Lecture 4

Time-independent Perturbation Theory

▲ problem: solved H_0 prob. exactly

want to know soln for $H = H_0 + H_1$

where perturbing Hamiltonian $H_1 << H_0$

Ex. H_0 Coulomb field of e & nucleus

H_1 is an additional E or B fields.

time-independent p.t.: H_1 is const in t.

▲ solution:

A. Nondegenerate case of H_0.

know $|n^0\rangle$, E_n^0 i.e. solved $H_0|n_0\rangle = E_n^0|n_0\rangle$

$\Rightarrow$ take: $|n\rangle = |n_0\rangle + |n_1\rangle + |n_2\rangle + \dots$

$$E_n = E_{n0} + E_{n1} + \dots$$

$|n_k\rangle$, E_n^k — k^{th} order (in powers of H_1) correction to unperturbed approximation.

A. Nondegenerate Perturbation theory: (4.2)

What are these?

$$H|n\rangle = E_n|n\rangle$$

$$(H_0 + H_1)\left[|n^\circ\rangle + |n'\rangle + \dots\right] = (E_n^\circ + E_n' + \dots)\left[|n^\circ\rangle + \dots\right]$$

now iteratively solve above eqn in $H_1 << H_0$

- 0th order: $H_0|n^\circ\rangle = E_n^\circ|n^\circ\rangle \Rightarrow E_n^\circ = E_n$
- 1st order: $H_0|n'\rangle + H_1|n^\circ\rangle = E_n^\circ|n'\rangle + E_n'|n^\circ\rangle$

$\langle n^\circ| \Rightarrow$

$$\cancel{\langle n^\circ|H_0|n'\rangle} + \langle n^\circ|H_1|n^\circ\rangle = \cancel{E_n^\circ\langle n^\circ|n'\rangle} + E_n'\underbrace{\langle n^\circ|n^\circ\rangle}_{1}$$

$$\Rightarrow \boxed{E_n' = \langle n^\circ|H_1|n^\circ\rangle}$$

$\langle m^\circ| \quad (m \neq n) \Rightarrow$

$$\underbrace{\langle m^\circ|H_0|n'\rangle}_{E_m^\circ\langle m^\circ|n'\rangle} + \langle m^\circ|H_1|n^\circ\rangle = E_n^\circ\langle m^\circ|n'\rangle + E_n'\underbrace{\langle m^\circ|n^\circ\rangle}_{0}$$

$$\Rightarrow \langle m^\circ|n'\rangle = \frac{\langle m^\circ|H_1|n^\circ\rangle}{E_n^\circ - E_m^\circ}$$

What about $\langle n^\circ|n'\rangle$? via overall normalization

$$1 = \langle n|n\rangle = \Big(\langle n^\circ| + \langle \underbrace{n_\perp'}_{\text{no } |n^\circ\rangle \text{ contrib.}}| + \langle \underbrace{n_\parallel'}_{\propto |n^\circ\rangle}|\Big)\big(|n^\circ\rangle + \dots\big)$$

4.3

$$\Rightarrow 1 = \langle n^\circ | n^\circ \rangle + \langle n^1_{\parallel} | n^\circ \rangle + \langle n^\circ | n^1_{\parallel} \rangle$$

(used $\langle n^\circ | n^1_\perp \rangle = 0$)

$$\Rightarrow \langle n^1_{\parallel} | n^\circ \rangle + \langle n^\circ | n^1_{\parallel} \rangle = 0$$

$$\Rightarrow \langle n^\circ | n^1_{\parallel} \rangle = i\alpha$$

purely imaginary

$$\Rightarrow |n\rangle = |n^\circ\rangle e^{i\alpha} + \sum_{m \neq n} C^{(1)}_m |m^\circ\rangle$$

$$C^{(1)}_m = \frac{\langle m^\circ | H' | n^\circ \rangle}{E^\circ_n - E^\circ_m}$$

can drop $e^{i\alpha}$ by redefinition $|n\rangle \to e^{i\alpha}|n\rangle$

& dropping α in $|n'\rangle$ to 1^{st} order in H_1

note: $\langle n' | n^\circ \rangle = 0$

- 2nd order:

$$H^\circ |\underbrace{n^2}_{?}\rangle + H' |n'\rangle = E^\circ_n |\underbrace{n^2}_{?}\rangle + E'_n |n'\rangle + \underbrace{E^2_n}_{?} |n^\circ\rangle$$

$\langle n^\circ | \Rightarrow$

$$\cancel{\langle n^\circ | H^\circ | n^2 \rangle} + \langle n^\circ | H' | n' \rangle = \cancel{E^\circ_n \langle n^\circ | n^2 \rangle} + E'_n \underbrace{\cancel{\langle n^\circ | n' \rangle}}_{0} + E^2_n \underbrace{\langle n^\circ | n^\circ \rangle}_{1}$$

$$\Rightarrow E^2_n = \langle n^\circ | H' | n' \rangle = \sum_m{}' \frac{\langle n^\circ | H' | m^\circ \rangle \langle m^\circ | H' | n^\circ \rangle}{E^\circ_n - E^\circ_m}$$

$$\boxed{E^2_n = \sum_m{}' \frac{|\langle n^\circ | H' | m^\circ \rangle|^2}{E^\circ_n - E^\circ_m}}$$

... can keep going to arbitrary order.

① $$|n\rangle = \left(|n^\circ\rangle + \sum_{m\neq n} \frac{\langle m^\circ|H'|n^\circ\rangle}{E_n^\circ - E_m^\circ}|m^\circ\rangle\right)N$$

② $$E_n = E_n^\circ + \langle n^\circ|H'|n^\circ\rangle + \sum_{m\neq n}\frac{|\langle m^\circ|H'|n^\circ\rangle|^2}{E_n^\circ - E_m^\circ}$$

where N is normalization of perturbed state $|n\rangle$

$N = ?$

$$\langle n|n\rangle = N^2\left(1 + \sum_m{}' |C_m|^2\right)$$

$$\Rightarrow N = \frac{1}{\sqrt{1 + \sum_m' |C_m|^2}} \simeq 1 - \frac{1}{2}\sum_m{}' |C_m|^2 + \cdots$$

can one calculate E_n via $\langle n|H|n\rangle$ instead of ②? Yes, but need to keep track of N above:

$$H = H_0 + H'$$

$$E_n = \langle n|H_0 + H'|n\rangle = \langle n|H_0|n\rangle + \langle n|H'|n\rangle$$
$$= N^2\Big[\Big(\langle n^\circ| + \sum_m{}' C_m^* \langle m^\circ|\Big) H_0 \Big(|n^\circ\rangle + \sum_m{}' C_m|m^\circ\rangle\Big)$$
$$+ \Big(\langle n^\circ| + \sum_m{}' C_m^*\langle m^\circ|\Big) H' \Big(|n^\circ\rangle + \sum_m{}' C_m|m^\circ\rangle\Big)\Big]$$

$$E_n = N^2\Big[E_n^0 + \sum_m{}' |C_m|^2 E_m^0 + \langle n^0|H'|n^0\rangle$$

$$+ \sum_m{}'\left(C_m^* \langle m^0|H'|n^0\rangle + C_m \langle n^0|H'|m^0\rangle\right)$$

$$+ \text{high order terms}\Big]$$

$$E_n = \left(1 - \frac{1}{2}\sum_m{}' |C_m|^2\right)^2 \Big[\;\ldots\;\Big] \qquad \left(\frac{\langle m^0|H'|n^0\rangle}{E_n^0 - E_m^0}\right)^2 \quad (3^{\text{rd}}\text{ order})$$

$$E_n \simeq \Big[E_n^0 - \sum_m{}' |C_m|^2 (E_n^0 - E_m^0) + \langle n^0|H'|n^0\rangle$$

$$+ 2\sum_m{}' \frac{|\langle m^0|H'|n^0\rangle|^2}{E_n^0 - E_m^0} + \mathcal{O}(3^{\text{rd}})\Big]$$

$$\boxed{E_n \simeq E_n^0 + \langle n^0|H'|n^0\rangle + \sum_m{}' \frac{|\langle m^0|H'|n^0\rangle|^2}{E_n^0 - E_m^0}}$$

✓ agrees w/ 2^{nd} order p.t.

Comments:

- strongest effect from nearby levels due to small denominator
- 2^{nd} order correction $E_0^{(2)} < 0$
- level repulsion
- connection to variational method:

recall $E_0^{\text{variat}} = \langle \Psi | H | \Psi \rangle$

$$= \langle n^0 | H_0 + H_1 | n^0 \rangle$$

e.g. $|\Psi\rangle = |n^0\rangle = E_0^{(0)} + \underbrace{\langle n^0 | H_1 | n^0 \rangle}_{E_0^{(1)}}$

simplest choice

but pert. theory shows that

$$E_0^{\text{var}} > E_0 = E_0^{(0)} + E_0^{(1)} - |E_0^{(2)}|$$

as expected since E_0^{var} is upper bound

- P.T. is only ok if $\left| \frac{|\langle m^0 | H_1 | n^0 \rangle|}{E_n^0 - E_m^0} \right| \ll 1$

want large gaps in unperturbed spectrum, fails with gapless excitations $\rightarrow$ nondegenerate.

- $|n\rangle = |n^0\rangle + \underbrace{\sum_{m \neq n} c^{(m)} |m^0\rangle}_{\text{admixture of states other than } |n\rangle}$

- selection rules essential; e.g $\langle m | H_1 | n \rangle$ might vanish!

Examples

1. Shifted harmonic oscillator: 'toy' model of dc Stark shift

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 - q\mathcal{E}x$$

- Exact soln: (recall final exam P5250)

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 \Big(x - \underbrace{\frac{q\mathcal{E}}{m\omega^2}}_{\substack{\text{shift} \\ \text{in } \langle x\rangle = \alpha}}\Big)^2 - \underbrace{\frac{q^2\mathcal{E}^2}{2m\omega^2}}_{\text{in } E_n}$$

$$\Rightarrow E_n = \hbar\omega(n+\tfrac{1}{2}) - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

$$\psi_n(x) = N_n H_n\left(\frac{x-\alpha}{x_0}\right) e^{-\frac{(x-\alpha)^2}{2x_0^2}}$$

Note: $\underbrace{\alpha = \frac{q\mathcal{E}}{m\omega^2}}_{\text{shift}}$ is also a classical equilibrium

Taylor expand E_n, ψ_n in $\left(\frac{\alpha}{x_0}\right)^2 = \frac{q^2\mathcal{E}^2/2m\omega^2}{\hbar\omega} << 1$

$$E_n = E_n^{\circ} - \underbrace{\frac{q^2\mathcal{E}^2}{2m\omega^2}}$$

only quadratic correction → exact 2nd order p.t.
note $E_n^{(2)} < 0$ as expected.

$$\psi_0(x) = N_0 e^{-\frac{(x-\alpha)^2}{2x_0^2}} = \psi_0^{(0)}(x) \underbrace{e^{+\frac{x\alpha}{x_0^2}}}_{\substack{1 + \frac{\alpha}{x_0^2}x + \frac{\alpha^2}{2x_0^4}x^2 + \dots \\ H_1(x) + H_2(x) + \dots}} e^{-\frac{\alpha^2}{2x_0^2}} \leftarrow \text{normaliz. correction.}$$

<u>more formally</u> translation op. by a

$$|n\rangle = T(\alpha)\,|n^\circ\rangle \qquad \Big| \quad T(a)f(x) = e^{-a\partial_x} f(x) = f(x-a) \checkmark$$

$$= e^{-i\frac{\alpha}{\hbar}p}\,|n^\circ\rangle$$

$$\simeq \left(I - i\frac{\alpha}{\hbar}p\right)|n^\circ\rangle$$

$$= \left(I - i\frac{\alpha}{\hbar}\left(\frac{\hbar m\omega}{2}\right)^{1/2}\frac{a-a^+}{i}\right)|n^\circ\rangle$$

$$|n\rangle \simeq |n^\circ\rangle + \frac{q\mathcal{E}}{(2m\hbar\omega^3)^{1/2}}\left[(n+1)^{1/2}|(n+1)^\circ\rangle - n^{1/2}|(n-1)^\circ\rangle\right]$$

$$\boxed{\begin{aligned} x &= \frac{x_0}{\sqrt{2}}(a^+ + a) \\ p &= \frac{i\hbar}{\sqrt{2}x_0}(a^+ - a)\end{aligned}}$$

- <u>perturbation theory</u>:

$$H = H^\circ + H'$$

$\boxed{1^{st}\text{ order}}$

$$E_n' = \langle n^\circ|H'|n^\circ\rangle = -q\mathcal{E}\langle n^\circ|x|n^\circ\rangle$$

$\Rightarrow \underline{E_n' = 0}$ ← example of <u>selection rules</u>

parity ✓ ▲ coord. repres. $\langle n^\circ|x|n^\circ\rangle \propto \int_{-\infty}^{\infty} \underbrace{|\psi_n^\circ|^2 x}_{\text{odd in } x} = 0$

phonon conservation ✓ ▲ $x = \frac{x_0}{\sqrt{2}}(a^+ + a)$

$$\Rightarrow \langle n^\circ|x|n^\circ\rangle \propto \underbrace{\langle n^\circ|a^+|n^\circ\rangle}_{0} + \underbrace{\langle n^\circ|a|n^\circ\rangle}_{0}$$

<u>Physics</u>: dipolar interaction $\vec{d}\cdot\vec{\mathcal{E}}$, but $\langle\vec{d}\rangle = 0$ in all eigenstates of H.O. $\Rightarrow E_n' = 0$. But expect to 2^{nd} order $E_n^{(2)} \neq 0$ since $\vec{d}$ is induced to linear order in $\vec{\mathcal{E}}$: $\vec{d} = \chi\vec{\mathcal{E}} \Rightarrow \vec{d}_n\cdot\vec{\mathcal{E}} \simeq \frac{1}{2}\chi_n\mathcal{E}^2 = E_n^{(2)}$

$$|n\rangle = \underbrace{|n^\circ\rangle + \overbrace{|n'\rangle}^{\text{linear in } \mathcal{E}}}_{\text{exhibits } \vec{d} \,\propto\, \vec{\mathcal{E}}} + \ldots$$

$$\Rightarrow \langle n|\vec{x}\cdot\vec{\mathcal{E}}|n\rangle \propto \mathcal{E}^2 \checkmark$$

$$|n\rangle = |n^\circ\rangle + \sum_m{}' \, |m^\circ\rangle \frac{\langle m^\circ|\left(-q\mathcal{E}\left(\frac{\hbar}{2m\omega}\right)^{1/2}(a+a^\dagger)\right)|n^\circ\rangle}{E_n^\circ - E_m^\circ}$$

$$\boxed{|n\rangle = |n^\circ\rangle + \underbrace{q\mathcal{E}\left(\frac{1}{2m\hbar\omega^3}\right)^{1/2}}_{\propto \frac{q\mathcal{E}x_0}{\hbar\omega}} \underbrace{\left[(n+1)^{1/2}|n+1^\circ\rangle - n^{1/2}|n-1^\circ\rangle\right]}_{\text{admixture } \pm 1 \text{ vibrational quanta states.}}}$$

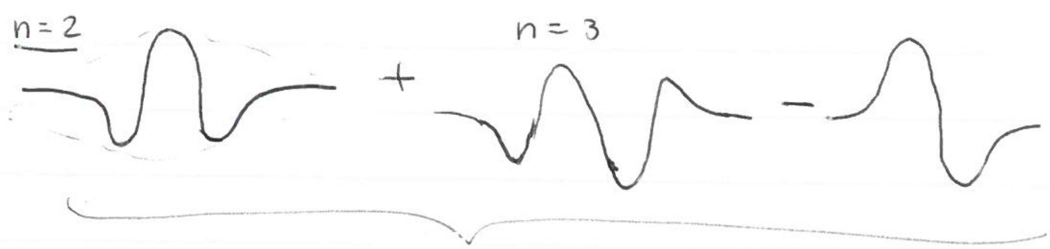
$\hbar\omega \leftarrow$ rigidity of spring

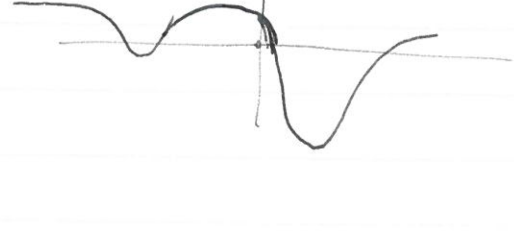
Note:

- response (admixture) $\rightarrow 0$ as $\omega \rightarrow \infty$
  $\nearrow$ as $q\mathcal{E} \nearrow$.

- in coord. representation:

$$\psi_n(x) = \psi_n^\circ(x) + \# \left(\psi_{n+1}^\circ(x)\sqrt{n+1} - \psi_{n-1}^\circ(x)\sqrt{n}\right)$$





biased toward
$x > 0 \Rightarrow d > 0$

$\boxed{2^{\text{nd}} \text{ order}}$

$$E_n^{(2)} = \langle n^0 | H' | n^1 \rangle = \sum_m{}' \frac{|\langle m^0 | H' | n^0 \rangle|^2}{E_n^0 - E_m^0}$$

$$= q^2 \mathcal{E}^2 \frac{\hbar}{2m\omega} \left(\frac{n+1}{-\hbar\omega} + \frac{n}{\hbar\omega} \right)$$

$$\boxed{E_n^{(2)} = -\frac{1}{2}\left(\frac{q^2}{m\omega^2}\right) \mathcal{E}^2}$$

$$\chi_n = \frac{q^2}{m\omega^2} \quad \text{— polarizability (linear)} \Rightarrow \underline{\text{units are } (\text{length})^3}$$

$$\underline{d} = -\frac{\partial E_n}{\partial \mathcal{E}} = \underline{\chi \mathcal{E}}$$

$$\frac{q^2}{m\omega^2} = x_0 \underbrace{\frac{q^2 / x_0}{\hbar\omega}}\ \frac{\hbar}{\underbrace{m\omega}_{x_0^2}} = \boxed{\frac{E_{coul}}{\hbar\omega} x_0^3}$$

Note: $E_n^{(2)} < 0$ since energy is reduced due to interaction of induced d with $\mathcal{E}$

All higher order corrections $E_n^{(k)} = 0$, from exact soln or explicit calculations to k^{th} order.

Digression on <u>Selection Rules</u>:

<u>general statement</u>:

special case $[\Omega, H'] = 0$

$\Rightarrow \langle \alpha_2 \omega_2 | H' | \alpha_1 \omega_1 \rangle = 0$, unless $\omega_1 = \omega_2$

$0 = \langle \omega_2 | [\Omega, H_1] | \omega_1 \rangle$

$= (\omega_2 - \omega_1) \langle \omega_2 | H_1 | \omega_1 \rangle \Rightarrow$

$\Rightarrow \langle \omega_2 | H_1 | \omega_1 \rangle = 0$ unless $\omega_1 = \omega_2$.

<u>Ex's</u>:

- $H_1 = Z$ — invnt under $U_{\hat{z}}$ rotation

$\Rightarrow [L_z, H_1] = 0 \Rightarrow$

$\langle m_2 | H_1 | m_1 \rangle = 0$, unless $m_1 = m_2$

i.e. conservation of z-component of L_z

- $H_1 = X^2$ — even under parity P

$[P, X^2] = 0 \Rightarrow \langle p | X^2 | p' \rangle = 0$

unless $p = p'$

i.e., $\langle + | X^2 | + \rangle \neq 0 \neq \langle - | X^2 | - \rangle$

but $\langle + | X^2 | - \rangle = 0$

when $[\Omega, H_1] = 0$

$\Rightarrow$ we say: " H_1 carries no Ω ", i.e. when acting on state, it imparts no Ω to it

i.e. $\Omega(H_1|\omega_1\rangle) = \omega_1(H_1|\omega_1\rangle)$

▲ generalization to H_1 that "carries Ω 'charge' "

$$[\Omega, H_1] = \Delta\omega\, H_1$$

$\Rightarrow$ H_1 acts like ladder op. wrt Ω charge ω raising it by $\Delta\omega$

$$\Omega(H_1|\omega_1\rangle) = (\omega_1 + \Delta\omega)(H_1|\omega_1\rangle)$$

$$\Rightarrow (H_1|\omega_1\rangle) = \#|\omega_1 + \Delta\omega\rangle \ !$$

$$\Rightarrow \langle\omega_2|H_1|\omega_1\rangle = \#\langle\omega_2|\omega_1 + \Delta\omega\rangle$$

$$= \#\,\delta_{\omega_2,\,\omega_1+\Delta\omega} \quad !$$

Ex's:

- $\Omega = \hat{n}$, $H_1 = a^+ \leftarrow$ has "charge" of $+1$

$\Rightarrow \langle n_2|a^+|n_1\rangle \propto \delta_{n_2, n_1+1}$ $\qquad [n, a^+] = a^+$

$\Rightarrow$ $H_1 = a$, $[\hat{n}, a] = -a \leftarrow$ "charge" $= -1$

$\Rightarrow \langle n_2|a|n_1\rangle \propto \delta_{n_2, n_1-1}$

- $\Omega = \mathbb{P}$, $H_1 = X$ odd under parity

$[\mathbb{P}, X] \neq 0$, actually $\mathbb{P}X + X\mathbb{P} = 0$

$$\mathbb{P}|p\rangle = \underset{\pm 1}{p}|P\rangle \Rightarrow \mathbb{P}(\underbrace{X|p\rangle}_{\text{changes parity}}) = -p(X|p\rangle)$$

+ → −
− → +

$$\Rightarrow \langle p|\underbrace{X|p'\rangle}_{|-p'\rangle}$$

$= \langle p|-p'\rangle = 0$ unless $p \neq p'$ i.e. opposite parity

- spherical tensor op's T_J^M

operators that transform under rotation like states with $(L, L_z) = (J, M)$ namely under rot.

$$\hat{U}^+ \hat{T}_J^M \hat{U} = \sum_{M'} R^{(J)}_{MM'} T_J^{M'}$$

$$\Rightarrow \langle j_2 m_2 | T_J^M | j_1 m_1 \rangle = 0$$

unless $\begin{cases} j_1 + J \geq J_2 \geq |j_1 - J| & \text{addition of } J\text{'s} \\ m_2 = m_1 + M & J_z \end{cases}$

tensor op carries angular momentum (J, M)
explicit real space representation are
<u>spherical harmonics</u>: $T_J{}^M = Y_{JM}(\theta, \varphi)$
(thought of as coord. repr. ops, rather than wavefncs)

⇒ Wigner - Eckart Thm

▲ $H_1 = Z \sim T_1^0$ ← $M=0$ component of $J=1$ ops.

$(T_1^{\pm 1} \propto X \pm iY)$

$\Rightarrow \langle j_2 m_2 | Z | j_1 m_1 \rangle = 0$

unless $\begin{cases} j_2 = j_1+1,\ j_1,\ j_1-1 \\ \underline{\text{and}}\quad m_2 = m_1 + 0 \end{cases}$

▲ $H = X$ or Y $(\sim T_1^{\pm 1})$

$\langle j_2 m_2 | X \text{ or } Y | j_1 m_1 \rangle = 0$

unless $\begin{cases} j_2 = j_1+1,\ j_1,\ j_1-1 \\ m_2 = m_1 \pm 1 \end{cases}$ and

▲ combine parity & $\vec{J}$ selection rules:

$\langle l_2 m_2 | Z | l_1 m_1 \rangle = 0$

unless $\begin{cases} l_2 = l_1 \pm 1 \\ m_2 = m_1 \end{cases}$ ($l_2 = l_1$ violates parity) since Z is odd & $|lm\rangle$ $P = (-1)^l \Rightarrow \underline{l_1 \neq l_2}$

⇒ dipole selection rules

$H_{dipole} = -q\vec{r} \cdot \vec{E} \Rightarrow \langle \vec{r} \rangle$

- Tensor operators (under rotation)

  - Scalars (tensors of rank 0)

$$T^{(0)} \xrightarrow[R]{} T'^{(0)} = U_R T^{(0)} U_R^{+} = T^{(0)}$$

i.e. using $U_R = e^{-\frac{i}{\hbar}\vec{J}\cdot\vec{\theta}}$ & looking at infinitesimal $\vec{\theta}$ $\Rightarrow$

$$[T^{(0)}, \vec{J}] = 0 \iff [J_\pm, T^{(0)}] = [J_z, T^{(0)}] = 0$$

Ex. of $T^{(0)}$ are: H, L^2, etc.

  - vectors (tensors of rank 1)

$$T_i^{(1)} \longrightarrow T_i'^{(1)} = U_R T_i^{(1)} U_R^{+} = \sum_j R_{ij} T_j^{(1)}$$

x, y, z 3 operators that mix with eachother 3x3 rot. matrix

$$\Rightarrow [T_i^{(1)}, J_j] = i\hbar \sum_j \epsilon_{ijk} T_k^{(1)}$$

Ex. of $T^{(1)}$ are: $\vec{J}$, $\vec{L}$, $\vec{S}$, $\vec{p}$, $\vec{r}$, ...

— Tensor of rank 2

$$T_{ij}^{(2)} \rightarrow T_{ij}^{\prime(2)} = U_R T_{ij}^{(2)} U_R^{+} = \sum_{i'j'} R_{ii'} R_{jj'} T_{i'j'}^{(2)}$$

<u>Cartesian Tensors</u>

9 operators that mix with each other under rotation

— <u>Cartesian</u> tensor operators of rank n

$T_{i_1 i_2 \ldots i_n}^{(n)}$ — 3^n operators that all mix under rotation.

<u>Examples</u>: $T^{(0)} = r^2$, $T_i^{(1)} = r_i = (x, y, z)$

$T_{ij}^{(2)} = r_i r_j = (x^2, y^2, z^2, xy, xz, yz)$, $T_{ijk}^{(3)} = r_i r_j r_k = (x^3, y^3, z^3, x^2 y, \text{etc})$

... but these do not transform <u>irreducibly</u> i.e. more of them mix than have to by properties of $\vec{J}$ & rotation group.

— <u>Spherical</u> tensors of rank j

T_j^m has $2j+1$ components $m = j, j-1, \ldots, -j$

$$T_j^m \xrightarrow[R]{} U_R T_j^m U_R^{+} = \sum_{m'} D_{mm'}^{(j)} T_j^{m'}$$

transforms <u>irreducibly</u> like $|j\,m\rangle$ eigenkets under $U_R |jm\rangle = \sum_{m'} D_{mm'}^{(j)} |jm'\rangle$

T_j^m are convenient because transform simply under rotation ; example $\underline{T_j^m = Y_{jm}(\theta, \varphi)}$

Ex. $j=0$; $T_0^0 = 1$.

$j=1$; $T_1^m = (T_1^{+1}, T_1^0, T_1^{-1}) =$

$= (x+iy, z, x-iy) = r Y_1^m(\theta,\varphi)$

→ Consider infinitesimal rot ⇒

$$[J_\pm, T_j^m] = \pm\hbar [j(j+1) - m(m\pm1)]^{1/2} T_j^{m}$$

$$[J_z, T_j^m] = \hbar m T_j^m$$

→ T_j^m are interesting b.c. transform simply and:

$$U_R\left(T_{j_1}^{m_1} |j_2 m_2\rangle\right) = U_R T_{j_1}^{m_1} U_R^\dagger U_R |j_2 m_2\rangle$$

$$= \sum_{\substack{m_1' \\ m_2'}} D^{(j_1)}_{m_1 m_1'} D^{(j_2)}_{m_2 m_2'} \left(T_{j_1}^{m_1'} |j_2 m_2'\rangle\right)$$

⇒ $T_{j_1}^{m_1} |j_2 m_2\rangle$ transforms like a direct product ket $|j_1 m_1\rangle \otimes |j_2 m_2\rangle$!

⇒ $T_{j_1}^{m_1}|j_2 m_2\rangle$ imparts j_1 angular momentum with component m_1 to $|j_2 m_2\rangle$ producing a ket with $j = j_1 + j_2, j_1+j_2-1, \ldots, |j_1 - j_2|$ & $m = m_1 + m_2$

$\Rightarrow$ know alot about matrix elements of T_j^m

$$\langle n_2 j_2 m_2 | T_j^m | n_1 j_1 m_1 \rangle = 0$$

unless $j_1 + j \geq j_2 \geq |j_1 - j|$, $m_2 = m_1 + m$

$\Rightarrow$ <u>Selection rules</u> required by conserv. of angular momentum (rot. invnce).

Hence given a tensor operator, it is very convenient to decompose it into spherical tensors T_j^m, whose matrix elements can be assessed to be 0 (or not) just by rot. invnce selection rules!

– Relation between Cartesian & spherical tensors

- <u>scalar</u> (rank 0), only one $\Rightarrow$ same.

$\Rightarrow$ Ex. $\langle n_2 j_2 m_2 | T_0^0 | n_1 j_1 m_1 \rangle = 0$

unless $j_1 = j_2$ & $m_1 = m_2$

- <u>vector</u> (rank 1) T_x, T_y, T_z cartesian

& $T_1^{+1}, T_1^0, T_1^{-1}$

$\Rightarrow T_1^{\pm} = T_x \pm i T_y$, $T_1^0 = T_z$

(e.g. $Y_1^{\pm} = (x \pm iy)\frac{1}{r} = e^{\pm i\phi}$, $Y_1^0 = \frac{z}{r} = \cos\theta$)

Ex's

$\Rightarrow \langle n_2 j_2 m_2 | T_x | n_1 j_1 m_1 \rangle = \langle n_2 j_2 m_2 | \frac{T_1^{-1} - T_1^{+1}}{\sqrt{2}} | n_1 j_1 m_1 \rangle$

$= 0$, unless $j_1 + 1 \geq j_2 \geq |j_1 - 1|$ & $m_2 = m_1 \pm 1$

$\langle n_2 j_2 m_2 | T_z | n_1 j_1 m_1 \rangle = \langle n_2 j_2 m_2 | T_1^0 | n_1 j_1 m_1 \rangle$

$= 0$, unless $j_1 + 1 \geq j_2 \geq |j_1 - 1|$, $m_2 = m_1$

- rank $n > 1$

3^n Cartesian tensors $T_{i_1 i_2, \dots, i_n}$

$>$

$2n+1$ spherical tensors $T_n^{m_n}$

$\ell = 2$: $m = \pm 2$ $\quad x^2 - y^2 \pm i\, 2xy \sim e^{\pm i 2\varphi}$

$m = \pm 1$ $\quad zx \pm i zy \sim e^{\pm i\varphi}$

$m = 0$ $\quad r^2 - 3z^2 = x^2 + y^2 - 2z^2$

$\ell = 1$ $\quad m = \pm 1$ $\quad \vec{r} \times \vec{p} = \vec{V} \Rightarrow V_x \pm V_y$

$m = 0$ $\quad V_z$

Ex. $n = 2 \Rightarrow 9$ T_{ij}'s

& $j = 2 \Rightarrow 5$ T_2^m's.

That is because Cartesian tensors are reducible, since they transform as n^{th} tensor product of rank tensor

$T_{ijk} = T_i \otimes T_j \otimes T_k$

recall for states $|j_1 m_1\rangle \otimes |j_2 m_2\rangle =$

$$= \sum_{\substack{m \\ j_1 + j_2 \geq j \geq |j_1 - j_2|}} |j\, m\rangle \underbrace{\langle j m | j_1 m_1; j_2 m_2 \rangle}_{\text{CG coeff.}}$$

$$\underline{\text{Ex}}.\quad T_{ij} = T_i \otimes T_j = \overbrace{T_0^{\,0}}^{1} + \overbrace{\sum_{m=1,0,-1} c_m^{(1)}\, T_1^{\,m}}^{3} + \underbrace{\sum_{m=\pm 2,\pm 1,0} c_m^{(2)}\, T_2^{\,m}}_{5}$$

$$\underline{3 \cdot 3 = 9 = 1 + 3 + 5}$$

$\Rightarrow$ T_{ij} consists of

3 irreducible representation: a scalar $(j=0)$, a vector $(j=1)$ and a rank-2 spherical tensor $(j=2)$.

$\Rightarrow$ <u>Wigner</u> - <u>Eckart</u> <u>Thm</u>:

$$\langle n_2\, j_2\, m_2 | T_j^{\,m} | n_1\, j_1\, m_1 \rangle$$

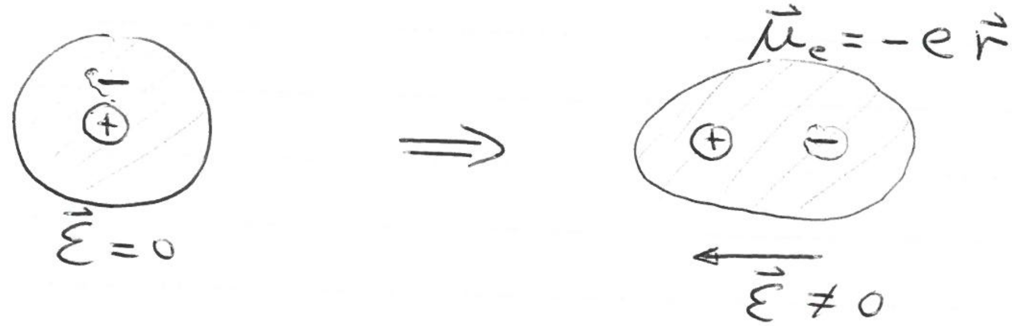
$$= \underbrace{\langle n_2\, j_2 \| T_j \| n_1\, j_1 \rangle}_{\substack{\text{an overall radial}\\ \text{factor independent}\\ \text{of orientation.}}} \underbrace{\langle j_2 m_2 | j\, m; j_1 m_1 \rangle}_{\substack{\text{selection rules}\\ = \underline{\text{C-G coeff}}}}$$

For more details see Shankar; Schiff, L&L.

4.13

2. Application of P.T. to Stark effect (Harton)
(utility of dipole selection rules)

Stark effect — response to constant $\vec{\mathcal{E}}$ field



$$H_1 = -e\phi(\vec{r}_-) + e\phi(\vec{r}_+)$$
$$= +e\underbrace{(\vec{r}_- - \vec{r}_+)}_{\vec{r}}\cdot\vec{\mathcal{E}} \equiv -\vec{\mu}_e\cdot\vec{\mathcal{E}}$$

$\vec{\mu}_e = -e\vec{r}$; take $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$

Complete analogy with shifted h. oscill.

1st order:

$$\underbrace{E'_{100}}_{g.s.} = \langle 100 | e\mathcal{E}z | 100\rangle$$
$= 0$ via parity, or Wigner-Eckart thm
$$= N\int_0^{\infty} dr\, r^3 |R(r)|^2 \underbrace{\int_0^{\pi} d\theta \sin\theta\cos\theta}_{=0} \int_0^{2\pi} d\phi$$

Physically: charge distribution is spherically symmetric in g.s. (in excited states at least azimuthally symmetric, which is enough) $\Rightarrow \langle\vec{\mu}_e\rangle = 0$

4.14

$$E_{100}^{(2)} = \sum_{nlm}{}' \frac{e^2\mathcal{E}^2 |\langle n l m | z | 100\rangle|^2}{\underbrace{E_{100}^0 - E_{nlm}^0}_{<0}}$$

∞ # of terms.

$$E_{100}^0 - E_{nlm}^0 = -E_{Ry}\left(1 - \frac{1}{n^2}\right) = -E_R \frac{n^2-1}{n^2} < 0$$

using dipole selection rules: $\frac{e^2}{2a_0}$, $a_0 = \frac{\hbar^2}{me^2}$

$$z \propto T_1^0 \Rightarrow l = 0+1 = 1, \quad m = 0$$

$Y_{00} \sim$ const

$$\Rightarrow E_{100}^{(2)} = \sum_{n=2}^{\infty} e^2\mathcal{E}^2 \frac{|\langle n 1 0 | z | 100\rangle|^2}{E_1^0 - E_n^0}$$

$Y_{10} \propto \cos\theta$

$\sim \cos\theta = Y_{10}$

setting bounds:

$$|E_{100}^{(2)}| \le \frac{e^2\mathcal{E}^2}{|E_{100}^0 - E_{200}^0|} \underbrace{\sum_{nlm}{}' |\langle n l m | z | 100\rangle|^2}$$

upper bound:

$$\Rightarrow \boxed{|E_{100}^{(2)}| \le \frac{8a_0^3\mathcal{E}^2}{3}}$$

$$= \langle 100 | z^2 | 100\rangle - \underbrace{\langle 100 | z | 100\rangle}_{0}{}^2$$

$$= a_0^2$$

lower bound:

$$|E_{100}^{(2)}| \ge \frac{e^2\mathcal{E}^2}{\underbrace{3e^2/8a_0}_{E_{Ry} =}} \underbrace{|\langle 210 | z | 100\rangle|^2}_{\frac{2^{15}a_0^2}{3^{10}} \simeq 0.55 a_0^2}$$

take only 1st term in sum

$$\Rightarrow |E_{100}^{(2)}| \ge (0.55)\frac{8a_0^3\mathcal{E}^2}{3}$$

Actually can do sum exactly (see Shankar pg 462)

$$\boxed{|E_{100}^{(2)}| = (0.84)\frac{8a_0^3\mathcal{E}^2}{3}}$$

✓

4.15

Induced moment $\vec{\mu} = \langle -e\vec{r} \rangle$

$$dW = +e\vec{\mathcal{E}}\cdot d\vec{r} = -\vec{\mathcal{E}}\cdot d\vec{\mu}$$

$$\vec{\mu} = \chi \vec{E}$$

$$\Rightarrow dW = -\chi \vec{\mathcal{E}}\cdot d\vec{\mathcal{E}}$$

$$\Rightarrow W = -\frac{1}{2}\chi \mathcal{E}^2 = E_{100}^2$$

$$\Rightarrow \boxed{\chi = \frac{18}{4} a_0^3} \simeq 0.56\ \mathring{A}^3$$

exact:

$$\langle n10|z|100\rangle = \frac{1}{\sqrt{3}}\int_0^\infty r^2 dr\ R_{n10}(r)\ r\ R_{100}(r)$$

$$|\qquad\qquad|^2 = \frac{1}{3}\frac{2^8 n^7 (n-1)^{2n-5}}{(n+1)^{2n+5}} a_0^2$$

B. Degenerate perturbation theory.

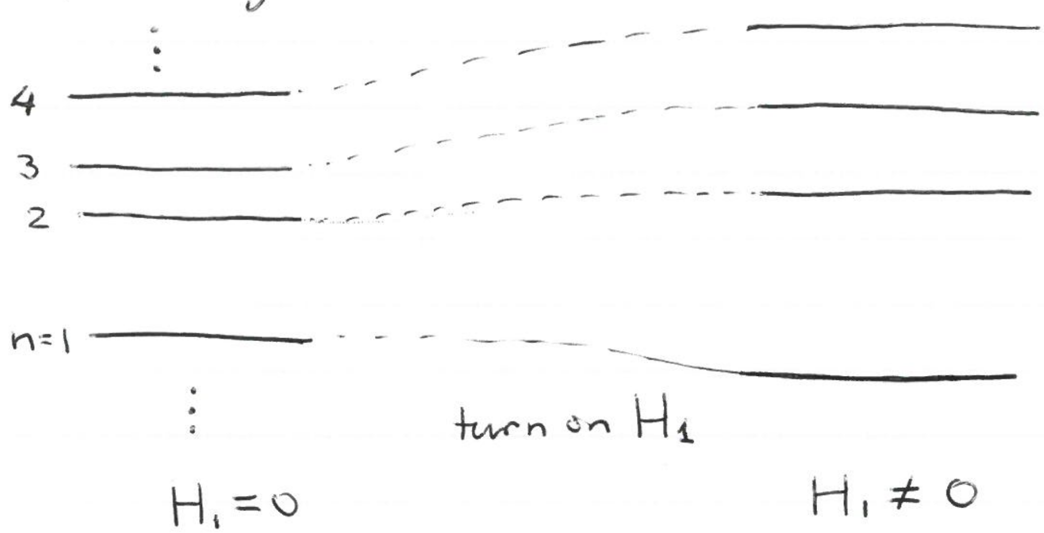
Clearly p.t (nondegen.) breaks down

e.g. $E_n^{(2)} = \sum_m{}' \frac{|\langle m | H' | n \rangle|^2}{E_n^\circ - E_m^\circ} \to \infty$ when

there is degeneracy.

Need to treat degenerate set of states (also nearly degener. ones too) as a set

Physically:



levels never cross, large gaps $\Rightarrow$ p.t. (nondegen.) is good.

$H_0 | n, m \rangle = E_n^\circ | n\, m \rangle$

E_n° is degenerate wrt m (independent of m)

$\Rightarrow | n, m \rangle$, for $m = 1, 2, \ldots M$ are degenerate.

what to do? $\Rightarrow$ diagonalize H_1 in this (usually) finite degenerate subspace

$\langle m | H_1 | m' \rangle = H^1_{mm'}$

using basis $|\bar{m}\rangle = \sum_m c_m |m\rangle$

that diagonalizes

$H^1_{mm'}$ gaurantees that E^2_n is finite

since $\frac{|\langle \bar{m} | H_1 | \bar{m}' \rangle|^2}{E_m - E_{m'}} = 0$ ✓

More formally, derivation of d.p.t.:

$|n\rangle = \sum_i \alpha_i^{(n)} |n_i^0\rangle + \sum_i \beta_i^{(n)} |n_i^1\rangle + \dots$

$E_n = E_n^0 + E_n^1 + \dots$

$\Rightarrow (H_0 + H_1)(|n\rangle) = (E_n^0 + E_n^1 + \dots)|n\rangle$

0th order: $H_0 \sum_i \alpha_i^n |n_i^0\rangle = E_n^0 \sum_i \alpha_i^n |n_i^0\rangle$

$\Rightarrow H_0 |n_i^0\rangle = E_n^0 |n_i^0\rangle$

N-fold degenerate space of states $|n_i^0\rangle$, $i = 1, 2, \dots N$
with eigenvalue E_n^0.

1st order: $H_0 \sum_i \beta_i^{(n)} |n_i^1\rangle + H_1 \sum_i \alpha_i^{(n)} |n_i^0\rangle$

$$= E_n^{(0)} \sum_i \beta_i^{(n)} |n_i^1\rangle + E_n^{(1)} \sum_i \alpha_i^{(n)} |n_i^0\rangle .$$

$$\langle n_j^{(0)}| \Rightarrow E_n^{(0)} \sum_i \beta_i^{(n)} \cancel{\langle n_j^0 | n_i^1\rangle} + \sum_i \overbrace{\langle n_j^0 | H_1 | n_i^0\rangle}^{H'_{ij}} \alpha_i^{(n)} =$$

$$= \cancel{E_n^{(0)} \sum_i \beta_i^{(n)} \langle n_j^0 | n_i^1\rangle} + E_n^{(1)} \sum_i \alpha_i^{(n)} \delta_{ji}$$

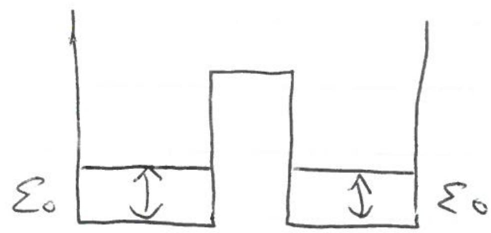
$$\boxed{\begin{aligned} &\Rightarrow \sum_j H'_{ij} \alpha_j^{(n)} = E_n^{(1)} \alpha_i^{(n)} \\ &\Rightarrow E_{nm}^{(1)},\ \alpha_{jm}^{(n)} \end{aligned}}$$

$\leftarrow$ $N \times N$ eigenvalue problem.

, $m = 1, 2, \ldots, N$ $\leftarrow$ eigenstates generally no longer degenerate.

Normalization: $\sum_{i=1}^{N} |\alpha_{im}^{(n)}|^2 = 1$.

Ex:



$H^{(0)}_{\text{Left/right}}$ diagonalized

$$H^0_{L/R} |n^0_{L,R}\rangle = \varepsilon_0 |L, R\rangle$$

$$\langle i | H^0 | j \rangle = \begin{array}{c|cc} & L & R \\ \hline L & \varepsilon_0 & 0 \\ R & 0 & \varepsilon_0 \end{array}$$

$$\langle i | H' | j \rangle = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix}$$

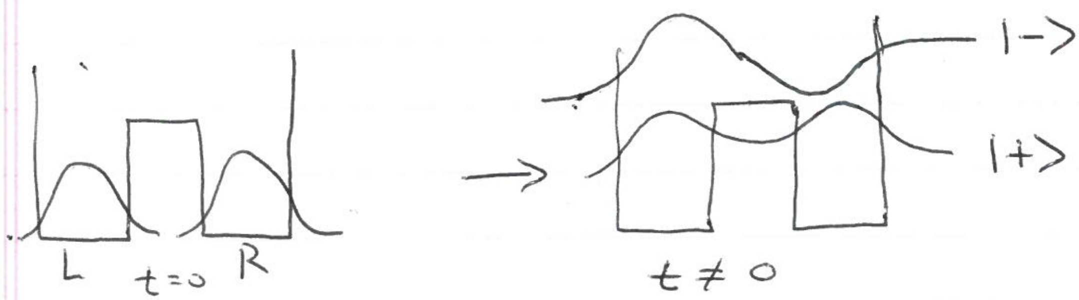
$$H'_{ij}\,\alpha_j = E^{(1)}\alpha_i$$

$$\Rightarrow \alpha_i^{\pm} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm 1\end{pmatrix}, \quad E^{(1)}_{\pm} = \mp|t|$$

independent of t

$$\Rightarrow \underline{E_{\pm} = \varepsilon_0 \mp |t|}$$

δE linear in $|t|$



More generally:

what if $H^0|L/R\rangle = E^0_{L/R}|L/R\rangle$

& $E^0_L \neq E^0_R$ i.e. close but not degenerate

but $E^0_L - E^0_R \ll |E^0_{L,R} - E^0_{n\neq L,R}|$

$\Rightarrow$ focus on $|L\rangle, |R\rangle$ subset of Hilbert space, to lowest order dropping all other states.

$H_{ij} = \langle i|H|j\rangle$, $|i\rangle = |L\rangle, |R\rangle$

diagonalize H_{ij} in this 2×2 subspace.

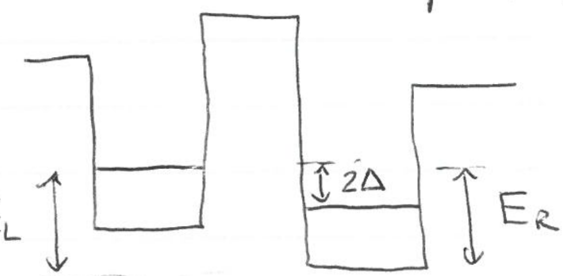
$$(H_0 + H_1)(\alpha_L |L\rangle + \alpha_R |R\rangle + |n'\rangle + \ldots)$$

$$= E(\alpha_L |L\rangle + \alpha_R |R\rangle + |n'\rangle + \ldots)$$

$$\begin{pmatrix} E_L^0 & H'_{LR} \\ H'_{RL} & E_R^0 \end{pmatrix} \begin{pmatrix} \alpha_L \\ \alpha_R \end{pmatrix} = E \begin{pmatrix} \alpha_L \\ \alpha_R \end{pmatrix}$$

$H'_{LR} = (H'_{RL})^*$ since $H = H^+$ (Hermitian operator)

$$\det \begin{pmatrix} E_L^0 - E & -t \\ -t^* & E_R^0 - E \end{pmatrix} = 0$$



$$\Rightarrow \quad (E_L^0 - E)(E_R^0 - E) = |t|^2$$

$$E^2 - (E_L^0 + E_R^0)E + E_L^0 E_R^0 - |t|^2 = 0$$

$$\Rightarrow \quad \underline{E_\pm = E_0 \pm \sqrt{\Delta^2 + |t|^2}} \qquad \left(\begin{aligned} E_0 &= \tfrac{1}{2}(E_L^0 + E_R^0) \\ \Delta &= \tfrac{1}{2}(E_L - E_R) \end{aligned} \right)$$

linear

two limits:

1. $\Delta << |t|$: $E_\pm \simeq E_0 \mp |t|$ (degenerate p.t.)

2. $\Delta >> |t|$: $E_\pm \simeq \underbrace{E_0 \mp \Delta}_{E_{L,R}} \mp \dfrac{|t|^2}{2\Delta}$ (nondegen. p.t.)

quadratic

2nd order:

$$|\nu\rangle = \underbrace{\sum_i \alpha_i^{(\nu)} |i\rangle}_{\text{nearly degenerate subspace}} + \underbrace{\sum_{n \notin i} \alpha_n^{(\nu)} |n\rangle}_{\text{set separated by a large gap from } i\text{'s.}}$$

$$(H_0 + H_1)|\nu\rangle = E_\nu |\nu\rangle$$

$$\langle j| \Rightarrow \left(\sum_i E_j^0 \delta_{ij} + \sum_i \langle j|H_1|i\rangle\right)\alpha_i^{(\nu)} + \sum_{n\notin i} \langle j|H_1|n\rangle \alpha_n^{(\nu)}$$

$$= \left(\alpha_j^{(\nu)}\right) E_\nu$$

$$\left(E_j^0 \delta_{ij} + H_{ji}^1\right)\alpha_i^{(\nu)} + \sum_{n\neq i} H'_{jn}\, \alpha_n^{(\nu)} = E_\nu \alpha_j^{(\nu)}$$

$$\left(\Rightarrow \text{to lowest order: } \alpha_{0i}^{(\nu)} \text{ soln of } H_{ij}\, \alpha_{0j}^{(\nu)} = E_\nu^0 \alpha_{0i}^{(\nu)}\right)$$

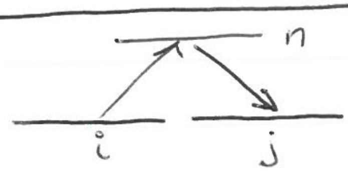
$$\langle m| \Rightarrow \sum_i \langle m|H_1|i\rangle \alpha_i^{(\nu)} + \sum_{n\notin i} \underbrace{\langle m|H_1|m\rangle \alpha_n}_{\approx 0 \text{ 3nd order}}$$

$$+ E_m \alpha_m^{(\nu)} = E^{(\nu)} \alpha_m^{(\nu)}$$

$$\Rightarrow \alpha_m^{(\nu)} \simeq \sum_i \frac{H'_{mi}\, \alpha_i^{(\nu)}}{E_0^{(\nu)} - E_m^0}$$

$$\Rightarrow \sum_i \left[E_j^0 \delta_{ij} + H'_{ji} + \sum_{n\neq i} \frac{H'_{jn} H'_{ni}}{E_i^0 - E_m^0}\right] \alpha_i^{(\nu)} = E^{(\nu)} \alpha_j^{(\nu)}$$

to 2nd order accuracy



H_{ij}^{eff} effective H in ij subspace.

Note: For exact degeneracy of i states

$$H_{ij} = E_0 \begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & \ddots & 1 \end{pmatrix} + H^1_{ij}$$

$\Rightarrow$ diagonalizing H_{ij} is identical to diagonalizing H^1_{ij} since $H^0_{ij} = E_0 \delta_{ij}$ does not change under U^+ (since $\propto \mathbb{1}$)

$$\Rightarrow \quad H^1_{ij} \rightarrow E^1_i \delta_{ij} \Rightarrow H_{ij} \rightarrow (E_0 + E^1_i)\delta_{ij} \checkmark$$

4.24

Examples of degenerate P.T.:

1. Stark effect in the $n=2$ levels of Hydrogen.
(ignore spin since H_0, H_1 are spin independent)

$$H_1 = -\vec{\mu}_e \cdot \vec{\mathcal{E}} = e z \mathcal{E}$$

unlike g.s. $|100\rangle$ (that is nondegenerate)

$|2lm\rangle$ is 4-fold degenerate, i.e.,

$$\underbrace{|200\rangle, \; |210\rangle}_{\text{by special prop. of } \frac{1}{r} \text{ potential}}, \; |21-1\rangle, \; |211\rangle$$

$|210\rangle, |21-1\rangle, |211\rangle$: by conservation of $\vec{L}$

by special prop. of $\frac{1}{r}$ potential (conservation of Lenz-Runge vector $\hat{n} = \frac{\vec{p} \times \vec{L}}{m} - \frac{e^2}{r}\vec{r}$)

How is this degeneracy lifted by $e\mathcal{E}z$?

Diagonalize: $\langle 2lm | H_1 | 2l'm' \rangle$

$= e\mathcal{E} \langle 2lm | z | 2l'm' \rangle \leftarrow$ 4x4 matrix.

$$= e\mathcal{E} \begin{pmatrix} \langle 200|z|200\rangle & \langle 200|z|210\rangle & \langle 200|z|211\rangle & \langle 200|z|21-1\rangle \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

Selection rules:

$[Z, L_z] = 0 \Rightarrow Z$ conserves $m \Rightarrow \propto \delta_{m,m'}$

also parity allows finite matrixelement s.t. $\delta_{\ell,\ell'\pm 1}$

$\Rightarrow \langle 2\ell m | Z | 2\ell m \rangle = 0$, etc.

only $\langle 200 | Z | 210 \rangle \neq 0$ (also its c.c.)

(all others vanish!)

$$\Rightarrow \quad H'_{\substack{\ell m \\ \ell' m'}} = \begin{array}{c c} & \begin{array}{cccc} 200 & 210 & 211 & 21\text{-}1 \end{array} \\ \begin{array}{c} 200 \\ 210 \\ 211 \\ 21\text{-}1 \end{array} & \begin{pmatrix} 0 & \Delta & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array}$$

$$\Delta = \langle 200 | Z | 210 \rangle e\mathcal{E} = -3e\mathcal{E}a_0 .$$

$=$

use coord. representation:

$$\phi_{200} = \left(\frac{1}{2a_0}\right)^{3/2} 2\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{0,0}$$

$$\phi_{21\pm1} = \left(\frac{1}{2a_0}\right)^{3/2} 3^{-1/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{1,\pm1}$$

$$\phi_{210} = \left(\frac{1}{2a_0}\right)^{3/2} 3^{-1/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{1,0} .$$

$$\Rightarrow \langle 200 | Z | 210 \rangle = \int_0^\infty r^2 dr\, (2a_0)^{-3} e^{-r/a_0} \frac{2r}{\sqrt{3}\,a_0}\left(1 - \frac{r}{2a_0}\right) r \oint d\Omega\, Y_{00}^* \cos\theta\, Y_{10}$$

$$= -3a_0$$

n^2

$\vdots$

$1 = 3^2$ $\quad n=3$ $\quad$ —— $\overbrace{\overbrace{0,0}^{1};\ \overbrace{1,0,\pm 1}^{3};\ \overbrace{2,0,\pm 1,\pm 2}^{5}}^{9};$

$= 2^2$ $\quad n=2$ $\quad$ —— $\underbrace{l=0, m=0;\ l=1, m=0,\pm 1}_{4} \otimes s = \pm 1/2$

$1 = 1^2$ $\quad n=1$ $\quad$ —— $\otimes \underbrace{s = \pm 1/2}_{1}$

- Multi-electron atoms.

→ true many-body problem, impossible to treat analytically.

→ Hartree approximation is simplest with each electron obeying single e S. Eqn in a potential, self-consist. determined due to nucleus $-\frac{Ze^2}{r}$ + repulsive Coulomb potential due to N−1 other e's.

$$V_{eff}(r) = -\frac{Ze^2}{r} - e\phi(r)$$

where $\phi(r)$ solves $-\nabla^2\phi = \rho_{N-1}(r)$

$-e\rho(r)$

$= -e\sum_{n\ell m} |\Psi_{n\ell m}|^2$

self-consist determined

$\Psi^{Hartree}_{n\ell m}$, but $E_{n\ell}$ no degeneracy wrt $\underline{\ell}$

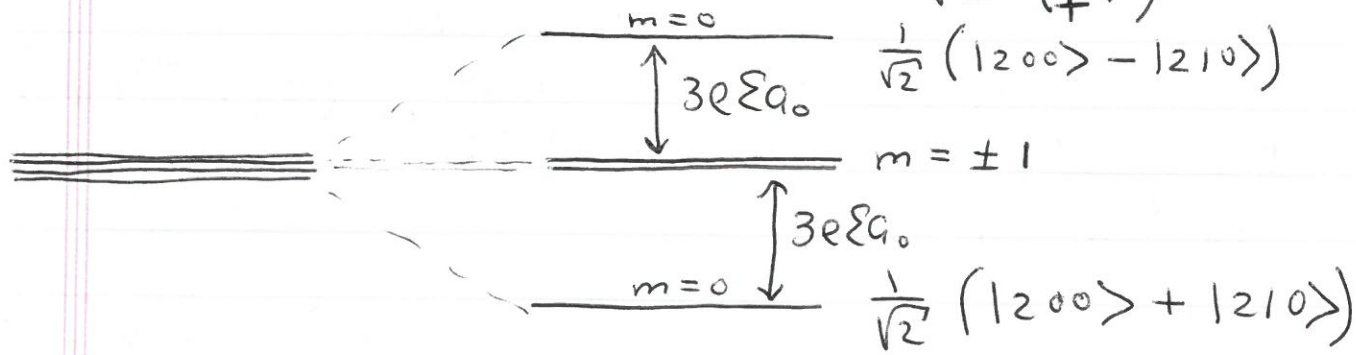
since $V(r) \neq \frac{1}{r}$

$E_{n\ell}$ goes up with ℓ since higher ℓ, nucleus is more screened, less attractive.

Filling these single particle Hartree states generates Mendeleev's table (1869) & explains props of atoms, affinities etc. ⇒ Chemistry.

$$\Rightarrow \quad E^{(1)} = \pm\, 3e\mathcal{E}a_0 \;, \quad |2,\pm\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \mp 1 \end{pmatrix}$$

$\Rightarrow$



2. Relativistic corrections $\Rightarrow$ fine structure

A. Kinetic energy:

$$H_{\text{kinetic}} = \frac{p_p^2}{2M_p} + \left(p_e^2c^2 + m_e^2c^4\right)^{1/2} - m_e c^2$$

$$\simeq \underbrace{\frac{p_p^2}{2M_p} + \frac{p_e^2}{2m_e}}_{\underbrace{\frac{p_{cm}^2}{2M} + \frac{p^2}{2\mu}}_{H_0}} \underbrace{- \frac{1}{8}\frac{p_e^4}{m_e^3c^2}}_{H_1}$$

$\Rightarrow$ other relativistic corrections

$\Rightarrow$ quantum treatment of E&M $\Rightarrow$ QED (photon)

$\Rightarrow$ Lamb shift

$\langle p_e \rangle = \alpha m c$

Compare:
$$\frac{\langle H_1\rangle}{\langle H_0\rangle} \simeq \frac{\langle p_e^4\rangle}{m_e^3c^2\frac{\langle p_e^2\rangle}{2m_e}} \simeq \frac{\langle p^2\rangle}{m^2c^2} \Downarrow \alpha^2 \ll 1. \qquad \sim 10^{-5}$$

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$

diagonal in $|l\,m\rangle$ basis.

$$E_T^1 = -\frac{1}{8m^3c^2}\langle nlm|\,p^4\,|nlm\rangle = -\frac{1}{2mc^2}\langle nlm|\left(H_0 + \frac{e^2}{r}\right)^2|nlm\rangle$$

$$= -\frac{1}{2mc^2}\left[\left(E_n^0\right)^2 + 2E_n^0\, \underbrace{e^2\left\langle\frac{1}{r}\right\rangle_{nlm}}_{-2E_n^0} + e^4\left\langle\frac{1}{r^2}\right\rangle_{nlm}\right]$$

$-2E_n^0$ (via virial thm $\langle\vec{r}\cdot\vec{p}\rangle = 0$)

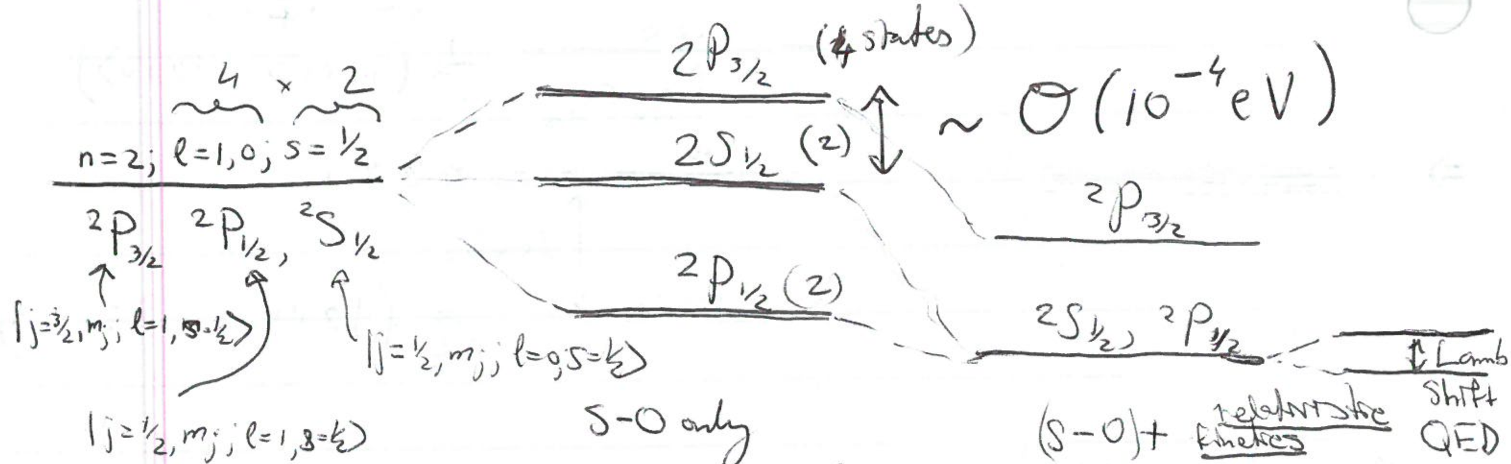
$$\partial_t\langle\vec{r}\cdot\vec{p}\rangle = 0 = \left\langle\frac{\partial H}{\partial p}\cdot p\right\rangle - \left\langle r\cdot\frac{\partial H}{\partial r}\right\rangle \Rightarrow 2K = -\langle V_{coul}\rangle$$

$$\left\langle\frac{e^4}{r^2}\right\rangle_{nlm} = \frac{e^4}{a_0^2 n^3(l+\frac{1}{2})}$$

$$\Rightarrow \quad E_T^1 = -\frac{1}{2}\left(mc^2\right)\alpha^4\left[-\frac{3}{4n^4} + \frac{1}{n^3(l+\frac{1}{2})}\right]$$

splits l-degen.

Note: no off-diagonal terms in ll' mm' space. p^4 is a scala



$\vec{S}\cdot\vec{L} \propto (J^2 - L^2 - S^2)$

$\Rightarrow$ same J but higher L is lower!

only depends on j! not l.

(relativity)

B. Spin-orbit interaction:

Recall charged particle moving in $\vec{\mathcal{E}}$ field sees in its rest frame $\vec{B} = -\frac{\vec{v}}{c} \times \vec{\mathcal{E}}$

$\Rightarrow$ e in proton's coulomb field $\vec{\mathcal{E}} = -\vec{\nabla} V_c = \frac{e}{r^3}\vec{r}$

$$\Rightarrow \vec{B} = -\frac{e}{c}\frac{\vec{v}\times\vec{r}}{r^3}$$

$$\Rightarrow \mathcal{H}_{s.o} = -\vec{\mu}\cdot\vec{B} = \frac{-e}{mc}\frac{\vec{\mu}\cdot\vec{L}}{r^3}$$

$$H_{so} = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L} \left(= \frac{-Ze^2}{2m^2c^2}\frac{e}{r}\vec{\nabla}V\,\vec{S}\cdot\vec{L}\right)$$

extra Thomas factor (automatic from Dirac eqn).

$\Rightarrow \vec{S}$ & $\vec{L}$ coupled into $\vec{J} = \vec{S} + \vec{L}$

$$J^2 = S^2 + L^2 + 2\vec{S}\cdot\vec{L}$$

$$\Rightarrow \vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - L^2 - S^2)$$

$$\Rightarrow H_{so} = \frac{e^2}{4m^2c^2r^3}\left[J^2 - L^2 - S^2\right]$$

$$\Rightarrow \langle j'm'; l', \tfrac{1}{2} | H_{so} | j, m; l; \tfrac{1}{2}\rangle = \delta_{jj'}\delta_{mm'}\delta_{ll'}\frac{e^2}{4m^2c^2}\left\langle\frac{1}{r^3}\right\rangle_{nl} \cdot \hbar^2\left[j(j+1) - l(l+1) - 3/4\right]$$

See Shankar 17.3.4:

$$\left\langle\frac{1}{r^3}\right\rangle_{nl} = \frac{1}{a_0^3}\frac{1}{n^3 l(l+\frac{1}{2})(l+1)}$$

$l + 1/2 = j$ ← Only term for $l=0$ $\Rightarrow$ finite limit even for $l \to 0$

$l - \frac{1}{2} = j$

$$\Rightarrow E^1_{s.o} = \frac{1}{4}mc^2\alpha^4 \{l, -(l+1)\} / n^3(l)(l+1/2)(l+1)$$

$$\Rightarrow \boxed{E^{(1)}_{\text{fine structure}} = E^1_T + E^1_{s.o} = -\frac{mc^2\alpha^2}{2n^2}\frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)}$$

Hartree Approx to multi-e' atom

$$H = \underbrace{\sum_i \frac{p_i^2}{2m} + \underbrace{V_{ion}(r_i)}_{\frac{-Ze^2}{|\vec{r}_i|}}}_{\sum_i H_i^0} + \frac{1}{2}\sum_{i \neq j} \underbrace{V_{ee}(|\vec{r}_i - \vec{r}_j|)}_{\frac{e^2}{|\vec{r}_i - \vec{r}_j|}}$$

many body Sch. Eqn:

$$\Big[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{ion}(r_i) + \underbrace{\sum_{j\neq i} V_{ee}(r_i - r_j)}\Big]\Psi(r_1, r_2, \ldots r_N) = E\,\Psi(r_1, r_2, \ldots r_N)$$

$$\equiv V_{ee}^{eff}(r_i) = \sum_{j \neq i} V_{ee}(r_i - r_j)$$

$$\simeq \int dr\, V_{ee}(\vec{r}_i - \vec{r})\,\rho(\vec{r})$$

$$\rho(\vec{r}) = -e\,P(\vec{r}) = -e \sum_{n\ell m} |\psi_{n\ell m}(r)|^2$$

2) Hartree: reduce to 1-body problem:

$$\Big[-\frac{\hbar^2}{2m}\nabla_i^2 + V^{Hartree}(r_i)\Big]\Psi(r_1 \ldots r_N) = E\,\Psi$$

$$V^{Hartree}(r_i) = V_{ion}(r_i) + \int dr\, V_{ee}(\vec{r}_i - \vec{r})\,\rho(\vec{r})$$