Selection Rules

Matrix elements of a perturbation $\underset{\sim}{H}'$ are sometimes 0.

For example, the eigenkets of $\underset{\sim}{H}^0$ are often eigenkets of other operators, like $\underset{\sim}{L}^2$, or $\underset{\sim}{L}_z$, or parity $\underset{\sim}{\Pi}$. Call one of these $\underset{\sim}{\Omega}$. Obviously $[\underset{\sim}{H}^0, \underset{\sim}{\Omega}] = 0$. $\Omega \rightarrow$ Hermitian

Then say: $\underset{\sim}{\Omega}|\alpha_1 \omega_1\rangle = \omega_1 |\alpha_1 \omega_1\rangle$

e.v. of $\underset{\sim}{\Omega}$

$\underset{\sim}{\Omega}|\alpha_2 \omega_2\rangle = \omega_2 |\alpha_2 \omega_2\rangle$

The symbol α_1 represents all the quantum numbers other than ω that might describe the state. If $\underset{\sim}{\Omega}$ is $\underset{\sim}{L}_z$, α might include radial & l quantum numbers.

Then, $\langle \alpha_2 \omega_2 | \underset{\sim}{H}' | \alpha_1 \omega_1 \rangle = 0$ "selection rule" when $\omega_1 \neq \omega_2$

when $[\underset{\sim}{\Omega}, \underset{\sim}{H}'] = 0$

To see this: $0 = \langle \alpha_2 \omega_2 | [\underset{\sim}{\Omega}, \underset{\sim}{H}'] | \alpha_1 \omega_1 \rangle$

$= \langle \alpha_2 \omega_2 | [\underbrace{\underset{\sim}{\Omega}}_{\text{right}} \underset{\sim}{H}' - \underset{\sim}{H}' \underbrace{\underset{\sim}{\Omega}}_{\text{left}}] | \alpha_1 \omega_1 \rangle$

$0 = \underbrace{(\omega_2 - \omega_1)}_{\neq \text{ by assumption}} \underbrace{\langle \alpha_2 \omega_2 | \underset{\sim}{H}' | \alpha_1 \omega_1 \rangle}_{\text{must then } = 0}$

"$\underset{\sim}{H}'$ carries no $\underset{\sim}{\Omega}$" means $\dashrightarrow$

$$\underset{\sim}{\Omega}(\underset{\sim}{H}'|\omega_1\rangle) = \underset{\sim}{H}'\underset{\sim}{\Omega}|\omega_1\rangle = \underset{\sim}{H}'(\omega_1|\omega_1\rangle) = \omega_1(\underset{\sim}{H}'|\omega_1\rangle)$$

because $[\underset{\sim}{\Omega}, \underset{\sim}{H}'] = 0$

$\underset{\sim}{\Omega}\underset{\sim}{H}' - \underset{\sim}{H}'\underset{\sim}{\Omega} = 0$

$\underset{\sim}{\Omega}\underset{\sim}{H}' = \underset{\sim}{H}'\underset{\sim}{\Omega}$

$\underset{\sim}{H}'|\omega_1\rangle$ still an eigenstate of $\underset{\sim}{\Omega}$ with same eigenvalue ω_1 when $[\underset{\sim}{\Omega}, \underset{\sim}{H}'] \neq 0$ then things like

$\underset{\sim}{H}'|\omega_1\rangle \propto |\omega_1\rangle + \alpha|\omega_2\rangle$ happen

more or less "$\underset{\sim}{\Omega}$"

$\rightarrow \underset{\sim}{H}'$ carries $\underset{\sim}{\Omega}$ when $[\underset{\sim}{H}', \underset{\sim}{\Omega}] \neq 0$

Example

Suppose $\underset{\sim}{H}' \propto \underset{\sim}{z}$, $= \alpha\underset{\sim}{z}$

note: $[\underset{\sim}{L}_z, \underset{\sim}{H}'] = \alpha[\underset{\sim}{L}_z, \underset{\sim}{z}] = 0$

because $\underset{\sim}{L}_z = \underset{\sim}{X}P_y - \underset{\sim}{Y}P_x \leftarrow$ no P_z!

so $\langle \underbrace{n'l'm'}_{\text{SHO or Hydrogen}} | \underset{\sim}{H}' | nlm \rangle \propto \delta_{m'm}$

(won't cover Wigner-Eckart theorem, but this example is W.E.T.)

<u>Parity</u> when $[\underset{\sim}{\Pi}, \underset{\sim}{H}'] = 0$

and $[\underset{\sim}{\Pi}, \underset{\sim}{H}^0] = 0$

then $\langle m^0 | \underset{\sim}{H}' | n^0 \rangle = 0$ unless $|m^0\rangle, |n^0\rangle$ have <u>same</u> parity.

A related case: suppose $\underset{\sim}{\Pi} |n^0\rangle = \underset{\uparrow}{\Pi} |n^0\rangle$

+1 or −1

consider $\underset{\sim}{\Pi} \begin{Bmatrix} \underset{\sim}{x} \\ \underset{\sim}{y} \\ \underset{\sim}{z} \\ p_x \\ p_y \\ p_z \end{Bmatrix} |n^0\rangle = -\Pi \begin{Bmatrix} \underset{\sim}{x} \\ \underset{\sim}{y} \\ \underset{\sim}{z} \\ p_x \\ p_y \\ p_z \end{Bmatrix} |n^0\rangle$

since $\underset{\sim}{\Pi}\underset{\sim}{x} = -\underset{\sim}{x}\underset{\sim}{\Pi}$

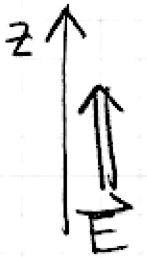
so states like $\underset{\sim}{x}|n^0\rangle$ have parity opposite to $|n^0\rangle$. So, for

$\langle m^0 | \underset{\sim}{x} | n^0 \rangle$ to be non-zero, $|m^0\rangle, |n^0\rangle$ must have <u>opposite</u> parity

or $\underset{\sim}{y}, \underset{\sim}{z}, p_x, p_y, p_z$

Stark ~~Effect~~ in ground state

Put a hydrogen atom in an electric field, $\vec{E} = \mathcal{E}\hat{k} = \mathcal{E}\hat{z}$.



$\phi = -\mathcal{E} z$

z_e o electron

z_p • proton

$$H' = -\mathcal{E}(\underset{-e}{q_e} z_e + \underset{+e}{q_p} z_p)$$

$$H' = e\mathcal{E}(\underbrace{z_e - z_p}_{z\text{, the relative coordinate}})$$

$$H' = e\mathcal{E} z$$

First Order: $E^1_{100} = \langle 100|e\mathcal{E}z|100\rangle$

ground state $n=1$

$$= e\mathcal{E}\underbrace{\langle 100|z|100\rangle}_{0 \text{ by parity}}$$

no shift... another view is:

$$\int \underbrace{d^3x\,|\psi_{100}(\vec{x})|^2}_{\text{spherically symmetric}} z$$

$\frac{1}{2}+,\ \frac{1}{2}- \Rightarrow$ nulls out.

so $E_0^1 = 0$

means omit 100 or generally, the state being perturbed

Second Order: $$E^2_{100} = \sum_{n\ell m}{}' \frac{e^2\mathcal{E}^2\langle 100|z|n\ell m\rangle\langle n\ell m|z|100\rangle}{E_{100} - E_{n\ell m}}$$

note that $E_{100} - E_{n\ell m} < 0$ because $E_{n\ell m} > E_{100}$. The numerator is ≥ 0 since $\langle 100|z|n\ell m\rangle\langle n\ell m|z|100\rangle = |\langle 100|z|n\ell m\rangle|^2$

so, $E^2_{100} \leq 0$ ← to second order, ground state lowers energy

<u>Method #1</u> Try to bracket $|E^2_{100}|$

$$|E_{100} - E_{n\ell m}| \geq |E_{100} - E_{200}| = \frac{e^2}{2a_0}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$
$$= \frac{3}{8}\frac{e^2}{a_0}$$

so $$|E^2_{100}| = e^2\mathcal{E}^2\left|\sum{}' \frac{|\langle 100|z|n\ell m\rangle|^2}{E_{100} - E_{n\ell m}}\right|$$

$$\leq \frac{e^2\mathcal{E}^2}{\frac{3}{8}\frac{e^2}{a_0}}\left(\underbrace{\sum{}' |\langle 100|z|n\ell m\rangle|^2}_{\text{remember, missing 100 in sum (the ' means this)}}\right)$$

$$E^2_{100} \leq \frac{8}{3}a_0\mathcal{E}^2\Big(\sum \langle 100|z|n\ell m\rangle\langle n\ell m|z|100\rangle$$
$$- \langle 100|z|100\rangle\langle 100|z|100\rangle\Big)$$

no '

subtract this to make up for ' removal

but $\sum |n\ell m\rangle\langle n\ell m| = 1$

$$E^2_{100} \leq \frac{8}{3}a_0\mathcal{E}^2\left(\langle 100|z^2|100\rangle - \underbrace{\langle 100|z|100\rangle^2}_{0}\right)$$

$$\langle 100|z^2|100\rangle = \int d^3x\, |\psi_{100}(\vec{x})|^2 z^2$$

p. 357 $$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-\frac{r}{a_0}} \qquad z = r\cos\theta \qquad \mu \equiv \cos\theta$$

$$= \frac{1}{\pi a_0^3}\int_0^\infty dr\, r^4 e^{-2r/a_0} \underbrace{\int_{-1}^{1} d\mu\, \mu^2}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$\langle 100|z^2|100\rangle = \frac{2a_0^2}{2^5} \times \frac{2}{3} \times \underbrace{\int_0^\infty d\rho\, \rho^4 e^{-\rho}}_{4! = 2^2\cdot 3\cdot 2 = 2^3\cdot 3}$$

$$= \frac{2^2\cdot 2^3\cdot 3}{2^5\cdot 3}\cdot a_0^2 = a_0^2$$

so $\boxed{E_{100}^2 \leq \frac{8}{3} a_0^3 \mathcal{E}^2}$

Method #2 Dalgarno + Lewis

→ idea is to cancel out the energy denominator by figuring out a way to get $\underset{\sim}{H}^0$ back in the picture

→ "new" operator $\underset{\sim}{\Omega}$ (to be found)

→ satisfies $\underset{\sim}{H}^1 = [\underset{\sim}{\Omega}, \underset{\sim}{H}^0]$.

then $$E_{100}^2 = \sum{}' \frac{\langle 100|\underset{\sim}{H}^1|nlm\rangle\langle nlm|\underset{\sim}{H}^1|100\rangle}{E_{100} - E_{nlm}}$$

$$= \sum{}' \frac{\langle 100|\underset{\sim}{H}^1|nlm\rangle\langle nlm|[\underset{\sim}{\Omega}, \underset{\sim}{H}^0]|100\rangle}{E_{100} - E_{nlm}}$$

$$= \sum{}' \frac{\langle 100|\underset{\sim}{H}^1|nlm\rangle\langle nlm|\underset{\sim}{\Omega}\underset{\sim}{H}^0 - \underset{\sim}{H}^0\underset{\sim}{\Omega}|100\rangle}{E_{100} - E_{nlm}}$$

$$= \sum{}' \frac{\langle 100|\underset{\sim}{H}^1|nlm\rangle\cancel{(E_{100} - E_{nlm})}\langle nlm|\underset{\sim}{\Omega}|100\rangle}{\cancel{(E_{100} - E_{nlm})}}$$

$$= \sum{}' \langle 100|\underset{\sim}{H}^1|nlm\rangle\langle nlm|\underset{\sim}{\Omega}|100\rangle$$

$$= \sum \langle 100|\underset{\sim}{H}'|nlm\rangle\underbrace{\langle nlm|}_{\text{complete (now)}}\underset{\sim}{\Omega}|100\rangle - \langle 100|\underset{\sim}{H}'|100\rangle\langle 100|\underset{\sim}{\Omega}|100\rangle$$

$$E^2_{100} = \langle 100|\underset{\sim}{H}'\underset{\sim}{\Omega}|100\rangle - \langle 100|\underset{\sim}{H}'|100\rangle\langle 100|\underset{\sim}{\Omega}|100\rangle$$

To find $\underset{\sim}{\Omega}$, only really need: $\quad \underset{\sim}{H}'|100\rangle = [\underset{\sim}{\Omega}, \underset{\sim}{H}^0]|100\rangle$

but $\underset{\sim}{H}'|100\rangle \rightarrow e\mathcal{E}z\left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$

$$= e\mathcal{E}r\cos\theta\left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

assert with:

$$\underset{\sim}{\Omega} = -\frac{m a_0 e\mathcal{E}}{\hbar^2}\left[\frac{r^2\cos\theta}{2} + a_0 r\cos\theta\right]$$

then $[\underset{\sim}{\Omega}, \underset{\sim}{H}^0]|100\rangle = \underset{\sim}{H}'|100\rangle$

$$\underset{\sim}{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \qquad |100\rangle = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

a bit of work to prove ... grungy.

exact value: $\boxed{E^2_{100} = -\frac{27}{32} \times \frac{8}{3} a_0^3 \mathcal{E}^2}$