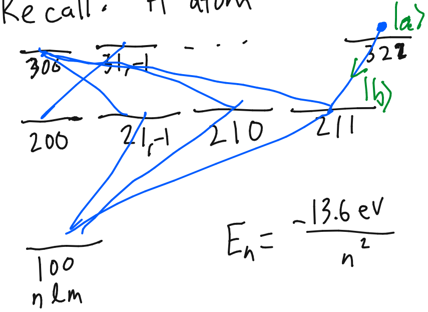
PHYS 5040
Algebra and Topology in Physics
Spring 2021

Lecture 9

February 11

1 Introduce the concept of selection rules in atomic/molecular physics.

Recall: H atom



$$E_n = \frac{-13.6\,\text{eV}}{n^2}$$

selection rules:

$\Delta \ell = \pm 1 \qquad \Delta m = 0, \pm 1$

using semiclassical arguments or (baby) QED...

$$\Gamma_{a\to b} = \frac{e^2 (E_a - E_b)^3}{3\pi \varepsilon_0 c^3 \hbar^4} \underbrace{|\langle a|\vec{p}|b\rangle|^2}_{\text{dipole matrix element}}$$

transition rate

selection rules: (group theory) which can be non-zero

$\boxed{2}$ Use representation theory to constrain the selection rules.

Hamiltonian H, symmetry group G (finite)

$[H, U(g)] = 0$ ↳ irreps $R_1, \ldots, R_n$

from Schur's Lemma: eigenstates of H classified by irrep;

$$H|n, R, k\rangle = E_{nR}|n, R, k\rangle$$

energy level ↑ n, irrep ↑ R, ↑ $k = 1, \ldots, \dim(R)$

comes in irrep P

$$\langle n_1 R_1 k_1 | P_\alpha | n_2 R_2 k_2\rangle = ?$$

$\alpha = (x, y, z)$

Claim: matrix element $\neq 0$ only when $R_1 \subset P \otimes R_2$ [or $R_2 \subset P \otimes R_1 \ldots$] [if $\chi^{(R)}(g)$ is real]

"Proof": Suppose mat $\neq 0$

$$\langle n_1 R_1 k_1 | P_\alpha | n_2 R_2 k_2\rangle = \overbrace{\langle n_1 R_1 k_1 | U^\dagger}\,\overbrace{U P_\alpha U^\dagger}\,U | n_2 R_2 k_2\rangle$$

$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix}$

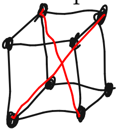
$$= \sum_{k_1' k_2' \alpha'} R_1(g)_{k_1 k_1'} \langle n_1 R_1 k_1' | P_{\alpha'} | n_2 R_2 k_2\rangle P(g)_{\alpha\alpha'} R_2(g)_{k_2 k_2'}$$

$$\sum_{g \in G} \frac{1}{|G|} \cdots =$$

by G.O.T. $R_1 \subset R_1 \oplus \cdots \oplus$

$$(R_1 \oplus R_2 \oplus \cdots) \simeq (P \otimes R_2)_{k_2\alpha, k_2'\alpha'}$$

3 Consider a crystal with symmetry group $O_h = S_4 \times \mathbb{Z}_2$. Give the character table and label the representations. Which irrep(s) does the dipole moment correspond to?



direct product group: irreps of $O_h \to (R_1, R_2)$

R_1: irrep of S_4 R_2: irrep of $\mathbb{Z}_2$

n_c	S_4	1	1′	2	3	3′
1	1	1	1	2	3	3
6	(12)	1	−1	0	1	−1
8	(123)	1	1	−1	0	0
6	(1234)	1	−1	0	−1	1
3	(12)(34)	1	1	2	−1	−1

character table for $S_4 \times \mathbb{Z}_2$ is tensor product of tables...

denote irreps of O_h as $(R_1)_\pm$ (R_1: S_4, $\pm$: $\mathbb{Z}_2$)

$$\chi^{(3_-)}((g,h)) = \chi^{(3)}(g)\,\chi^{(-)}(h)$$

$(x,y,z) \to (-x,-y,-z)$

$\mathbb{Z}_2$	+	−
1	1	1
5	1	−1

find dipole moment is 3_-

4 Consider an ~~atom~~ electron (in a crystal with this symmetry group) in a $\mathbf{3}_-$ (p) orbital. Into which irreps' orbitals can it decay via single-photon spontaneous emission?

$\langle \underset{\uparrow \text{init.}}{a} | \vec{p} | \underset{\leftarrow \text{Fin.}}{b} \rangle$ $\langle a, \cancel{ph}\, p | H_{QED} | b, \text{no phot} \rangle$

Compare w/ H atom:

$3_- \rightarrow \ell = 1$

$\ell = 1 \rightarrow \ell = 0$ or $\ell = 2$

selection rules: $\underset{\text{starting orbital}}{3_-} \otimes \underset{\text{photon/dipole mom.}}{3_-} = \underbrace{1_+ \oplus 2_+ \oplus 3_+ \oplus \cancel{3}3'_+}_{\text{final orbital}}$

S_4

if $3 \otimes 3 = R$, then $3_- \otimes 3_- = R_+$

in S_4: $3 \otimes 3 = 1 \oplus 2 \oplus 3 \oplus 3'$

$\chi^{(3\otimes 3)}(1) = \chi^{(3)}(1)^2 = 3^2 = 9$

$\chi^{(3\otimes 3)}[(12)] = \chi^{(3)}((12))^2 = 1$

$\chi^{(3\otimes 3)}((123)) = 0$

$\chi^{(3\otimes 3)}((1234)) = 1$

$\chi^{(3\otimes 3)}((12)(34)) = 1$

$\chi^{3\times 3}$ χ^{1} n_a

$$n_1 = \frac{1}{24}\Big[\underbrace{9\cdot 1\cdot 1}_{1} + \underbrace{1\cdot 6\cdot 1}_{(12)} + \underbrace{1\cdot 8\cdot 0}_{(123)} + \underbrace{1\cdot 6\cdot 1}_{(1234)} + \underbrace{1\cdot 3\cdot 1}_{(12)(34)}\Big] = 1$$

$$n_2 = \frac{1}{24}\Big[\underbrace{9\cdot 2\cdot 1}_{1} + 1\cdot 0\cdot 1 + \cdots \underbrace{3\cdot 2\cdot 1}_{(12)(34)}\Big] = 1$$

⋮

$n_{1'} = 0$ $n_{3'} = 1$ $n_3 = 1$

5 What is the Wigner-Eckart Theorem?

Calculating: $\langle n_1 R_1 k_1 | P_\alpha | n_2 R_2 k_2 \rangle \neq 0$ only if $R_1 \subset P \otimes R_2$

Assume that R_1, R_2, P are all irreps of G.

(generalized) Wigner-Eckart Thm:

$$\langle n_1 R_1 k_1 | P_\alpha | n_2 R_2 k_2 \rangle = \underbrace{\langle n_1 R_1 \| P \| n_2 R_2 \rangle}_{\text{const. from QM, not math}} \cdot \underbrace{\langle R_1 k_1 | P \alpha \; R_2 k_2 \rangle}_{\text{Clebsch-Gordan coefficients}}$$

Note: assuming R_1 shows up once in $P \otimes R_2$

6 What are Clebsch-Gordan coefficients?

Change perspective: start w/ smaller Hilbert space... irrep $P \otimes R_2$

dim(P)-space

$|P\alpha\rangle \otimes |R_2k_2\rangle$

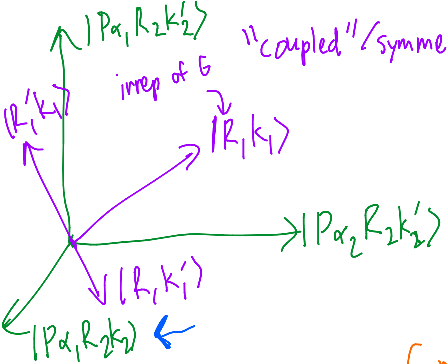
$\alpha=1,\ldots,\dim(P)$

$k_2=1,\ldots,\dim(R_2)$

"uncoupled"/product basis

$|P\alpha\, R_2k_2\rangle$ [spin: $|j_1m_1j_2m_2\rangle$]

"coupled"/symmetry basis



C-G coefficients:

change of basis coefficients!

$$|P\alpha_1 R_2k_2\rangle = \sum_{R_1k_1} |R_1k_1\rangle \underbrace{\langle R_1k_1|P\alpha_1 R_2k_2\rangle}_{\text{C-G coeff.}}$$

Comment: if $R_1 \notin P\otimes R_2$, we still define $\langle R_1k_1|P\alpha R_2k_2\rangle = 0$ $\forall k_1,k_2,\alpha$

7 Sketch how to calculate Clebsch-Gordan coefficients.

$$|R_1 k_1\rangle\langle R_1 k_1'| := \frac{d_{R_1}}{|G|}\sum_{g\in G} \overline{R_1(g)}_{k_1 k_1'}\,(P\otimes R_2)(g)$$

Step #1: $k_1=0\ldots$

$$\langle P\alpha R_2 k_2|\underbrace{R_1 0\rangle\langle R_1 0}_{\text{projector}}|P\alpha R_2 k_2\rangle = c^2 \qquad c>0$$

Step #2:

$$\langle P\alpha R_2 k_2|\underbrace{R_1 0\rangle\langle R_1 k_1}_{\text{projector}}|P\alpha' R_2 k_2'\rangle = c\,\langle R_1 k_1|P\alpha' R_2 k_2'\rangle$$

8 In D_8, what are the Clebsch-Gordan coefficients $\langle Rk|\mathbf{2}i\mathbf{2}j\rangle$?