1 Abstract Group Theory

Lagrange's Theorem:

- For a subgroup H of G: $\frac{|G|}{|H|} = i \in \mathbb{N}^+$

  index i: number of distinct cosets

  $\implies$ Groups of prime order are cyclic

  pitfall: you can have none or more than one subgroup of the same order

Abelian groups:

- Group containing only second order elements are Abelian.
- Cyclic groups are Abelian.

  $\implies$ A group of prime order is Abelian.

- all subgroups of an Abelian group are invariant

First group isomorphism theorem:

- $f : G \to L$ is injective (isomorphism) if $\ker(f) = E$
- a matrix representation is faithful / isomorphic to G if $D(g) \neq I$ for $g \neq E$

$\implies$ no other element has the same character as E

Schur's Lemmas: $D^{(i)}(G)M = MD^{(j)}(G) \implies M = \delta_{ij}\alpha I$

1.1 Conjugate Classes

- identity E forms a class of its own
- conj. elements have same order: $g^k = E \implies (g')^k = E$
- G is abelian iff every conjugacy class has size one

Point Groups:

- conjugation changes axis of rotation

  $\implies$ classes consist of (im)proper rotations of the same angle, such that their axes can be mapped onto each other

- conjugating a rotation by a reflection yields the inverse rotation

  $\implies$ C_n and C_n^{-1} belong to the same class if the group contains σ_v or S_n

1.2 Generators

Finite groups: Elements whose products generate the whole group. Often not unique.

example: generate C_{3v} from products of C_3 and σ_v

2 Character Table Completion

1. # IRREPs = # Conjugate Classes
2. First column $\chi(E)$ using $\sum_j n_j^2 = |G| = \sum_C n_C$
3. homomorphism: $g^n = E \iff D(g)^n = I$
   - Abelian $\implies$ 1D IRREP $\implies$ $\chi(g) = \exp\left(i\frac{2\pi}{n}k\right)$
   - g, g^{-1} in same class $\implies$ $\chi(g) = \chi(g)^*$ is real
   - then, if n odd (e.g. C_5) then it is $+1$
4. Row and column orthogonality

Row orthogonality

$$(\chi^{(i)}, \chi^{(j)}) = \sum_g \chi^{(i)}(g)^* \chi^{(j)}(g) = |G|\delta_{ij}$$

Column orthogonality

$$\sum_i n_C (\chi^{(i)}(C))^* \chi^{(i)}(C') = |G|\delta_{CC'}$$

The basis functions $|k_i\rangle$ of an IRREP k are defined as

$$\hat{T}(g)\,|k_i\rangle = \sum_j D(g)_{ji}^{(k)}\,|k_j\rangle$$

3 Degeneracy and Lifting

A $n \times n$ IRREP has n degenerate eigenfunctions ψ as a basis.

- Perturbation can only decrease symmetry $G' \subset G$
- new rep: select from $D(G)$ the matrices $D(g' \in G')$
  - If new rep. is reducible: lift degeneracy; split level
  - guess or use character orthogonality to decompose

trick: In questions about lifting degeneracy, use only rotational subgroup SO(3). For selection rules, use full O(3).

pitfall: Example $\Gamma^2 = A_1 \oplus 2E$, then the 2 E have different energies in general (each with 2-fold degeneracy).

4 Normal Modes in Molecules

Normal modes transform as (form basis of) IRREPs of the symmetry group of the potential

- basis: 3N-component N-atom displacement vectors
- representation matrices $D^{(3N)} = R \otimes A$
  - R exchanges equilibrium positions of N atoms
  - $A(g)$ is action on each atom (e.g. rotation)
- n_g: number of atoms that stay in place after g

In practice, find normal modes IRREPs as follows:

1. Write down table (group elements, n_g, φ, (im)proper)
2. Decompose into IRREPs: $\chi^{(\text{vib})} = \sum_i a_i \chi^{(i)}$

$$a_i = \frac{1}{m} \sum_g \chi^{(i)}(g)^* \chi^{(\text{vib})}(g)$$

3. if IRREP turns up twice ($a_i \neq 1$), cannot deduce normal modes / eigenstates
   - normal mode is lin. comb. of projection op. results

Projection operators:

$$\hat{P}^{(i)}_{jk} \propto \sum_g D^{(i)}_{jk}(g)^* \hat{T}(g)$$

5 Selection Rules

- $\langle\psi_i| \hat{T}'_\alpha |\psi_j\rangle \neq 0$ only if $D^{(i)} \otimes D' \otimes D^{(j)}$ contains A_{1g}
  - Calculate $\chi^{(D^{(i)} \otimes D' \otimes D^{(j)})}(g) = \chi^{(i)}(g)\chi'(g)\chi^{(j)}(g)$
  - Scalar product with $\chi^{(A_1)}$ is 0 $\implies$ forbidden
- fundamental transition $|0\rangle \to |1\rangle$: ground state transforms as totally symmetric IRREP A_{1g}

  trick (PS10) use direct product parity rules

$$\text{gerade:} \quad \chi_g \otimes \chi_g = \chi_u \otimes \chi_u = \bigoplus \chi_g$$

$$\text{ungerade:} \quad \chi_g \otimes \chi_u = \bigoplus \chi_u \neq A_{1g}$$

5.1 Perturbation of spherically symmetric $\hat{H}$

For degeneracy, only use SO(3), but for transitions, need O(3)

- Since $\hat{i} Y_{lm} = (-1)^l Y_{lm}$, have extra factor $(-1)^l$

$$\chi^{(l)}(i \otimes R(\varphi)) = (-1)^l \chi^{(l)}(R(\varphi))$$

- Can then calculate characters with

$$S_n(\varphi) = iC_n(\varphi + \pi)$$

  e.g.:

$$\chi(\sigma_h) = \chi(i \otimes C_2) = \chi(i \otimes R(\pi))$$
$$\chi(S_4) = \chi(i \otimes C_4^{-1}) = \chi(i \otimes R(\frac{\pi}{2}))$$
$$\chi(S_n) = \chi(i \otimes C_2 \otimes C_n) = \chi(i \otimes R(\pi + \frac{2\pi}{n}))$$

O(3)	$R(\varphi)$	$i = i \otimes E$	$i \otimes R(\varphi)$	basis
$\chi^{(l)}$	$\frac{\sin[(2l+1)\,\varphi/2]}{\sin(\varphi/2)}$	$(-1)^l(2l+1)$	$(-1)^l \chi^{(l)}(R(\varphi))$	Y_{lm}

- perturbation example: Octahedral arrangement
  - new $\hat{H}$ has symmetry of rotational subgroup of O_h
  - calculate characters $\chi^{(l)}(O_h)$ via table
  - decompose into IRREPs of O_h
    * $l = 2$ level is split into $\chi^{(2)} = E \oplus T_2$
  - selection rules between split states
    * use symmetry (g / u) arguments

6 Selection Rules and Wigner Eckart

Perturbation $V = V_0 \underbrace{xy\ldots}_{\omega \text{ factors}}$

Selection rules:
Have matrix elements $\langle j'm'| V |jm\rangle$

1. write $V \propto \sum_\mu Y_{\omega,\mu}$ using spherical coordinates
2. Clebsch-Gordan series

$$D^{(\omega)} D^{(j)} = \bigoplus_{L=|\omega-j|}^{\omega+j} D^{(L)} = D^{|\omega-j|} \oplus \cdots \oplus D^{\omega+j}$$

$$\implies |j' - j| \leq \omega$$

3. selection rules for $\langle j'm'| Y^{(\omega)}_\mu |jm\rangle$ are

$$j' = j + \omega, \ldots, |j - \omega|$$
$$\text{C-G coeff.:} \quad m' = \mu + m$$
$$(\text{left}) = (\text{center}) + (\text{right})$$

4. finally, using parity $(-1)^j$,

   V even: $1 = (-1)^{j+j'}$, so $\Delta j = 0, 2, \ldots$

   V odd: $1 = (-1)^{j+j'+1}$, so $\Delta j = 1, 3, \ldots$

Wigner-Eckert theorem:

$$\langle N'j'm'| \hat{T}^{(\omega)}_\mu |Njm\rangle = C^{j\omega j'}_{m\mu m'} \underbrace{\langle N'j'| \left|\hat{T}^{(\omega)}\right| |Nj\rangle}_{\text{reduced matrix element}}$$

where

$$\hat{T}^{(\omega)}_\mu = r^\omega Y_{\omega,\mu}$$

1. Find $\langle 0,0||T^\omega|\rangle\, N,\omega \propto C^{-1} r^\omega_{0N}$
2. then other matrix elements are written down as (e.g.)

$$\langle 0,0,0| \underbrace{r^2 Y_{2,\mp 2}}_{T^{(2)}\mp 2} |N,2,\pm 2\rangle = C^{022}_{0\pm 2\mp 2} \langle 0,0| \left|T^{(2)}\right| |N,2\rangle$$

6.1 Spherical Harmonics

- First spherical harmonic: $Y_{0,0} = \frac{1}{\sqrt{4\pi}}$
- symmetry under inversion: $(-1)^l$

	C_n	σ_v	σ_h
φ	$\varphi + \frac{2\pi}{n}$	-φ	
θ			$\pi - \theta$

Table 1: Action of symmetry operations