Lecture 22 – 11/27

Remember: Final presentations!

Timeline:
→ suggestion of topic (in person or via email): Wednesday

→ first draft (in person or via email): Tu next week

→ Presentation: Thu, Dec 7,
10am – 2pm
will provide lunch
· Science Center 309

Finish group theory for AMO general
- basis fcts ($\hat{=}$ eigenstates)
- continuous groups (spherical symm.)
- without & with spin

• Basis functions

What does group theory teach us about the eigenstates of a Hamiltonian?

Remember:

"Hamiltonian is symmetric under (operation) $\hat{R}$" $\hat{=}$

$[\hat{H}, \hat{R}] = 0$

$\Rightarrow$ $\hat{H}$ and $\hat{R}$ can share a set of eigenstates.

What are the eigenstates of $\hat{R}$?

G: group of the Schr. Eq.

Each $g \in G$ has associated a 3D rotation, w/ matrix R_g

$$\vec{r}\,' = R_g \vec{r}$$

$$\boxed{P_g\, f(\vec{r}) \equiv f(R_g^{-1} \vec{r})}$$ for $R_g \hat{=} \Gamma(g)$

R_g are isomorphic representations of G if we are looking only at 3D-rotation symmetry.

Example: rotation by 90° around $\hat{x}$:

$\Rightarrow x' = x\,;\; y' = z\,;\; z' = -y\;:\; R_g = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$

$\rightarrow P_g\, f(x,y,z) = f(R_g^{-1}\vec{r}) = f(x,-z,y)$

$[H, P_g] = 0 \quad \Rightarrow \quad P_g |\psi_n\rangle$ is also eigenfct

$H|\psi_n\rangle = E_n |\psi_n\rangle$ with same energy.

$\Rightarrow$ given one eigenfct $\psi_n^{(\kappa)}$, we can generate other $\psi_n^{(\nu)}$ with all P_g !

If this produce $\psi_n^{(\kappa)} \Rightarrow$ degeneracy is "normal"

otherwise, degeneracy is "accidental"

Example: np_x, np_y, np_z – normal

np, ns – accidental

(but: not accidental/degenerate under Dirac eq.!)

<u>normal:</u>

$$P_g \psi_n^{(\kappa)} = \sum_{\nu=1}^{l_n} \psi_n^{(\nu)} \Gamma^{(n)}(g)_{\nu\kappa}$$

l_n: degeneracy of E_n

$\Gamma^{(n)}$ is l_n-dim. rep.

$\Gamma^{(n)}$ is (can be) irreducible

If $\psi_n^{(\nu)}$ orthonormal basis $\Leftrightarrow \Gamma^{(n)}$ unitary

$\Rightarrow$ The set of l_n degenerate eigenfcts $\psi_n^{(\nu)}$ for eigenvalue E_n form basis fcts for l_n-dimensional irred. rep $\Gamma^{(n)}$ of Schr. group.

Trivial extension:

Different set $\psi_n^{(\nu)'} \mathrel{\hat{=}} \Gamma^{(n)'} = S^{-1} \Gamma^{(n)} S$

$\Rightarrow$ <u>same</u> space, <u>equivalent</u> irred. rep.

<u>Properties</u>:

- n and κ, ν (row, col. indices of $\Gamma^{(n)}$) are "good q. numbers."
- dimension of irred. reps. gives all possible (normal) degeneracies.

- all eigenfct w/ different $\{m, \kappa, \nu\}$ are orthogonal.
- perturbation H' lifts degeneracies iff it changes symm. group and dim. of irred. representation.

<u>Defs:</u> $\psi_n^{(\nu)}$ "transforms according to $\Gamma^{(m)}$" or
$\psi_n^{(\nu)}$ "belongs to" $\Gamma^{(m)}$ or
the $\psi_n^{(\nu)}$ "generate" $\Gamma^{(m)}$

- <u>How to form Basis functions?</u> $\varphi_n^{(\nu)}$

Remember: $P_g \varphi_n^{(\nu)} = \sum_{\kappa=1}^{l_m} \varphi_n^{(\kappa)} \Gamma^{(m)}(g)_{\kappa\nu}$

multiply from left: $\sum_{g\in G} \Gamma^{(m)*}(g)_{\kappa'\nu'} \cdot |$

$\Rightarrow \sum_{g\in G} \Gamma^{(m)*}(g)_{\kappa'\nu'} P_g \varphi_n^{(\nu)} = \frac{h}{l_m} \delta_{nm} \delta_{\kappa\kappa'} \delta_{\nu\nu'} \varphi_n^{(\kappa)}$ (orthogonality theorem!)

$\Rightarrow$ define: $\mathcal{P}_{\kappa\nu}^{(m)} \equiv \frac{l_m}{h} \sum_{g\in G} \Gamma^{(m)*}(g)_{\kappa\nu} P_g$

$\Rightarrow \mathcal{P}_{\kappa\nu}^{(m)} \varphi_n^{(\xi)} = 0$ unless $\xi = \nu$. If $\xi = \nu$: $\mathcal{P}_{\kappa\nu}^{(m)} \varphi_n^{(\nu)} = \varphi_n^{(\kappa)}$

$\Rightarrow \mathcal{P}_{\nu\nu}^{(m)}$ is projector onto $\varphi_n^{(\nu)}$!

$\Rightarrow \mathcal{P}_{\nu\nu}^{(m)} F = f_n^{(\nu)} \propto \varphi_n^{(\nu)}$

any function!

$\mathcal{P}_{\nu\nu}^{(m)}$ projector on $\varphi_n^{(\nu)}$ (can be constructed)

Then: $P_{\kappa\nu}^{(m)}$ (with $\kappa \neq \nu$) yield all "partners".
(<u>Def</u>: different $\psi_n^{(\nu)}$ are called partners.)

<u>Use characters instead:</u>

$\mathcal{P}^{(m)} \left(\equiv \sum_{\kappa=1}^{l_m} \mathcal{P}_{\kappa\kappa}^{(m)}\right) = \frac{l_m}{h} \sum_{g\in G} \chi^{(m)}(g) P_g$ projects onto space of $\Gamma^{(m)}$, E_n

$\rightarrow \mathcal{P}^{(m)} F = f^{(m)}$ ($\propto$ span $(\varphi_n^{(\nu)})$)

Example: $G = \{e, \sigma_x\}$ (mirror $\perp \hat{x}$)

	e	σ_x
$\Gamma^{(1)}$	1	1
$\Gamma^{(2)}$	1	-1

$$\mathcal{P}^{(1)} = \frac{\ell}{h} \sum_{g \in G} \chi^{(1)}(g) P_g = \frac{1}{2}(P_e + P_{\sigma_x})$$

$$\mathcal{P}^{(2)} = \qquad\qquad = \frac{1}{2}(P_e - P_{\sigma_x})$$

any $F(\vec{r}) = F(x, y, z)$

$$f^{(1)/(2)}(x,y,z) = \frac{1}{2}\left(F(x,y,z) \pm F(-x,y,z)\right)$$

orthogonal! (+ normalize)

c) Representation + characters of continuous (rotation) groups

- cyclic group: $G = \{a, a^2, \dots, a^n = e\}$

Abelian $\Rightarrow$ only 1D irred. rep's

$\Gamma(a)^n = a^n = e \Rightarrow \chi^{(p)}(a) = e^{2\pi i \frac{p}{n}}$

$\Gamma^{(p)}(a) = \chi^{(p)}(a) = e^{2\pi i \frac{p}{n}}$, $p = 1, \dots, n$ ($l = h$)

- Bloch theorem

periodic potential with k a-periods (ring or linear with periodic boundary conditions)

$$P_a \psi(x) = \psi(x+a) = \Gamma(a) \psi(x) = e^{ika} \psi_k(x)$$

$$k = \frac{2\pi p}{L}$$

$$\psi_k(x) = u_k(x) e^{ikx}$$

where $u_k(x+a) = u_k(x)$

- infinite rotation in 2D

($\hat{=}$ infinite-order cyclic group)

$$\Gamma^{(m)}(\varphi) = e^{im\varphi} = \chi^{(m)}(\varphi)$$

$\psi_m(r,\vartheta,\varphi) = f(r,\vartheta)\, e^{im\varphi}$

$\Gamma^{(m)}(\pi) \overset{!}{=} \Gamma^{(m)}(-\pi) \Rightarrow e^{im\pi} \overset{!}{=} e^{-im\pi}$

$\Rightarrow m = 0, \pm 1, \pm 2, \dots$

- 3D proper rotation group $SO(3)$ $(O^+(3))$

One obvious representation:

$R(\alpha,\beta,\gamma)$ Euler angles

$R(\alpha,\beta,\gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma)$

$$R_z(\varphi) = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad R_y = \dots$$

- $R^T R = \mathbb{1}$ $\det R = 1$
- <u>not</u> Abelian
- "three-parameter" group
- <u>Basis functions</u>

We know that

Definition for $D^{(\ell)}_{m'm}$

$$P_R(\alpha,\beta,\gamma)\, Y_{\ell m}(\vartheta,\varphi) = \sum_{m'=-\ell}^{\ell} Y_{\ell m'}(\vartheta,\varphi)\, D^{(\ell)}_{m'm}(\alpha,\beta,\gamma)$$

with $Y_{\ell m}$ spherical harmonics = basis functions

and $D^{(\ell)}(\alpha,\beta,\gamma) = \Gamma^{(2\ell+1)}$: $(2\ell+1)$-dim irred. rep

(These are listed in tables

"D" for "Darstellung" - due to Wigner)

- Rotations by <u>same</u> angle about any axis are in same class!

(Proof: $R_{z'}(\varphi) = R(z\to z')\, R_z(\varphi)\, R^{-1}(z\to z')$)

- characters of $D^{(\ell)}(\varphi)$

$$\boxed{\chi^{(2\ell+1)}(\varphi) = \frac{\sin\left[(\ell+\frac{1}{2})\varphi\right]}{\sin \varphi/2}}$$

Proof: Rotate axes by $-\alpha$ about $\hat{z}$:

$$P_\alpha Y_{\ell m}(\vartheta,\varphi) \equiv Y_{\ell m}(\vartheta,\varphi-\alpha) = e^{im\alpha} Y_{\ell m}(\vartheta,\varphi)$$

$$D^{(\ell)}(\alpha) = \begin{pmatrix} e^{-i\ell\alpha} & & & \\ & e^{-i(\ell-1)\alpha} & & \\ & & \ddots & \\ & & & e^{i\ell\alpha} \end{pmatrix} ; \quad \chi^{(2\ell+1)}(\alpha) = \sum_{m=-\ell}^{\ell} e^{im\alpha}$$

$\square$

- These are the only (odd-dim) irr. rep's of SO(3)

(proof: characters have to be orthogonal $\Rightarrow$ new $\chi(\alpha)$ also orthogonal to $\chi^{(2\ell+1)}(\alpha) - \chi^{(2\ell-1)}(\alpha) = 2\cos\ell\alpha$

$\Rightarrow$ $\chi(\alpha)$ needs to be orthogonal to cos-Fourier series!

Rotations by α, $-\alpha$ in same class $\Rightarrow \chi(\alpha) = \chi(-\alpha) \Rightarrow$

$\lightning$: can never be orthogonal to all cos-Fourier series! $\square$

- With spin: SU(2) + double groups

Q: Even rep's for SO(3)?

$D^{(j)}$ for half-integer j?

$$\Rightarrow \chi^{(j)}(\alpha) = \frac{\sin\left((j+\frac{1}{2})\alpha\right)}{\sin \alpha/2} \quad \text{works!}$$

But $Y_{\ell m}$ only for $\ell \in \mathbb{Z}$!

$\Rightarrow$ use $|j,m\rangle$ as basis

($\Rightarrow$ combined angular & spin wave functions)

$$P_R |j,m\rangle = \sum_{m'=-j}^{j} |j,m'\rangle D^{(j)}_{R\, m'm}$$

$$\chi^{(2j+1)}(\alpha+2\pi) = \frac{\sin\left((j+\frac{1}{2})(\alpha+2\pi)\right)}{\sin\frac{\alpha+2\pi}{2}} = (-1)^{2j} \chi^{(2j+1)}(\alpha)$$

$\Rightarrow$ for half-integer j, the Hilbert space is taken into itself only by 4π-rotation!

Remedy: define $r \neq e$, $r^2 = e$ as new group element!

$\Rightarrow$ group doubles, i.e., for each group element g, there now also exists an $r \cdot g$!

$\Rightarrow$ $G' = \{e, g_2, g_3, \dots g_n, r, r \cdot g_2 \dots, r \cdot g_n\}$

is called "double group" of G.

SU(2) is double group of SO(3)

<u>Remark</u>: For finite groups there are double as many group elements, but not necessarily double as many classes: cf O vs O'

- Mapping between SO(3), SU(2)

SO(3) are all proper rotations in 3D real space

SU(2) are all proper rotations in 2D complex space

$\Rightarrow$ unitary mces U with $\det U = 1$ is isomorphic rep.

Any x, y, z can be mapped to 2D traceless Hermitian matrix:

$$X = \begin{pmatrix} z & x+iy \\ x-iy & -z \end{pmatrix}$$ is most general such matrix

One general way to write U:

$$U = e^{i\vec{\sigma}\cdot\vec{\varphi}/2} = \cos\frac{\varphi}{2}\,\mathbb{1} + i\hat{\varphi}\cdot\vec{\sigma}\,\sin\frac{\varphi}{2}$$

$\vec{\varphi}$: $|\vec{\varphi}|$ is angle, $\hat{\varphi}$ is axis of rot.

$\vec{\sigma}$: vector of Pauli mces.

$$R^T \vec{r} R \;\hat{=}\; U^+ X U$$

But: both U and $-U$ give same rotation R!

(e.g. $U_z(2\pi) = \begin{pmatrix} e^{-i\pi} & \\ 0 & e^{i\pi} \end{pmatrix} = -\mathbb{1}$)

- Direct - product groups

often: complete symmetry can be broken up into distinct operations, ① and ②, where ① and ② commute.

Example: H_2 ① exchange protons
② exchange e^-
③ rotating molecule
⋮

can be written as "direct product group"

$G_1 = \{e, a_2, \dots a_h\}$, $G_2 = \{e, b_2, \dots, b_k\}$

$G' \equiv G_1 \times G_2 = \{e, a_1 \dots, b_1 \dots \; a_1 b_1, a_1 b_2 \dots\}$

order: $h \cdot k$, $\Gamma_{1,ij} \cdot \Gamma_{2,lm} \equiv (\Gamma_1 \times \Gamma_2)_{ij,lm}$

$\chi_{12} \equiv \chi_1 \cdot \chi_2$, ...

example: G_1 (equilateral triangle): "D_3" (in xy-plane)

D_3	e	$2C_3$	$3\sigma_i$
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	1	-1
$\Gamma^{(3)}$	2	-1	0

G_2: mirroring along $\hat{z}$ $\mathcal{S} = \{e, \sigma\}$

$\mathcal{S}$	e	σ_h
$\Gamma^{(1)}$	1	1
$\Gamma^{(2)}$	1	-1

$G_1 \times G_2 \equiv D_3 \times \mathcal{S} = D_{3h}$ 

D_{3h}	e	$2C_3$	3σ	σ_h	$2\sigma_h C_3$	$3\sigma_h\sigma_i$
$\Gamma^{(1)}$	1	1	1	1	1	1
$\Gamma^{(2)}$	1	1	-1	1	1	-1
$\Gamma^{(3)}$	2	-1	0	2	-1	0
$\Gamma^{(4)}$	1	1	1	-1	-1	-1
	1	1	-1	-1	-1	1
	2	-1	0	-2	1	0

- Direct-product representation

(within a group: e.g. $2e^-$ in He)

$\Gamma^{(i)}, \Gamma^{(j)}$ rep's of same group

$\Gamma^{(i)} \otimes \Gamma^{(j)} \Rightarrow ?$ $\quad \chi = \chi^{(i)} \cdot \chi^{(j)}$

$$\Gamma = \Gamma^{(i)} \otimes \Gamma^{(j)} = \sum_{k\,\text{irr.}} a_{ijk} \Gamma^{(k)}$$

$$\chi = \sum_k a_{ijk} \chi^{(k)}$$

$$\boxed{\begin{aligned} a_{ijk} &= \frac{1}{h} \sum_{g \in G} \chi^{(i)}(g)\, \chi^{(j)}(g)\, \chi^{(k)*}(g) \\ &= \frac{1}{h} \sum_{c\,(\text{classes})} N_c\, \chi^{(i)}(\mathcal{C}_c)\, \chi^{(j)}(\mathcal{C}_c)\, \chi^{(k)*}(\mathcal{C}_c) \end{aligned}}$$

d) Nomenclature: irred. rep's for point groups

"point groups": 32 groups of crystal symm.

two types:
1) one main axis
2) higher symm. (O, T)

classes: C_j : j-fold symm. about principal axis

$C_j'^{(\prime\prime)}$: — " — , about other axis

σ : reflection

i : inversion

irred. rep.

A : 1D ; $\chi(C_i) = 1$

B : 1D ; $\chi(C_1) = -1$

E : 2D

T : 3D

(3D is highest dim. for irred. rep's in 32 point groups!
(cf. level scheme XIV centers!)

Example:

Consider, for example, the group C_{2v}. Its character table is:

C_{2v}			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

Our notation here is such that σ_v is reflection in the xz plane and σ_v' is reflection in the yz plane. Then we can write out symbolically the effect of each of these operations (or its inverse, which is the same in this example) on the three coordinate functions as follows:

$$P_E\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\y\\z\end{pmatrix}\quad P_{C_2}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\-y\\z\end{pmatrix}\quad P_{\sigma_v}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\-y\\z\end{pmatrix}\quad P_{\sigma_v'}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\y\\z\end{pmatrix}$$

Comparing the results with the character table, and using the fact that $\chi^{(i)}(R) = \Gamma^{(i)}(R)$ for a one-dimensional representation, we have, for example,

$$P_{C_2}x = \Gamma^{(B_1)}(C_2)x$$

or more generally $$P_R x = \Gamma^{(B_1)}(R)x$$

Similarly, $$P_R y = \Gamma^{(B_2)}(R)y$$

and $$P_R z = \Gamma^{(A_1)}(R)z$$

We summarize these results by saying that, under the group C_{2v}, x transforms according to B_1, y according to B_2, and z according to A_1. From these results it follows that xy transforms according to $B_1 \times B_2 = A_2$, etc.

Basis fct: in group tables:

linear + quadratic, combinations

$x, y, z, x^2, \dots, x^2+y^2, -, xy, \dots$

R_x, R_y, R_z + comb's : axial, i.e. even under i (inversion)

(see table previous page)

e) Crystal field splitting:

What is the effect of lowering symmetry?

Example: O : proper rotations of  $(h=24)$

(Tables here....)

Tinkham:

O				E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
$\cancel{\Gamma_1}$	$\cancel{\alpha}$	Γ_1	A_1	1	1	1	1	1
$\cancel{\Gamma_2}$	$\cancel{\beta'}$	Γ_2	A_2	1	1	1	-1	-1
$\cancel{\Gamma_{12}}$	$\cancel{\gamma}$	Γ_3	E	2	-1	2	0	0
$\cancel{\Gamma'_{15}}$	$\cancel{\delta'}$	Γ_4	T_1	3	0	-1	-1	1
$\cancel{\Gamma'_{25}}$	$\cancel{\epsilon}$	Γ_5	T_2	3	0	-1	1	-1

$$\chi(C_2) = \chi(\pi) = (-1)^L$$

$$\chi(C_3) = \chi\left(\frac{2\pi}{3}\right) = \begin{cases} 1 & L = 0, 3, \ldots \\ 0 & L = 1, 4, \ldots \\ -1 & L = 2, 5, \ldots \end{cases}$$

$$\chi(C_4) = \chi\left(\frac{\pi}{2}\right) = \begin{cases} 1 & L = 0, 1, 4, 5, \ldots \\ -1 & L = 2, 3, 6, 7, \ldots \end{cases}$$

Crystal field splitting → spherically symm → cubic

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
D_3	7	1	−1	−1	−1
D_4	9	0	1	1	1

compare characters of classes

$$\boxed{D_L = \sum a_i\Gamma_i} \qquad \text{where} \qquad a_i = (24)^{-1}\sum N_k\chi_i(\mathscr{C}_k)\chi_L(\mathscr{C}_k)$$

$D_0 = A_1$ cannot split since it is only one-dimensional.

$D_1 = T_1$, by comparison of the characters. Since D_1 remains a single irreducible representation, a P state ($L = 1$) is not split by a cubic field.

$D_2 = E + T_2$. D_2 *must* split, since there are no five-dimensional *irreducible* representations of O. The actual decomposition shows that a D state ($L = 2$) is split into a twofold and a threefold degenerate level in a cubic field.

$D_3 = A_2 + T_1 + T_2$. Thus an F state is split into a nondegenerate and two threefold degenerate states.

$D_4 = A_1 + E + T_1 + T_2$. Thus a G state splits into a nondegenerate state, a doubly degenerate state, and two triply degenerate states.

Example:

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