_{A_2}(S_N) = \frac{1}{6}(1E + 1C_3^+ + 1C_3^- - 1\sigma_v - 1\sigma_v' - 1\sigma_v'')(S_N)$$

$$= \frac{1}{6}(S_N + S_N + S_N - S_N - S_N - S_N) = 0$$

$$P_E(S_N) = \frac{2}{6}(2E - C_3^+ - C_3^-)(S_N) = 0$$

$$P_{A_1}(S_1) = \frac{1}{6}(1E + 1 \cdot C_3^{+} + 1C_3^{-} + 1\sigma_v + 1\sigma_v' + 1\sigma_v'')(S_1)$$

$$= \frac{1}{6}(1 \cdot S_1 + 1 \cdot S_3 + S_2 + S_1 + S_3 + S_2) = \frac{1}{3}(S_1 + S_2 + S_3)$$

$$\Rightarrow \text{Normalization } \frac{1}{\sqrt{3}}(S_1 + S_2 + S_3)$$

$$P_{A_1}(S_2) = \frac{1}{\sqrt{3}}(S_1 + S_2 + S_3) = P_{A_1}(S_3)$$

$$P_{A_2}(S_1) = \frac{1}{6}(1E + 1C_3^{+} + 1C_3^{-} - 1\sigma_v - 1\sigma_v' - 1\sigma_v'')(S_1)$$

$$= \frac{1}{6}(S_1 + S_2 + S_3 - S_1 - S_3 - S_2) = 0$$

$$P_{A_2}(S_2) = P_{A_2}(S_3) = 0$$

$$P_E(S_1) = \frac{2}{6}(2E - 1C_3^+ - 1C_3^-)(S_1) = \frac{2}{6}(2S_1 - S_2 - S_3)$$

$$\overset{\text{Normalization}}{=} \frac{1}{\sqrt{6}}(2S_1 - S_2 - S_3)$$

$$P_E(S_2) = \frac{2}{6}(2E - 1C_3^+ - 1C_3^-)(S_2) = \frac{2}{6}(2S_2 - S_1 - S_3)$$

$$P_E(S_3) = \frac{2}{6}(2E - 1C_3^+ - 1C_3^-)(S_3) = \frac{2}{6}(2S_3 - S_2 - S_1)$$

→ linear combination

$$\Rightarrow \frac{1}{3}(S_2 - S_3)$$

Normalization $\Rightarrow \frac{1}{\sqrt{2}}(S_2 - S_3)$

* 두개의 linearly dependent basis function ψ_1, ψ_2를 linear combination 해서 하나의 orthogonal basis function ψ'를 만드는 일반적인 방법은 Gram-Schmidt의 방법에 의해 $\psi' = \psi_1 - \frac{\langle \psi_1 | \psi_2 \rangle}{\langle \psi_1 | \psi_2 \rangle} \psi_2$ 이다.

이 방법은 서로 linearly dependent한 $\{\psi_1, \ldots, \psi_n\}$을 linear combination하여 새로운 orthogonal set를 다음과 같이 만들수 있다.

$$\psi_1' = \psi_1 - \frac{\langle \psi_1 | \psi_2 \rangle}{\langle \psi_1 | \psi_1 \rangle}\psi_2 - \frac{\langle \psi_1 | \psi_3 \rangle}{\langle \psi_1 | \psi_1 \rangle}\psi_3 - \cdots - \frac{\langle \psi_1 | \psi_n \rangle}{\langle \psi_1 | \psi_1 \rangle}\psi_n$$

$$\vdots$$

$$\psi_i' = -\frac{\langle \psi_i | \psi_1 \rangle}{\langle \psi_i | \psi_i \rangle}\psi_1 - \frac{\langle \psi_i | \psi_2 \rangle}{\langle \psi_i | \psi_i \rangle}\psi_2 \cdots + \psi_i - \cdots \frac{\langle \psi_i | \psi_n \rangle}{\langle \psi_i | \psi_i \rangle}\psi_n$$

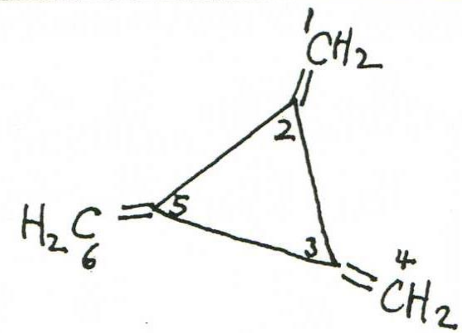
$$(i = 1, \cdots, n-1)$$

(연습) 옆의 분자의 6개의 탄소 P_z orbital을

a) 선형결합하여 reduce하면 어떤 symmetry representation을 갖는가?

b) 3개의 normalized SALC는 각각 무엇인가?

c) 이 3개의 SALC-MO를 가지고 만든 secular equation에 Hückel approximation을 적용하여 각 representation의 orbital wavefunction과 energy를 구하라.



풀이)

a) 6개의 P_z orbital을 $\{\phi_1, \phi_4, \phi_6\}$와 $\{\phi_2, \phi_3, \phi_5\}$의 두 subgroup으로 나누면 편리하다.

D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$
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

$\chi\{\phi_1, \phi_4, \phi_6\} = \{3, 0, 1, -3, 0, -1\}$

$a(A_1') = \frac{1}{12}(3\cdot1\cdot1 + 1\cdot1\cdot3 + (-3)\cdot1\cdot1 + (-1)\cdot1\cdot3) = 0$

$a(A_2') = \frac{1}{12}(3\cdot1\cdot1 + 1\cdot(-1)\cdot3 + (-3)\cdot1\cdot1 + (-1)(-1)\cdot3) = 0$

$a(A_2'') = \frac{1}{12}(3\cdot1\cdot1 + 1\cdot1\cdot3 + (-3)(-1)\cdot1 + (-1)(-1)\cdot3) = 1$

$a(A_1'') = \frac{1}{12}(3\cdot1\cdot1 + (-1)\cdot1\cdot3 + (-3)(-1)\cdot1 + (-1)\cdot1\cdot3) = 0$

$a(E') = \frac{1}{12}(3\cdot2\cdot1 + 1\cdot0\cdot3 + (-3)\cdot2\cdot1 + (-1)\cdot0\cdot3) = 0$

$a(E'') = \frac{1}{12}(3\cdot2\cdot1 + 1\cdot0\cdot3 + (-3)(-2)\cdot1 + (-1)\cdot0\cdot3) = 1$

$\therefore \Gamma_{\phi_1\phi_4\phi_6} = A_2'' + E''$ 마찬가지로 $\Gamma_{\phi_2\phi_3\phi_5} = A_2'' + E''$

$\therefore \Gamma_{\phi_1\phi_2\cdots\phi_6} = \underline{2A_2'' + 2E''}$

b). Normalized SALC-MO :

A_2'' : $\psi_1 = \frac{1}{\sqrt{3}}(\phi_2 + \phi_3 + \phi_5)$

$\psi_2 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_4 + \phi_6)$

E'' : $\psi_3 = \frac{1}{\sqrt{6}}(2\phi_2 - \phi_3 - \phi_5)$ $\qquad$ $\psi_5 = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_4 - \phi_6)$

$\psi_4 = \frac{1}{\sqrt{2}}(\phi_3 - \phi_5)$ $\qquad$ $\psi_6 = \frac{1}{\sqrt{2}}(\phi_4 - \phi_6)$

c) Secular Determinant는 아래와 같다.

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-S_{21} & 0 & 0 & 0 & 0 \\ H_{21}-ES_{21} & H_{22}-ES_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{33}-ES_{33} & H_{34}-S_{34} & H_{35}-S_{35} & H_{36}-S_{36} \\ 0 & 0 & H_{43}-S_{43} & H_{44}-ES_{44} & H_{45}-S_{45} & H_{46}-S_{46} \\ 0 & 0 & H_{53}-S_{53} & H_{54}-S_{54} & H_{55}-ES_{55} & H_{56}-S_{56} \\ 0 & 0 & H_{63}-S_{63} & H_{64}-S_{64} & H_{65}-S_{65} & H_{66}-ES_{66} \end{bmatrix} = 0$$

$H_{ij} = \langle \psi_i | H | \psi_j \rangle$

$S_{ij} = \langle \psi_i | \psi_j \rangle = \delta_{ij}$

$$\Rightarrow \begin{vmatrix} H_{11}-E & H_{12} & 0 & 0 & 0 & 0 \\ H_{21} & H_{22}-E & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{33}-E & H_{34} & H_{35} & H_{36} \\ 0 & 0 & H_{43} & H_{44}-E & H_{45} & H_{46} \\ 0 & 0 & H_{53} & H_{54} & H_{55}-E & H_{56} \\ 0 & 0 & H_{63} & H_{64} & H_{65} & H_{66}-E \end{vmatrix} = 0$$

이 secular determinant는 symmetry에 의해 block-diagonalized 되었다.

A_2'' symmetry를 갖는 block-diagonalized secular determinant는

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0$$

$$H_{11} = \frac{1}{3}\langle \phi_2 + \phi_3 + \phi_5 | H | \phi_2 + \phi_3 + \phi_5 \rangle = \frac{1}{3}\langle 3\alpha + 6\beta \rangle = \alpha + 2\beta$$

$$H_{22} = \frac{1}{3}\langle \phi_1 + \phi_4 + \phi_6 | H | \phi_1 + \phi_4 + \phi_6 \rangle = \frac{1}{3}(3\alpha) = \alpha$$

$$H_{21} = H_{12} = \frac{1}{3}\langle \phi_1 + \phi_4 + \phi_6 | H | \phi_2 + \phi_3 + \phi_5 \rangle = \frac{1}{3}(\beta + \beta + \beta) = \beta$$

$$\therefore \begin{bmatrix} \alpha+2\beta-E & \beta \\ \beta & \alpha-E \end{bmatrix} = 0 \qquad E = \alpha + (1 \pm \sqrt{2})\beta$$

$E = \alpha + (1+\sqrt{2})\beta$일때 $\left[\begin{array}{l} \begin{pmatrix} (1-\sqrt{2})\beta & \beta \\ \beta & -(1+\sqrt{2})\beta \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \\ C_1^2 + C_2^2 = 1 \end{array}\right] \rightarrow \begin{array}{l} C_1 = 0.924 \\ C_2 = 0.382 \end{array}$

$$\therefore \psi^{(1)}_{A_2''} = 0.924\,\psi_1 + 0.382\,\psi_2$$
$$= 0.533(\phi_2 + \phi_3 + \phi_5) + 0.221(\phi_1 + \phi_4 + \phi_6)$$

$E = \alpha + (1-\sqrt{2})\beta$일때 $\left[\begin{array}{l} \begin{pmatrix} (1+\sqrt{2})\beta & \beta \\ \beta & -(1-\sqrt{2})\beta \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \\ C_1^2 + C_2^2 = 1 \end{array}\right] \rightarrow \begin{array}{l} C_1 = -0.383 \\ C_2 = 0.924 \end{array}$

$$\psi^{(2)}_{A_2''} = -0.383\,\psi_1 + 0.924\,\psi_2$$
$$= 0.533(\phi_1 + \phi_4 + \phi_6) - 0.221(\phi_2 + \phi_3 + \phi_5)$$

E'' symmetry를 갖는 block-diagonalized secular determinant는

$$\begin{bmatrix} H_{33}-E & H_{34} & H_{35} & H_{36} \\ H_{43} & H_{44}-E & H_{45} & H_{46} \\ H_{53} & H_{54} & H_{55}-E & H_{56} \\ H_{63} & H_{64} & H_{65} & H_{66}-E \end{bmatrix} = 0$$

$$H_{33} = \frac{1}{6}\langle 2\phi_2 - \phi_3 - \phi_5 | H | 2\phi_2 - \phi_3 - \phi_5 \rangle = \frac{1}{6}(4\alpha + \alpha + \alpha - 2\beta - 2\beta \quad -2\beta + \beta - 2\beta + \beta)$$

$$= \frac{1}{6}(6\alpha + 6\beta) = \alpha + \beta = H_{55}$$

$$H_{44} = \frac{1}{2}\langle \phi_3 - \phi_5 | H | \phi_3 - \phi_5 \rangle = \frac{1}{2}(2\alpha + 2\beta) = \alpha + \beta = H_{66}$$

$$H_{34} = H_{43} = \frac{1}{\sqrt{12}}\langle 2\phi_2 - \phi_3 - \phi_5 | H | \phi_3 - \phi_5 \rangle = \frac{1}{\sqrt{12}}(-2\alpha + 2\alpha + 2\beta - 2\beta + \beta - \beta) = 0$$

$$H_{35} = H_{53} = \frac{1}{6}\langle 2\phi_2 - \phi_3 - \phi_5 | H | 2\phi_1 - \phi_4 - \phi_6 \rangle = \frac{1}{6}(4\beta - \beta - \beta) = \frac{1}{3}\beta$$

$$H_{36} = H_{63} = \frac{1}{\sqrt{12}}\langle 2\phi_2 - \phi_3 - \phi_5 | H | \phi_4 - \phi_6 \rangle = \frac{1}{\sqrt{12}}(-\beta + \beta) = 0$$

$$H_{45} = H_{54} = \frac{1}{\sqrt{12}}\langle \phi_3 - \phi_5 | H | 2\phi_1 - \phi_4 - \phi_6 \rangle = \frac{1}{\sqrt{12}}(-\beta + \beta) = 0$$

$$H_{46} = H_{64} = \frac{1}{6}\langle \phi_3 - \phi_5 | H | \phi_4 - \phi_6 \rangle = \frac{1}{6}(\beta + \beta) = \frac{1}{3}\beta$$

$\therefore$ E'' symmetry 의 secular determinant 는

$$\begin{array}{c|c} & \begin{array}{cccc} 3 & 4 & 5 & 6 \end{array} \\ \begin{array}{c} 3 \\ 4 \\ 5 \\ 6 \end{array} & \begin{bmatrix} \alpha+\beta-E & 0 & \frac{1}{3}\beta & 0 \\ 0 & \alpha+\beta-E & 0 & \frac{1}{3}\beta \\ \frac{1}{3}\beta & 0 & \alpha+\beta-E & 0 \\ 0 & \frac{1}{3}\beta & 0 & \alpha+\beta-E \end{bmatrix} \end{array}$$

Secular equation은 다음과 같이 다시 쓰는 것이 좋다
(즉 4와 5의 순서를 바꾼다)

$$\begin{array}{c} 3 \\ 5 \\ 4 \\ 6 \\ \\ \end{array} \begin{array}{c} \begin{bmatrix} \alpha+\beta-E & \frac{1}{3}\beta & 0 & 0 \\ \frac{1}{3}\beta & \alpha+\beta-E & 0 & 0 \\ 0 & 0 & \alpha+\beta-E & \frac{1}{3}\beta \\ 0 & 0 & \frac{1}{3}\beta & \alpha+\beta-E \end{bmatrix} \\ \begin{matrix} 3 & \quad\quad 5 & \quad\quad 4 & \quad\quad 6 \end{matrix} \end{array} \begin{pmatrix} C_3 \\ C_5 \\ C_4 \\ C_6 \end{pmatrix} = 0$$

$$\begin{bmatrix} \alpha+\beta-E & \frac{1}{3}\beta \\ \frac{1}{3}\beta & \alpha+\beta-E \end{bmatrix} = 0$$ 을 풀면 $E = \alpha+\beta \pm \frac{1}{3}\beta$.

$E = \alpha+\beta+\frac{1}{3}\beta = \alpha+\frac{4}{3}\beta$ 일때 $\begin{pmatrix} -\frac{1}{3}\beta & \frac{1}{3}\beta \\ \frac{1}{3}\beta & -\frac{1}{3}\beta \end{pmatrix}\begin{pmatrix} C_3 \\ C_5 \end{pmatrix} = 0$ $\quad C_3 = C_5 = \frac{1}{\sqrt{2}}$

$$\psi^{(3)}_{E''} = \frac{1}{\sqrt{2}}(\psi_3 + \psi_5) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{6}}(2\phi_2 - \phi_3 - \phi_5) + \frac{1}{\sqrt{6}}(2\phi_1 - \phi_4 - \phi_6)\right)$$
$$= \frac{1}{\sqrt{12}}(2\phi_1 + 2\phi_2 - \phi_3 - \phi_4 - \phi_5 - \phi_6)$$

같은 방법으로 $\psi_{E''}^{(4)} = \frac{1}{\sqrt{2}}(\psi_4 + \psi_6) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}(\phi_3 - \phi_5) - \frac{1}{\sqrt{2}}(\phi_4 - \phi_6)\right)$

$$= \frac{1}{\sqrt{2}}(\phi_3 + \phi_4 - \phi_5 - \phi_6)$$

$E = \alpha + \beta - \frac{1}{3}\beta = \alpha + \frac{2}{3}\beta$ 일 때

$$\begin{pmatrix} \frac{1}{3}\beta & \frac{1}{3}\beta \\ \frac{1}{3}\beta & \frac{1}{3}\beta \end{pmatrix}\begin{pmatrix} C_3 \\ C_5 \end{pmatrix} = 0 \qquad C_3 = -C_5 = \frac{1}{\sqrt{2}}$$

$$\therefore \quad \psi_{E''}^{(5)} = \frac{1}{\sqrt{2}}(\psi_3 - \psi_5) = \frac{1}{\sqrt{12}}(2\phi_1 - 2\phi_2 - \phi_3 + \phi_4 - \phi_5 - \phi_6)$$

같은방법으로 $\psi_{E''}^{(6)} = \frac{1}{\sqrt{2}}(\psi_4 - \psi_6) = \frac{1}{2}(\phi_3 - \phi_4 - \phi_5 - \phi_6)$

energy level 은 다음과 같다.

$\alpha + (1-\sqrt{2})\beta \qquad \psi_{A_2''}^{(2)} = 0.533(\phi_1 + \phi_4 + \phi_6) - 0.221(\phi_2 + \phi_3 + \phi_5)$

$$\alpha + \frac{2}{3}\beta \qquad \psi^{(5),(6)} = \begin{cases} \frac{1}{\sqrt{12}}(2\phi_1 - 2\phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6) \\ \frac{1}{2}(\phi_3 - \phi_4 - \phi_5 - \phi_6) \end{cases}$$

$$\alpha + \frac{4}{3}\beta \qquad \psi_{E''}^{(3)(4)} = \begin{cases} \frac{1}{\sqrt{12}}(2\phi_1 + 2\phi_2 - \phi_3 - \phi_4 - \phi_5 - \phi_6) \\ \frac{1}{2}(\phi_3 + \phi_4 - \phi_5 - \phi_6) \end{cases}$$

$\alpha + (1+\sqrt{2})\beta \qquad \psi_{A''}^{(1)} = 0.533(\phi_2 + \phi_3 + \phi_5) + 0.221(\phi_1 + \phi_4 + \phi_6)$