PHYS 4410
Quantum Mechanics 2
Spring 2023

Lecture 32

Selection rules

April 14

$\boxed{1}$ Last time: absorption/emission of photons:

$$R_{i\to f} \sim |\langle f|\vec{p}|i\rangle|^2$$

↖ electric dipole. usually $\vec{p} = -e\vec{r}$.

Today: selection rules, or symmetry constraints on $\langle f|\vec{p}|i\rangle$.

Example: parity symmetry $x \to -x$ (P)

Classify states as:

even: $P|\psi\rangle = +|\psi\rangle$ $\quad \psi_e(x) = \psi_e(-x)$

odd: $P|\psi\rangle = -|\psi\rangle$ $\quad \psi_o(x) = -\psi_o(-x)$

Suppose: $\langle f|p|i\rangle = -e\langle f|x|i\rangle$

$\langle f|x|i\rangle = 0$ if: i & f both even or odd

$\boxed{2}$ Suppose: $P|f\rangle = \pi_f |f\rangle$ and $P|i\rangle = \pi_i |i\rangle$

π_f: $\uparrow$ ± 1

$\psi_f(x) = \pi_f \psi_f(-x)$ and $\psi_i(x) = \pi_i \psi_i(-x)$.

$$\langle f|x|i\rangle = \int_{-\infty}^{\infty} dx\, \psi_f^*(x)\, x\, \psi_i(x) = \int_0^{\infty} dx\, \psi_f^*(x)\, x\, \psi_i(x) + \int_{-\infty}^{0} dx \cdots$$

$(z = -x)$

$$= \int_0^{\infty} dz\, \psi_f^*(-z)(-z)\psi_i(-z)$$

$$= \int_0^{\infty} dz\, (\pi_f \cdot \pi_i \cdot -1)\, \psi_f^*(z)\, z\, \psi_i(z)$$

$$= \boxed{(1 - \pi_f \pi_i)} \int_0^{\infty} dz\, \psi_f^*(z)\, z\, \psi_i(z)$$

$\langle f|x|i\rangle = 0$ $\quad \pi_f \pi_i = 1$ (both i/f even/odd)

$\boxed{3}$ Suppose $\langle f | \phi \rangle \neq 0$. Then f & ϕ both odd/even.

each has definite parity

$$\langle f | P | \phi \rangle = \langle f | \big(P | \phi \rangle \big) = \langle f | \phi \rangle \pi_\phi$$
$$= \big(\langle f | P \big) | \phi \rangle = \pi_f \langle f | \phi \rangle$$

$$\langle f | P | \phi \rangle - \langle f | P | \phi \rangle = \langle f | \phi \rangle \pi_\phi - \langle f | \phi \rangle \pi_f = \underbrace{\langle f | \phi \rangle (\pi_\phi - \pi_f)}_{} = 0$$

either $\langle f | \phi \rangle = 0$ or $\pi_\phi = \pi_f$.

Back to selection rules: $\langle f | x | i \rangle = \langle f | \phi \rangle$ where $\underline{| \phi \rangle = x | i \rangle}$.

$P | i \rangle = \pi_i | i \rangle$ $\qquad$ $P \big(x | i \rangle \big) = -x P | i \rangle = (-\pi_i) x | i \rangle$

$$x \quad | i \rangle \quad = \quad | \phi \rangle$$

$$\text{odd} \otimes \begin{cases} \text{even} \\ \text{odd} \end{cases} = \begin{cases} \text{odd} \\ \text{even} \end{cases}$$

<u>Summary</u>: $| i \rangle$ & $| f \rangle$ have opposite parity

$\boxed{4}$ Rotation symmetry in 3d: $\langle f|\underline{\vec{r}}|i\rangle$

$l_f m_f \quad l_r m_r \quad l_i m_i$

Classify i & f in terms of:

orbital angular momentum

$l = 0, 1, 2, \ldots \qquad [m = -l, \ldots, l-1, l]$

$z|i\rangle = |\phi\rangle$

"$l_\phi m_\phi$"

$$\vec{r} \otimes |i\rangle = |\phi\rangle$$

If $\langle f|\phi\rangle \neq 0$, need $l_f = l_\phi$

$m_f = m_\phi$

$$l_r \otimes l_i = |l_i - l_r| \oplus \cdots \oplus (l_i + l_r - 1) \oplus (l_i + l_r)$$

$(m_r) \qquad (m_i) \qquad\qquad m_i + m_r$

uncoupled basis $\qquad$ coupled basis

need non-vanishing C-G coefficients: $\underline{\langle l_f m_f | l_r m_r l_i m_i \rangle \neq 0}$

$l_r = 1$

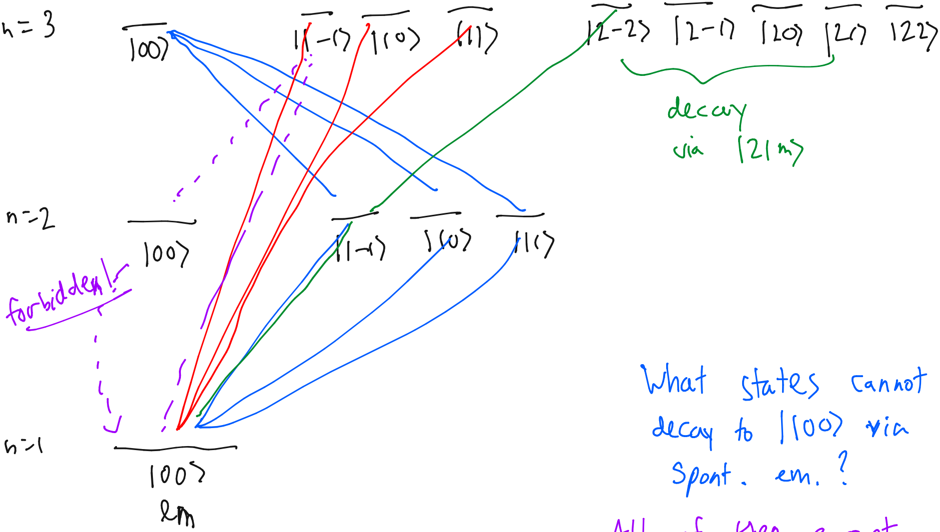
$m_r = 0, \pm 1$

$1 \otimes l_i = \boxed{(l_i - 1)} \oplus l_i \oplus \boxed{(l_i + 1)}$ one of these $= l_f$.

$m_i + m_r = m_f$, so $\underline{|m_i - m_f| = 0 \text{ or } 1}$.

Claim: $\underline{|l_i - l_f| = 1}$. Because $\vec{r} \to -\vec{r}$: $|lm\rangle \to (-1)^l |lm\rangle$

$\boxed{5}$ Take $n=1,2,3$ hydrogen:



What states cannot decay to $|100\rangle$ via spont. em.?

All of them except $|200\rangle$!

at first order.