Group Theory

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3 j symbols

SU(n) symmetries

Literature

1963 Chemical Application of Group Theory - F.A. Cotton; John Wiley

1973 Group Theory and Chemistry, D.M. Bishop, Clarendon Press, and Sons

1964 Group Theory and Quantum Mechanics, M. Tinkham, Mc Graw-Hill.

1. Groups and Point Groups

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

Symmetry operations : symmetry of the Hamiltonian.

$$\mathcal{H} = \sum_{el.} -\frac{(\hbar/2)\bar{\nabla}_i^2}{2m} - \sum_{el.} \frac{Ze^2}{r_{ne}} + \sum_{el.} \frac{e^2}{r_{ij}} + \sum \bar{L}.G.\bar{S} + \sum \bar{S}.\underline{g}.\bar{S}$$

$$+ V_{pot.}$$

Symmetry of $\mathcal{H}$:

- inversion $\quad \bar{r} \to -\bar{r} \quad (x,y,z) \to (-x,-y,-z)$
- rotational symmetry
- reflection $\quad (x,y,z) \to (x, y\cos\theta, z\sin\theta)$
- translation $\quad (x,y,z) \to (x+a, y, z)$
- permutation

Symmetry of Interaction or of environment.

~~$R\mathcal{H}\psi = \mathcal{H}R\psi \quad R\mathcal{H}R^{-1}R\psi$~~

Solution: $\mathcal{H}\varphi_i = E_i\varphi_i$,

$R\varphi_i \to \mathcal{H}\,\underline{R\varphi_i} = E_i\,\underline{R\varphi_i}$

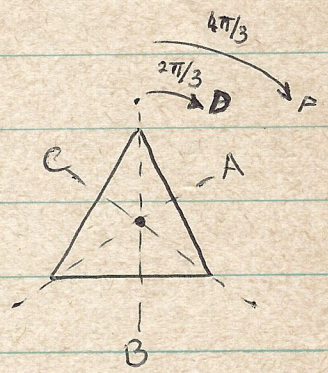
φ_i, $R\varphi_i$ degenerated.

Group: closed $AB = C \quad C \in G$

associative $(AB)C = A(BC)$ h: order.

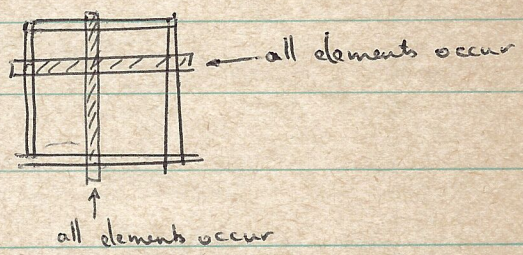
Unit Element $EA = AE$

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



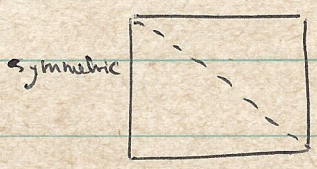
Group multiplication table:

	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

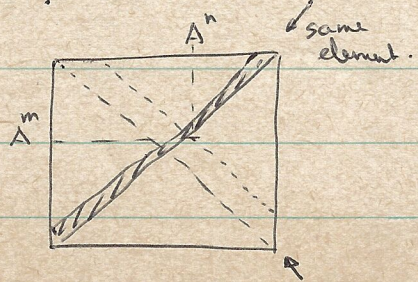


$R_i R_j \quad \forall_j$

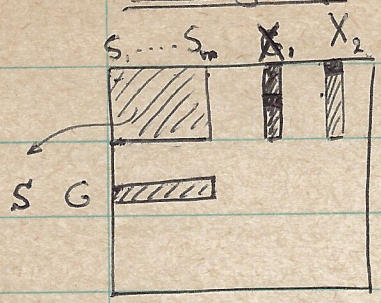
Abelian $AB = BA$



Cyclic $A, A^2, A^3 \ldots A = E$



Subgroup



$S_i X$ right coset

$X S_i$ left coset

Two cosets are diffent in all elements

If $S_i X_1 = S_j X_2$ then $\forall_k \; S_k X_1 = S_l S_i X_1 = S_l S_j X_2 = S_m X_2$

(S_k, S_m)

S : g order — x different cosets : $xg + g$ diffel elements

C : l order — l

$\Rightarrow l = (x+1)g$

Order g of subgroup integral divisor of entire group $l/g = x+1$

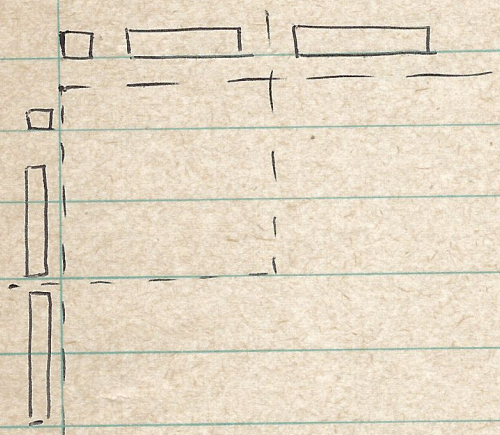
	E	D	F	A	B	C
E	E	D	F	A	B	C
D	D	F	E	C	A	B
F	F	E	D	B	C	A

Conjugated Elements

B is conjugate to A
C " " to A
} B to C

$B = X A X^{-1}$

Class : all conjugated elements



~~Normal divisor~~ : subgroup consisting of complete classes.
invariant subgroup

Isomorphy : Same multipl. table

Homomorphic : $A \longleftrightarrow A'_1 \dots A'_a$

$B \longleftrightarrow B'_1 \dots B'_b$ $\quad AB = C \quad A'_i B'_j = C'_k$

⋮ one-to-many correspondence

E is homomorphic to any group

Class Multiplication

class: $C = \{C_i\}$ $\quad \boxed{X\{C'_i\}X^{-1} = \{C'_i\}}$ ← each elem of left is diff

because $X C_i X^{-1} = X C_j X^{-1} \rightarrow C_i = C_j$

$\{C''_i\}\{C'_j\} = X^{-1}\{C''_i\}\{C'_j\}X$

{

Class C $\quad X\{C_i\}X^{-1} = \{C_i\} \quad XC_iX^{-1} = XC_jX^{-1} \rightarrow C_i = C$

If $X\{C_i\}X^{-1} = \{C_i\} \longrightarrow C$ classes complete

$$\{C_i^{(k)}\}\{C_j^{(l)}\} = \sum_m c_{klm}\{C^{(m)}\}$$

$C^{(1)} = E$

$C^{(2)} = A\ B\ C$ $\qquad C^{(1)}C^{(2)} = C^{(2)}$

$C^{(3)} = D,\ F$ $\qquad C^{(2)}C^{(2)} = 3C^{(1)} + 3C^{(3)}$

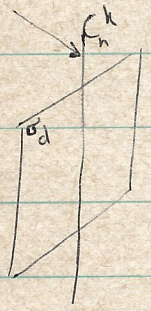
$C^{(2)}C^{(3)} = 2C^{(2)}$

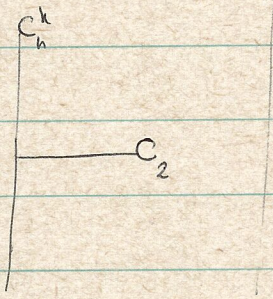
Each ... belonging ... → ... conjugate class

Point groups : symmetry group of molecule, while we leave center of mass fixed.

1. E, i, σ_h are classes by themselves ← (commutative with all)

2. C_n^k and C_n^{-k} are in same class ; C_n^k, C_n^l $n \nmid k-l$ in same class.

if 

if 

3. σ and σ' in same class if $\exists$ a symmetry operator in the point group which moves all point in plane σ to plane σ'.

C_n^k, $C_n^{k'}$ in same class if ... all point on C_n^k to $C_n^{k'}$ ... different axes.

32 point groups in crystal but much more in molecule.

T : 12 regular tetrahedron

T_d : T + reflections

T_h + inversion

O octahedron

O_h $O + i$

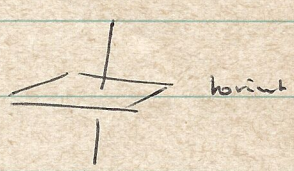
Point Groups

Symmetry operations (5)

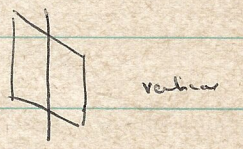
1 Identical operation E

2 rotation —//— C_n $2\pi/n$

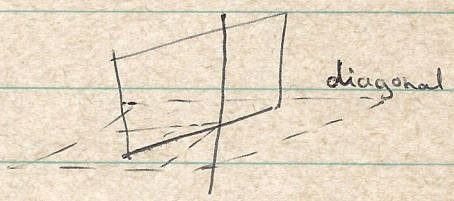
3 reflection —//— σ_h



σ_v

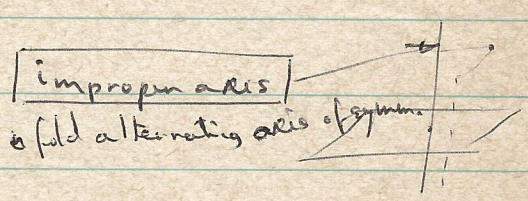


$\boxed{\sigma^2 = E}$



4 rotation - reflection S_n

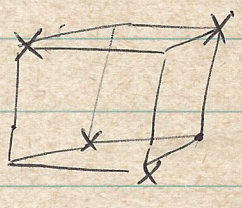
$S_n^k = \sigma_h C_n^k$



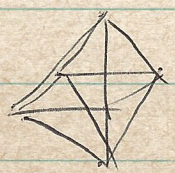
$S_n^2 = C_n^2$

5 Inversion i $S_1 = \sigma$ $S_2 = i$

Tetrahedral molecule S_4



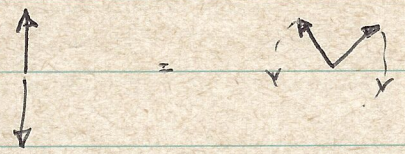
Octahedron



Voorbelden.

Dipole moment. : if well defined symmetry axis.

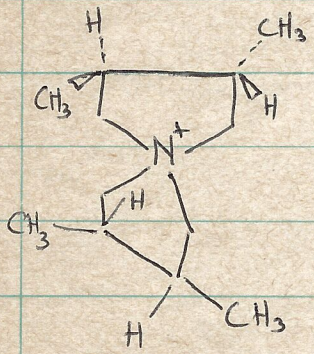
Optical activity : Rotate the plane of polarization



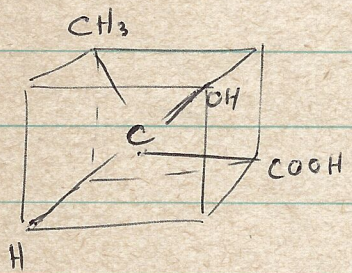
Necessary and sufficient condition for substance to exhibit opt. act is molecule cannot be superimposed on mirror reflection.

Enantiomers : molecule with S_n axis is not opt active

then → without S_n axis is opt. active in principle



S_4 tetramethyl spiro (1,1') dipyrrolidinium inactive



form of lactic acid active

2. Representation

Matrices A

Identity $A_{ij} = \delta_{ij}$

Diagonal $A_{ij} = d_i \delta_{ij}$

Symm M $A = \tilde{A}$ trasposed

real M $A = A^*$ conjucate

Hermitian M $A = A^\dagger$ adjoint

Unitary M $A^\dagger = A^{-1}$

Orthogonal M $\tilde{A} = A^{-1}$

Unitary trasformation $Q^{-1} A Q = B$

Trace $\mathrm{tr}\, A =$

Determinant $\det A =$

Eigenstates (values) $H \bar{x}_i = h_i \bar{x}_i$

$U^{-1} H U = D$ $\quad D \underbrace{U^{-1} \bar{x}_i}_{\begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix}} = h_i U^{-1} \bar{x}_i$

Representation : group of matrices $\Gamma(A)\,\Gamma(B) = \Gamma(AB)$

Multiplication table similar

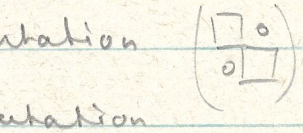
all matrices diffent <u>isomorphic</u>

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad A = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad B = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \quad C = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$$

$$D = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad E = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad F = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

- $E = A = B = C = D = E = F = 1$ identical representation
- $E = 1$ D, E, F
- $A = -1$ B, C

<u>Equivalent</u> representation $\Gamma'(A) = S^{-1}\,\Gamma(A)\,S$

<u>reducable</u> representation  possible to get blocks

<u>irreducable</u> representation impossible to get blocks.

× Any representation is equivalent to a unitary matrix

× <u>Great orthogonality theorem</u> : If we consider all inequivalent irreducable unitary representations of a group, then

$$\sum_R \Gamma^{(i)}(R)^*_{\mu\nu}\, \Gamma^{(j)}(R)_{\alpha\beta} = \frac{h}{l_i}\, \delta_{ij}\, \delta_{\mu\alpha}\, \delta_{\nu\beta}$$

TABLE 3-7.1

A flow chart for determining the point group of a molecule

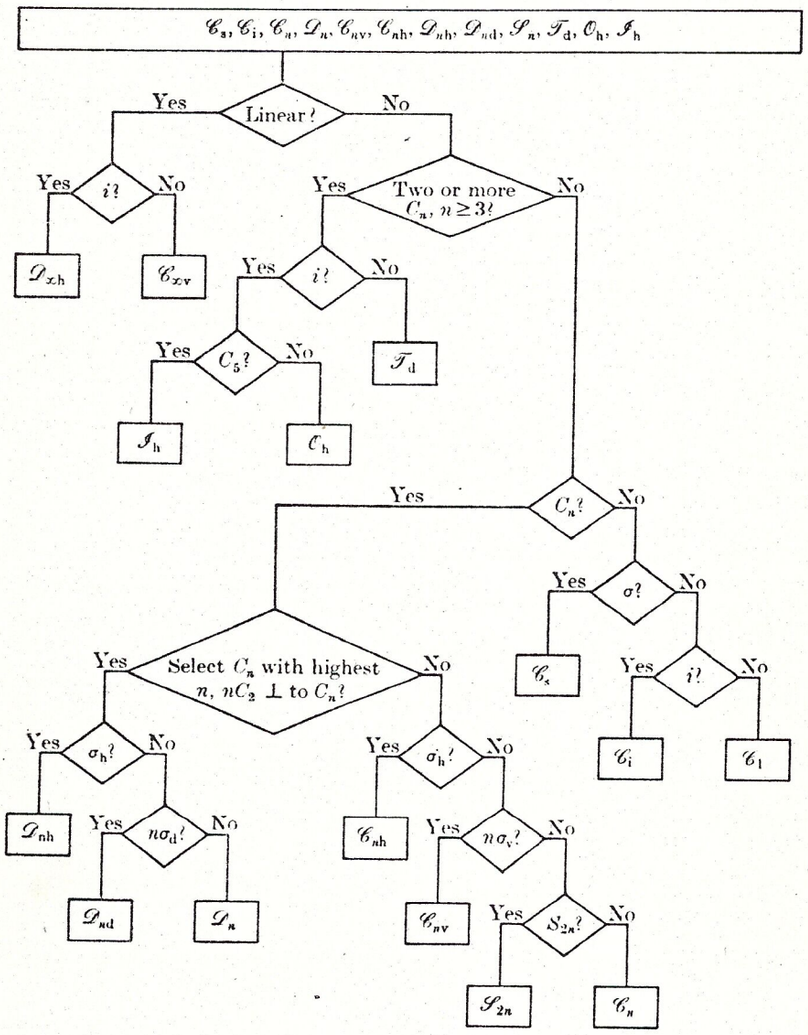


TABLE 3-6.3

The point groups and all their symmetry elements†

Point group	*Symmetry elements*
$\mathscr{C}_s$	E, σ_h
$\mathscr{C}_i$	E, i
$\mathscr{C}_1$	E
$\mathscr{C}_2$	E, C_2
$\mathscr{C}_3$	E, C_3–C_3^2
$\mathscr{C}_4$	E, C_4–C_2–C_4^3
$\mathscr{C}_5$	E, C_5–C_5^2–C_5^3–C_5^4
$\mathscr{C}_6$	E, C_6–C_3–C_2–C_3^2–C_6^5
$\mathscr{C}_7$	E, C_7–C_7^2–C_7^3–C_7^4–C_7^5–C_7^6
$\mathscr{C}_8$	E, C_8–C_4–C_8^3–C_2–C_8^5–C_4^3–C_8^7
$\mathscr{D}_2$	E, three C_2 (mutually perpendicular)
$\mathscr{D}_3$	E, C_3–C_3^2, three C_2 (perpendicular to C_3)
$\mathscr{D}_4$	E, C_4–C_2–C_4^3, four C_2 (perpendicular to C_4)‡
$\mathscr{D}_5$	E, C_5–C_5^2–C_5^3–C_5^4, five C_2 (perpendicular to C_5)
$\mathscr{D}_6$	E, C_6–C_3–C_2–C_3^2–C_6^5, six C_2 (perpendicular to C_6)‡
$\mathscr{C}_{1v}$	same as $\mathscr{C}_s$
$\mathscr{C}_{2v}$	E, C_2, two σ_v
$\mathscr{C}_{3v}$	E, C_3–C_3^2, three σ_v
$\mathscr{C}_{4v}$	E, C_4–C_2–C_4^3, four σ‡
$\mathscr{C}_{5v}$	E, C_5–C_5^2–C_5^3–C_5^4, five σ_v
$\mathscr{C}_{6v}$	E, C_6–C_3–C_2–C_3^2–C_6^5, six σ‡
$\mathscr{C}_{\infty v}$	E, infinite number of coincidental rotational axes, infinite number of σ_v
$\mathscr{C}_{1h}$	same as $\mathscr{C}_s$
$\mathscr{C}_{2h}$	E, C_2, i, σ_h
$\mathscr{C}_{3h}$	E, C_3–C_3^2–S_3–S_3^5,§ σ_h
$\mathscr{C}_{4h}$	E, C_4–C_2–C_4^3–S_4–S_4^3, σ_h, i
$\mathscr{C}_{5h}$	E, C_5–C_5^2–C_5^3–C_5^4–S_5–S_5^7–S_5^3–S_5^9,§ σ_h
$\mathscr{C}_{6h}$	E, C_6–C_3–C_2–C_3^2–C_6^5–S_6–S_3–S_3^5–S_6^5,§ σ_h, i
$\mathscr{D}_{2h}$	E, three C_2 (mutually perpendicular), i, three σ (mutually perpendicular)
$\mathscr{D}_{3h}$	E, C_3–C_3^2–S_3–S_3^5,§ three C_2 (perpendicular to C_3), σ_h, three σ_v
$\mathscr{D}_{4h}$	E, C_4–C_2–C_4^3–S_4–S_4^3, four C_2 (perpendicular to C_4),‡ i, σ_h, four σ‡
$\mathscr{D}_{5h}$	E, C_5–C_5^2–C_5^3–C_5^4–S_5–S_5^7–S_5^3–S_5^9,§ five C_2 (perpendicular to C_5), σ_h, five σ_v
$\mathscr{D}_{6h}$	E, C_6–C_3–C_2–C_3^2–C_6^5–S_6–S_3–S_3^5–S_6^5,§ six C_2 (perpendicular to C_6),‡ i, σ_h, six σ‡
$\mathscr{D}_{\infty h}$	E, infinite number of coincidental rotational C and alternating S axes, ($S_1 = \sigma_h$), infinite number of σ_v, i, infinite number of C_2 axes
$\mathscr{D}_{2d}$	E, C_2–S_4–S_4^3, two C_2 (perpendicular to each other and to the other C_2), two σ_d (through S_4)
$\mathscr{D}_{3d}$	E, C_3–C_3^2–S_6–S_6^5, three C_2 (perpendicular to C_3), i, three σ_d
$\mathscr{D}_{4d}$	E, C_4–C_2–C_4^3–S_8–S_8^3–S_8^5–S_8^7, four C_2 (perpendicular to C_4), four σ_d
$\mathscr{D}_{5d}$	E, C_5–C_5^2–C_5^3–C_5^4–S_{10}–S_{10}^3–S_{10}^7–S_{10}^9, five C_2 (perpendicular to C_5), i, five σ_d
$\mathscr{D}_{6d}$	E, C_6–C_3–C_2–C_3^2–C_6^5–S_{12}–S_4–S_{12}^5–S_{12}^7–S_4^3–S_{12}^{11}, six C_2 (perpendicular to C_6), six σ_d
$\mathscr{S}_1$	same as $\mathscr{C}_s$
$\mathscr{S}_2$	same as $\mathscr{C}_i$
$\mathscr{S}_3$	same as $\mathscr{C}_{3h}$
$\mathscr{S}_4$	E, C_2–S_4–S_4^3
$\mathscr{S}_5$	same as $\mathscr{C}_{5h}$
$\mathscr{S}_6$	E, C_3–C_3^2–S_6–S_6^5, i
$\mathscr{S}_7$	same as $\mathscr{C}_{7h}$
$\mathscr{S}_8$	E, C_4–C_2–C_4^3–S_8–S_8^3–S_8^5–S_8^7
$\mathscr{T}_d$	E, four C_3–C_3^2, three C_2–S_4–S_4^3 (mutually perpendicular), six σ_d (see Fig. 3-6.2)
$\mathscr{O}_h$	E, four C_3–C_3^2–S_6–S_6^5, three C_4–C_2–C_4^3–S_4–S_4^3 (mutually perpendicular), six C_2, i, three σ_h, six σ_d (See Fig. 3-6.3)

† Axes which coincide are linked, e.g. C_3–C_3^2–S_6–S_6^5.

‡ For reasons which will become clear later on, the σ planes in $\mathscr{C}_{4v}$, $\mathscr{C}_{6v}$, $\mathscr{D}_{4h}$, and $\mathscr{D}_{6h}$ and the C_2 axes in $\mathscr{D}_4$, $\mathscr{D}_6$, $\mathscr{D}_{4h}$, and $\mathscr{D}_{6h}$ are conventionally separated into two types: the planes into σ_v and σ_d planes and the axes into C_2' and C_2'' axes. These distinctions are shown in Fig. 3-6.1, where it is apparent that in $\mathscr{C}_{4v}$ and $\mathscr{C}_{6v}$, the planes labelled σ_d do not fulfill the requirement of Table 2-3.1. Nonetheless, the notation given is that recommended by R. S. Mulliken, (*Journal of Chemical Physics* **23**, 1997 (1955)). We will not bother with the differences between the C_2' and C_2'' axes in $\mathscr{D}_4$ and $\mathscr{D}_6$ as these point groups have no chemical significance.

§ S_3^5 is the element corresponding to rotation about an axis by $5{\cdot}2\pi/3$ (or $2{\cdot}2\pi/3$) followed by a reflection in the plane perpendicular to that axis. We cannot use the symbol S_3^2 as this is identical with C_3^2 (see § 2–3 page 13). A similar argument holds for S_6^7 and S_6^9.

TABLE 3-6.1

The point groups and their essential symmetry elements

Point group	*Essential symmetry elements*†
$\mathscr{C}_s$	One symmetry plane
$\mathscr{C}_i$	A centre of symmetry
$\mathscr{C}_n$	One n-fold axis of symmetry
$\mathscr{D}_n$	One C_n axis plus n C_2 axes perpendicular to it
$\mathscr{C}_{nv}$	One C_n axis plus n vertical planes σ_v
$\mathscr{C}_{nh}$	One C_n axis plus a horizontal plane σ_h
$\mathscr{D}_{nh}$	Those of $\mathscr{D}_n$ plus a horizontal plane σ_h
$\mathscr{D}_{nd}$	Those of $\mathscr{D}_n$ plus n dihedral planes σ_d
$\mathscr{S}_n$ (n even)	One n-fold alternating axis of symmetry
$\mathscr{T}_d$	Those of a regular tetrahedron
$\mathscr{O}_h$	Those of a regular octahedron or cube
$\mathscr{I}_h$	Those of a regular icosahedron
$\mathscr{K}_h$	Those of a sphere

† These elements are all in addition to the identity element E which is possessed by all point groups.

*

$$\sum_R \Gamma^{(i)}(R)^*_{\mu\nu}\, \Gamma^{(j)}(R)_{\alpha\beta} = \frac{h}{l_i}\, \delta_{ij}\, \delta_{\mu\alpha}\, \delta_{\nu\beta}$$

$$\sum_R \left|\Gamma^{(i)}_{\alpha\beta}(R)\right|^2 = \frac{h}{l_i}$$

I $$\boxed{\sum_i l_i^2 = h}$$

Character: $\mathrm{tr}\, \Gamma^{(i)}(R) = \chi^{(i)}(R)$

$$\sum_{\alpha,\beta} \sum_R \Gamma^{(i)}_{\alpha\alpha}(R)^*\, \Gamma^{(j)}_{\beta\beta}(R) = \frac{h}{l_i}\, \delta_{ij} \overbrace{\sum_{\alpha,\beta} \delta_{\alpha\beta}}^{l_i} = h\, \delta_{ij}$$

A_m, A_k in Class $\Gamma^{(i)}$: conjugated if $A_n^{-1} A_m A_n = A_k$

$$\mathrm{tr}\, \Gamma^{(i)}(A_n^{-1})\, \Gamma^{(i)}(A_m)\, \Gamma^{(i)}(A_n) = \mathrm{tr}\, \Gamma(A_k)$$

Character of representation element of class are equal.

II $$\boxed{\sum_k \chi^{(i)}(C^{(k)})^* \chi^{(j)}(C^{(k)})\, N_k = h\, \delta_{ij}} \quad \text{(rows)}$$

	$\Gamma^{(1)}$		$\Gamma^{(j)}$	
$C^{(1)}$	$\chi^{(1)}(C^{(1)})$		$\chi^{(j)}(C^{(1)})$	
$C^{(k)}$			$\chi^{(j)}(C^{(k)})$	

$$\sum_k \left|\chi^{(i)}(C^{(k)})\right|^2 = h/N_k$$

III $$\boxed{\text{number of irreducible representations} = \text{number of classes}}$$

Character table: (Triangle  $C_3, 3C_2$

	$C^{(1)}$	$3C^{(2)}$	$2C^{(3)}$
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	-1	1
$\Gamma^{(3)}$	2	0	-1

$$\sum_i \chi^{(i)}(C^{(k)})^* \chi^{(i)}(C^{(l)}) = \frac{h}{N_k}\delta_{kl}$$ columns

Construction of Character table! :

	1	1	1	1	1	...
l_2						
l_3						
l_4						
⋮						

Reducable representation

Suppose we have $\Gamma(R)$ with $\chi(R)$

Irreducable reprsn are $\chi^{(i)}(R)$

$$\text{Thus} \quad \chi(R) = \sum_i a_i \chi^{(i)}(R)$$

Now

$$\sum_R \chi(R)\chi^{(j)}(R) = \sum_R \sum_i a_i \chi^{(i)}(R)\chi^{(j)}(R) = a_j h$$

$$\Rightarrow \quad a_j = h^{-1}\sum_R \chi(R)\chi^{(j)}(R) = h^{-1}\sum_k N_k \chi(C^{(k)})\chi^{j}(C^{(k)})$$

Direct product Groups.

Suppose our triangle $D_3 + \sigma_h \rightarrow \boxed{D_{3h} = D_3 \times \sigma_h}$

Suppose two Groups and all elements of one group are

commutative with all element of other group.

$A: \{A_i\}$ $B\{B_j\} \rightarrow \{A_i B_j\}$ = Direct product group

$G = A \times B$ is group of $h_a h_b$ elements.

$G_k = A_i B_j \quad k = 1, \ldots - h_a h_b$

Let us take irreducible representations of A $\Gamma^{(m)}(A_i) \; \ell^A_{mm}$

$\Gamma^{(n)}(B_j) \; \ell^B_{nn}$

~~Define~~ Then:

$$\Gamma(G_k) = \Gamma^{(m)}(A_i) \otimes \Gamma^{(n)}(B_j) \qquad \begin{pmatrix} * & & \\ & * & \\ & & * \end{pmatrix} \begin{pmatrix} * & & \\ & * & \\ & & * \end{pmatrix} \rightarrow \begin{pmatrix} * & & & & & \\ & * & & & & \\ & & * & & & \\ & & & * & & \\ & & & & * & \\ & & & & & * \end{pmatrix}$$

is irreducible representation!

$$\sum_m \left(\ell^A_{mm}\right)^2 = h_A \qquad \sum_n \left(\ell^B_{nn}\right)^2 = h_B$$

$$\sum_{m,n} \left(\ell^G_{\substack{kk \\ mn}}\right)^2 = \sum_{m,n} \ell^{A^2}_{mm} \ell^{B^2}_{nn} = h_A h_B \Rightarrow$$

There are no more irred. representations than the direct products!

$$\chi(G_k) = \sum_{\alpha,\beta} \Gamma^{(m)}_{\alpha\alpha}(A_i) \Gamma^{(n)}_{\beta\beta}(B_j) = \sum \Gamma \sum \Gamma = \chi^{(m)}(A_i) \chi^{(n)}(B_j)$$

D_3 σ_h (Abelian : each element = class ⇒ num of elems = num of classes = 1 dim)

C_s / S	E	σ_h
$\Gamma^{(+)}$	1	1
$\Gamma^{(-)}$	1	-1

Number of classes or irred rep : $3 \times 2 = 6$

D_{3h}	E	$3C_2$	$2C_3$	σ_h	$3(C_2\sigma_h)$	$2(C_3\sigma_h)$
$\Gamma^{(1+)}$	1	1	1	1	1	1
$\Gamma^{(2+)}$	1	-1	1	1	-1	1
$\Gamma^{(3+)}$	2	0	-1	2	0	-1
$\Gamma^{(1-)}$	1	1	1	-1	-1	-1
	1	-1	1	-1	1	-1
	2	0	-1	-2	0	+1

C_1 (1)	E
A	1

C_2 (2)			E	C_2
x^2, y^2, z^2, xy	R_z, z	A	1	1
xz, yz	x, y / R_x, R_y	B	1	-1

C_3 (3)			E	C_3	C_3^2
$x^2 + y^2, z^2$	R_z, z	A	1	1	1
(xz, yz) / $(x^2 - y^2, xy)$	(x, y) / (R_x, R_y)	E	1	ω	ω^2
			1	ω^2	ω

$\omega = e^{2\pi i/3}$

C_4 (4)			E	C_2	C_4	C_4^3
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1
$x^2 - y^2, xy$		B	1	1	-1	-1
(xz, yz)	(x, y) / (R_x, R_y)	E	1	-1	i	$-i$
			1	-1	$-i$	i

C_5 (5)			E	C_5	C_5^2	C_5^3	C_5^4
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1
(xz, yz)	(x, y) / (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4
			1	ω^4	ω^3	ω^2	ω
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	ω	ω^3
			1	ω^3	ω	ω^4	ω^2

$\omega = e^{2\pi i/5}$

C_6 (6)			E	C_6	C_3	C_2	C_3^2	C_6^5
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1	1
		B	1	-1	1	-1	1	-1
(xz, yz)	(x, y) / (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4	ω^5
			1	ω^5	ω^4	ω^3	ω^2	ω
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	1	ω^2	ω^4
			1	ω^4	ω^2	1	ω^4	ω^2

$\omega = e^{2\pi i/6}$

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

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

C_{4v} (4mm)			E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1	1
	R_z	A_2	1	1	1	-1	-1
$x^2 - y^2$		B_1	1	1	-1	1	-1
xy		B_2	1	1	-1	-1	1
(xz, yz)	(x, y) / (R_x, R_y)	E	2	-2	0	0	0

C_{5v} (5m)			E	$2C_5$	$2C_5^2$	$5\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1
	R_z	A_2	1	1	1	-1
(xz, yz)	(x, y) / (R_x, R_y)	E_1	2	$2\cos x$	$2\cos 2x$	0
$(x^2 - y^2, xy)$		E_2	2	$2\cos 2x$	$2\cos 4x$	0

$x = \frac{2\pi}{5}$

C_{6v} (6mm)			E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1	1	1
	R_z	A_2	1	1	1	1	-1	-1
		B_1	1	-1	1	-1	-1	1
		B_2	1	-1	1	-1	1	-1
(xz, yz)	(x, y) / (R_x, R_y)	E_1	2	-2	-1	1	0	0
$(x^2 - y^2, xy)$		E_2	2	2	-1	-1	0	0

C_{1h} (m)			E	σ_h
x^2, y^2, z^2, xy xz, yz	R_z, x, y R_x, R_y, z	A' A''	1 1	1 −1

$C_{2h}(2/m)$			E	C_2	σ_h	i
x^2, y^2, z^2, xy	R_z	A_g	1	1	1	1
	z	A_u	1	1	−1	−1
xz, yz	R_x, R_y	B_g	1	−1	−1	1
	x, y	B_u	1	−1	1	−1

$C_{3h} = C_3 \times \sigma_h$ $(\bar{6})$			E	C_3	C_3^2	σ_h	S_3	$(\sigma_h C_3^2)$
$x^2 + y^2, z^2$	R_z	A'	1	1	1	1	1	1
	z	A''	1	1	1	−1	−1	−1
$(x^2 - y^2, xy)$	(x, y)	E'	1	ω	ω^2	1	ω	ω^2
			1	ω^2	ω	1	ω^2	ω
(xz, yz)	(R_x, R_y)	E''	1	ω	ω^2	−1	$-\omega$	$-\omega^2$
			1	ω^2	ω	−1	$-\omega^2$	$-\omega$

$\omega = e^{2\pi i/3}$

$C_{4h} = C_4 \times i$ $(4/m)$

$C_{5h} = C_5 \times \sigma_h$ $(\overline{10})$

$C_{6h} = C_6 \times i$ $(6/m)$

S_2 $(\bar{1})$			E	i
$x^2, y^2, z^2, xy, xz, yz$	R_x, R_y, R_z x, y, z	A_g A_u	1 1	1 −1

S_4 $(\bar{4})$			E	C_2	S_4	S_4^3
$x^2 + y^2, z^2$	R_z	A	1	1	1	1
	z	B	1	1	−1	−1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	1	−1	i	$-i$
			1	−1	$-i$	i

$S_6 = C_3 \times i$ $(\bar{3})$

D_2 (222)			E	C_2^z	C_2^y	C_2^x
x^2, y^2, z^2		A_1	1	1	1	1
xy	R_z, z	B_1	1	1	−1	−1
xz	R_y, y	B_2	1	−1	1	−1
yz	R_x, x	B_3	1	−1	−1	1

D_3 (32)			E	$2C_3$	$3C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1
	R_z, z	A_2	1	1	−1
(xz, yz) $(x^2 - y^2, xy)$	(x, y) (R_x, R_y)	E	2	−1	0

D_4 (422)			E	$C_2 = C_4^2$	$2C_4$	$2C_2'$	$2C_2''$
$x^2 + y^2, z^2$		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	−1	−1
$x^2 - y^2$		B_1	1	1	−1	1	−1
xy		B_2	1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	−2	0	0	0

D_5 (52)			E	$2C_5$	$2C_5^2$	$5C_2'$
$x^2 + y^2, z^2$		A_1	1	1	1	1
	R_z, z	A_2	1	1	1	−1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2\cos x$	$2\cos 2x$	0
$(x^2 - y^2, xy)$		E_2	2	$2\cos 2x$	$2\cos 4x$	0

$x = \frac{2\pi}{5}$

D_6 (622)			E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$x^2 + y^2, z^2$		A_1	1	1	1	1	1	1
	R_z, z	A_2	1	1	1	1	−1	−1
		B_1	1	−1	1	−1	1	−1
		B_2	1	−1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	−2	−1	1	0	0
$(x^2 - y^2, xy)$		E_2	2	2	−1	−1	0	0

D_{2d} ($\bar{4}2m$)			E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$
x^2+y^2, z^2		A_1	1	1	1	1	1
	R_z	A_2	1	1	1	−1	−1
x^2-y^2		B_1	1	1	−1	1	−1
xy	z	B_2	1	1	−1	−1	1
(xz, yz)	(x, y) / (R_x, R_y)	E	2	−2	0	0	0

$D_{3d} = D_3 \times i \quad (\bar{3}m)$

$D_{2h} = D_2 \times i \quad (mmm)$

$D_{3h} = D_3 \times \sigma_h$ ($\bar{6}m2$)			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
x^2+y^2, z^2		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
(x^2-y^2, xy)	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0

$D_{4h} = D_4 \times i \quad (4/mmm)$

$D_{5h} = D_5 \times \sigma_h \quad (\bar{1}0m2)$

$D_{6h} = D_6 \times i \quad (6/mmm)$

T (23)		E	$3C_2$	$4C_3$	$4C_3'$
	A	1	1	1	1
	E	1	1	ω	ω^2
		1	1	ω^2	ω
(R_x, R_y, R_z) / (x, y, z)	T	3	−1	0	0

$\omega = e^{2\pi i/3}$

$T_h = T \times i \quad (m3)$

O (432)		E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2$	$6C_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
$(x^2-y^2, 3z^2-r^2)$	E	2	−1	2	0	0
(R_x, R_y, R_z) / (x, y, z)	T_1	3	0	−1	−1	1
(xy, yz, zx)	T_2	3	0	−1	1	−1

$O_h = O \times i \quad (m3m)$

T_d ($\bar{4}3m$)		E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
	A_1	1	1	1	1	1
	A_2	1	1	1	−1	−1
	E	2	−1	2	0	0
(R_x, R_y, R_z)	T_1	3	0	−1	−1	1
(x, y, z)	T_2	3	0	−1	1	−1

$C_{\infty v}$ (∞m)			E	$2C_\phi$	σ_v
x^2+y^2, z^2	z	$A_1(\Sigma^+)$	1	1	1
	R_z	$A_2(\Sigma^-)$	1	1	−1
(xz, yz)	(x, y) / (R_x, R_y)	$E_1(\Pi)$	2	$2\cos\phi$	0
(x^2-y^2, xy)		$E_2(\Delta)$	2	$2\cos 2\phi$	0
		...	...	...	...

$D_{\infty h}$ (∞/mm)			E	$2C_\phi$	C_2'	i	$2iC_\phi$	iC_2'
x^2+y^2, z^2		$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1
		$A_{1u}(\Sigma_u^-)$	1	1	1	−1	−1	−1
	R_z	$A_{2g}(\Sigma_g^-)$	1	1	−1	1	1	−1
	z	$A_{2u}(\Sigma_u^+)$	1	1	−1	−1	−1	1
(xz, yz)	(R_x, R_y)	$E_{1g}(\Pi_g)$	2	$2\cos\phi$	0	2	$2\cos\phi$	0
	(x, y)	$E_{1u}(\Pi_u)$	2	$2\cos\phi$	0	−2	$-2\cos\phi$	0
(x^2-y^2, xy)		$E_{2g}(\Delta_g)$	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
		$E_{2u}(\Delta_u)$	2	$2\cos 2\phi$	0	−2	$-2\cos 2\phi$	0
		...	...	...	...	...	...	...

prepare notes!

X

Note!

1. Abelian group : each element's a class $\Rightarrow$ all irred. reps are order 1

2. Cyclic group $\quad A, A^2, A^3, \dots A^h = E$

$$\Gamma(E) = 1$$

If $\Gamma(A) = r \quad \rightarrow \quad \Gamma(A^2) = r^2 \qquad \Gamma(A^h) = r^h = 1$

$$r = e^{2\pi i p/h} \qquad p = 1, 2, \dots, h$$

XX 3. Direct Product representation within group

Suppose $f_1^{(i)} \dots f_p \dots f_n^{(i)}$ form basis for $\Gamma^{(i)}$

$f_1^{(j)} \dots \dots \dots f_m^{(j)}$ " " " $\Gamma^{(j)}$

Then $f_p^{(i)} f_q^{(j)}$ form a basis for a representation

$\Gamma = \Gamma^{(i)} \otimes \Gamma^{(j)}$ representation with basis $\{f_p^{(i)} f_q^{(j)}\}$

In general $\Gamma = \sum_k a_k \Gamma^{(k)}$

$$\chi^{(i\otimes j)}(A_i) = \chi^{(i)}(A_i)\, \chi^{(j)}(A_i)$$

$$a_k = \frac{1}{h} \sum_n \chi^{(i\otimes j)}(A_n)\, \chi^{(k)}(A_n) = \frac{1}{h} \sum_n \chi^{(i)}(A_n)\, \chi^{(j)}(A_n)\, \chi^{(k)}(A_n)$$

$$= \frac{1}{h} \sum_m N_k^2\, \chi^{(i)}(C^{(m)})\, \chi^{(j)}(C^{(m)})\, \chi^{(k)}(C^{(m)})$$

The group of the Schrödinger equation

1. Representations by operations on vectors.

Consider group $\{A_i\}_h$ and representation $D(A_i)$:

$$D(A_i)\begin{pmatrix}x_1\\x_2\\x_3\end{pmatrix} = \begin{pmatrix}D_{11}(A_i)x_1 + D_{12}(A_i)x_2 + D_{13}(A_i)x_3\\ D_{21}(A_i)x_1 + D_{22}(A_i)x_2 + D_{23}(A_i)x_3\\ D_{31}(A_i)x_1 + D_{32}(A_i)x_2 + D_{33}(A_i)x_3\end{pmatrix} = \begin{pmatrix}x_1'\\x_2'\\x_3'\end{pmatrix}$$

$$D(A_i)\,D(A_j) = D(A_k) \quad \text{when} \quad A_i A_j = A_k$$

2. Representations by operations on function space

Consider group $\{A_i\}_h$ and function space : $f_1, f_2, \cdots f_n$ $\left(\int f_n f_m \, d\tau = \delta_{nm}\right)$

$$P(A_i)\begin{pmatrix}f_1\\f_2\\\vdots\\f_n\end{pmatrix} = \begin{pmatrix}P_{11}(A_i)f_1 + P_{21}(A_i)f_2 + \cdots + P_{n1}(A_i)f_n\\ \vdots\\ P_{1n}(A_i)f_1 + P_{2n}(A_i)f_2 + \cdots + P_{nn}(A_i)f_n\end{pmatrix}$$

$$P(A_i)\,f_\nu(\vec{x}) = f_\nu(D(A_i)^{-1}\vec{x}) \equiv \sum_\mu P_{\mu\nu}(A_i)\,f_\mu(\vec{x})$$

Representation $P(A_i)$ is unitary when f_i's orthogonal.

Representation $P(A_i)$ is reducible or irreducible.

There exist function spaces which form bases for irreducible representations.

3. Hamiltonian and its symmetry.

$$\mathcal{H}\varphi_n = E_n\varphi_n$$

$P(A_i)$ is representation of $\{A_i\}$ with basis $\{\varphi_i\}$ and $\{\ \}$ is the group of the Hamiltonian

Then $P(A_i)\,\mathcal{H}\,\varphi_n = P(A_i)\,E_n\,\varphi_n$

and $\mathcal{H}\,P(A_i)\,\varphi_n = E_n\,P(A_i)\,\varphi_n$

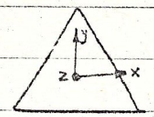
and $\varphi_n, P(A_1)\varphi_n, \cdots, P(A_i)\varphi_n, \cdots P(A_h)\varphi_n$ are degenerate.

The set of normal degenerate eigenfunctions form a basis for an irreducible representation.

The orders of the irreducible representations give the possible number of normal degenerate eigenfunctions

Every set of normal degenerate eigenfunctions can be characterized by its irreducible representation.

Example 1. The representation of D_3 in the function space p_x, p_y, p_z



$$D(E)\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}$$

$$D(C_3)\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}&+\frac{1}{2}\sqrt{3}&0\\-\frac{1}{2}\sqrt{3}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}x+\frac{1}{2}\sqrt{3}y\\-\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\\z\end{pmatrix}$$

$$D(C_3^2)\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}&-\frac{1}{2}\sqrt{3}&0\\\frac{1}{2}\sqrt{3}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}x-\frac{1}{2}\sqrt{3}y\\\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\\z\end{pmatrix}$$

$$D(C_2)\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}-x\\y\\-z\end{pmatrix}$$

$$D(C_2')\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}1/2&1/2\sqrt{3}&0\\\frac{1}{2}\sqrt{3}&-\frac{1}{2}&0\\0&0&-1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}\frac{1}{2}x+\frac{1}{2}\sqrt{3}y\\\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\\-z\end{pmatrix}$$

$$D(C_2'')\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}\frac{1}{2}&-\frac{1}{2}\sqrt{3}&0\\-\frac{1}{2}\sqrt{3}&-\frac{1}{2}&0\\0&0&-1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix} = \begin{pmatrix}\frac{1}{2}x-\frac{1}{2}\sqrt{3}y\\-\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\\-z\end{pmatrix}$$

With $p_x = x$; $p_y = y$; $p_z = z$

$P(E) = D(E)$ $\quad \chi(E) = 3$

$P(C_3) = D(C_3^2)$ $\quad \chi(C_3) = 0$

$P(C_2) = D(C_2)$ $\quad \chi(C_2) = -1$

P	E	$2C_3$	$3C_2$
	3	0	−1

D_3			
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Decomposition of P : $a_{A_1} = \frac{1}{6}(3.1 + 2.0.1 + 3.-1.1) = 0$

$a_{A_2} = \frac{1}{6}(3.1 + 2.0.1 + 3.-1.-1) = 1$

$a_E = \frac{1}{6}(3.2 + 2.0.-1 + 3.-1.0) = 1$

Basis for irreducible representations

$\{p_z\}$ function space for A_2

$\{p_y, p_x\}$ -"- -"- -"- E

Example 2. The representation of D_3 in function space $d_1 \dots d_5$

$$P(E)\begin{pmatrix}x^2-y^2\\xy\\xz\\yz\\3z^2-r^2\end{pmatrix} = \begin{pmatrix}x^2-y^2\\xy\\xz\\yz\\3z^2-r^2\end{pmatrix}, \quad \chi(E) = 5$$

$$P(C_3)\begin{pmatrix}x^2-y^2\\xy\\xz\\yz\\3z^2-r^2\end{pmatrix} = \begin{pmatrix}\left(-\frac{1}{2}x-\frac{1}{2}\sqrt{3}y\right)^2-\left(\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\right)^2\\\left(\frac{1}{2}x-\frac{1}{2}\sqrt{3}y\right)\left(\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\right)\\\left(\frac{1}{2}x-\frac{1}{2}\sqrt{3}y\right)z\\\left(\frac{1}{2}\sqrt{3}x-\frac{1}{2}y\right)z\\3z^2-r^2\end{pmatrix} = \begin{pmatrix}-\frac{1}{2}(x^2-y^2)+\dots\\-\frac{1}{2}xy+\dots\\\frac{1}{2}xz+\dots\\-\frac{1}{2}yz+\dots\\3z^2-r^2\end{pmatrix}, \quad \chi(C_3) = -1$$

$$P(C_2)\begin{pmatrix}x^2-y^2\\xy\\xz\\yz\\3z^2-r^2\end{pmatrix} = \begin{pmatrix}(-x)^2-y^2\\-xy\\-x\cdot z\\y\cdot z\\3(-z)^2-r^2\end{pmatrix} = \begin{pmatrix}x^2-y^2\\-xy\\xz\\-yz\\3z^2-r^2\end{pmatrix}, \quad \chi(C_2) = 1$$

P	E	$2C_3$	$3C_2$
	5	−1	1

$a_{A_1} = \frac{1}{6}(5.1 + 3.1.1 + 2.-1.1) = 1$ basis $\{3z^2-r^2\}$

$a_E = \frac{1}{6}(5.2 + 2.-1.1 + 3.1.0) = 2$ bases $\{xz, yz\}$, $\{x^2-y^2, xy\}$

(5)

Example. Direct product representation of two p-electrons in symmetry D_3

assignment 1- 2- electron

$p_x p_x$

$p_x p_y$

$p_y p_x$

$p_y p_y$

$p_x p_z$

$p_y p_z$

$p_z p_x$

$p_z p_y$

$p_z p_z$

$\Gamma^{(E)} \otimes \Gamma^{(E)}$

	E	$2C_3$	$3C_2$
	4	1	0

$a_{A_1} = \frac{1}{6}(4 \cdot 1 + 2 \cdot 1 \cdot 1) = 1$

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

$a_E = \frac{1}{6}(4 \cdot 2 + 2 \cdot -1 \cdot 1) = 1$

$\Gamma^{(A_2)} \otimes \Gamma^{(E)}$

	E	$2C_3$	$3C_2$
	2	-1	0

$a_{A_1} = 0$

$a_{A_2} = 0$

$a_E = 1$

$\Gamma^{(E)} \otimes \Gamma^{(A_2)}$

	E	$2C_3$	$3C_2$
	2	-1	0

$\Gamma^{(A_2)} \otimes \Gamma^{(A_2)}$

	E	$2C_3$	$3C_2$
	1	1	1

$a_{A_1} = 1$

$a_{A_2} = 0$

$a_E = 0$

1 electron

E —— p_x, p_y

A_2 —— p_z

2 electron

$p_x p_x, p_x p_y, p_y p_x, p_y p_y$ —— E, A_1, A_2

$p_x p_z, p_y p_z$
$p_z p_x, p_z p_y$ —— E, E

$p_z p_z$ —— A_1

XXX

Example. Find basis for irreducible representations of two p-electrons in D_3

$\mathcal{P}^{(i)} \equiv \sum_n \chi^{(i)}(A_n) \mathbb{P}(A_n)$: Projection operator

$\mathcal{P}^{(i)} g = \frac{h}{l_i} \sum_\alpha a_{i\alpha} f_\alpha^{(i)}$ if $g = \sum_i \sum_\alpha a_{i\alpha} f_\alpha^{(i)}$

If $\{g_s\}$ space contains diffent basis sets for the same irr. repr.

then all the basis sets show up: $g_s = \sum_i \left\{ \sum_\alpha a_{i\alpha} f_\alpha^{(i)} + \sum_\alpha b_{i\alpha} f_\alpha^{(i)'} \right\}$

$\mathcal{P}^{(i)} g_s = \frac{h}{l_i} \sum_\alpha a_{i\alpha} f_\alpha^{(i)} + \frac{h}{l_i} \sum_\beta b_{i\beta} f_\beta^{(i)'}$ etc.

$\mathcal{P}^{(A)} = \mathbb{P}(E) + \mathbb{P}(C_3) + \mathbb{P}(C_3^2) + \mathbb{P}(C_2') + \mathbb{P}(C_2'') + \mathbb{P}(C_2''')$

$\mathcal{P}^{(A_2)} = \mathbb{P}(E) + \mathbb{P}(C_3) + \mathbb{P}(C_3^2) - \mathbb{P}(C_2') - \mathbb{P}(C_2'') - \mathbb{P}(C_2''')$

$\mathcal{P}^{(E)} = 2\mathbb{P}(E) - \mathbb{P}(C_3) - \mathbb{P}(C_3^2)$

	$p_z p_z$	$p_x p_z$	$p_y p_z$	$p_x p_x$	$p_y p_y$	$p_x p_y$
$\mathcal{P}^{(A_1)}$	$6 p_z p_z$	0	0	$3(p_x p_x + p_y p_y)$	$3(p_x p_x + p_y p_y)$	0
$\mathcal{P}^{(A_2)}$	0	0	0	0	0	$3(p_x p_y - p_y p_x)$
$\mathcal{P}^{(E)}$	0	$3 p_x p_z$	$3 p_y p_z$	$\frac{3}{2}(p_x p_x - p_y p_y)$	$\frac{3}{2}(p_x p_x - p_y p_y)$	$\frac{3}{2}(p_x p_y + p_y p_x)$

e.g. $\mathcal{P}^{A_1} p_x p_x = p_x p_x + (-\frac{1}{2} p_x + \frac{1}{2}\sqrt{3} p_y)(-\frac{1}{2} p_x + \frac{1}{2}\sqrt{3} p_y) + (-\frac{1}{2} p_x - \frac{1}{2}\sqrt{3} p_y)(-\frac{1}{2} p_x - \frac{1}{2}\sqrt{3} p_y)$
$+ (-p_x)(-p_x) + (\frac{1}{2} p_x + \frac{1}{2}\sqrt{3} p_y)(\frac{1}{2} p_x + \frac{1}{2}\sqrt{3} p_y) + (\frac{1}{2} p_x - \frac{1}{2}\sqrt{3} p_y)(\frac{1}{2} p_x - \frac{1}{2}\sqrt{3} p_y)$
$= 3(p_x p_x + p_y p_y)$

The group of the Schrödinger equation

1. Representations by operations on vectors

Consider group $\{A_i\}_h$ and representation $D(A_i)$:

$$D(A_i)\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} D_{11}(A_i)x_1 + D_{12}(A_i)x_2 + D_{13}(A_i)x_3 \\ D_{21}(A_i)x_1 + D_{22}(A_i)x_2 + D_{23}(A_i)x_3 \\ D_{31}(A_i)x_1 + D_{32}(A_i)x_2 + D_{33}(A_i)x_3 \end{pmatrix} = \begin{pmatrix} x_1' \\ x_2' \\ x_3' \end{pmatrix}$$

$$D(A_i)\,D(A_j) = D(A_k) \quad \text{when} \quad A_i A_j = A_k$$

2. Representations by operations on function space

Consider group $\{A_i\}_h$ and function space : $f_1, f_2, \dots f_n$ $\left(\int f_n f_m \, d\tau = \delta_{nm}\right)$

$$\mathbb{P}(A_i)\begin{pmatrix} f_1 \\ f_2 \\ \vdots \\ f_n \end{pmatrix} = \begin{pmatrix} P_{11}(A_i)f_1 + P_{21}(A_i)f_2 + \dots + P_{n1}(A_i)f_n \\ \vdots \\ P_{1n}(A_i)f_1 + P_{2n}(A_i)f_2 + \dots + P_{nn}(A_i)f_n \end{pmatrix}$$

$$\mathbb{P}(A_i)\, f_\nu(\bar{x}) = f_\nu\left(D(A_i)^{-1}\bar{x}\right) \equiv \sum_\mu P_{\mu\nu}(A_i)\, f_\mu(\bar{x})$$

Representation $P(A_i)$ is unitary when f_i's orthogonal.

Representation $P(A_i)$ is reducible or irreducible.

There exist function spaces which form bases for irreducible representations.

3. Hamiltonian and its symmetry.

$$\mathcal{H}\varphi_n = E_n\varphi_n$$

$P(A_i)$ is representation of $\{A_i\}$ with basis $\{\varphi_i\}$ and $\{A_i\}$ is the group of the Hamiltonian

Then $P(A_i)\,\mathcal{H}\,\varphi_n = P(A_i)\,E_n\,\varphi_n$

and $\mathcal{H}\,P(A_i)\,\varphi_n = E_n\,P(A_i)\,\varphi_n$

and $\varphi_n, P(A_1)\varphi_n, \cdots, P(A_i)\varphi_n, \cdots P(A_h)\varphi_n$ are degenerate.

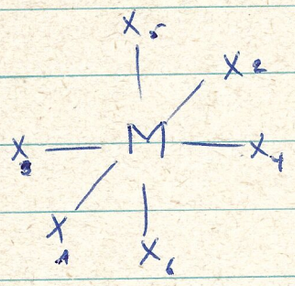
The set of normal degenerate eigenfunctions form a basis for an irreducible representation.

The orders of the irreducible representations give the possible number of normal degenerate eigenfunctions

Every set of normal degenerate eigenfunctions can be characterized by its irreducible representation.

Transition Metals

Elements with partly filled d (and f) shells.



M: metal

X: ligands

Two approaches to solve the electronic wave functions/energy levels.

1) MO - from basis set of atomic functions and calculate the real ~~one~~ eigenstates, where we ought to know all interactions.

2) ~~The~~ Ligand field. Crystal field assume simple electrostatic forces only look upon ligands as point charges or dipoles. Parameters in crystal field are some how fictitious replacing covalence etc in terms of electrostatic interactions.

MO $\hat{H}\psi = E\psi$ - Secular equation det $(H_{ij} - \varepsilon S_{ij}) =$

Coside MX_6 : Basis set of atomic functions:

M: 5 d-functions

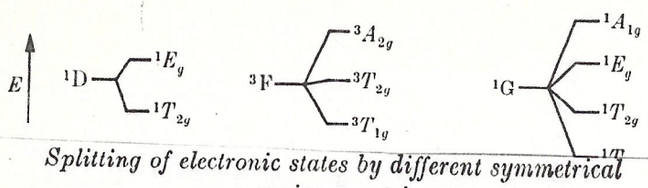
3 p-functions

1 s-function

X: 1 s-function s

3-p functions σ, π, π'

33 functions Linear Combin of Atom. Orbitals



Splitting of electronic states by different symmetrical environments†

Free ion states	*Split states*‡				
	$\mathcal{O}_h$	$\mathcal{T}_d$	$\mathcal{D}_{4h}$	$\mathcal{D}_3$	$\mathcal{D}_{2d}$
S	A_{1g}	A_1	A_{1g}	A_1	A_1
P	T_{1g}	T_1	A_{2g}, E_g	A_2, E	A_2, E
D	E_g, T_{2g}	E, T_2	$A_{1g}, B_{1g}, B_{2g}, E_g$	$A_1, E(2)$	A_1, B_1, B_2, E
F	A_{2g}, T_{1g}, T_{2g}	A_2, T_1, T_2	$A_{2g}, B_{1g}, B_{2g}, E_g(2)$	$A_1, A_2(2), E(2)$	$B_1, A_2, B_2, E(2)$
G	$A_{1g}, E_g, T_{1g}, T_{2g}$	A_1, E, T_1, T_2	$A_{1g}(2), A_{2g}, B_{1g}, B_{2g}, E_g(2)$	$A_1(2), A_2, E(3)$	$A_1(2), A_2, B_1, B_2, E(2)$
H	$E_g, T_{1g}(2), T_{2g}$	$E, T_1(2), T_2$	$A_{1g}, A_{2g}(2), B_{1g}, B_{2g}, E_g(3)$	$A_1, A_2(2), E(4)$	$A_1, A_2(2), B_1, B_2, E(3)$
I	$A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}(2)$	$A_1, A_2, E, T_1, T_2(2)$	$A_{1g}(2), A_{2g}, B_{1g}(2), B_{2g}(2), E_g(3)$	$A_1(3), A_2(2), E(4)$	$A_1(2), A_2, B_1(2), B_2(2), E(3)$

† The states are derived from d^n configurations only and hence for $\mathcal{O}_h$ and $\mathcal{D}_{4h}$ the split states all have g character.

‡ The numbers in parentheses refer to the number of states of the given symmetry, e.g. the 13 degenerate total wavefunctions for the state I form a reducible representation for $\mathcal{D}_3$ which can be decomposed as

$$\Gamma^I = 3\Gamma^{A_1} \oplus 2\Gamma^{A_2} \oplus 4\Gamma^E.$$

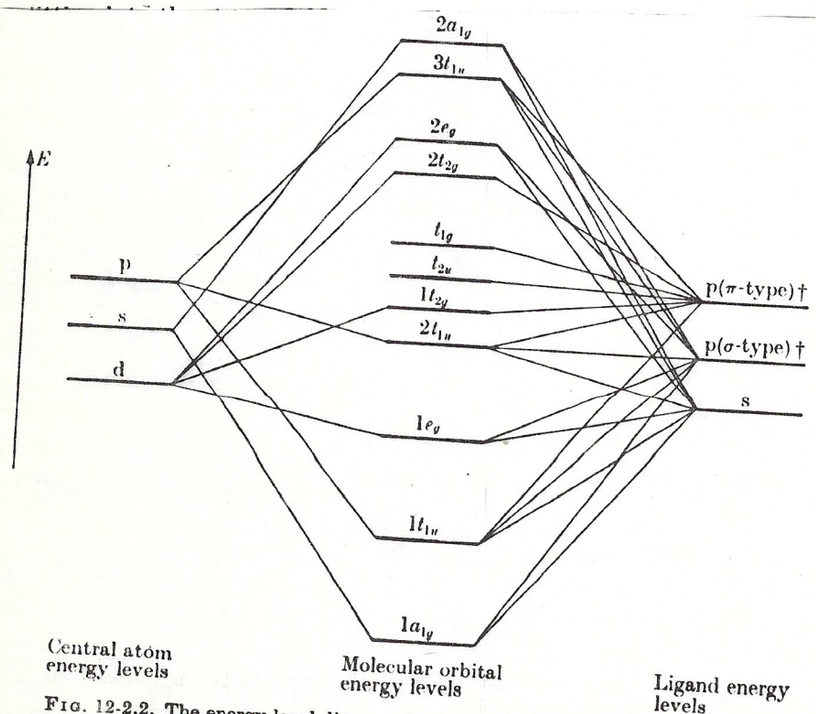
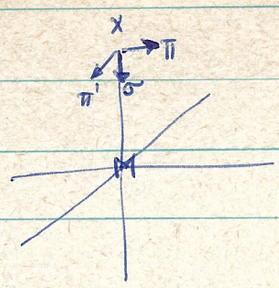


FIG. 12-2.2. The energy level diagram for an octahedral MX_6 molecule or ion.

O_h



Operations do not mix M- and X functions. $\Rightarrow$ $\mathbb{P}(A_m)\left(\quad\right) =$

$$\Gamma^{AO} = \Gamma^{M} + \Gamma^{X}$$

Γ^M

s	$\Gamma^{A_{1g}}$
ϕ_x, p_y, p_z	$\Gamma^{T_{1u}}$
$d_{z^2}, d_{x^2-y^2}$	Γ^{E_g}
d_x, d_y, d_z	$\Gamma^{T_{2g}}$

For the X's s, σ, π are not mixed:

$$\Gamma^X = \Gamma^s + \Gamma^\sigma + \Gamma^\pi$$

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
χ^s	6	0	2	2	0	0	0	4	0	2
χ^σ	6	0	2	2	0	0	0	4	0	2
χ^π	12	0	-4	0	0	0	0	0	0	0

Exercise ✱ no check

$$\Gamma^s = \Gamma^{A_{1g}} + \Gamma^{E_g} + \Gamma^{T_{1u}}$$

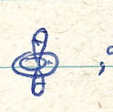
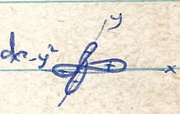
$$\Gamma^\sigma = \Gamma^{A_{1g}} + \Gamma^{E_g} + \Gamma^{T_{1u}}$$

$$\Gamma^\pi = T^{T_{1g}} + \Gamma^{T_{2g}} + T^{T_{1u}} + T^{T_{2u}}$$

Exercise ✱ no check

Eigenfuctions can be calculated by projection operators
Hard to perform ⇒

Common Sense:

	$\underline{S}$	
A_{1g}	$S_1+S_2+S_3+S_4+S_5+S_6/\sqrt{6}$	
E_g	$2(S_5+S_6)-S_1+S_2-S_3-S_4/\sqrt{12}$	similar to d_{z^2}  , $d_{x^2-y^2}$  .
	$S_1+S_2-S_3-S_4$	
T_{1u}	$(S_1-S_2)/\sqrt{2}$	similar p_x, p_y, p_z 
	$(S_3-S_4)/\sqrt{2}$	
	$(S_5-S_6)/\sqrt{2}$	

etc

Look in Bishop p. 248, 249

⇒ will bring secular equation in block form with ψ_i belongs to $\Gamma^{A_{1g}}$

3x3	$\Gamma^{A_{1g}}$	
4x4	$\Gamma^{T_{1u}}$	3 X

etc

real calculation begins this lecture

Copy p. 251 diagram.

We put the electrons in: each level two electrons etc.

Exam

1. Construct character $D_{3d} = D \times i$

D_3	E	$2C_3$	$3C_2'$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

i	E	i
A_g	1	1
A_u	1	−1

D_{3d}	E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$
	1	1	1	1	1	1
	1	1	−1	1	1	−1
	2	−1	0	2	−1	0
	1	1	1	−1	−1	−1
	1	1	−1	−1	−1	1
	2	−1	0	−2	1	0

$E\,i = i$

$C_3\,i = S_6$

$C_2\,i = \sigma_d$



2.

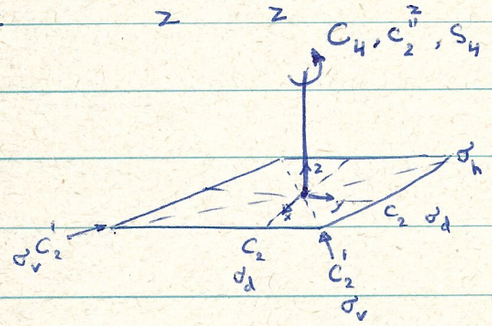
Exercise

2 Calculate the reprents of D_{4h} and T_d with d fnctions as a basis. Decompose this representation. Check your result with a bases in character table.

D_{4h}

take one of them!

E	$2C_4$	C_2''	$2C_2'$	$2C_2$	σ_h	$2\sigma_v$	$2\sigma_d$	$2S_4$	i
x	x	y	-x	y	x	x	y	-x	y
y	y	-x	-y	x	-y	y	x	y	-x
z	z	z	-z	-z	-z	z	z	-z	-z



xy	xy	-xy	xy	xy	-xy	xy	xy	-xy	-xy
xz	xz	-xz	-xz	-yz	-xz	-xz	yz	-xz	-yz
yz	yz	yz	-yz	-xz	+yz	-yz	xz	yz	xz
x^2-y^2	x^2-y^2	$-(x^2-y^2)$	x^2-y^2	y^2-x^2	x^2-y^2	x^2-y^2	y^2-x^2	x^2-y^2	y^2-x^2
$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	$3z^2-r^2$	
$\chi(E)=5$	$\chi(C_4)=-1$	1	1	1	1	1	1	-1	5

χ	5	-1	1	1	1	1	1	1	-1	5

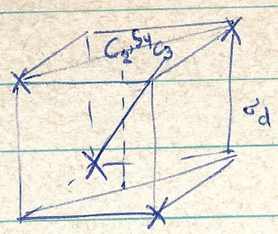
$\frac{1}{16}\{5 \pm 2 + +2 + 2 + + 2 + 2 - 2 + 5\}$

$\chi(A_g) = \frac{16}{16} = 1$; $\chi(B_{1g}) = 5+2+1+2-2 \dots = 1$

$\chi(E_g) = 1$ $\chi(B_{2g}) = 1$

} from character table
Look at sign functions in table

Exer T_d



$E \quad 8C_3 \quad 3C_2 \quad 6S_4 \quad 6\sigma_d$

Same way and look at bases in character table.

---

2 To what irred. repr. can the following direct product representation be reduced.

a) $\Gamma^{A_2''} \otimes \Gamma^{E''}$ for D_{3h} & b) $\Gamma^{E_1} \otimes \Gamma^{E_2}$ for C_{5v}

a)

χ	2	-1	0	2	-1	0

This is a just $\chi(E_1')$

b)

χ	4	$4\cos\alpha\cos2\alpha$	$4\cos\alpha\cos2\alpha$	0	$\alpha = 72°$

$2(\cos\alpha + \cos2\alpha) =$

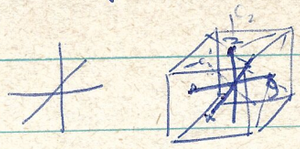
$\cos\alpha\cos2\alpha =$))

$\sum a_{E_1}^2 = 1$

$a_{E_2}^2 = 1.$

Exam

4 According to which irreducable representation of O does $xyz^2 f(r)$ transform.



E	$xyz^2 \to xyz^2$	1	A_2
C_3	$xyz^2 \to yzx = xyz^2$	1	
C_2	$xyz^2 \to -x\cdot -y\cdot z = xyz^2$	1	
C_4	$xyz^2 \to y\cdot -x\cdot z = -xyz^2$	-1	
C_4^3	$xyz^2 \to z\cdot -y\cdot x = -xyz^2$	-1	

E all operations of O $f(r) \to f(r)$ A_1

$$\Gamma^{A_1} \otimes \Gamma^{A_2} = \Gamma^{A_2}$$

5 To what irred. repr. must $\varphi^{(i)}$ belong if the integral

$$\int \varphi^{(i)} x^{(k)} \varphi^{(i)} \neq 0$$

a) D_{6h} $\Gamma^{(k)} = \Gamma(E_{1u})$ $\Gamma^{(i)} = \Gamma(E_{2u})$

b) T_d $\Gamma^{(k)} = \Gamma(T_2)$ $\Gamma^{(i)} = \Gamma(T_1)$

a) $\Gamma^{E_{1u}} \otimes \Gamma^{E_{2u}} = ?$ | 4 -4 1 -1 0 0 4 -4 1 1 0 0

($\Gamma^{E_{1g}} \otimes \Gamma^{E_{2g}}$ = same)

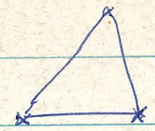
$$B_{1g} + B_{2g} + E_{1g}$$

b) $\Gamma(T_1) \otimes \Gamma(T_2) = A_2 + E + T_1 + T_2$

by trying we can find this too!

Exo 6

D_3 , $\alpha\alpha\alpha$, $\alpha\alpha\beta$ etc



	E	$2C_3$	$2C_2'$	
$\alpha\alpha\alpha$	$\alpha\alpha\alpha$	$\alpha\alpha\alpha$	$\alpha\alpha\alpha$	
	$\beta\alpha\alpha$	$\alpha\alpha\beta$	$\alpha\alpha\beta$	
	$\alpha\alpha\beta$	$\beta\alpha\beta$	$\alpha\beta\alpha$	
	$\alpha\beta\alpha$	$\alpha\beta\alpha$	$\beta\alpha\alpha$	
	$\beta\alpha\beta$	$\beta\alpha\beta$	$\alpha\beta\beta$	
	$\beta\beta\alpha$	$\alpha\beta\beta$	$\beta\alpha\beta$	
	$\alpha\beta\beta$	$\beta\alpha\beta$	$\beta\beta\alpha$	
$\beta\beta\beta$	$\beta\beta\beta$	$\beta\beta\beta$	$\beta\beta\beta$	

	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

χ	8	2	4	decomp with character table → $4A_1 + 2E$

$\Psi(A_1)$ $|\alpha\alpha\alpha\rangle = |\alpha\alpha\alpha\rangle$

$|\alpha\alpha\beta\rangle = (\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle + |\alpha\alpha\beta\rangle$

$|\alpha\beta\beta\rangle = |\alpha\beta\beta\rangle + |\beta\alpha\beta\rangle + |\beta\beta\alpha\rangle$

$|\beta\beta\beta\rangle = |\beta\beta\beta\rangle$

$\Psi(E)$ $|\alpha\alpha\beta\rangle = \{2|\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle - |\alpha\beta\alpha\rangle\}$ — 2 indep

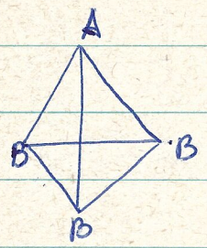
$|\alpha\beta\alpha\rangle = \{2|\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle\}$

$|\beta\alpha\alpha\rangle = \{2|\beta\alpha\alpha\rangle - |\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle\} = -\{\ \} = +\{\ \}$

$\Psi(F)$ $|\alpha\beta\beta\rangle$ etc.

Exercise

Find degenerate and non degenerate eigenfunctions of spin wave function of AB_3 system in NMR. What are the allowed transitions?



C_3, C_3^2, σ_v, σ_v, σ_v

$\alpha\alpha\alpha$
$\alpha\alpha\beta$
$\beta\beta\alpha$
$\beta\beta\beta$
$\alpha\beta\alpha$
$\beta\alpha\alpha$
$\alpha\beta\beta$
$\beta\alpha\beta$

2^4 = Functions 16

2×8

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

	E	$2C_3$	$3\sigma_v$
χ	16	4	8

$a_{A_1} = \frac{1}{6}\{16 + 8 + 24\} = \frac{48}{6} = 8$

$a_{A_2} = \frac{1}{6}\{16 + 8 - 24\} = 0$

$a_E = \frac{1}{6}\{32 - 8\} = \frac{24}{6} = 4$

8
+
8
16

$\Gamma(A_1)$ $|\alpha_A\alpha\alpha\alpha\rangle = |\alpha_A\alpha\alpha\alpha\rangle$ and $|\alpha_\beta\alpha\alpha\alpha\rangle$

$|\alpha_A\alpha\alpha\beta\rangle = |\alpha_A\alpha\alpha\beta\rangle + |\alpha_A\beta\alpha\alpha\rangle + |\alpha_A\alpha\beta\alpha\rangle$ and $|\alpha_\beta \dashrightarrow\rangle$

$|\alpha_A\beta\beta\alpha\rangle$ ~~$|\alpha_A\beta\alpha\alpha\rangle$~~ $+ |\alpha_A\alpha\beta\alpha\rangle + |\alpha_A\beta\alpha\beta\rangle$ $|\alpha_\beta \dashrightarrow\rangle$

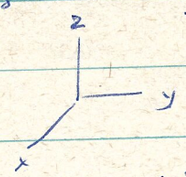
$|\alpha_A\beta\beta\beta\rangle = |\alpha_A\beta\beta\beta\rangle$ $|\alpha_\beta \dashrightarrow\rangle$

$\Gamma(E)$ $|\alpha_A\alpha\alpha\beta\rangle = |\alpha_A \dashrightarrow\rangle$ same as in Exercise 6

Allowed transition are only between eigenstate with same irred. repr.

Exerc

8 The character of translation is generated by real vector rotation.



$\chi(E) = 3$

$\chi(C(\theta)) = 1 + 2\cos\theta$

$\chi(S(\theta)) = -1 + 2\cos\theta$

$\chi(i) = -3$

$C(\theta)$ x → $\cos\theta$ x ---
y → $\cos\theta$ y ---
z → z

$S(\theta)$ x → $\cos\theta$ x ---
y → $\cos\theta$ y ---
z → $-z$

Characte of rotation by pseudo vector

$\chi(E) = 3$

$\chi(C(\theta)) = 1 + 2\cos\theta$

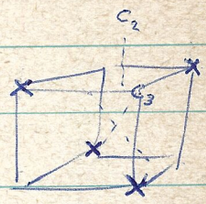
$\chi(S(\theta)) = 1 - 2\cos\theta$

$\chi(i) = +3$

Elève

9 Allowed transitions in Raman : CH_4, CH_3D

a) CH_4 T_d point group



$\Gamma^{Raman} = \Gamma^{A_1} + \Gamma^{E} + \Gamma^{T_2}$ $3N = 12$

2y

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\chi^{(6)}$	12	0	0	0	2

$\Gamma^{(6)} = A_1 + E + T_1 + 2T_2$

$\Gamma^{tr} = T_2$ from character table (x, y, z)

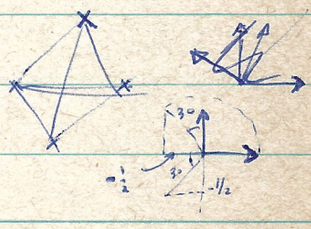
$\Gamma^{rot} = T_1$ ——— (R_x, R_y, R_z)

$\Gamma^{vib} = A_1 + E + T_2$

Raman active are A_1, E and T_2.

IR active are T_2

CH_3D C_{3v} (by character table)



$\Gamma^{Raman} = A_1 + E$

$\Gamma^{tr} = A_1 + E$

$\Gamma^{vib} = A_2 + E$

6

	E	$2C_3$	$3\sigma_v$
$\chi^{(6)}$	12	0	2

$\Gamma^{(6)} = 3A_1 + A_2 + 4E$ $\Gamma^{vib} = 2A_1 + 2E$

Raman : $2A_1 + 2E$; IR $2A_1 + 2E$.

Exam

$P(B_2)$ $q_1 = q_1 + q_4 + q_4 + q_1 = q_1 + q_4$ *

$q_2 = q_2 - q_5 - q_5 + q_2 = q_2 - q_5$ *

$q_3 = 0$

$q_7 = q_7 + q_7 + q_7 + q_7 = q_7$ *

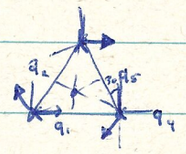
$q_8 = q_8 - q_8 - q_8 + q_8 = 0$

$q_9 = q_9 + q_9 - q_9 + q_9 = 0$

$q_1 + q_4 + q_7$ traslation

$q_1 + q_4 - q_7$
$q_2 - q_5$
} vibration + rotation

Rotation of form



q_7 +

etc

Full Rotation Group.

1) Angular momentum in QM.

A free atom in space is invariant under all rotations R:

$$R H \psi = H R \psi$$

When $[R, H] = 0$ then we can find a set of fuctions φ_n in which R and H are simultaniously diagonal:

$$R \varphi_n = r \varphi_n \quad \text{and} \quad H \varphi_n = E \varphi_n$$

This is so for every possible rotation and it is clear that there must be an operator which is independent of rotation angle and which is commutative with H.

Unitary R can be written as

$$R_p(\theta) = e^{-iS_p(\theta)} \qquad p = x, y, z \qquad \text{with } S \text{ Hermitian}$$

$$R(\theta_x, \theta_y, \theta_z) = e^{-iS(\theta_x, \theta_y, \theta_z)}$$

$$= \sum_{n=0}^{\infty} \frac{(-iS)^n}{n!}$$

In Taylor expansion we have for $\theta \ll 1$

$$R_p = 1 - i\theta_x J_p \qquad p = x, y, z$$

$$R = e^{-i\theta_x J_x} e^{-i\theta_y J_y} e^{-i\theta_z J_z}$$

From invariance of H under rotations we get:

$$[H, J_k] = 0 \qquad \forall\ k = x, y, z \qquad 1)$$

$$[H, \vec{J}^2] = 0 \qquad \vec{J}^2 = J_x^2 + J_y^2 + J_z^2 \qquad 2)$$

* We can prove (see later) $[J_x, J_y] = i J_z$ etc

$$\Rightarrow [J_z, \vec{J}^2] = 0 \qquad 3)$$

1), 2), 3) $\Rightarrow$ We can find φ_n's so that J_z, $\vec{J}^2$ and H are diagonal

$$\left.\begin{aligned} J_z \varphi_n &= j_z \varphi_n \\ \vec{J}^2 \varphi_n &= j^2 \varphi_n \\ H \varphi_n &= h \varphi_n \end{aligned}\right\}$$

* We can prove (see later)

$$J_z \varphi_n = m \varphi_n \qquad \varphi_n : \varphi_{j,m}$$
$$\vec{J}^2 \varphi_n = j(j+1) \varphi_n$$

$$j = 0, \tfrac{1}{2}, 1, \dots \qquad m = -j, \dots, j$$

$$J_\pm = J_x \pm i J_y$$

$$J_\pm \varphi_{j,m} = \left[(j \mp m)(j \pm m - 1)\right]^{1/2} \varphi_{j, m \pm 1}$$

$\Rightarrow$ Pauli matrices. define $\tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$; $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$; $\tfrac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

Conclusion : J is a good quantum number for electronic wave function of a free atom.

These wave functions can be defined by the operation of the angular momentum operator and we do not have to know the real functional form.

In particular an electron in a Hydrogen wave function has a well defined angular momentum (orbital) as

s, 1
p, 2
d, 3

} In this case we talk about L (instead of J)
Here functions are not eigenfunctions of L_z

but $L^2|p\rangle = l(l+1)|p\rangle = 6|p\rangle$

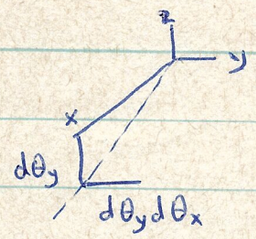
Electron have also spin angular momentum. This has expectation values $+\frac{1}{2}$ or $-\frac{1}{2}$.

The total J of a combination of electrons with each there L and S value can be of diffent values.

!? How do there angular momentum combine !?

I $[J_x, J_y] = i J_z$

Prove Infinitesimal rotation.



$e^{-i d\theta_x J_x} \quad e^{-i d\theta_y J_y} \qquad P(1,0,0)$

$P(1,0,0) \xrightarrow{1} P(1,0,d\theta_y) \rightarrow P(1, d\theta_y d\theta_x, d\theta$

$e^{-i d\theta_y J_y} \quad e^{-i d\theta_x J_x}$

$P(1,0,0) \rightarrow P(1,0,0) \rightarrow P(1, d\theta_y, 0)$

$e^{-i d\theta_x J_x} \; e^{-i d\theta_y J_y} - e^{-i\theta_y J_y} \; e^{-i d\theta_x J_x} = e^{-i d\theta_y d\theta_x J_z}$ from second order terms

$\Rightarrow J_x J_y - J_y J_x = i J_z$

II $\varphi_{J,m}$ etc.

III Classical angular momentum

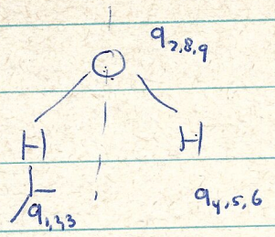
Orbital momentum :

Classical momentum :

Exo 10

H_2O Raman and IR active

C_{2v}



$3N = 9$

	E	C_2	σ_v	σ_v'	
$\chi^{(9)}$	9	-1	1	3	

χ $\Gamma^{tr} = A_1 + B_1 + B_2$

$\Gamma^{rot} = A_2 + B_1 + B_2$

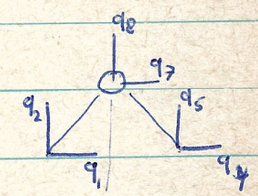
$\Gamma^{(9)} = 3A_1 + A_2 + 2B_1 + 3B_2$

$\Gamma^{vib} = 2A_1 + B_2$

$\Gamma^{Raman} = A_1 + A_2 + B_1 + B_2$

$\Gamma^{IR} = A_1 + B_1 + B_2$

} all active.



$\Gamma(A_1)$ $q_1 = q_1 - q_4 - q_4 + q_1 = q_1 - q_4$ *

$q_2 = q_2 + q_5 + q_5 + q_2 = q_2 + q_5$ *

$q_3 = q_3 - q_6 + q_6 - q_3 = 0$

$q_7 = q_7 - q_7 - q_7 + q_7 = 0$

$q_8 = q_8 + q_8 + q_8 + q_8 = q_8$ *

$q_9 = q_9 - q_9 + q_9 - q_9$

Translation : $q_2 + q_5 + q_8$ // vibration $q_1 - q_4$; $q_2 + q_5 - q_8$

2. 3-dimensional rotation Group

All three dimensional rotations form a infinite group

⇒ infinite number of classes.

All rotations of $\alpha°$ are in <u>one</u> class.

How do we find irred. representations

Take basis set Spherical Harmonics $Y_\ell^m(\theta,\varphi) \propto P_\ell^m e^{im\varphi}$

$$R\, Y_\ell^m = \sum D^\ell_{m',m}\, Y_\ell^{m'}$$

⇒ $(2\ell+1)$ functions are base for R

Rotation around z axis

$$R_z(\alpha)\, Y_\ell^m = e^{-im\alpha}\, Y_\ell^m$$

$$\chi^{(\ell)}(\alpha) = \sum_{m=-\ell}^{\ell} e^{-im\alpha} = \frac{\sin(\ell+1/2)\alpha}{\sin \alpha/2}$$

$\chi(180°) = (-1)^\ell$

$\chi(\frac{2\pi}{3}) = \begin{cases} 1 & \ell = 0, 3 \\ 0 & \ell = 1, 4 \\ -1 & \ell = 2, 5 \end{cases}$

$\chi(\pi/2) = \begin{cases} 1 & \ell = 0, 4, 5 \\ -1 & \ell = 2, 3, 6, 7, \dots \end{cases}$

Spherical Harmonics of order ℓ form the basis for the only distinct irred. representation of dimension $(2\ell+1)$ of the full rotation group. Irreducible repres.: "D_ℓ".

<u>E.g.</u> Crystal field on electrons

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
D_0	1	1	1	1	1
D_1	3	0	−1	−1	1
D_2	5	−1	1	1	−1
⋮					

In O point group by decomposition

$P\ (l=1) \quad D_1 = T_1$

$P\ (l=2) \quad D_2 = E + T_2$

In <u>strong field</u>:

1. Inequivalent $(D_1 \times D_1)$ e.g. $(2p^1\ 3p^1)$

χ	q	0	1	1	1

$\Rightarrow D_1 \times D_1 = A_1 + E + T_1 + T_2$

2. Equivalent $(2p^2)$

Pauli principle $L = 1,\ S = 1 \Rightarrow {}^3P$

Crystal field only on orbital part $\Rightarrow$ (character table)

${}^3P = {}^3T_1$

3. <u>Weak crystal field</u>:

First Spin - Orbid coupling: How do S and L couple?

Representations of Full rotation group.

Rotation of coordinate system:

Euler angles
1) α° about z axis $\rightarrow x', y', z'$ $\quad z' = z$
2) β° about y' axis $\rightarrow x'', y'', z''$ $\quad y' = y''$
3) γ about z'' axis $\rightarrow x''', y''', z'''$ $\quad z'' = z'''$

1) γ about z axis
β about y axis
α about x axis same result.

$P(\alpha, \beta, \gamma)\ \varphi_m^j$? Notice if $PH = HP \Rightarrow$ all φ_m^j $\forall m$ degenerated

We know that: $J_z\ \varphi_m^j = m\ \varphi_m^j$

$J_x\ \varphi_m^j = \sqrt{\quad}\ \varphi_{m+1}^j + \sqrt{\quad}\ \varphi_{m-1}^j$

$$P(\alpha,\beta,\gamma) = e^{-\alpha i J_z/\hbar}\ e^{-\beta i J_y/\hbar}\ e^{-\gamma i J_x/\hbar}$$

$$P_{z''}(\gamma)\ P_{y'}(\beta)\ P_z(\alpha) = P_z(\alpha)\ P_y(\beta)\ P_z(\gamma)$$

$$\boxed{P(\alpha,\beta,\gamma)\ \varphi_m^{(j)} = \sum_{m'} \varphi_{m'}^j\ D^{(j)}_{m'm}(\alpha,\beta,\gamma)}$$

Because of choice of z as diagonal and with $P = e^{-\varphi J/\hbar}$:

$$P(\alpha,\beta,\gamma)\varphi_m^j = \sum_{m'} \varphi_{m'}^j\ e^{-i\alpha m'}\ d^j_{m'm}(\beta)\ e^{-i\gamma m}$$

$$\boxed{D^{j}(\alpha,\beta,\gamma)_{m'm} = e^{-im'\alpha}\, d^{(j)}_{m'm}(\beta)\, e^{-im\gamma}}$$

A General form of rotation ~~of~~ matrix of eigenfunctions of J_z and J^2, or eigenfunctions of H for $HP = PH$ with P all possible rotations.

Calculation results in

$$D^{j}(\alpha,\beta,\gamma)_{m'm} = e^{-im'\alpha}\, e^{-im\gamma} \sum_{\kappa} \left[\frac{(-1)^{\kappa} \{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!\}^{1/2}}{\kappa!\,(j+m-\kappa)!\,(j-m'-\kappa)!\,(\kappa+m'-m)!} \times \left(\cos\frac{\beta}{2}\right)^{2j-2\kappa-m'+m} \left(-\sin\frac{\beta}{2}\right)^{2\kappa+m'-m} \right]$$

$\Downarrow$

$\rightarrow$ **Wigner Matrices**

Calculation after some general comments on addition of Angular momentum.

Addition of Angular momentum

Consider two systems with angular momentum j_1 and j_2

~~Total~~ dimensions $(2j_1+1) \times (2j_2+1)$

$$P_R(\alpha\beta\gamma)\, u^{j_1}_{m_1} = \sum_{m_1'} u^{j_1}_{m_1'}\, D^{j_1}_{m_1' m_1}$$

$$P_R(\alpha\beta\gamma)\, v^{j_2}_{m_2} = \sum_{m_2'} v^{j_2}_{m_2'}\, D^{j_2}_{m_2' m_2}$$

The direct (coupled) product functions behave under rotation as:

$$P_R \, u^{j_1}_{m_1} v^{j_2}_{m_2} = \sum_{m_1' m_2'} u^{j_1}_{m_1'} v^{j_2}_{m_2'} \underbrace{D^{j_1}_{m_1' m_1} D^{j_2}_{m_2' m_2}}_{\mathbb{D}_{m_1' m_2' m_1 m_2}}$$

$$\chi(\mathbb{D}) = \chi^{j_1}(\alpha\beta\gamma)\,\chi^{j_2}(\alpha\beta\gamma)$$

by decomposition $= \sum_J a_{j_1 j_2 J}\,\chi^J(\alpha\beta\gamma)$, we must end up with well defined angular momentums (J).

To do so we should sum over number of ~~infi~~ classes, but this numbe is infinite!

But we know

$$\chi^{j_1}(\alpha)\,\chi^{j_2}(\alpha) = \sum_{m_1, m_2}^{j_1, j_2} e^{-i(m_1+m_2)\alpha}$$

$$= \sum_{J=0}^{\infty} a_{j_1 j_2 J} \sum_{M=-J}^{J} e^{-iM\alpha}$$

$\Rightarrow$ For all α $\rightarrow$ $|M| \leq j_1 + j_2$ $\rightarrow$ $a_{j_1 j_2 J} = 0$ $|J| > j_1 + j_2$

$\rightarrow$ one possible $M = j_1 + j_2$ $\rightarrow$ $a_{j_1 j_2 (j_1+j_2)} = 1$.

$\Rightarrow M = j_1 + j_2 - 1 \rightarrow M = (j_1 - 1) + j_2$ or $j_1 + (j_2 - 1)$

$$\chi \cdot \chi \cdots = e^{-i(j_1+j_2-1)\alpha} + e^{-i(j_1-1+j_2)\alpha} \cdots = \overset{1}{\overset{\shortparallel}{a_{j_1 j_2 (j_1+j_2)}}} e^{-i(j_1+j_2)\alpha} + \cdots$$

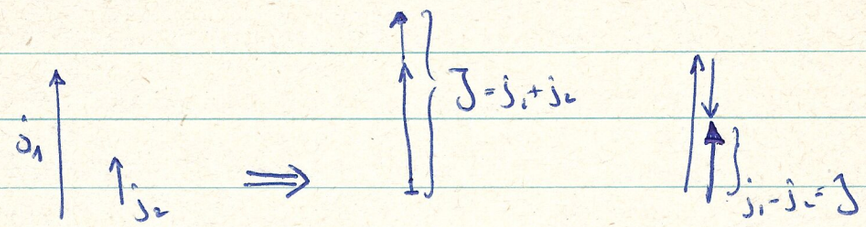
$\Rightarrow$ $a_{j_1 j_2 (j_1+j_2-1)} = 1$ $\Rightarrow$ all $a_{j_1 j_2 J} = 1$ for $J \leq j_1 + j_2$

<u>etc</u>

$$\chi^{j_1}(\alpha)\,\chi^{j_2}(\alpha) = \sum_{J=|j_1-j_2|}^{j_1+j_2} 1 \sum_{M=-J}^{J} e^{-iM\alpha}$$

$$\boxed{D^{(j_1)} \times D^{(j_2)} = \sum_{J=|j_1-j_2|}^{J=j_1+j_2} D^{(J)}}$$

Two systems with angular momentum j_1 and j_2 are possibly combined to any angular momentum allowed by elementary vector model.



What are the basis fuctions of the irred. representations of the direct products?

$$\psi_M^J = \sum_{m_1 m_2} u_{m_1}^{j_1} v_{m_2}^{j_2} \left(\tilde{A}^{-1}\right)_{m_1 m_2, JM}$$

$$u_{m_1}^{j_1} v_{m_2}^{j_2} = \sum_{JM} \underbrace{A_{J,M,m_1,m_2}^{j_1 j_2}} \psi_M^J$$

Wigner coefficients
Clebsh-Gordan coefficients.

Rotation $(\alpha\beta\gamma)$: $\left\{ D_{M'M}^J(\alpha\beta\gamma)\, \psi_M^J \right.$

$\left. D_{m_1' m_1}^{j_1} D_{m_2' m_2}^{j_2} u_{m_1}^{j_1} v_{m_2}^{j_2} \right\} \Longrightarrow$

$$\boxed{D_{m_1' m_1}^{j_1}(\alpha\beta\gamma)\, D_{m_2' m_2}^{j_2}(\alpha\beta\gamma) = \sum_{J,M,M'} A_{m_1', m_2', J, M'}^{-1} D_{M'M}^J A_{m_1, m_2, J, M}}$$

From this equation we see that A's are functions of D's and by lengthy calculation A's can be calculated. In this course we are not going to do so but rather give the result only.

$$A^{j_1 j_2 J}_{m_1 m_2 M} = \text{(pag 121 Tinkham)} \qquad M = m_1 + m_2$$

$$P_R \psi^J_M = e^{-i\alpha M} \sum_{m_1 m_2} u_{m_1} v_{m_2} A^{-1}_{m_1 m_2 J M}$$

$$= \sum_{m_1 m_2} e^{-i(m_1+m_2)\alpha} u_{m_1} v_{m_2} A^{-1}_{m_1 m_2 J M}$$

Racah : $V(j_1 j_2 j_3 , m_1 m_2 m_3) = (-1)^{j_3 - m_3} (2j_3+1)^{-\frac{1}{2}} A^{j_1 j_2 j_3}_{m_1 m_2 -m_3}$

Wigner : 3j symbol : $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_3 + j_2 - j_1} V(j_1 j_2 j_3 , m_1 m_2 m_3)$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} \text{ etc}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix}$$

Example:

$j_2 = \frac{1}{2}$ $\quad m_2 = \frac{1}{2}$ $\quad m_2 = -\frac{1}{2}$

$j = j_1 + \frac{1}{2}$	$\left(\frac{j_1 + m + \frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$	$\left(\frac{j_1 - m + \frac{1}{2}}{2j_1+1}\right)^{1/2}$
$j = j_1 - \frac{1}{2}$	$-\left(\frac{j_1 - m + \frac{1}{2}}{2j_1+1}\right)^{1/2}$	$\left(\frac{j_1 + m + \frac{1}{2}}{2j_1+1}\right)^{1/2}$

$A^{j_1 1/2, J}_{m_1 \pm 1/2, m \pm 1/2}$

$j_2 = 1$ $\quad m_2 = 1$ $\quad m_2 = 0$ $\quad m_2 = -1$

$j = j_1 + 1$ $\quad \left[\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{1/2}$

~~$j = j_2$~~

$j = j_1$ $\quad -\left[\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{1/2}$

etc p 124 Fritzsch

$j = j_1 + 1$ $\quad \left[\frac{(j_1-m)(j_1-m+1)}{2j_1(j_1+2)}\right]^{1/2}$

Hund rules

1. Maximum value of S consistent with Pauli principle
2. 
3. If shell less half $J = L - S$
4. If shell more $J = L + S$

§ Weak field only on L and S is not changed.
Strong

Calculation of $D^{(j)}_{mm'}(\alpha, \beta, \gamma)$

Relation between 2×2 u-matrix and 3×3 real rotation R-matrix

In general $u = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$ form of all unitary matrices?

$u^{-1} = u^\dagger$

$|a|^2 + |b|^2 = 1$

$$u^{-1} = \begin{pmatrix} a^* & -b \\ b^* & a \end{pmatrix} = u^\dagger$$

Define 3 Pauli matrices $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

In general any traceless matrix

$$h = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} = r \cdot \sigma = \begin{pmatrix} z & x - iy \\ x + iy & -z \end{pmatrix} \rightarrow \begin{cases} z = h_{11} = -h_{22} \\ x = \dfrac{h_{12} + h_{21}}{2} \\ y = \dfrac{h_{21} - h_{12}}{2i} \end{cases}$$

Unitary trasformation: $h' = u h u^{-1} = r' \cdot \sigma$

$$\Rightarrow \quad x' = \frac{h'_{21} + h'_{12}}{2} = \frac{1}{2}(a^2 + a^{*2} - b^2 - b^{*2})\, x + \frac{i}{2}(-a^2 + a^{*2} - b^2 + b^{*2})\, y - (ab + a^* b^*)\, z$$

$y' = \ldots$

$z' = \ldots$

$$\Rightarrow \quad r' = R(u)\, r$$

e.g. $R_{11}(u) = \frac{1}{2}(a^2 + a^{*2} - b^2 - b^{*2})$ etc $\Rightarrow$ homomorphism between 2×2 matrices ($|u| = 1$) and three dimensional rotation.

IF

$$u_1(\alpha) = \begin{pmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{pmatrix} \Rightarrow R(\alpha) = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

↑ general diagonal form

$$u_2(\beta) = \begin{pmatrix} \cos\beta/2 & \sin\beta/2 \\ -\sin\beta/2 & \cos\beta/2 \end{pmatrix} \Rightarrow R(\beta) = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & & \cos\beta \end{pmatrix}$$

↑ general real form

$$u(\alpha,\beta,\gamma) = u_1(\gamma)\, u_2(\beta)\, u_1(\alpha)$$

$$= \begin{pmatrix} e^{i(\alpha+\gamma)/2}\cos\frac{\beta}{2} & e^{-i(\gamma-\alpha)/2}\sin\beta/2 \\ -e^{-i(\gamma-\alpha)/2}\sin\frac{\beta}{2} & e^{-i(\alpha+\gamma)/2}\cos\beta/2 \end{pmatrix}$$

Euler angles are ~~only~~ defined by $0 \le \alpha,\beta,\gamma \le 2\pi \rightarrow u(\alpha,\beta,\gamma)$ only defined for angles till π. ⇒ there is an ambiguity in the angle or u and $-u$ are both representations of R.

$R(\alpha,\beta,\gamma)$ is defined on the coordinates and therefore $u(\alpha,\beta,\gamma)$ corresponds to coordinate transformation. To obtain $D^{(1/2)}_{mm'}$, defined on the functions, we get:

$$D^{1/2}(\alpha,\beta,\gamma) = u(-\gamma,-\beta,-\alpha)$$

$$= \begin{pmatrix} e^{-i(\alpha+\gamma)/2}\cos\frac{\beta}{2} & -e^{-i(\alpha-\gamma)/2}\sin\beta/2 \\ -e^{-i(\gamma-\alpha)/2}\sin\beta/2 & e^{i(\alpha+\gamma)/2}\cos\beta/2 \end{pmatrix}$$

0

Remember $D^0(\alpha,\beta,\gamma) = 1$

U is two dimensional representation of rotation group.

Take eigenfunctions $\varphi_1^{(1/2)}$ and $\varphi_2^{(1/2)}$

$$U\varphi_1^{(1/2)} = a\varphi_1 - b^*\varphi_2$$
$$U\varphi_2 = -b^*\varphi_1 + a^*\varphi_2^*$$

Example:

Consider now eigenfunctions $f_1^{(1)} = \varphi_1^2$

$$f_2^{(3)} = \varphi_1\varphi_2$$

$$f_3^{(3)} = \varphi_2^2$$

$$P(u) f_1^3 = (a\varphi_1 - b^*\varphi_2)^2 = a^2 f_1^3 - ab^* f_2^3 + b^{*2} f_3^3$$

$$P(u) f_i^{(3)} = \sum_{j=1}^{3} U_{ij}(u) f_j^3$$

In general

$$P(u) f_m^j = \sum_{m'} f_{m'}^j U_{m'm}^{(j)}(u)$$

$f_p^n \Rightarrow f_m^j$ with $2j = n$, $p = j + m$

Straightforward

$$U_m^{(j)} = \sum_k \frac{(-1)^k \left[(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!\right]^{1/2}}{k!\,(j+m-k)!\,(j-k+m')!\,(k+m'-m)!} \cdot a^{j+m-k} (a^*)^{j-k-m'} b^{k+m'-m} (b^*)^k$$

with $a = e^{-i(\alpha+\gamma)/2}\cos\frac{\beta}{2}$

$b = -e^{-i(\alpha-\gamma)}\sin\frac{\beta}{2}$

and $D^j(\alpha,\beta,\gamma) = U^j(u(-\gamma,-\beta,-\alpha))$

$\Longrightarrow D_{m'm}^{(j)}$

Comment

~~Assume~~

1) By changing u to $-u$ $U^{(j)}$ and $D^{(j)}$ changes and we get two possible representations.

Or

for $j = 1/2, 3/2,$ etc rotation of 2π in α, β, γ do not give the same D-matrix $\Rightarrow$ spinor character of 4π

for $j = 1, 2, \ldots$ rotation of 2π in α, β, γ do give same D.

2) Functions are rotated with respect to fixed axes $\Rightarrow$

$$P(\alpha)\, P(\beta)\, P(\gamma).$$

3) Notice D rotated $\varphi_{-1}, \varphi_0, \varphi_1$ and not x, y, z.

$$\Rightarrow \quad \varphi_1 = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\varphi} = -\sqrt{\frac{3}{8\pi}} \frac{x+iy}{r}$$

$$\varphi_0 = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$\varphi_{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\varphi} = \sqrt{\frac{3}{8\pi}} \frac{x-iy}{r}$$

D is given in eigenstate $\varphi_1, \varphi_0, \varphi_{-1}$ and therefore

$$Dx = D\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \text{and not} \quad Dx = D\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

Irreducible Tensors

Tensor as physical property

In classical mechanics : values of an property of object.

" quantum —"— operator —"—

$$T_{ij\ldots} \qquad i,j,\ldots = x,y,z$$

Cartesian Operators

The behave under coordinate trasformation according to $R\,\bar{r} = \bar{r}'$. $R(\alpha,\beta,\gamma)$

Under rotation :

$$T\varphi \longrightarrow T'\varphi'$$

$$T \longrightarrow R\,T\,R^{-1}$$

Example :

Cartesian Tensor $T_{xy} \longrightarrow$

E.F Gradient $\dfrac{\partial}{\partial x \partial y} \xrightarrow{45^\circ \text{ Rotation of } y} \dfrac{1}{r_2}\left(\dfrac{\partial}{\partial x \partial y} - \dfrac{\partial}{\partial z \partial y}\right) = \dfrac{1}{r_2}\left(T_{xy} - T_{zy}\right)$

$$T'_{ij} = \sum_{k,l} R_{ik}\,R_{jl}\,T_{kl}$$

or

$$T'_{ijk} = \sum_{k,l,m} R_{ik}\,R_{jl}\,R_{km}\,T_{klm}$$

We write the Cartesian tensor as

$$T = T_0^{(0)} + T^{(1)}_{\alpha} + T^{(2)}_{\alpha\beta} + \cdots$$

and define these tensors as :

$$T_0^{(0)\prime} = T_0^{(0)}$$

$$T^{(1)\prime}_{\alpha'} = \sum_{m'_1} P_{\alpha\alpha'} T^{(1)}_{\alpha} \qquad (P_{\alpha\alpha'} \sim R_{ij})$$

$$T^{(2)\prime}_{\alpha'\beta'} = \sum_{m'_2} P P\, T^{(2)}_{\alpha\beta} \qquad (P_{\beta\beta'} \sim R_{ij} R_{kl})$$

$T_0^{(0)}$ Scalar Operator

Example : Hamiltonian of a atom : $\langle N' \varphi^{j'}_{m'} | T_0^{(0)} | N \varphi^{j}_{m} \rangle$

$$= \delta_{jj'} \delta_{mm'} \langle N' j' \| T_0^{(0)} \| N j \rangle$$

Cartesian Vector Operator

$T^{(1)}_x, T^{(1)}_y, T^{(1)}_z$ like a vector rotation $\alpha = x, y, z$

$$T_i^{(1)\prime} = \sum R_{ji} T_j^{(1)}$$

R_{ij} coordinate transformation

Cartesian Rank = 2 operator

$T_{i,j}$ Is this reducable?

Example

$T_{i,j}$ $i,j = x,y,z$

trace $X = T_{xx} + T_{yy} + T_{zz} \Rightarrow$ Scalar (like r^2)

~~invariant~~ trace invariant under rotation

antisymm. combination

$$Y_z = \frac{1}{2}(T_{xy} - T_{yx})$$
$$Y_x = \frac{1}{2}(T_{yz} - T_{zy})$$
$$Y_y = -\frac{1}{2}(T_{zx} - T_{xz})$$

} Vector (like vector product $(v \times u)_z = v_x u_y - v_y u_x$ etc)

left

$$S_{ij} = \frac{1}{2}(T_{ij} + T_{ji}) - \frac{1}{3} X \qquad i \neq j \quad 3$$
$$i = j \quad \underline{2} \quad (+ \text{trace} = 3)$$

$$T_{ij} = X + Y_\alpha + S_\beta$$

//

Spherical Tensors

Spherical Harmonics $\quad Y_0^{(1)} = z$

$$Y_{-1}^{(1)} = \frac{x - iy}{\sqrt{2}}$$

$$Y_1^{(1)} = -\frac{x + iy}{\sqrt{2}}$$

Rotation given by $\underline{\underline{D^{(1)}}}$ Wigner Matrix.

$$T = T_0^{(0)} + T_{m_1}^{(1)} + T_{m_2}^{(2)} + \cdots$$

$$T_0^{(0)\prime} = T_0^{(0)}$$

$$T_{m_1}^{(1)\prime} = \sum_{m_1'} D_{m_1' m_1}^{(1)} T_{m_1'}^{(1)\prime}$$

$$T_{m_2}^{(2)\prime} = \sum_{m_2'} D_{m_2' m_2}^{(2)} T_{m_2'}^{(2)}$$

Irreducable tensors.

Vector operator = Tensor of rank = 1

$$T_1 = -\frac{T_x + i T_y}{\sqrt{2}} \equiv -T_+$$

$$T_0 = T_z$$

$$T_{-1} = \frac{T_x - i T_y}{\sqrt{2}} \equiv T_-$$

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$= \frac{x + iy}{\sqrt{2}}\left(\frac{\vec{i} - \vec{j}}{\sqrt{2}}\right) + \frac{x - iy}{\sqrt{2}}\left(\frac{\vec{i} + \vec{j}}{\sqrt{2}}\right) + z\vec{k}$$

$$= -r_1 \bar{e}_{-1} - r_{-1} \bar{e}_1 + r_0 e_0$$

$$= \sum (-1)^q r_{-q} \bar{e}_q$$

Representation of the Rotation Group by Representations of the Unitary Group

$$D^{(j)}(\alpha,\beta,\gamma)_{m'm} = e^{-im'\alpha}e^{-im\gamma}\sum_{\kappa}\frac{(-1)^{\kappa}\sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{\kappa!\,(j+m-\kappa)!\,(j-m'-\kappa)!\,(\kappa+m'-m)!} \times\left(\cos\frac{\beta}{2}\right)^{2j-2\kappa-m'+m}\left(-\sin\frac{\beta}{2}\right)^{2\kappa+m'-m} \quad \blacktriangleright \text{ (5-35)}$$

$$\mathbf{D}^{(1)}(\alpha,\beta,\gamma)=\begin{bmatrix} e^{-i\alpha}\dfrac{1+\cos\beta}{2}e^{-i\gamma} & -e^{-i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\dfrac{1-\cos\beta}{2}e^{i\gamma} \\ \dfrac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & -\dfrac{\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\dfrac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\dfrac{1+\cos\beta}{2}e^{i\gamma} \end{bmatrix}$$

$$\mathbf{D}^{(\frac{1}{2})}(\alpha,\beta,\gamma)=\begin{pmatrix} e^{-i(\alpha+\gamma)/2}\cos\dfrac{\beta}{2} & -e^{-i(\alpha-\gamma)/2}\sin\dfrac{\beta}{2} \\ e^{i(\alpha-\gamma)/2}\sin\dfrac{\beta}{2} & e^{i(\alpha+\gamma)/2}\cos\dfrac{\beta}{2} \end{pmatrix}$$

Notation, Tabulations, and Symmetry Properties of the Wigner Coefficients

$$\psi_M{}^J = \sum_m a^{(j_1j_2)}_{J,m,M-m}u^{(j_1)}_m v^{(j_2)}_{M-m} = \sum_m A^{j_1j_2J}_{m,M-m,M}u^{(j_1)}_m v^{(j_2)}_{M-m} \quad \blacktriangleright \text{ (5-49)}$$

Since $M = m_1 + m_2$ in all cases, we shall often abbreviate the latter notation from $A^{j_1j_2J}_{m_1m_2M}$ to $A^{j_1j_2J}_{m_1m_2}$.

$$A^{j_1j_2J}_{m_1m_2M} = a^{(j_1j_2)}_{Jm_1m_2}$$
$$= \frac{[(J+j_1-j_2)!\,(J-j_1+j_2)!\,(j_1+j_2-J)!\,(J+m_1+m_2)!\,(J-m_1-m_2)!]^{\frac{1}{2}}}{[(J+j_1+j_2+1)!\,(j_1-m_1)!\,(j_1+m_1)!\,(j_2-m_2)!\,(j_2+m_2)!]^{\frac{1}{2}}}$$
$$\times\sum_{\kappa}\frac{(-1)^{\kappa+j_2+m_2}\sqrt{(2J+1)}\,(J+j_2+m_1-\kappa)!\,(j_1-m_1+\kappa)!}{(J-j_1+j_2-\kappa)!\,(J+m_1+m_2-\kappa)!\,\kappa!\,(\kappa+j_1-j_2-m_1-m_2)!}$$

Wigner coefficients for $j_2 = \frac{1}{2}$

$j_2 = \frac{1}{2}$	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j = j_1 + \frac{1}{2}$	$\left(\dfrac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$	$\left(\dfrac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$
$j = j_1 - \frac{1}{2}$	$-\left(\dfrac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$	$\left(\dfrac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$

The Wigner coefficients for $j_2 = 1$

$j_2 = 1$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j = j_1 + 1$	$\left[\dfrac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$	$\left[\dfrac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right]^{\frac{1}{2}}$	$\left[\dfrac{(j_1-m)(j_1-m+1}{(2j_1+1)(2j_1+2)}\right.$
$j = j_1$	$-\left[\dfrac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$	$\dfrac{m}{[j_1(j_1+1)]^{\frac{1}{2}}}$	$\left[\dfrac{(j_1-m)(j_1+m+1}{2j_1(j_1+1)}\right.$
$j = j_1 - 1$	$\left[\dfrac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$-\left[\dfrac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$\left[\dfrac{(j_1+m+1)(j_1+m}{2j_1(2j_1+1)}\right.$

$$V(j_1j_2j_3, m_1m_2m_3) = (-1)^{j_3-m_3}(2j_3+1)^{-\frac{1}{2}}A^{j_1j_2j_3}_{m_1m_2-m_3}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_3+j_2-j_1}V(j_1j_2j_3, m_1m_2m_3)$$

$$\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix}$$
$$= (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Irreducible tensor

$$\left(T^{L'}_{M'}\right)' = \sum_{M} D^{L}_{M'M}\, T^{L}_{M}$$

Example

1) (x, y, z) vector.

$$\left.\begin{aligned} T^1_0 &= z \\ T^1_{-1} &= \frac{x - iy}{\sqrt{2}} \\ T^1_{+1} &= -\frac{x + iy}{\sqrt{2}} \end{aligned}\right\} \quad D'_{M'M}$$

$$z = t_0$$

$$-\frac{x + iy}{\sqrt{2}} = t_{+1}$$

$$\frac{x - iy}{\sqrt{2}} = t_{-1}$$

*

2) $\{t_i\, t_j\}$ $\qquad D^{(1)} \times D^{(1)} = D^{(2)} + D^{(1)} + D^{(0)}$

$$T^2_2 = A^{112}_{112}\, t_1\, t_1 .$$

$$T^2_{-2} = A^{112}_{-1-1-2}\, t_{-1}\, t_{-1}$$

$$T^2_{\pm 1} = A^{112}_{\pm 101}\, t_{\pm 1}\, t_0 + A^{112}_{0\pm 11}\, t_0\, t_{\pm 1}$$

$$T^2_0 = t_{\pm 1}\, t_{\mp 1} + t_0\, t_0$$

$$T^1_{\pm 1} = A^{111}_{\pm 10\pm 1}\, t_{\pm 1}\, t_0 - t_0\, t_{\pm 1}$$

$$T^0_0 = A^{110}_{0\pm 10}\, t_{+1}\, t_{-1} + t_{-1}\, t_{+1}$$

$$\vec{V} \cdot \vec{W} = \sum_{\alpha} V_{-\alpha} W_{\alpha} (-1)^{\alpha}$$

Second Rank Tensor

$T_{ij} \simeq x_i^{(1)} x_j^{(2)}$ $\quad i,j = x,y,z$

$T_{ij} \simeq r_{\alpha}^{(1)} r_{\beta}^{(2)}$ $\quad \alpha,\beta = -1, 0, 1$

$T_{ij}^{\bullet} = r_{\alpha} r_{\beta}$ Direct product of $D^{(1)}$

$$D^{(1)} \times D^{(1)} = D^{(2)} + D^{(1)} + D^{(0)}$$

$$T_0^0 = \sum_{\alpha} (-1)^{\alpha} r_{\alpha}(1)\, r_{-\alpha}(2) \qquad \text{scalar}$$

$$T^{(1)}_{\pm 1} \sim \left(r_1(1)\, r_0(2) - r_0(1)\, r_1(2) \right)$$

$$T^1_{-1} \sim \left(r_{-1}(1)\, r_0(2) - r_0(1)\, r_{-1}(2) \right)$$

$$T^1_0 \sim r_{-1}(1)\, r_{+1}(2) - r_{-1}(1)\, r_{+1}(2)$$

$$T^2_{\pm 2} \sim \left(r_{\pm 1}(1)\, r_{\pm}(2) \right)$$

$$T^2_{\pm 1} \sim \left(r_{\pm 1}(1)\, r_0(2) + r_0(1)\, r_{\pm}(2) \right)$$

$$T^2_0 \sim \left(2 r_0\, r_0 + (r_1 r_{-1} + r_{-1} r_1) \right)$$

$A\begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \\ 1 & 0 & -1 \end{pmatrix}$

$A\begin{pmatrix} 1 & 1 & 2 \end{pmatrix}$

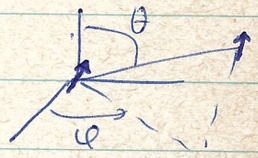
etc

$$T^{L}_{M} = \sum_{\substack{M_1 \\ M_2 = M - M_1}} A^{L_1 L_2 L}_{M_1 M_2 M} \; T^{L_1}_{M_1} \; T^{L_2}_{M_2}$$

Example

Dipole - Dipole interaction.

Class. $$\frac{\bar{\mu}_1 \cdot \bar{\mu}_2}{r_{12}^3} - \frac{3(\bar{\mu}_1 \cdot \bar{r}_{12})(\bar{\mu}_2 \cdot \bar{r}_{12})}{r_{12}^5}$$



$$\mu = \gamma \hbar I \qquad \frac{\gamma^2 \hbar^2}{r_{12}^3} \left\{ \bar{I}_1 \cdot \bar{I}_2 - 3 \frac{I_{1\alpha} I_{2\beta} r_{12\alpha} r_{12\beta}}{r_{12}^2} \right\}$$

Full rotation invariant.

$$\Rightarrow \quad H = \sum (-1)^{\alpha} Y^{2}_{\alpha} T^{2}_{-\alpha}$$

and Tinkham p. 130.

Note

Racah:

$$[J_{\pm}, T^{(\omega)}_{\mu}] = [\omega(\omega+1) - \mu(\mu \pm 1)]^{1/2} T^{(\omega)}_{\mu \pm 1}$$

$$[J_z, T^{(\omega)}_{\mu}] = \mu \, T^{(\omega)}_{\mu}$$

Wigner Eckart Theorem

Matrix Elements

$$\langle N \varphi^{j}_{m} | \; T^{J}_{M} \; | N' \varphi^{j'}_{m'} \rangle = A^{j' J j}_{m' M m} \; \langle N j \| T^{J} \| N' j' \rangle$$

$$m = M + m'$$

$$(j' - J) \leq j \leq (j' + J)$$

Selection rules :

$$T^{J}_{M} \quad : \quad \left. \begin{array}{l} \Delta m = (m_{\varepsilon} - m') = M \\ \Delta j = (j - j) \leq J \end{array} \right\}$$

If we know T^{J}_{M} between j and j' $\Rightarrow$ we know all $jm, j'm'$.
Two diffent tensors of same rank are equivalent.

$$T^{1}_{m} : \langle \varphi^{J\pm1}_{M\pm1} | \; T^{1}_{\pm1} \; | \varphi^{J}_{M} \rangle \qquad \langle \varphi^{J\pm1}_{M} | \; T^{1}_{0} \; | \varphi^{J}_{M} \rangle$$

$$\langle \varphi^{J}_{M\pm1} | \; T^{1}_{\pm1} \; | \varphi^{J}_{M} \rangle \qquad \langle \varphi^{J}_{M} | \; T^{1}_{0} \; | \varphi^{J}_{M} \rangle$$

Example

Two nuclear dipoles $I = 1/2$ $\quad D^{(1/2)} \times D^{1/2} = D^{(1)} + D^{(0)}$

$\{\alpha, \beta\}$ $\qquad A^{1/2\ 1/2\ 1}_{\pm 1/2 \pm 1/2\ M}$

$$\psi^{1}_{+1} = \alpha\alpha$$

$$\psi^{1}_{0} = \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha)$$

$$\psi^{1}_{-1} = \frac{1}{\sqrt{2}} (\beta\beta$$

$$\psi^{0}_{0} = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

Example

Matrix elements of Dipole dipole:

$\langle \psi^j_m | T^2_M | \psi^1_{\pm 1} \rangle$ $\quad j = 3, 2, 1$ $\quad m = M \pm 1$ $\quad \| \quad \langle \varphi^j_m | \; | \varphi^0_0 \rangle$

$\langle \varphi^j_m | T^2_M | \varphi^0_0 \rangle$

$j = 2$

$m = 0$

	ψ^1_1	ψ^1_0	ψ^1_{-1}	ψ^0_0
ψ^1_1	T^2_0	T^2_{-1}	T^2_{-2}	0
ψ^1_0	T^2_{+1}	T^2_0	T^2_{-1}	0
ψ^1_{-1}	T^1_{+2}	T^2_{+1}	T^2_0	0
ψ^0_0	0	0	0	0

$A^{121}_{mMm'} = a_{mMm'}$

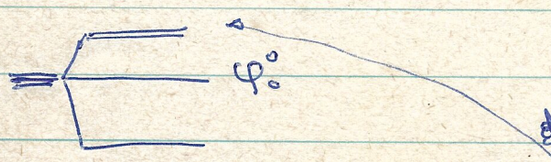
$\langle N'1 \| T^2 \| N1 \rangle = T$

$$T \begin{pmatrix} a_{101} & a_{1-10} & a_{1-2-1} & 0 \\ a_{011} & a_{000} & a_{0-1-1} & 0 \\ a_{-121} & a_{-110} & a_{-10-1} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad a_{000} = 1$$

$\langle \psi^1_0 | T^2_0 | \psi^1_0 \rangle = \langle N1 \| T \| N1 \rangle$

$\left\langle \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \right| \left(3 I_{z1} I_{z2} - I_1 \cdot I_2 \right) \left| \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \right\rangle$

$= 1$



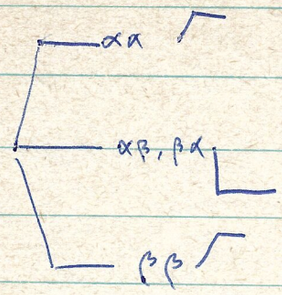
degeneracy

$a_{-1,2,1} = a_{1,-2,1}$; $a_{0,-1,1} = a_{1,0,-1}$

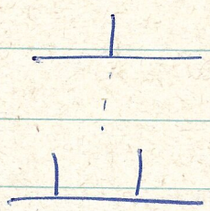
$a_{1,-1,0} = a_{0,1,-1}$

$a_{1,0,1} = a_{-1,0,-1}$

In high field. $H = -\gamma_H H_0 I_z = -\gamma_H H_0 T_0^1$



Truncation only T_0^2 left.





Selection Rule

$$\int \psi_1 \, X \, \psi_2 \, d\tau$$

or $\int \varphi_\nu^{(i)} \, X^{(k)} \, \varphi_\mu^{(j)} \, d\tau$ belong to $\Gamma^{(i)}$, $\Gamma^{(k)}$, $\Gamma^{(j)}$

1. Direkt product of two irr. repr. contains the total symm. representation A_1 once or not at all

$$\chi^{(i)\otimes(j)} = \chi^{(i)} \chi^{(j)} \qquad a_1 = \frac{1}{h} \sum_n \chi^{(i)} \chi^{(l)} \chi^{(j)} = \frac{1}{h} \sum_h \chi^{(i)} \chi^{(j)}$$

$\chi^{(i)}: \varphi_j$

$$\chi^{(l)}(A_n) = 1 \qquad \mathcal{P}(A_1) = \frac{1}{h} \Sigma \mathbb{P}(A_n)$$

$$\chi^{(l)} = 1 \rightarrow a_1 = \delta_{ij}$$

2. $$\int F(r)\, d\tau = \int \mathbb{P}(A_n) F(r)\, d\tau = \frac{1}{h} \int \Sigma \mathbb{P}(A_n) F(r)\, d\tau$$

$$= \frac{1}{h} = \int \mathcal{P}(A_1) F(r)\, d\tau = \int f^{(l)} d\tau \quad \text{if } a_1 = 1$$

$$= 0 \quad \text{if } a_1 = 0$$

$\Rightarrow$ if $F(r)$ contains A_1 irred. repr. $\int F(r)\, d\tau \neq 0$

$\Rightarrow$ $\Gamma^{(i)} \otimes \Gamma^{(j)} = \Sigma a_k \Gamma^{(k)}$ if $a_k = 0 \rightarrow \int \varphi^{(i)} \chi^{(k)} \varphi^{(j)} = 0$

$a_k \neq 0$

Reviews

Group : Elements, Multiplication (Table) A_n

Conjugated Elements $X^{-1} A_n X$

Class $\{C_i\} = X^{-1}\{C_i\}X$

Point groups Identity, Rotation, Reflection, Rotation-reflection, Inversion

Representation : same multiplication table. Most Matrices.

Equivalent representations $\Gamma'(A_n) = S^{-1}\Gamma(A_n)S$

Reducible repr.

Irreducible repres.

$\sum_i l_i^2 = h$ l_i dimens of i-th irred. repr.

Orthogonality rel. of characters of classes

Number of irred reps = number of classes

Direct product of Groups $A_n B_n \rightarrow$ Product of irr. rep are irred.

→ Decomposition of ind. repr. $a_j = h^{-1} \sum_R \chi(R)\,\chi^{(j)}(R)$

$= h^{-1} \sum_k N_k \chi(C^{(k)})\,\chi^{j}(C^{(k)})$

Reducable representations : Operators on vectors $D(A_i)\,\bar{x} = \bar{x}'$

—"— —"— : Operators of function $\mathbb{P}(A_i)\,f_\mu = \sum_\nu P_{\mu\nu}(A_i) f_\nu$

If $\{f_\nu\}$ creates irred. repr. $\Rightarrow \{f_\nu\}$ basis for irred. repr.

If $\{A_i\}$ is group of Hamiltonian $\Rightarrow$ $\mathbb{P}(A_i)\varphi_n$ have same E_n

$\varphi_n, \mathbb{P}(A_1)\varphi_n, \dots, \mathbb{P}(A_h)\varphi_n$ same energy normal degeneration

If φ_n are basis for irred. representations then
order of irred. repr. give possible numb of degenerate eigenf.

$\Rightarrow$

Every set of normal degen. eigenfunctions are characterized by irrad. repr.

Before examples: Direct product representations of product functions of same group.

$$\chi(A_n) = \chi_1(A_n)\,\chi_2(A_n)$$

Projection operators to find irred. repr.

$$\varphi^{(i)} \equiv \sum_n \chi^{(i)}(A_n)\,\mathbb{P}(A_n)$$

$$\varphi^{(i)} g = \frac{h}{l_i} \sum_\alpha a_{i\alpha} f_\alpha^{(i)}$$

Selection rules

$$\int \varphi_\nu^{(i)} X^{(k)} \varphi_\mu^{(j)}\, d\tau$$

If $\varphi_\nu^{(i)} X^{(k)} \varphi_\mu^{(j)}$ contains the A_1 irred. repr. then $= \int \mathbb{P}(A_n) f^{(i)} d\tau \neq 0$

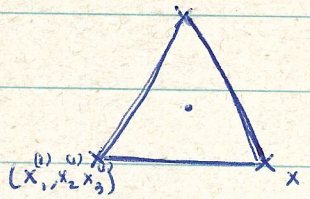
Direct product of two irred. repr. contains A_1 or once or not at all (and irred. repr. are equal then $a_{A_1} = 0$)

If $\Gamma^{(i)} \otimes \Gamma^{(j)} = \sum a_\ell \Gamma^{(\ell)}$ and $a_k = 0 \Rightarrow \int = 0$

$a_k \neq 0 \Rightarrow$

Molecular Vibrations

1) What are the energy levels of vibrating molecule
2) What are the allowed transitions in i.r. and raman.



Kinetic energy of nuclei $T = \frac{1}{2} \sum_{n=1}^{N} \sum_{i=1}^{3} M_n \dot{x}_i^{(n)\,2}$

$q_i^{(n)} = \sqrt{M_n}\, x_i^{(n)}$

mass-weighted displ. coor.

$= \frac{1}{2} \sum_{n=1}^{N} \sum_{i=1}^{3} \dot{q}_i^{(n)\,2}$ $\qquad q_i^{(n)} \equiv q_k$

$= \frac{1}{2} \sum_{k=1}^{3N} \dot{q}_k^2 = \frac{1}{2} \sum_{k=1}^{3N} \sum_{l=1}^{3N} \delta_{kl}\, \dot{q}_k \dot{q}_l$

Potential energy $V = \sum_k \left(\frac{\partial V}{\partial q_k}\right)_0 q_k + \frac{1}{2} \sum_k \sum_l \underbrace{\left(\frac{\partial^2 V}{\partial q_l \partial q_k}\right)}_{B_{ij}\text{ harmonic force constants (approx)}} q_k q_l$

(the $\left(\frac{\partial V}{\partial q_k}\right)_0$ term $= 0$)

Classical eqn. of motion is [illegible],

$$\frac{\partial V}{\partial q_k} = -\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_k} \qquad \left[\tfrac{1}{2} m v^2 \to m v \to m a\right]$$

$$\frac{1}{2} \sum_k B_{kl} q_l + \frac{1}{2} \sum_l \delta_{kl} \frac{d^2 q_l}{dt^2} = 0 \qquad k = 1, \ldots 3N$$

$$\sum_l B_{kl} q_l + \sum_l \delta_{kl} \frac{d^2 q_l}{dt^2} = 0 \qquad k = 1, \dots 3N$$

Take now C_k's

$$\sum_k C_k \left\{ \sum_l B_{kl} q_l + \sum_l \delta_{kl} \frac{d^2 q_l}{dt^2} \right\} = 0 \quad \text{so that}$$

$$\lambda Q + \frac{d^2 Q}{dt^2} = 0 \qquad Q = \sum_j C_j q_j$$

Can show that C_i are solution of $\sum_{k=1}^{3N} (B_{kl} - \lambda \delta_{kl}) C_k = 0$ for $l = 1, \dots 3N$

$\Rightarrow$ there are $3N$ equations $\rightarrow$ there are $3N$ sets of $3N$ C_k's:

with λ : $\det(B - \lambda E) = 0$

There are $3N$ λ's :

λ_1 : $C_{11}, \dots C_{3N,1}$ $\quad Q_1 = \sum_l C_{l,1} q_l$

λ_i : $C_{1i} \dots C_{3Ni}$ $\quad Q_i = \sum_l C_{li} q_l$

Q_i Normal coordinates

$$\frac{d^2 Q_k}{dt^2} + \lambda_k Q_k = 0 \qquad k = i, \dots 3N$$

$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$

$$V = \frac{1}{2} \sum \lambda_k Q_k^2$$

Quantum Mech eigenvalues and functions

$$-\frac{\hbar^2}{8\pi^2}\sum_i \frac{1}{M_i}\nabla_i^2 \psi_n(X_n) + V_n \psi_n(X_n) = E\,\psi_n(X_n)$$

Nuclear equation

Possible to approximate: $\psi_n = \psi^{tr}\psi^{rot}\psi^{vib}$

three eigenvalues eq E^{tr}, E^{rot}, E^{vib}

$E = E^{tr} + E^{rot} + E^{vib} + E^{e}$

Vibr equation:

$$\psi^{vib} = \prod_{l=1}^{3N-6} \varphi_l(Q_l)$$ product of independent single vibrational normal coordinates

$$W^{vib} = \sum W_l$$

$$\sum_{l=1}^{3N-6}\left(\frac{\hbar^2}{8\pi^2}\frac{d^2\varphi_l(Q_l)}{dQ_l^2} + \left(\tfrac{1}{2}\lambda_l Q_l^2 - W_l\right)Q_l\right) = 0$$

$$\Rightarrow \boxed{\frac{d^2\varphi_l(Q_l)}{dQ_l^2} + \frac{8\pi^2}{\hbar^2}\left(W_l - \tfrac{1}{2}\lambda_l Q_l^2\right)\varphi_l(Q_l) = 0}$$

One dimensional oscillator $\Rightarrow$

$$\varphi_l(Q_l) = N_l\, e^{-\frac{1}{2}\alpha_l Q_l^2} H_n(\sqrt{\alpha_l}\,Q_l)$$

↳ vibrational quantum number
Hermit polynomials.

$$W_l = \left(n + \tfrac{1}{2}\right)h\nu_l$$

$\alpha_i = \frac{4\pi\nu_i}{h}$, $\nu_i = \frac{\sqrt{\lambda_i}}{2\pi}$, $H_0 = 1$, $H_1(x) = 2x$

Total ~~ground~~ Energy

$$\sum_{l=1}^{3N-6} \left(n_l + \tfrac{1}{2}\right) h\nu_l$$

Ground state $W_0^{v.b} = \sum_{l=1}^{3N-6} \tfrac{1}{2} h\nu_l$ zero point energy

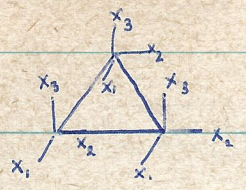
$$\Psi_0^{v.b} = N e^{-\frac{1}{2}\sum \alpha_l Q_l^2}$$

Fundamental levels are

$$n_1 = 0 \; \ldots \; n_{3N-1} = 0 \qquad n_k \neq 0$$

Energy $W_0^{v.b} + h\nu_k$

wave function $\propto \Psi_0^{v.b} Q_k$



Molecular Vibrations

position of nucleus i : $\{x_1^{(i)}(t),\ x_2^{(i)}(t),\ x_3^{(i)}(t)\}$

Kinetic energy $T = \frac{1}{2}\sum_{n=1}^{N}\sum_{i=1}^{3} M_n \dot{x}_i^{(n)2} = \frac{1}{2}\sum_{k=1}^{3N}\dot{q}_k^2 = \frac{1}{2}\sum_{k=1}^{3N}\sum_{l=1}^{3N} \delta_{kl}\dot{q}_k\dot{q}_l$

with $q_k = q_i^{(n)} = \sqrt{M_n}\, x_i^{(n)}$ and $k = 1, 2, \dots, 3N$

Potential energy $V = V_0 + \sum_k \left(\frac{\partial V}{\partial q_k}\right)_0 q_k + \frac{1}{2}\sum_l\sum_k \left(\frac{\partial^2 V}{\partial q_l \partial q_k}\right)_0 q_k q_l + \dots \cong \frac{1}{2}\sum_l\sum_k B_{kl} q_k q_l$

($V_0 = 0$, $\left(\frac{\partial V}{\partial q_k}\right)_0 = 0$; B_{kl}: harmonic force constant)

Classical equation of motion : $\frac{\partial V}{\partial q_k} = -\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_k}$

$$\boxed{\sum_l B_{kl} q_l + \sum_l \delta_{kl}\frac{d^2 q_l}{dt^2} = 0 \quad , \ k = 1, 2, \dots 3N}$$

It is possible to find coefficients C_{kl} so that

$$\boxed{\frac{d^2 Q_k}{dt^2} + \lambda_k Q_k = 0 \quad , \ k = 1, 2, \dots, 3N}$$

with $\boxed{Q_k = \sum_{l=1}^{3N} C_{lk}\, q_l}$ and

λ_k and C_{lk} given by $\det(\underline{\underline{B}} - \lambda \underline{\underline{E}}) = 0$

and $\sum_{k=1}^{3N}(B_{kl} - \lambda_l \delta_{kl})C_{kl} = 0$

Q_k are normal coordinates and the solution of the equation of motion is

$$Q_k = A_k \cos(\sqrt{\lambda_k}\, t + \varepsilon_k)$$

and

$$q_l = \sum_k C_{kl} A_k \cos(\sqrt{\lambda_k}\, t + \varepsilon_k)$$

Furthermore $T = \frac{1}{2}\sum_{k=1}^{3N}\dot{Q}_k^2$ and $V = \frac{1}{2}\sum_{k=1}^{3N}\lambda_k Q_k^2$

Quantum Mechanical eigenvalue equation

Approximations: nuclear wavefunction $\psi_n = \psi^{tr}\,\psi^{rot}\,\psi^{vib}$

energies $E_n = E^{tr} + E^{rot} + E^{vib} + E^{o}$

From classical $T = \frac{1}{2}\sum_{k=1}^{3N}\left(\frac{dQ_k}{dt}\right)^2$ and $V = \frac{1}{2}\sum_{k=1}^{3N}\lambda_k Q_k^2$

(*) and with $\psi^{vib} = \prod_{l=1}^{3N-6}\varphi_l(Q_l)$ and $E^{vib} = \sum_{l=1}^{3N-6}E_l$

$$\sum_{k=1}^{3N-6} -\frac{h^2}{8\pi^2}\frac{d^2\varphi_k(Q_k)}{d^2Q} + \sum_{k=1}^{3N-6}\frac{1}{2}\lambda_k Q_k^2\varphi_k = \sum_{k=1}^{3N-6}E_l\,\varphi_k(Q_k)$$

$$\boxed{\frac{d^2\varphi_k(Q_k)}{d^2Q_k} + \frac{8\pi^2}{h^2}\left(E_k - \frac{1}{2}\lambda_k Q_k^2\right)\varphi_k(Q_k) = 0}$$

This represents one dimensional oscillator $\Rightarrow$

$$\varphi_l^{(n)}(Q_l) = N_l\, e^{-\frac{1}{2}\alpha_l Q_l^2}\, H_n\left(\sqrt{\alpha_l}\,Q_l\right)$$

↳ Hermit polynomial

n: quantum number

$$E_l = \left(n+\tfrac{1}{2}\right)h\nu_l \qquad \alpha_l = \frac{4\pi^2\nu_l}{h}$$

$$\nu_l = \sqrt{\lambda_l}/2\pi$$

$$H_0(x) = 1$$

$$H_1(x) = 2x$$

(*) There are 3 degrees of freedom for translation with $\lambda_l = 0$ and 3 degrees of freedom for rotation with $\lambda_l = 0$

$n=1$ $\left\{\right.$ $\varphi_1^{(0)} Q_1 \varphi_2^{(0)} \cdots \varphi_{3N-6}^{(0)}$ $\quad E_0 + h\nu_1$; $E_0 + h\nu_2$; ---- ; $\left(\varphi_1^{(0)} \varphi_2^{(0)} \cdots \varphi_k^{(0)} Q_k \varphi_{k+1}^{(0)} \cdots \varphi_{3N-6}^{(0)}\right)$ $\quad E_0 + h\nu_k$; ---- ; $E_0 + h\nu_{3N-6}$

$n=0$ $\left\{\right.$ $\underline{\sum_\ell \varphi_\ell^{(0)} = \sum_\ell N_\ell \exp(-\tfrac{1}{2}\alpha_\ell Q_\ell^2)}$ $\quad E_0 = \frac{1}{2} h \sum_{\ell=1}^{3N-6} \nu_\ell$

for $n=1$ $\qquad \varphi_\ell^{vib} = Q_\ell \prod_{k=1}^{3N-6} \varphi_k^{(0)}$

$\equiv$

$\#$

What are the degeneracies of the $n=1$ levels !

What are the (symmetry) irreducible representations of the molecule and what are the their basis functions.

! We know $\varphi_\ell^{vib} \propto Q_\ell$ and therefore Q_ℓ's must be a basis for the irreducable representations !

The result of a calculation of the characters of the representation with basis $\{Q_\ell\}$ will tell us which Q_ℓ belongs to ~~not~~ which irred. repr. If two Q_ℓ's belong to same irred. repr. then the λ_ℓ's will be equal.

With $a_j = h^{-1} \sum_n \chi(A_n) \chi^{(j)}(A_n)$ and $P^{(j)} = \frac{1}{h} \sum_n \chi^{(j)}(A_n) P(A_n)$ all questions could be solved but how do we find χ's ?!

We can however find the representation of the basis set $\{q_\ell\}$ and ~~the~~ obtain the characters. With the relation

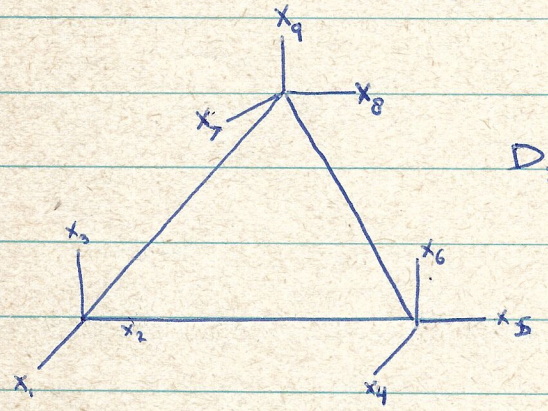
$$Q_\ell = \sum_k C_{k\ell}\, q_k$$

we get

$$\Gamma^{(i)}(Q_\ell) = C^{-1}\, \Gamma^{(i)}(q)\, C$$

and

$$\chi_Q(A_n) = \chi_q(A_n)$$



D_{3h}

$$P(A_n)\begin{pmatrix} q_1 \\ \vdots \\ q_g \end{pmatrix} = \underline{P}\begin{pmatrix} q_1 \\ \vdots \\ q_g \end{pmatrix}$$

Character table: (number of coordinates which are unchanged under A_n)

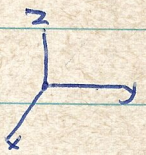
	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
χ^0	9	0	−1	3	0	1

What are the translational and rotational irred. repr. and there characters.

$$\chi^{vib} = \chi^0 - \chi^{tr} - \chi^{rot}$$

Translational

The three Q_i's corresponding to translation are generating a three dimentional representation Γ^{tr}. This representation is equivalent to representation of (x, y, z):

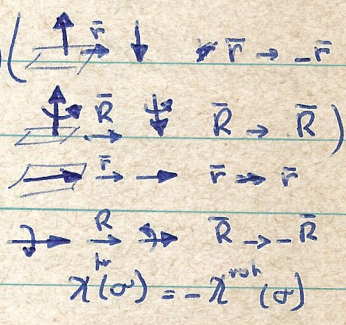


	E	$2C_3$	$3C_3$	σ_h	$2S_3$	$3\sigma_v$
χ^{tr}	3	0	−1	1	−2	1
$\chi^{o}\cdot\chi^{tr}$	6	0	0	2	2	0

Rotational

The three Q_i's corresponding to rotation are generating a three dimentional representation Γ^{rot}. This representation is equivalent to representation of pseudo-vector (R_x, R_y, R_z)

($\underline{R}$ is different from $\underline{r}$ only by reflection)



	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
χ^{rot}	3	0	−1	−1	2	−1

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\chi^{o}\cdot\chi^{tr}\cdot\chi^{rot}$	3	0	1	3	0	1

Decomposition of representation Γ^{o}

Γ^{tr} is given in character table $\quad \Gamma^{E'}, \Gamma^{A_2''}$

Γ^{rot} —"— —"— $\quad \Gamma^{E''}, \Gamma^{A_2'}$

$$\boxed{\Gamma^{vib} = \Gamma^{A_1'} + \Gamma^{E'}}$$

$$a_{A_1'} = \frac{1}{12}(3.1 + 1.1.3 + 3.1 + 1.1.3) = 1 \quad \to 1$$

$$a_{E'} = \frac{1}{12}(3.2 + 3.2) = 1$$

Basis functions are :

$$\varphi^{A_1'} = \sum \chi^{A_1'}(A_n)\, \mathbb{P}(A_n)$$

$$= 1\,\mathbb{P}(E) + 1\,(\mathbb{P}(C_3) + \mathbb{P}(C_3^2)) + \cdots$$

$$\varphi^{A_1'}$$

$$q_1 = q_1 + q_4 + q_7 - q_1 - q_4 - q_7 - q_1 - q_4 - q_7 + q_1 + q_4 + q_7 = 0$$

$$q_2 = q_2 + \tfrac{1}{2}\sqrt{3}\,q_6 - \tfrac{1}{2}q_5 - \tfrac{1}{2}\sqrt{3}\,q_9 - \tfrac{1}{2}q_8 + \tfrac{1}{2}\sqrt{3}\,q_3 + \tfrac{1}{2}q_2 - x_5 - \tfrac{1}{2}\sqrt{3}\,x_9 - \tfrac{1}{2}x_8$$

(C_3, C_3, C_2, C_2, C_2)

$$+ q_2 + \tfrac{1}{2}\sqrt{3}\,q_6 - \tfrac{1}{2}q_5 - \tfrac{1}{2}\sqrt{3}\,q_9 - \tfrac{1}{2}q_8 + \tfrac{1}{2}\sqrt{3}\,q_3 + \tfrac{1}{2}q_2 - x_5 - \tfrac{1}{2}\sqrt{3}\,x_9 - \tfrac{1}{2}x_8$$

(σ_h, S_3, S_3, σ_v, σ_v, σ_v)

$$= (1 + \tfrac{1}{2} + 1 + \tfrac{1}{2})\,q_2 + (\tfrac{1}{2}\sqrt{3} + \tfrac{1}{2}\sqrt{3})\,q_3 + (-\tfrac{1}{2} - 1 - \tfrac{1}{2} - 1)\,q_5$$

$$(\tfrac{1}{2}\sqrt{3} + \tfrac{1}{2}\sqrt{3})\,q_6 + (-\tfrac{1}{2} - \tfrac{1}{2} - \tfrac{1}{2} - \tfrac{1}{2})\,q_8 + (-\tfrac{1}{2}\sqrt{3} - \tfrac{1}{2}\sqrt{3} - \tfrac{1}{2}\sqrt{3} - \tfrac{1}{2}\sqrt{3})\,q_9$$

$$= 3q_2 - 3q_5 - 2q_8 + \sqrt{3}\,q_3 + \sqrt{3}\,q_6 - 2\sqrt{3}\,q_9 \equiv Q_{A_1'}$$

[redacted]

etc

Exercises

1. Show that:

	E	$C(\theta)$	σ	$S(\theta)$	i
χ^{tr}	3	$1+2\cos\theta$	1	$-1+2\cos\theta$	-3
χ^{rot}	3	$1+2\cos\theta$	-1	$1-2\cos\theta$	3

2. Calculate the irreducible representations (translational, rotational and vibrational) of the fundamental vibrational levels of H_2O. Calculate the normal coordinates of this the molecule and ~~show~~ the schematic picture of these vibrations.

Infrared Spectroscopy

Irradiation field E interacts with electric dipole moment of molecul

$$-\bar{\mu} \cdot \bar{E}$$

Transition probability between two levels $\psi^{(0)}$ and $\psi^{(l)}$ is according to golden rule proportional to

$$\left| \int \psi^{(0)} \mu \psi_l^{(l)} \, d\tau \right|^2$$

Selection rule $\int \psi^{(0)} \bar{\mu} \psi_l^{(l)} \, d\tau \neq$ or $= 0$

$\psi^{(0)} : \Gamma^{(A_1)}$

$\psi_l^{(l)} : \Gamma^{vib} = \sum a_i \Gamma^{(i)}$

$\bar{\mu} : \Gamma^{tr} = \sum_i b_i \Gamma^{(i)}$

$\bar{\mu}$ behaves like vector and therefore it is a basis for Γ^{tr} representation just like translation vector it self.

If $a_i \neq 0$ and $b_i \neq 0$ for same ith irrad. repr. $\Rightarrow$ the direct product functions $\bar{\mu} \psi_l^{(l)}$ contains Γ^{A_1} and with $\psi^{(0)}$ als $\Gamma^{(A_1)}$ the integral is non zero

Example

$\Gamma^{vib} = \Gamma^{A_1} + \Gamma^{E'}$

$\Gamma^{tr} = \Gamma^{E'} + \Gamma^{A_2''}$

} only level with E' is allowed for IR spectroscopy.

Raman Spectra

Irradiation ν is scattered ν, $\nu \pm \nu_p$
└ fundamental frequency.

Irradiation induces dipole moment:

$$M_k = \sum_{j=1}^{3} \alpha_{kj} E_j$$

↳ polarizability

α_{kl} is trasformed by symmetry operations in same way as

$x_1^2, x_2^2, x_3^2, \dots x_i x_j$ 6 fuctions → representation Γ^{α}

⟹ irred. basis set is given in character tables

Probability $\int \psi^{(0)} \alpha_{ij} \psi_p^{(1)} d\tau$

$\Gamma^{(\alpha)}$ for D_{3h} A_1', E', E''.

Exercise

Calculate the allowed fundamental Raman and ir transition

Test 6. July 6, 1978

Group Theory and Chemistry

by Shimon Vega

1. Is the function x^2z a basis function of an irreducible representation of C_{4v}?

   If yes; Which irreducible representation. Calculate the corresponding basis functions of this representation.

   If not: Calculate the basis functions, containing the term x^2z, of the irreducible representations.

2. a. Calculate the full rotational product functions of the eigen functions (α and β) of two nuclear spins ($j=\frac{1}{2}$). Using Clebsh-Gordon coefficients. Assign these functions according to their total angular momentum coefficients J and M.

   b. Which matrix element between these product functions are different from zero for

      (i) a Zeeman field Hamiltonian ($\gamma\hbar H_0 I_z$).
      (ii) a nuclear dipole-dipole Hamiltonian (see your notes)

   c. Show the schmatic energy level diagrams for these two cases.

3. Consider the correlation diagram of two d-electrons at an action in a tetrahedral environment (fig. 1).

   a. Five a full description of the energy level assignments in this figure.

   b. How does the corresponding diagram for two p-electrons look like.

   c. What will happen to fig. 1 if the symmetry is lowered by making $a \neq b = c$ in fig. 2.

4. a. Calculate the degeneracies of the fundamental vibrational levels of A_3B_3 (fig. 3).

   b. What are the allowed Raman and I.R. transitions and calculate some of the normal modes.

   c. What will happen with the fundamental levels and the allowed transitions when A=B.

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