Advanced Quantum Mechanics

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Lecture #3

Symmetries and Quantum Mechanics

Recap of Last Class

- Conjugacy Classes and Examples

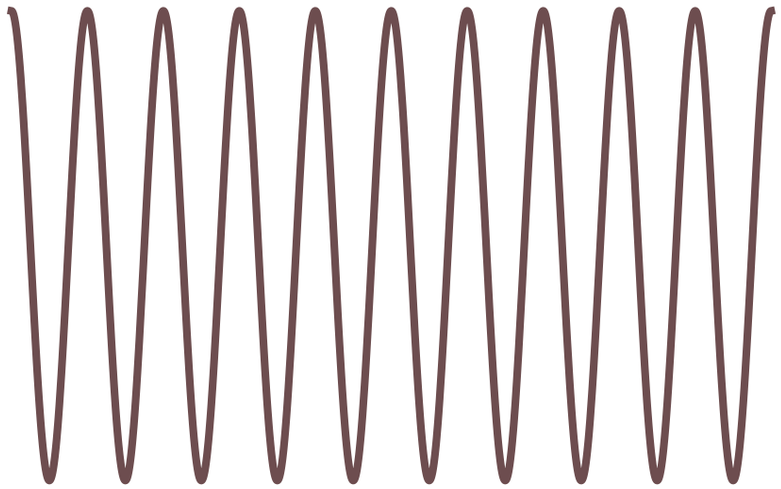
- Representation of Groups: Examples of construction: position space, function space

- Irreps, Characters and Orthogonality relation

- Reduction of a representation into irreps: Use of character Tables

- Example with parity (space inversion)

Applications: Lattice Translation Invariance



Bloch's Theorem

For a particle moving in a periodic potential $V(\vec{r}+\vec{R}) = V(\vec{r})$ the eigenfunctions can be written in the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \qquad \text{where} \quad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$$

The Symmetry group is the translation by lattice vectors with representation $\mathcal{T}(\vec{R})\psi(\vec{r}) = \psi(\vec{r}-\vec{R})$

The corresponding group is an Abelian group, so irreps are 1-D. Matrix elements are just numbers

$$\mathcal{T}(\vec{R})\psi(\vec{r}) = c(\vec{R})\psi(\vec{r})$$

Now

$$\mathcal{T}(\vec{R})\mathcal{T}(\vec{R}') = \mathcal{T}(\vec{R}+\vec{R}') \longrightarrow c(\vec{R})c(\vec{R}') = c(\vec{R}+\vec{R}') \longrightarrow c(\vec{R}) = e^{i\vec{k}\cdot\vec{R}}$$

Hence $\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$

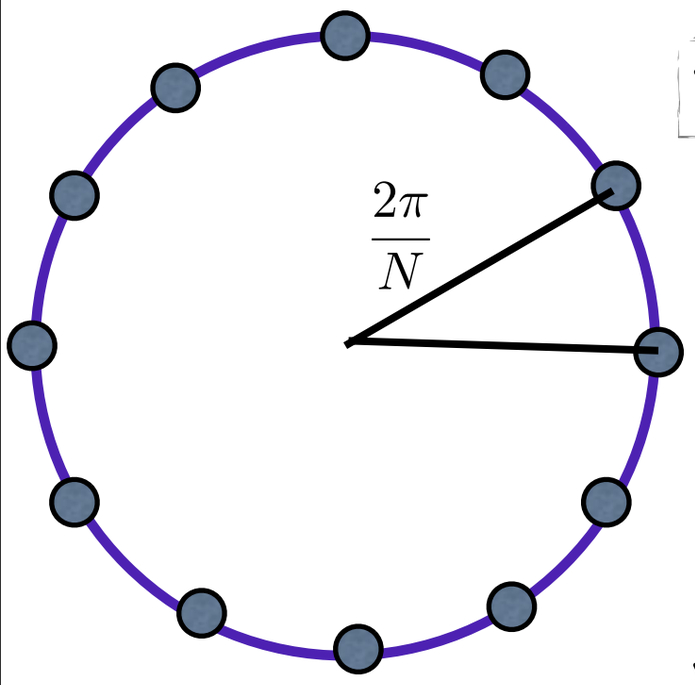
The general solution of this equation is given by the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \qquad \text{where} \quad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$$

k provides the quantum no.

Applications: Lattice Translation Invariance

Possible values of k : Brillouin zone and crystal momentum



We will show this for 1-D lattice of N sites with Periodic Boundary Cond.

Bloch's Theorem: $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$ where $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$

Now, $\psi_{k+\frac{2\pi n}{a}}(r) = e^{i\left(k+\frac{2\pi n}{a}\right)r} u_{k+\frac{2\pi n}{a}}(r)$

When r= ma, with integer m $\psi_{k+\frac{2\pi n}{a}}(r) = e^{ikr} u_{k+\frac{2\pi n}{a}}(r)$

This suggests that one can restrict values of k between $-\pi/a$ and π/a, and use n as an additional quantum number. This is the basic idea of working in the "First Brillouin Zone" [$-\pi/a < k < \pi/a$] with a number of bands [n becomes the band index].

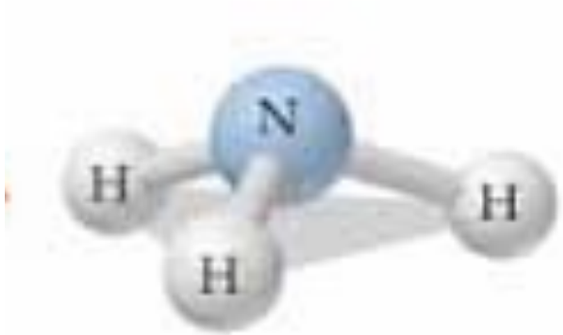
$$\psi_k^n(r) = e^{ikr} u_k^n(r) \qquad u_k^n(r) = u_k^n(r+a)$$

With P.B.C. $\psi_k^n(r) = \psi_k^n(r+Na) = e^{ik(r+Na)} u_k^n(r)$ $k = \frac{2\pi}{a}\frac{p}{N}$ p=0,1,...N-1

Applications: NH_3 molecule

12 D problem
(3 D for each atom)

Symmetries of NH_3



Molecular geometry
(trigonal pyramidal)

Group : $C_{3\nu}$

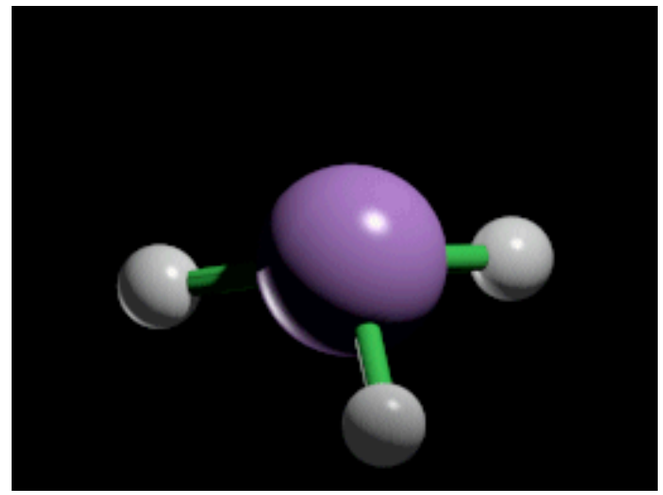
Rotations about axis perp to H plane

{E}

All 4 atoms are
fixed in this transf.

{R,R^2 } ⟶ 2C_3

R= rotn by $2\pi/3$
leaves only N atom fixed

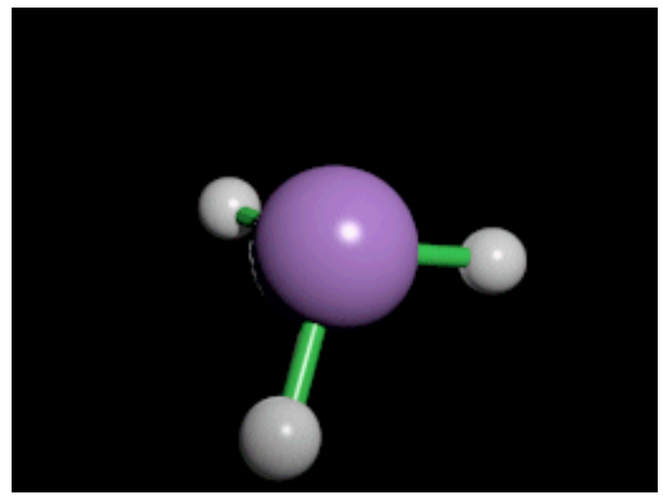


Reflection about plane cont. N and H

$$3\sigma_\nu = \{\sigma_1, \sigma_2, \sigma_3\}$$

↓

N and H atom forming
reflection plane are fixed



Vibrational Modes of NH_3 :CM

Unknown $V(r_1, ..r_4)$, but it must respect the symmetries of the molecule.

Small amplitude oscillations are governed by the expansion of V around the eqbm. config.

$$H = \sum_i \frac{1}{2} m_i \dot{q}_i^2 + \frac{1}{2} \sum_{ij} B_{ij} q_i q_j \qquad B_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \qquad q_i = r_i - r_i^0$$

Define $D_{ij} = \dfrac{B_{ij}}{\sqrt{m_i m_j}}$ and $\alpha_i = \sqrt{m_i} q_i$ $\longrightarrow$ $H = \dfrac{1}{2} \sum_i \dot{\alpha}_i^2 + \dfrac{1}{2} \sum_{ij} D_{ij} \alpha_i \alpha_j$

Normal Co-ord: $\alpha_i = \sum_k a_{ik} Q_k$ where $\sum_j D_{ij} a_{jk} = \omega_k^2 a_{ik}$ $\longrightarrow$ Eigenvalue Eqn

$$H = \frac{1}{2} \sum_k \dot{Q}_k^2 + \omega_k^2 Q_k^2$$

Independent Harmonic Oscillators

D_{ij} has symmetries of the molecule, we will treat this as eigenvalue problem

We wish to use symmetries to classify the normal modes Q_k and frequencies ω_k

Vibrational Modes of NH_3: CM

12 D problem
(3 D for each atom)

Molecular geometry
(trigonal pyramidal)

- Transformations of atomic displacements in 12 dim space will provide a representation of the group. $T^{(3N)}$
- If we can find the reduction of this group into irreps, we would be able to classify normal modes

$$T^{(3N)} = \oplus_\alpha m^{(\alpha)} T^{(\alpha)}$$

Reduction of representation -----> Characters $\chi_p = \sum_\alpha m^{(\alpha)} \chi_p^{(\alpha)}$

$$\frac{1}{g}\sum_p c_p \chi_p^{(\beta)*} \chi_p = \frac{1}{g}\sum_p c_p \chi_p^{(\beta)*} \sum_\alpha m^{(\alpha)} \chi_p^{(\alpha)} = \frac{1}{g}\sum_\alpha m^{(\alpha)} \sum_p c_p \chi_p^{(\beta)*} \chi_p^{(\alpha)} = m^{(\beta)}$$

Character Table of the Group:

	E	$2C_3$	$3\sigma_\nu$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Need to find the characters of the 12 dim representation $\chi^{(3N)}$

Vibrational Modes of NH_3: CM

Characters of the 12 dim representation $\chi^{(3N)}$

Let $\mathbf{e}_{ti}$ be the i^{th} displacement of t^{th} atom

$$T^{(3N)}(G_a)\mathbf{e}_{ti} = \sum_{t'j} T^{(3N)}_{t'j,ti}(G_a)\mathbf{e}_{t'j} \longrightarrow \chi^{(3N)}(G_a) = \sum_{ti} T^{(3N)}_{ti,ti}(G_a)$$

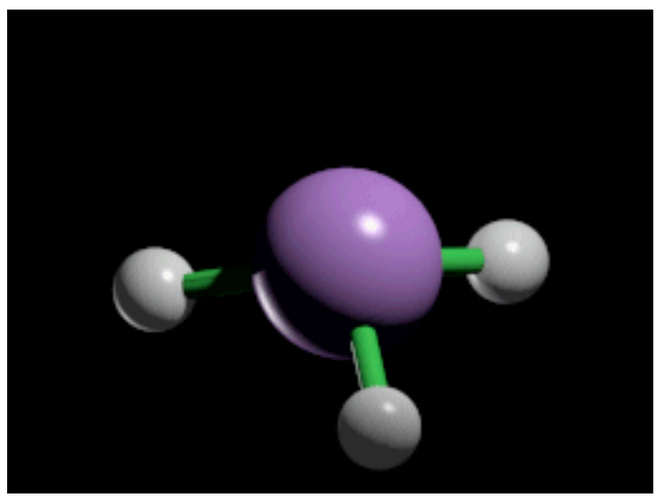
Only atoms unmoved in a transform contribute to the character

E conjugacy class: Obviously $\chi^{(3N)}(E) = 3N = 12$

$2C_3$ conjugacy class:

For proper rotation of an atom co-ord,

$$T(R_\theta) = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \theta = \frac{2\pi}{3}$$



$$\chi^{(3N)}(R_\theta) = N(R_\theta)(2\cos\theta + 1)$$

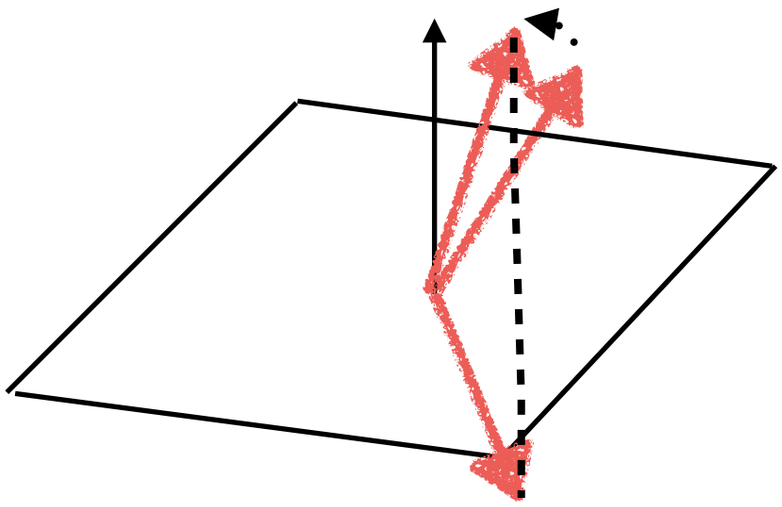
where $N(R_\theta)$= no. of unmoved atom = 1

Vibrational Modes of NH_3: CM

Characters of the 12 dim representation $\chi^{(3N)}$

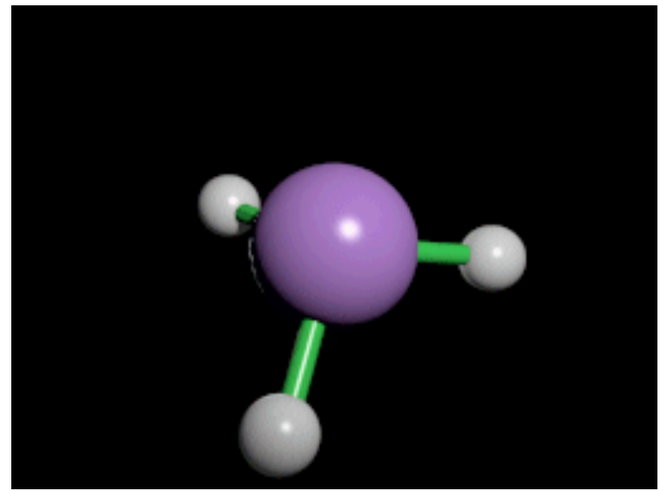
$3\sigma_v$ conjugacy class:

For improper rotation of an atom co-ord, (rotn. followed by reflection)



$$T(S_\theta) = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

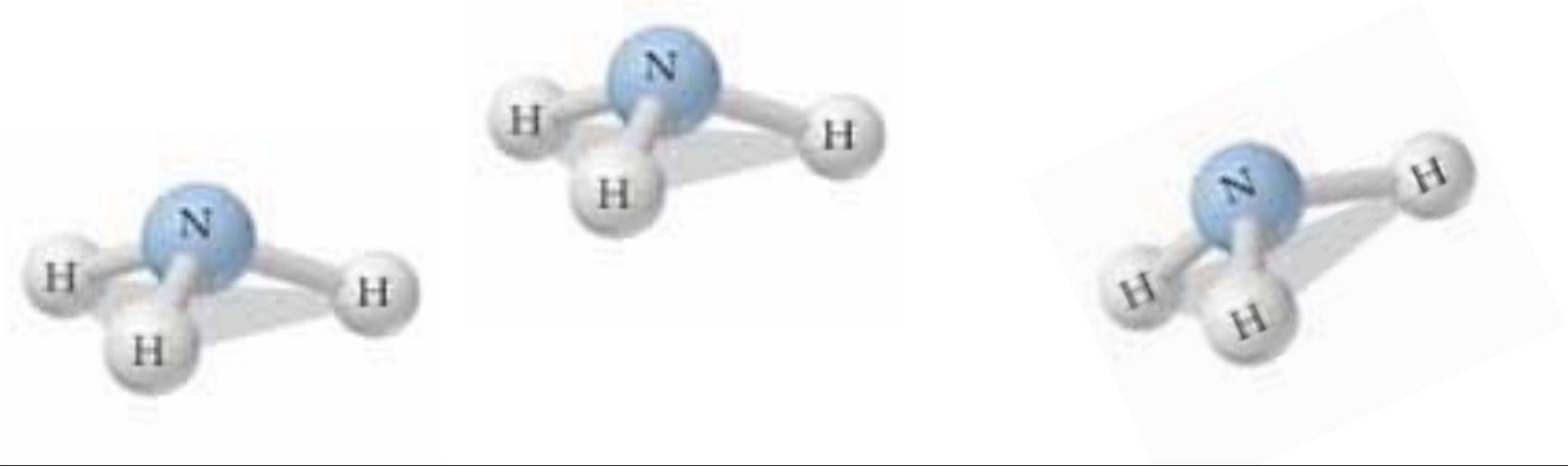
$$\theta = 0$$



$$\chi^{(3N)}(S_\theta) = N(S_\theta)(2\cos\theta - 1)$$ where $N(S_\theta)$= no. of unmoved atom = 2

These normal modes, as written, include translation and rotation of the center of mass of the molecule.

We are not interested in these modes and will subtract their contribution from the calculated characters.



Vibrational Modes of NH_3: CM

Character contribution of the translation and rotation modes:

For translation modes, $\chi_t(R_\theta) = (2\cos\theta + 1)$ $\chi_t(S_\theta) = (2\cos\theta - 1)$ $\chi_t(E) = 3$

For rotation modes, $\chi_r(R_\theta) = (2\cos\theta + 1)$ $\chi_r(S_\theta) = -(2\cos\theta - 1)$ $\chi_r(E) = 3$

For vibration modes: $\chi_\nu(R_\theta) = \chi^{(3N)}(R_\theta) - \chi_t(R_\theta) - \chi_r(R_\theta) = [N(R_\theta) - 2][2\cos\theta + 1]$

For $2C_3, \quad \theta = 2\pi/3, \quad N(R_\theta) = 1$

$$\chi_v(2C_3) = (1-2)\left(2\frac{-1}{2} + 1\right) = 0$$

$$\chi_v(S_\theta) = \chi^{(3N)}(S_\theta) - \chi_t(S_\theta) - \chi_r(S_\theta) = N(S_\theta)(2\cos\theta - 1)$$

For $3\sigma_\nu, \quad \theta = 0, \quad N(S_\theta) = 2$

$$\chi_v(3\sigma_\nu) = 2\,(2-1) = 2$$

$$\chi_v(E) = \chi^{(3N)}(E) - \chi_t(E) - \chi_r(E) = 12 - 3 - 3 = 6$$

Vibrational Modes of NH_3: CM

Character Table including vibrational modes.

$$m^{(\alpha)} = \frac{1}{g}\sum_p c_p \chi_p^{(\alpha)*} \chi_v$$

$$m^{A_1} = \frac{1}{6}\sum_p 1\times 6 + 2\times 1\times 0 + 3\times 1\times 2 = 2$$

$$m^{A_2} = \frac{1}{6}\sum_p 1\times 6 + 2\times 1\times 0 + 3\times (-1)\times 2 = 0$$

$$m^{E} = \frac{1}{6}\sum_p 2\times 6 + 2\times (-1)\times 0 + 3\times 0\times 2 = 2$$

	E	$2C_3$	$3\sigma_\nu$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
χ_v	6	0	2

Now we can reduce the representation as $2A_1 \oplus 2E$

So we will have 2 modes (say Q_1,Q_2)which transform according to A_1 irrep.

Their freq. are generically non-degenerate

2 sets of modes transform according to E irrep. Each of these are 2-fold degenerate (say Q_3,Q_4 is a degenerate pair transf. acc. to E and Q_5,Q_6 is another degenerate pair.)

Note: We can say all this without knowing any details of the atomic potentials.
We cannot compute the normal mode frequencies just from symmetry principles.

Vibrational Modes of NH_3: QM

The QM problem is that of a 6 dimensional Harmonic Oscillator (Q_1 ... Q_6)

$$H = \sum_k H_k \qquad H_k = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_k^2} + \frac{1}{2}\omega_k^2 Q_k^2 \qquad \omega_3 = \omega_4 \quad \omega_5 = \omega_6$$

Eigenenergies of the QM problem $\epsilon = \sum_k \hbar\omega_k(n_k + 1/2)$ n_k is occ. no. of k^{th} mode

Eigenstates of the QM problem $|n_1,n_2,...n_6\rangle$, with wavefn. $\Psi(Q_1,\dots Q_6) \sim \prod_{k=1}^{6} e^{-\omega_k Q_k^2/2} H_{n_k}(\omega_k^{1/2} Q_k)$

We know degeneracies of ω_k and transformation properties of Q_k (i.e. the irreps they transform according to)

What about symmetry properties of the eigenstates?

What about expectation value/ matrix elements of various operators between these states?

Can symmetries tell us anything about that?

Direct Product of Representations

Direct Product of Matrices:

The direct product of a n X n matrix A and a m X m matrix B is the mn X mn matrix, A X B with

$$(A \times B)_{ij,kl} = A_{ik} B_{jl}$$

Direct Product of Irrep:

$$T^{(\alpha\times\beta)}_{ij,kl}(G_a) = T^{(\alpha)}_{ik}(G_a) T^{(\beta)}_{jl}(G_a)$$

Show that these preserve group multiplication

Character of Direct Product of Irreps:

$$\chi^{(\alpha\times\beta)}(G_a) = \sum_{ij} T^{(\alpha\times\beta)}_{ij,ij}(G_a) = \sum_{ij} T^{(\alpha)}_{ii}(G_a) T^{(\beta)}_{jj}(G_a) = \chi^{(\alpha)}(G_a)\chi^{(\beta)}(G_a)$$

It is clear from the above character composition rule that direct product of irreps is generally not an irrep.

So, we should be able to reduce it as before using character tables

$$T^{(\alpha\times\beta)} = \oplus_\gamma m^{(\gamma)} T^{(\gamma)} \qquad m^{(\gamma)} = \frac{1}{g}\sum_p c_p \chi^{(\gamma)*}_p \chi^{(\alpha)}_p \chi^{(\beta)}_p$$

Direct Product of Representations

$$T^{(\alpha\times\beta)} = \oplus_\gamma m^{(\gamma)} T^{(\gamma)} \qquad m^{(\gamma)} = \frac{1}{g}\sum_p c_p \chi_p^{(\gamma)*}\chi_p^{(\alpha)}\chi_p^{(\beta)*}$$

Example:

$$E \times E = E + A_1 + A_2$$

$$A_2 \times A_2 = A_1$$

	E	$2C_3$	$3\sigma_\nu$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
E X E	4	1	0
A_2 X A_2	1	1	1

1) Eigenstates/Wfns transform according to irreps. Product of wfn.s transform according to direct product of irreps.

$$T(G_a)|\phi_i^{(\alpha)}\rangle|\phi_j^{(\beta)}\rangle = \sum_{lm} T_{li}^{(\alpha)}(G_a)|\phi_l^{(\alpha)}\rangle T_{mj}^{(\beta)}(G_a)|\phi_j^{(\beta)}\rangle = \sum_{lm} T_{li}^{(\alpha)}(G_a)T_{mj}^{(\beta)}(G_a)|\phi_l^{(\alpha)}\rangle|\phi_j^{(\beta)}\rangle$$

$$= \sum_{lm} T_{lm,ij}^{(\alpha\times\beta)}(G_a)|\phi_l^{(\alpha)}\rangle|\phi_j^{(\beta)}\rangle$$

$\phi_i^{(\alpha)}\phi_j^{(\beta)}$ transform according to the ij row of $T^{(\alpha\times\beta)}$

Example: Wfn.s of vibrational modes of NH_3

Eigenstates of the QM problem $|n_1,n_2,\ldots n_6\rangle$, with wavefn. $\Psi(Q_1,\ldots Q_6) \sim \prod_{k=1}^{6} e^{-\omega_k Q_k^2/2} H_{n_k}(\omega_k^{1/2} Q_k)$

where $H_n(x)$ is the Hermite polynomial of degree n and n_k is the occupancy of the k^{th} mode

- The ground state is invariant under the symmetries and transform according to A_1
- The states where one mode is occupied (n_k=1, n_i=0 for all others) ~ $H_1(Q_k)$~Q_k and transform acc. to respective irrep of Q_k
- The state where two modes corr. to E and A_1 each have occupancy of 1. This transforms as E X A_1 = E
- The states where the degenerate doublet of E is doubly occupied. We can only form 3 independent states from the doublet —— $H_2(Q_3)$, $H_2(Q_4)$ and $H_1(Q_3)H_1(Q_4)$, and not 4 as we would naively think about.

Thus product states of same irrep do not transform as direct product representation, only the symmetrized levels will survive.

$$\chi^{(\alpha)}_{sym}(G_a) = \frac{1}{2}[\chi^{(\alpha)}(G_a)]^2 + \frac{1}{2}\chi^{(\alpha)}(G_a^2)$$

$$\chi^{E\times E}_{sym} = E + A_1$$

	E	$2C_3$	$3\sigma_\nu$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$\chi^{E\times E}_{sym}$	3	0	1

Irreducible Set of Operators

Eigenstates are labelled by irreps of the symmetry group. For a s dimensional irrep α, consider the basis set $\{ |\varphi^{\alpha}_i\rangle \}$ in the corresponding invariant subspace.

$$T(G_a)|\phi_i^{(\alpha)}\rangle = \sum_l T_{li}^{(\alpha)}(G_a)|\phi_l^{(\alpha)}\rangle$$

The state (or equivalently the wfn) $\phi_i^{(\alpha)}$ transforms according to ith row of $T^{(\alpha)}$

Can we extend the concept of states transforming according to an irrep to operators?

Irreducible Set of Operators :

A set of operators, which transform among themselves in the sense

$$S_i^{(\alpha)'} \equiv T(G_a) S_i^{(\alpha)} T(G_a^{-1}) = \sum_j T_{ji}^{(\alpha)}(G_a) S_j^{(\alpha)}$$

are called irreducible operators transforming according to $T^{(\alpha)}$

These operators have support only in the invariant space spanned by the irrep.

Matrix Elements

2) If $\hat{O}_i^{(\alpha)}$ is an irreducible operator, transforming according to $T^{(\alpha)}$, and $|\varphi^{(\beta)}{}_j>$ a state which transforms according to $T^{(\beta)}$, then

$\hat{O}_i^{(\alpha)}|\phi_j^{(\beta)}\rangle$ transforms according to the ij row of $T^{(\alpha\times\beta)}$

Now let us reduce $T^{(\alpha\times\beta)} = \oplus_\gamma m^{(\gamma)} T^{(\gamma)}$

Consider the matrix element $\langle\phi_k^{(\gamma)}|\hat{O}_i^{(\alpha)}|\phi_j^{(\beta)}\rangle$

- The matrix element of $\hat{O}^{(\alpha)}$ between $\phi^{(\beta)}$ and $\phi^{(\gamma)}$ is non-zero only if $m^{(\gamma)} \neq 0$

i.e. if the irrep γ does not occur in the reduction of (αxβ), the corr. matrix element is zero

This is not surprising, the idea of irreps correspond to block diagonalizing matrices, so the off-block matrix elements are 0.

At the heart of huge simplification of complex problems

Matrix Elements: Some Applications

If we know the matrix elements of an observable A between energy eigenstates, then the expectation of the observable is given by

$$A(t) = \langle\psi(t)|A|\psi(t)\rangle = \sum_{nn'} c_n^*(0)c_{n'}(0)e^{i(E_n - E_{n'})t}A_{nn'} \qquad A_{nn'} = \langle n|A|n'\rangle$$

Time Independent Perturbation Theory: $E^{(1)} = \langle 0|H_1|0\rangle$ $E^{(2)} \sim -\sum_n \frac{\langle 0|H_1|n\rangle\langle n|H_1|0\rangle}{\epsilon_n - \epsilon_0}$

If we start with a system in an energy eigenstate |n>, and turn on a time dependent perturbation,

$$H_1 = \lambda e^{i\omega t}\hat{A}$$

the system makes transitions to different excited states |m> (of the unperturbed system)

with a rate

$$P_{mn} \sim \lambda^2 |\langle m|\hat{A}|n\rangle|^2$$

- Some of these matrix elements are 0 due to symmetry ..... forbidden transitions ..... selection rules

Matrix Elements: Some Applications

Example : Dipole Transitions

Light shining on charge neutral systems (like atoms). The dipole moment (induced) interacts with the Electric field by H1 ~ d.E. To see which transitions are allowed, we need the matrix element of the dipole operator between the states.

1-D Harmonic Oscillator:

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 \hat{x}^2$$

In 1D, the dipole operator ~ x, so we are interested in matrix elements of x

Irreps: {1,-1} Even and Odd states x transforms acc. to -1 irrep

Start with even state |2n>, x|2n> transforms according to -1 irrep

Start with odd state |2n+1>, x|2n+1> transforms according to 1 irrep

Transitions are allowed between odd n and even n states.

Transition between even-even and odd-odd states are forbidden

Selection Rule