서강대학교 SOGANG UNIVERSITY | 물리학과 Department of Physics

Group Theory, especially about Molecular Symmetry

P. Atkins and R.Friedman, Molecular Quantum Mechanics
F.Cotton, Chemical Applications of Group Theory
N.Cheung, Molecular Symmetry & Group Theory

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Why do we need studying Molecular Symmetry?

Molecular symmetry is used to

1. Determine whether an integral is zero or not

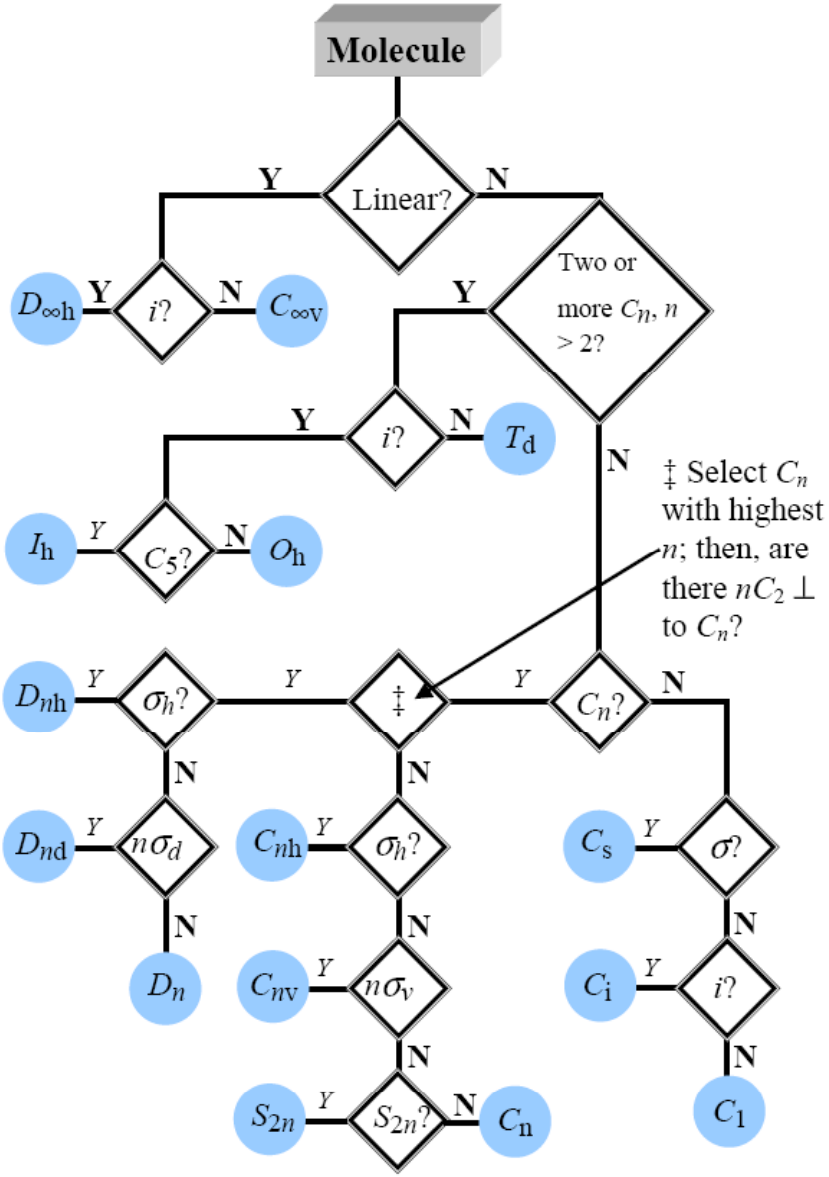
2. Determine whether the transition dipole moment is zero or not
   -> **Selection Rule**

3. Construct a molecular orbital

Molecular symmetry and Chirality
(https://people.ok.ubc.ca/wsmcneil/symm/symm.htm)

Symmetry Operations and Elements

1. E (identity)
2. C_n (n-fold rotation)
3. σ (reflection)
4. i (inversion)
5. S_n (n-fold improper rotation)



Group Theory

Group

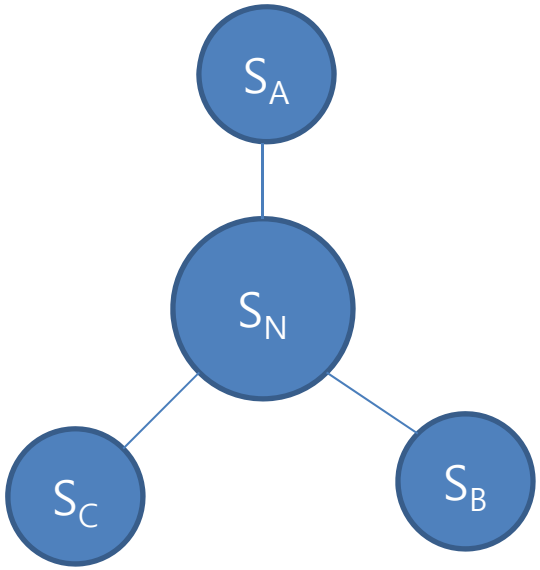
1. Group should have the identity
2. Group operation is associative
3. Elements in group has those inverse
4. Group operation is closed under multiplication

Matrix Representation

Consider a NH_3 molecule

* NH_3 molecule has a C_{3v} symmetry
  C_{3v} symmetry has six operations
  E(identity), C_3^+, C_3^- (rotation), σ_v, σ'_v, σ''_v (inversion)

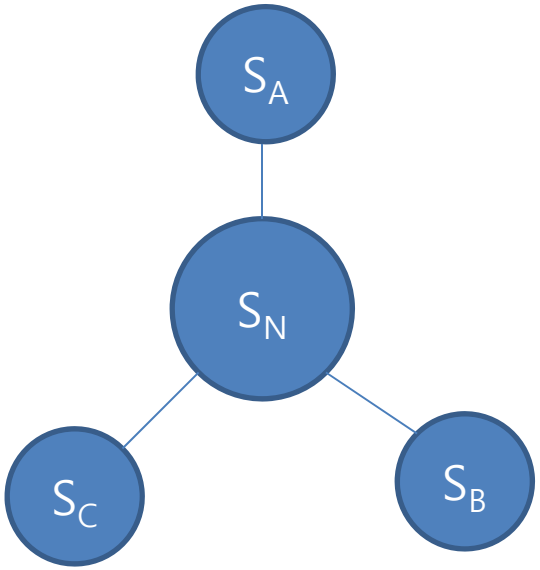
S_N, S_A, S_B and S_C are s-orbitals of H or N and Basis function also



(S_N, S_A, S_B, S_C)

Identity

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



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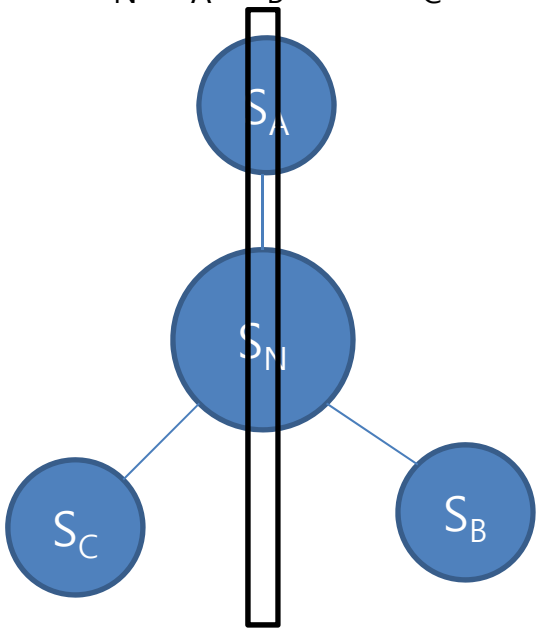
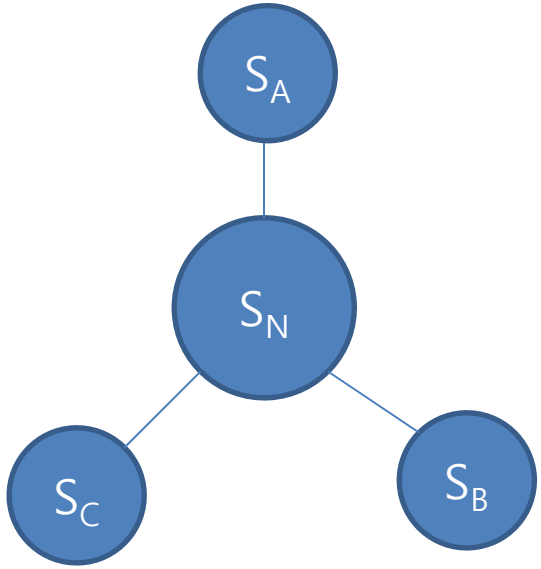


$$(S_N, S_A, S_B, S_C)$$

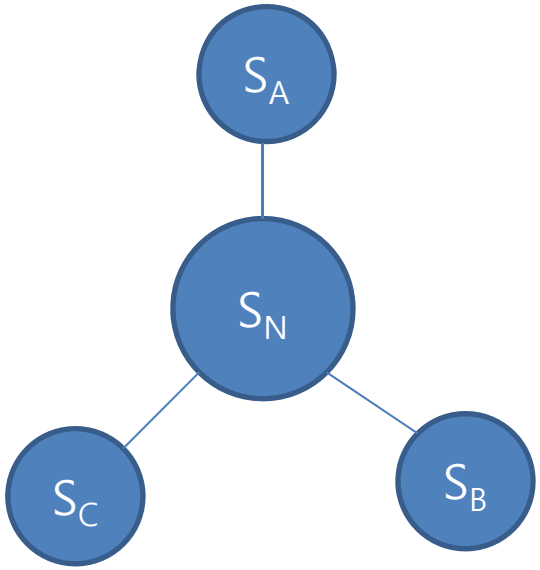
Inversion Sym.

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = D(\sigma_V)$$



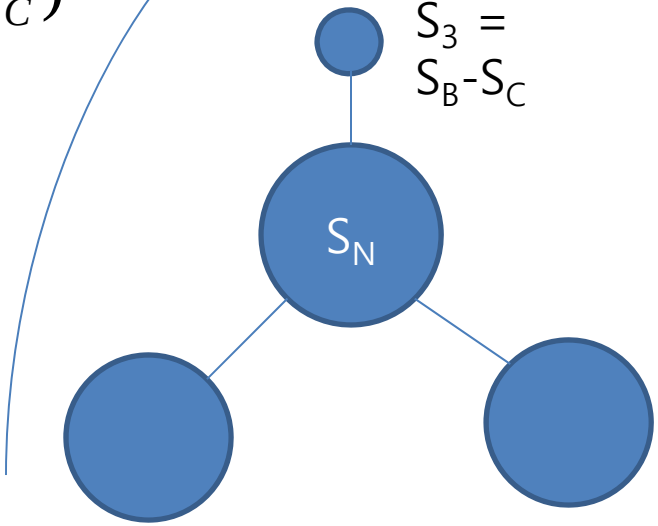
$$(S_N, S_A, S_C, S_B)$$

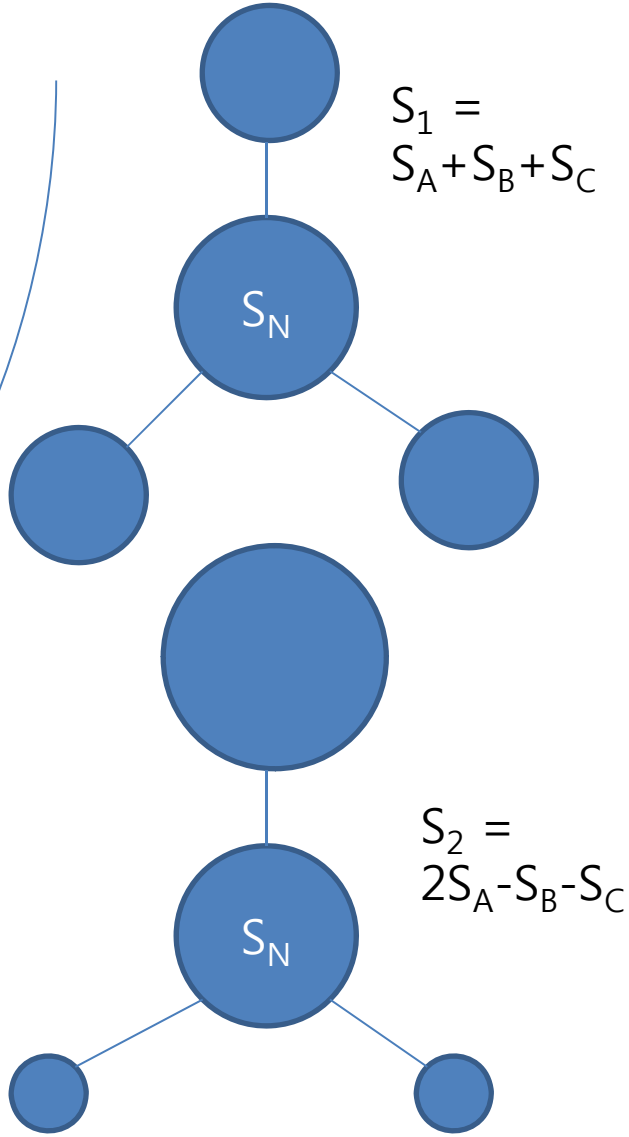
Matrix Representation II



(S_N, S_A, S_B, S_C)

WHY?
HOW?





(S_N, S_1, S_2, S_3)

Matrix Representation II

$$D(R) = (S_N, S_A, S_B, S_C) \longrightarrow D'(R) = (S_N, S_1, S_2, S_3)$$

Similarity Transformation
$D(R)=cD'(R)c^{-1}$

Character $\chi(R)$ (Trace of Matrix)
$tr\{D(R)\} = tr\{cD'(R)c^{-1}\} = tr\{D'(R)\}$

Character

Character $\chi(R)$ (Trace of Matrix)

$\mathrm{tr}\{D(R)\} = \mathrm{tr}\{cD'(R)c^{-1}\} = \mathrm{tr}\{D'(R)\}$

$D(E)$

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

$\chi(E) = 4$

Class 1

$D(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & 1/2 \\ 0 & 0 & -1/2 & -1/2 \end{bmatrix}$$

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

Class 2

$D(\sigma_v)$

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

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

Class 3

Irreducible Operator & Character Table

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & 1/2 \\ 0 & 0 & -1/2 & -1/2 \end{bmatrix}$$

Block-diagonal Form

$$D^{(1)} \oplus D^{(1)} \oplus D^{(2)}$$

Irreducible Representation

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

Character {1,1,1,1,1,1} – 1-Dim irreducible representation, A

Character {2,-1,-1,0,0,0} – 2-Dim irreducible representation, E

Irreducible Operator & Character Table

Character {1,1,1,1,1,1} – 1-Dim irreducible representation, A

Character {2,-1,-1,0,0,0} – 2-Dim irreducible representation, E

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

: Character Table

NH_3

$$(S_N, S_A, S_B, S_C) \longrightarrow (S_N, S_1, S_2, S_3) \longrightarrow 2A_1+E$$

How to Construct Character Table?

Little Orthogonality Theorm

$$\sum_R \chi^{(l)}(R) * \chi^{(l')}(R) = h\delta_{ll'}$$

- R: Symmetry operation
- $\chi^{(l)}(R)$: Dimension of operation
- h: Order of group

For C_{3v}

	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)

The order of C_{3v} (h) is 6.
Three classes of operation (R) exist in C_{3v}

1. When l=l'

$$d_{A_1}^2 + d_E^2 + d_X^2 = 6$$

$d_x=1$

2. others

1 * x * 1 + 2 * y * 1 + 3 * z *1 = 0
1 * x * 2 + 2 * y * -1 + 3 * z * 0 = 0

-> A_2 = {1,1,-1}

Direct Product

Direct Product Table for D_3, C_{3v}

	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + A_2 + E$

So what?

1. Wavefunction Overlap & the expection value

Only if the integrand is A_1, then the integral is not necessarily zero.

Wavefunction Overlap

Expection Value
$\langle d_{xy}|l_z|d_{xz}\rangle$ in C_{3v} molecule

	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)

	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1+ A_2+ E$

The Selection Rule for the Molecular Vibration mode

How do we get the molecular vibration mode ?

Total symmetry species –
(translational symmetry species (x, y ,z) +
rotational symmetry species (Rx, Ry, Rz))

Ex> H_2O (C_2V)

	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

H_2O : $3A_1 + A_2 + 3B_1 + 2B_2$

$H_2O_{vib} = H_2O_{tot}$

$-H_2O_{trans}$ $(A_1 + B_1 + B_2)$

$-H_2O_{rot}$ $(A_2 + B_1 + B_2)$

$= 2A_1 + B_1$

The Selection Rule for the Molecular Vibration mode
- IR & Raman activity

The Absorption of Infrared light is caused from the permanent dipole moment (p_x, p_y, p_z)

The Polarizability of molecules makes Stokes shift (d_{xz}, d_{yz}, d_{xy}, d_x^2, dx_2-y_2)

	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

The Selection Rule for the Molecular Vibration mode
- IR & Raman activity

Methane (T_d symmetry)

CH4 : A1 + E + T1 + 3T2

Trans : T2
Rot : T1

Raman : A1, E
IR : T2

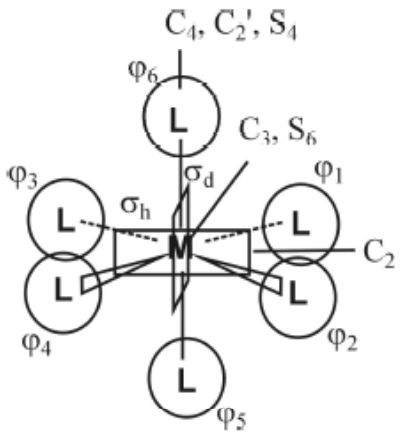
Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
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		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2		A_1	E	T_2	T_1
E			$A_1+ A_2+ E$	$T_1+ T_2$	$T_1+ T_2$
T_1				$A_1+ E + T_1+ T_2$	$A_2+ E + T_1+ T_2$
T_2					$A_1+ E + T_1+ T_2$

Molecular Orbital

Octahedral complex AB_6



Application of all symmetry operations to the set of ligand AOs and determination of the characters of the 6 dimensional representation:

Operation	$\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6$	χ
E (1)	$\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6$	6
C_3 (8)	$\varphi_2, \varphi_6, \varphi_4, \varphi_5, \varphi_3, \varphi_1$	0
C_2 (6)	$\varphi_2, \varphi_1, \varphi_4, \varphi_3, \varphi_6, \varphi_5$	0
C_4 (6)	$\varphi_2, \varphi_3, \varphi_4, \varphi_1, \varphi_5, \varphi_6$	2
C_2' (6)	$\varphi_3, \varphi_4, \varphi_1, \varphi_2, \varphi_5, \varphi_6$	2
i (1)	$\varphi_3, \varphi_4, \varphi_1, \varphi_2, \varphi_6, \varphi_5$	0
S_4 (6)	$\varphi_2, \varphi_3, \varphi_4, \varphi_1, \varphi_6, \varphi_5$	0
S_6 (8)	$\varphi_4, \varphi_5, \varphi_2, \varphi_6, \varphi_1, \varphi_3$	0

σ_h (3)	$\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_6, \varphi_5$	4
σ_d (6)	$\varphi_4, \varphi_3, \varphi_2, \varphi_1, \varphi_3, \varphi_4$	2

Analysis (analogous to tetrahedral case):

$$\Gamma_{\text{Ligand }\sigma\text{-AOs}} = A_{1g} + E_g + T_{1u}$$

MO diagram for octahedral σ-bonded ML_6 complex of 3d transition metal: