Clebsch - Gordan coefficients

<u>Def</u>: Consider direct product repre of two IRREPs,

$$\rho^{\mu\times\nu} = \rho^{\mu} \otimes \rho^{\nu}$$

with characters $\chi^{\mu\times\nu}(g) = \chi^{\mu}(g)\chi^{\nu}(g)$. Then the decomposition

$$\rho^{\mu\times\nu} = \bigoplus_{\sigma} m_{\sigma}^{\mu\times\nu} \rho^{\sigma}$$

is called Clebsh - Gordan series and the coefficients satisfy

$$m_{\sigma}^{\mu\times\nu} \equiv (\mu\nu\sigma) = \frac{1}{\# G} \sum_{g} \chi^{\sigma}(g)^{*} \chi^{\mu}(g)\chi^{\nu}(g)$$

- $(\mu\nu\sigma) = (\nu\mu\sigma)$ determined unambiguously for any finite or compact Lie $\left(\sum_{g} \to \int_{G} dg\right)$ group
- bases of invariant subspaces for respective ρ^{σ}:

$$\{\psi_j^{\mu}\varphi_e^{\nu}\} \to \{\psi_s^{\sigma,\lambda_\sigma} \,|\, s = 1,\dots,d_\sigma;\ \lambda_\sigma = 1,\dots,(\mu\nu\sigma)\}$$

$$\boxed{\psi_s^{\sigma,\lambda_\sigma} = \sum_{je} \psi_j^{\mu}\psi_e^{\nu}\,(\mu j, \nu e \,|\, \sigma \lambda_\sigma s)}$$

- $d_\mu d_\nu \times d_\mu d_\nu$ matrix $(\mu j, \nu e \,|\, \sigma \lambda_\sigma s)$ is matrix of Clebsch - Gordan coefficients (CGc)
- CGc not determined unambiguously:
  1, $(\mu\nu\sigma) = 1 \Rightarrow$ up to arbitrary phase factor $e^{i\omega}$
  2, $(\mu\nu\sigma) > 1 \Rightarrow$ up to $\mathbb{C}$ transf. matrix $(\mu\nu\sigma)\times(\mu\nu\sigma)$
  (we can "mix" subspaces corresp. to equivalent IRREPs)

- normalization of CGc:

- usually $\sum_{jl} |(\mu j, \nu l | \sigma \lambda_\sigma s)|^2 = 1$ (*)

$$\Rightarrow (\Psi_s^{\sigma, \lambda_\sigma} | \Psi_{s'}^{\sigma' \lambda_{\sigma'}}) = \delta_{\sigma\sigma'} \delta_{\lambda_\sigma \lambda_\sigma'} \delta_{ss'} \quad \text{for}$$

$$(\Psi_j^\mu \varphi_l^\nu | \Psi_{j'}^\mu \varphi_{l'}^\nu) = \delta_{jj'} \delta_{ll'}$$

$$\Rightarrow \Psi_s^{\sigma, \lambda_\sigma} = \sum_{jl} \Psi_j^\mu \varphi_l^\nu (\mu j \nu l | \sigma \lambda_\sigma s) \quad \text{is unitary transformation}$$

→ inverse transform.

$$\Psi_j^\mu \varphi_l^\nu = \sum_{\sigma \lambda_\sigma} \Psi_s^{\sigma, \lambda_\sigma} (\sigma \lambda_\sigma s | \mu j \nu l) = \sum_{\sigma \lambda_\sigma s} \Psi_s^{\sigma \lambda_\sigma} (\mu j \nu l | \sigma \lambda_\sigma s)^*$$

Unitarity conditions

$$\sum_{jl} (\mu j \nu l | \sigma \lambda_\sigma s)^* (\mu j \nu l | \sigma' \lambda_\sigma' s') = \delta_{\sigma\sigma'} \delta_{\lambda_\sigma \lambda_\sigma'} \delta_{ss'}$$

$$\sum_{\sigma, \lambda_\sigma, s} (\mu j \nu l | \sigma \lambda_\sigma s)^* (\mu j' \nu l' | \sigma \lambda_\sigma s) = \delta_{jj} \delta_{ll'}$$

Example (cf. tutorial MO-LCAO for H_3^{2+}) ; C_{3v} group

- $\Psi_1^E = \frac{1}{\sqrt{6}} (2\phi_1^{1s} - \phi_2^{1s} - \phi_3^{1s})$ $\qquad \varphi_1^E = (\ 2s\ )$

  $\Psi_2^E = \frac{1}{\sqrt{2}} (\phi_2^{1s} - \phi_3^{1s})$ $\qquad \varphi_2^E = (\ 2s\ )$

- we already have the matrices $D^E(g)$ from the tutorial & they correspond to the above basis (as the matrices were used to obtain these vectors)

- C_{3v} : $E \otimes E = A_1 \oplus A_2 \oplus E \Leftrightarrow (E E A_1) = (E E A_2) = (E E E) = 1$
  (C-G series)

- how do we construct the basis of $E \otimes E$?

1, it has sym & anti-sym. component & the antisym. component is 1D $\Rightarrow$ it must be A_2 & the corresp. vector is

$$\boxed{\Psi_1^{A_2} = \frac{1}{\sqrt{2}}\left(\psi_1^E \varphi_2^E - \psi_2^E \varphi_1^E\right)} \Rightarrow (E2, E1 \mid A_2 1 1) = -\frac{1}{\sqrt{2}}$$

2, A_1 IRREP: $P^{A_1} \psi_1^E \varphi_1^E = \frac{1}{\#G} \sum_g \chi^{A_1}(g)^* \, T(g) \psi_1^E \varphi_1^E$

$$= \frac{1}{\#G} \sum_g \sum_{jl=1}^{2} \psi_j^E \varphi_l^E D^E(g)^j_1 D^E(g)^l_1 = \frac{1}{6} (6 \times 2 \times 2 \text{ contribs})$$

$$= \frac{1}{6}\left(3 \psi_1^E \varphi_1^E + 3 \psi_2^E \varphi_2^E\right) \Rightarrow \boxed{\Psi_1^{A} = \frac{1}{\sqrt{2}}\left(\psi_1^E \varphi_1^E + \psi_2^E \varphi_2^E\right)}$$

3, E IRREP is generated by $\perp$ complement

$$\Rightarrow \boxed{\begin{aligned} \Psi_1^E &= \frac{1}{\sqrt{2}}\left(\psi_1^E \varphi_2^E + \psi_2^E \varphi_1^E\right) \\ \Psi_2^E &= \frac{1}{\sqrt{2}}\left(\psi_1^E \varphi_1^E - \psi_2^E \varphi_2^E\right) \end{aligned}} \Rightarrow (E1, E2 \mid E 1 1) = \frac{1}{\sqrt{2}}$$

Note: • ad 2, we do not need to compute anything due to the general observation:

- If repre D of G consists of OG matrices ($D^T D = \mathbb{1}$) then $\sum_i \psi_i \varphi_i$ is invariant subspace of trivial repre:

$$T(g) \sum_i \psi_i \varphi_i = \sum_i \sum_{kl} \psi_k \varphi_l D^k_i D^l_i = \sum_{kl} \psi_k \varphi_l \overbrace{\sum_i (D^T)_l^{\,i} D^k_i}^{\delta_{kl}} = \sum_k \psi_k \varphi_k$$

- useful for point groups as they are $\subset O(3)$

WIGNER - ECKART THEOREM

Def: Invariant scalar operator (under the action of G on $\mathcal{H}$) is an operator satisfying $(\mathcal{U}(g)^{-1} = \mathcal{U}(g)^{+})$

$$\Omega' \equiv \mathcal{U}(g)\Omega\,\mathcal{U}(g)^{+} = \Omega \iff \Omega\,\mathcal{U}(g) = \mathcal{U}(g)\Omega$$

- inspect matrix element

$$\boxed{M^{\mu\nu}_{kl} = \langle \psi^{\mu}_{k} | \Omega | \varphi^{\nu}_{l} \rangle}$$

for ψ^{μ}_{k} & φ^{ν}_{l} basis of two IRREPs ρ^{μ} & ρ^{ν}, resp.

a, $\mathcal{U}(g)\varphi^{\nu}_{l} = \sum \varphi^{\nu}_{i} D^{\nu}(g)^{i}_{l}$

b, $\tilde{\varphi}^{\nu}_{l} = \Omega\varphi^{\nu}_{l} \Rightarrow \mathcal{U}(g)\tilde{\varphi}^{\nu}_{l} = \mathcal{U}(g)\Omega\varphi^{\nu}_{l} = \Omega\,\mathcal{U}(g)\varphi^{l}_{\nu} = \Omega\sum_{i}\varphi^{\nu}_{i} D^{\nu}(g)^{i}_{l}$

$$= \sum \tilde{\varphi}^{\nu}_{i} D^{\nu}(g)^{i}_{l}$$

$\Rightarrow \tilde{\varphi}^{\nu}_{l}$ is again basis of the same IRREP ρ^{ν}

c, $M^{\mu\nu}_{kl}$ is invariant under the action of G (by def!)

- $\mathcal{U}(g) M^{\mu\nu}_{kl} \equiv \langle \mathcal{U}(g)\psi^{\mu}_{k} | \mathcal{U}(g)\Omega\,\mathcal{U}(g)^{+} | \mathcal{U}(g)\varphi^{\nu}_{l} \rangle \overset{\text{unitarity}}{=} \langle \psi^{\mu}_{k} | \Omega | \varphi^{\nu}_{l} \rangle$
  - holds for arbitrary (i.e., non-invariant)
- Ω invariant $\Rightarrow$ we can also write

$$\mathcal{U}(g) M^{\mu\nu}_{kl} = \langle \mathcal{U}(g)\psi^{\mu}_{k} | \mathcal{U}(g)\Omega\varphi^{\nu}_{l} \rangle \qquad /\Omega \text{ invar.}$$

$$= \langle \mathcal{U}(g)\psi^{\mu}_{k} | \Omega | \mathcal{U}(g)\varphi^{\nu}_{l} \rangle$$

$$= \sum_{ij} [D^{\mu}(g)^{i}_{k}]^{*} D^{\nu}(g)^{j}_{l} \langle \psi^{\mu}_{i} | \Omega | \varphi^{\nu}_{j} \rangle = M^{\mu\nu}_{kl} \quad / \sum_{g}$$

$$\Rightarrow \#G\, M^{\mu\nu}_{kl} = \sum_{ij} \langle \psi^{\mu}_{i} | \Omega | \varphi^{\nu}_{j} \rangle \frac{\#G}{d_{\mu}} \delta_{\mu\nu}\delta_{ij}\delta_{kl}$$

$$\Rightarrow \boxed{M^{\mu\nu}_{kl} = \delta_{\mu\nu}\delta_{kl}\, h^{\mu} \qquad h^{\mu} \equiv \frac{1}{d_{\mu}} \sum_{i} \langle \psi^{\mu}_{i} | \Omega | \varphi^{\nu}_{i} \rangle}$$

$\langle \psi_k^\mu | \Omega | \varphi_\ell^\nu \rangle = \delta_{\mu\nu} \delta_{k\ell} \, h^\mu$

$h^\mu = \frac{1}{d_\mu} \sum_i \langle \psi_i^\mu | \Omega | \varphi_i^\nu \rangle$ ... reduced matrix element
... indep. of k & ℓ !

$\Rightarrow$ selection rules for matrix elements

a) $M_{k\ell}^{\mu\nu} = 0$ for ρ^μ not equiv. to ρ^ν

b) $M_{k\ell}^{\mu\nu} = 0$ for $k \neq \ell$ (basis vectors corr. to the same IRREP but different column)

Generalization: tensor operator

- Let (ρ^μ, V^μ) & (ρ^ν, V^ν) be IRREPs of a group G & $A_1 : V^\mu \to V^\nu$ is a linear mapping. We define operator addition

$$(A_1 + A_2)\psi = A_1 \psi + A_2 \psi \in V^\nu \quad \forall \psi \in V^\mu$$

and multiplication of an operator by a scalar

$$(\alpha A)\psi = \alpha (A\psi) \in V^\nu \quad \forall \psi \in V^\mu \qquad (0A = 0 \text{ ... zero op.})$$

Then • $A_1 : V^\mu \to V^\nu$ forms a lin. vect. space $L(V^\mu, V^\nu)$ over the same field as V^μ & V^ν

- $\dim L(V^\mu, V^\nu) = d_\mu d_\nu$ (Shephard; Oliver & Boyd, 1966)

(motivation: $A_{ij} \psi_k = \delta_{ik} \varphi_j$ for ψ_k basis in V^μ & φ_j basis in V^ν $\Rightarrow$ A_{ij} is a basis of $L(V^\mu, V^\nu)$)

- action of G on $L(V^\mu, V^\nu)$:

$T^\mu(g)\psi^\mu = \psi'^\mu \qquad T^\nu(g)\varphi^\nu = \varphi'^\nu$ are ops from ρ^μ & ρ^ν

$\Rightarrow \tilde{T}(g) A \equiv T^\mu(g) A \, T^\nu(g)^{-1}$ is repre of G on $L(V^\mu, V^\nu)$:

$\tilde{T}(g) A$ is linear operator & $\tilde{T}(g_1 g_2) = \tilde{T}(g_1) \tilde{T}(g_2)$

- basis of the representation:

$$\tilde{T}(g) A_\mu = \sum_{m=1}^{\dim r} A_m \tilde{D}(g)^m_\mu$$

- decomposition of $\tilde{T}(g)$ to IRREPs, $\tilde{\rho} = \bigoplus_\sigma \rho^\sigma$

$\Rightarrow$ basis $\{A^\sigma_\mu\}_{\mu=1}^{d_\sigma}$ of ρ^σ forms set of irreducible tensor operators:

Def: A set of d_σ operators that under the action of G transforms as

$$T^\alpha(g) A^\sigma_\mu T^\nu(g)^{-1} = \sum_{m=1}^{d_\sigma} A^\sigma_m D^\sigma(g)^m_\mu ,$$

where $D^\sigma(g)$ is some d_σ-dim matrix IRREP of G, forms irreducible tensor operators of the IRREP ρ^σ of G.

Examples: • dipole operator $\vec{\mu} = e(x,y,z)$

Theorem XXVI: (Wigner-Eckart) (for finite or compact Lie group)

Let A^σ_m be irreducible tensor operators. Then matrix elements $M = \langle \psi^\alpha_k | A^\sigma_m | \varphi^\nu_\ell \rangle$ between vectors that transforms according to k-column of IRREP ρ^α and ℓ-col. of IRREP ρ^ν, resp., can be expressed in the form

$$M = \sum_{\lambda_\mu} (\sigma m \nu \ell | \mu \lambda_\mu k)^* (\psi^\alpha \| A^\sigma \| \varphi^\nu)_{\lambda_\mu} .$$

The reduced matrix element $(\psi^\alpha \| A^\sigma | \varphi^\nu)_{\lambda_\mu}$ is independent of k, ℓ, m but depends on λ_μ which number individual instances of the IRREP ρ^μ in decomposition of $\rho^{\sigma \times \nu}$ if $(\sigma \nu \mu) > 1$.

- recall $\rho^{\sigma \times \nu} = \bigoplus_\mu (\sigma \nu \mu) \rho^\mu$

Proof:

- we already know (for scalar operators)

$$\Omega\, \mathcal{U}(g) = \mathcal{U}(g)\,\Omega \Rightarrow \langle \Psi^{\mu}_{k} | \Omega | \Psi^{\nu}_{l} \rangle = h^{\mu} \delta_{\mu\nu} \delta_{kl}$$

- vectors $A^{\sigma}_{m} \varphi^{\nu}_{l}$ form basis of $\rho^{\sigma\times\nu} = \rho^{\sigma} \otimes \rho^{\nu}$:

$$T(g) A^{\sigma}_{m} \varphi^{\nu}_{l} = T(g) A^{\sigma}_{m} T(g)^{-1} T(g) \varphi^{\nu}_{l} = \sum_{mi} A^{\sigma}_{m} \varphi^{\nu}_{i} D^{\sigma}(g)^{m}_{m} D^{\nu}(g)^{i}_{l}$$

$$= \sum_{mi} A^{\sigma}_{m} \varphi^{\nu}_{i} \left[D^{\sigma}(g) \otimes D^{\nu}(g) \right]^{mi}_{ml}$$

$\Rightarrow$ / normalized CG coefs satisfying unitarity conditions /

$$A^{\sigma}_{m} \varphi^{\nu}_{l} = \sum_{\alpha \lambda_\alpha s} \Psi^{\alpha,\lambda_\alpha}_{s} (\sigma m \nu l | \alpha \lambda_\alpha s)^{*}$$

- $\Psi^{\alpha,\lambda_\alpha}_{s}$ is basis of ρ^{α}, $s = 1, \dots, d_\alpha$, $\lambda_\alpha = 1, \dots, (\sigma\nu\alpha)$

$$\Rightarrow M = \langle \Psi^{\mu}_{k} | A^{\sigma}_{m} | \varphi^{\nu}_{l} \rangle = \sum_{\alpha\lambda_\alpha s} (\sigma m \nu l | \alpha \lambda_\alpha s)^{*} \langle \Psi^{\mu}_{k} | \Psi^{\alpha,\lambda_\alpha}_{s} \rangle$$

$$= / \mathbb{1} \text{ is invar. scalar operator} / = \sum_{\alpha\lambda_\alpha s} (\quad)^{*} h^{\mu(\sigma,\nu)}_{\lambda_\mu} \delta_{\mu\alpha} \delta_{ks}$$

$$= \sum_{\lambda_\alpha} (\sigma m \nu l | \mu \lambda_\mu k)^{*} h^{\mu(\sigma,\nu)}_{\lambda_\mu}$$

$$h^{\mu(\sigma,\nu)}_{\lambda_\mu} = \frac{1}{d_\mu} \sum_{i} \langle \Psi^{\mu}_{i} | \Psi^{\mu(\sigma,\nu),\lambda_\mu}_{i} \rangle \equiv (\Psi^{\mu} \| A^{\sigma} \| \varphi^{\nu})_{\lambda_\mu}$$

$\boxtimes$

<u>SELECTION RULES</u> for irreducible tensor operators

1. $M = 0$ if $\rho^{\sigma} \otimes \rho^{\nu}$ does not contain ρ^{μ}
   $\Leftrightarrow$ if $\rho^{\mu} \otimes (\rho^{\sigma} \otimes \rho^{\nu})$ does not contain totally sym. IRREP

2. dependence on m, l, k only throug CG coefs (can be tabulated)

MOLECULAR VIBRATIONS & OPTICAL TRANSITIONS

1, normal coordinates

- $\vec{r}_i$ - atomic coordinates relative to equilibrium geometry

$$\vec{r}_1 = (x_1, x_2, x_3) \qquad m_1 = m_2 = m_3 = M_1$$
$$\vec{r}_2 = (x_4, x_5, x_6) \qquad m_4 = m_5 = m_6 = M_2$$
$$\vdots \qquad\qquad \vdots$$

- harmonic approximation - atomic interaction potential quadratic around equil. geom.

$$V(\{\vec{r}_i\}) = V_0 + \frac{1}{2}\sum_{ij=1}^{3N} V_{ij}\, x_i x_j \qquad T = \frac{1}{2}\sum_{i=1}^{3N} \frac{\dot{x}_i^2}{m_i}$$

(assume $V_0 = 0$ - just shift in energy)

- scaling of coordinates: $x_i = \frac{q_i}{\sqrt{m_i}}$

$$\Rightarrow \mathcal{L} = \frac{1}{2}\sum_i \dot{q}_i^2 - \frac{1}{2}\sum_{ij} B_{ij}\, q_i q_j$$

! B_{ij} depend on atomic masses !

- diagonalization of the symmetric matrix B

$$\Rightarrow \mathcal{L} = \frac{1}{2}\sum_i \dot{Q}_i - \frac{1}{2}\sum_i \lambda_i Q_i^2$$

$$Q_i = \sum_j c_i^j q_j \quad \& \quad c_i^j \text{ OG matrix } \quad C^T C = \mathbb{1}$$

$$\Rightarrow (Q_i | Q_{i'}) = \sum_{jj'} c_i^j c_{i'}^{j'} (q_j | q_{j'}) = \sum_j c_i^j c_{i'}^j = \delta_{ii'}$$

$$\Rightarrow T = \frac{1}{2}\sum_i \dot{q}_i^2 = \frac{1}{2}\sum_i \dot{Q}_i^2 \quad \text{, off-diag terms cancel}$$

! we assume q_i to be ON basis, not x_i ! (we can do it, it just defines our vec. space)

$\Rightarrow Q_i$ are so-called <u>normal coordinates</u>

$\rightarrow Q_1, Q_2, Q_3$ are translations ($\lambda_{1,2,3} = 0$) of the molec. center of mass $\Updownarrow$ no deformation

$\rightarrow Q_4, Q_5, Q_6$ are rotations of the molec. without deformation $\Rightarrow \lambda_{4-6} = 0$ (4-5 for diatomic molec.)

$\rightarrow Q_7, \dots, Q_{3N}$ ... vibrational modes, $\lambda_i \neq 0$

<u>Note:</u> • q_i can be directly chosen as generalized internal coordinates (band lengths, band angles, ...) corresponding ~~to~~ internal degrees of freedom

$\Rightarrow$ we do not need to deal with the (useless) transl. & rotational deg. of fr.

$\Rightarrow \mathcal{L}$ more complicated, namely the kinetic energy

(see, e.g., F-G matrix method - Cotton, Wiley 1990; Wilson, Molecular Vibrations, Dover 1980)

2, <u>Hamiltonian & transformations of normal coordinates</u> (under symmetry group)

$$H_{vib} = \sum_{i=7}^{3N} \left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \lambda_i Q_i^2 \right) \qquad H_{tr,rot} = -\frac{1}{2} \sum_{i=1}^{6} \frac{\partial^2}{\partial Q_i^2}$$

• H invariant under $Q_i \mapsto Q_i' = T(g) Q_i = \sum_j Q_j D(g)^j_i$ (for $T(g)$ belonging to the group of symmetry)

• $D(g)$ unitary $\Rightarrow$ kin. energy term is invariant (for any group)

- for $\sum_i \lambda_i Q_i^2 = \sum_i \lambda_i (T(g) Q_i)^2$ for any displacement (Q_i independent), normal coordinates associated wit the same $\lambda_i = \lambda$ must transform only among themselves

  a, λ_i nondeg. $\Rightarrow$ $Q_i' = \pm Q_i$

  b, λ_i deg. $\Rightarrow$ $\sum_{i:\lambda_i=\lambda} \lambda_i Q_i^2 = \lambda \sum_i Q_i^2 = \lambda \sum Q_i'^2$

  $$\Leftrightarrow Q_i' = T(g) Q_i = \sum_{j=1}^{d_\mu} D^\mu(g)_i^j Q_j$$

  D^μ ... IRREP of G (dim d_μ)

  $\Rightarrow$ Q_i corresp. to specific value of λ form basis of an IRREP of the sym. group

  $\Rightarrow$ Q_i can in fact be obtained by symmetrization of the basis of q_j

3, <u>wave functions</u>

$\Psi(Q_i) = \Psi^{tr}(Q_1, \dots, Q_6)\, \Psi^{vib}(Q_7, \dots, Q_{3N})$

Ψ^{tr} ... free particle in 6-dim space

Ψ^{vib} ... 3N−6 <u>non-interacting</u> harmonic oscilators (compare to phonons & other quasi-particles)

- <u>ground state</u>: $|\Psi_0^{vib}\rangle = N_0 \exp\left(-\sum \lambda_i^{1/2} Q_i^2\right) \Leftrightarrow$ totally sym. IRREP
- <u>(singly) excited states</u>: $|\Psi_{v_i=1}^{vib}\rangle = N_i H_1(Q_i \lambda_i^{1/4}) \exp(-\sum \dots)$

  $\Rightarrow |\Psi_{v_i=1}^{vib}\rangle \propto Q_i |\Psi_0^{vib}\rangle \Rightarrow$ transforms according the same IRREP as Q_i (ρ^i)

$\Rightarrow$ excited states wave functions transform according to IRREPs defined by the resp. normal coordinates

$\Rightarrow$ W-E theorem provides selection rules for mat. elements of tensor operators

Example :

1, infrared spectrum

- (de)excitation transitions between vibrational states via absorption/emission of a photon
- mediated by a dipole moment operator

$$\vec{\mu} = \mu_x \vec{e_x} + \mu_y \vec{e_y} + \mu_z \vec{e_z}$$

$\Rightarrow$ transforms as a (polar) vector as $\rho^{\vec{r}} = \sum_\nu \alpha_\nu^{\vec{r}} \rho^\nu$

- transition probability $P_{m\to n} \propto \left| \sum_i \langle m | \mu_i | n \rangle \right|^2$

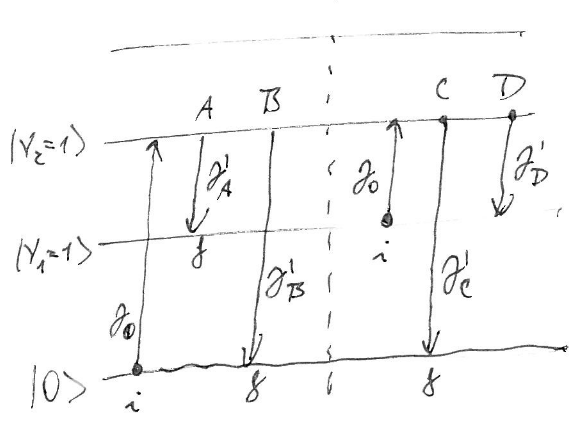
$\Rightarrow$ /W-E/ $P_{m\to n} \neq 0$ only if $\rho^{\vec{r}} \otimes \rho^n$ contains ρ^m

- usually we are interested in fundamental transitions

$|0\rangle \leftrightarrow |\nu_i = 1\rangle \Rightarrow \rho^m$ is totally symmetric IRREP

2, Raman (scattering) spectra

$$\boxed{P_{0\to \nu_i=1} \neq 0 \Leftrightarrow \langle 0 | \alpha_{kl} | \nu_i = 1 \rangle = 0 \text{ for at least one } kl}$$



A : Raman-Stokes line ; $\omega' < \omega_0$

B : Rayleigh , $\omega' = \omega_0$

C : Raman-anti-Stokes ; $\omega' > \omega_0$

D : Rayleigh , $\omega' = \omega_0$

- mediated by the change of induced dipole moment , $\vec{\mu} = \overleftrightarrow{\alpha} \vec{E}$

- $\overleftrightarrow{\alpha}$ — polarisability tensor ... symmetric, 6 indep. components ... transforms as $\{ \rho^{\vec{r}} \otimes \rho^{\vec{r}} \}$

(in a sense $\vec{\mu}^2$ — interactions with 2 photons)