Harmonic Oscillator

[operator method]

$\Rightarrow$ $$H = \frac{-\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega^2 x^2$$ [for harmonic oscillator]

$$H\psi = E\psi$$

we know, $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$, $n = 0, 1, 2, \ldots$

upon solving we get,

$$\psi_n(x) = N_n H_n\left(\frac{x}{a_0}\right) e^{-x^2/2a_0^2}$$, where $a_0 = \sqrt{\frac{\hbar}{M\omega}}$

and $p_0 = \sqrt{\hbar M\omega}$

$\psi_n(x)$ → oscillator wavefunction.

H_n → Hermite polynomial.

[If $H = \frac{-\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega^2 x^2 + \Delta$

then the energy states shift by Δ, i.e.,

$E_n = \left(n+\frac{1}{2}\right)\hbar\omega + \Delta$]

$\Rightarrow$ We can construct two operators,

$$a^+ = \frac{1}{\sqrt{2}}\left[\frac{x}{a_0} - \frac{i p_x}{p_0}\right]$$ and,

$$a = \frac{1}{\sqrt{2}}\left[\frac{x}{a_0} + \frac{i p_x}{p_0}\right]$$ where $p_x = -i\hbar\frac{d}{dx}$.

consider a dimensionless variable, $\eta = \frac{x}{a_0}$, then

$$a^+ = \frac{1}{\sqrt{2}}\left(\eta - \frac{d}{d\eta}\right) \text{ and } a = \frac{1}{\sqrt{2}}\left(\eta + \frac{d}{d\eta}\right)$$

thus $\boxed{[a, a^+] = 1}$

$\Rightarrow$ We can write $\eta = \frac{x}{a_0}$, as,

$$\eta = \frac{x}{a_0} = \frac{1}{\sqrt{2}}\left(a + a^{+}\right)$$

thus, $x = \frac{a_0}{\sqrt{2}}\left(a + a^{+}\right)$ and

$$P_x = \frac{i p_0}{\sqrt{2}}\left(a - a^{+}\right)$$

$\Rightarrow$ Consider, $\hat{N} = a^{+}a$, then,

$$H = \left(\hat{N} + \frac{1}{2}\right)\hbar\omega$$

and, $\boxed{\hat{N}\,\psi_n(x) = n\,\psi_n(x)}$

$\Rightarrow a^{+}\psi_n(x) = \sqrt{n+1}\,\psi_{n+1}(x)$ [creation operator]

$a\,\psi_n(x) = \sqrt{n}\,\psi_{n-1}(x)$ [antilliation operator]

we know that, $\psi_n(x) = \langle x|n\rangle$

thus, $\boxed{a^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle \text{ and } a|n\rangle = \sqrt{n}\,|n-1\rangle}$

$\Rightarrow$ Consider,

$\langle n|x^2|m\rangle$, then

$$x^2 = \left(\frac{a_0}{\sqrt{2}}(a+a^{+})\right)\left(\frac{a_0}{\sqrt{2}}(a+a^{+})\right) = \frac{a_0^2}{2}(a+a^{+})(a+a^{+})$$

substituting, we get,

$$\langle n|\left(\frac{a_0^2}{2}\left(a^2 + aa^{+} + a^{+}a + a^{+2}\right)\right)|m\rangle$$

$$= \frac{a_0^2}{2}\left[\langle n|\left(a^2 + aa^{+} + a^{+}a + (a^{+})^2\right)|m\rangle\right]$$

expanding and distributing, we get,

$$\frac{a_0^2}{2}\left[\langle n|(a^2 + aa^\dagger + a^\dagger a + (a^\dagger)^2)|m\rangle\right] = \frac{a_0^2}{2}\left[\langle n|a^2|m\rangle + \langle n|aa^\dagger|m\rangle + \langle n|a^\dagger a|m\rangle + \langle n|a^{\dagger 2}|m\rangle\right]$$

1st term,

$$\langle n|a^2|m\rangle = \langle n|a \cdot a|m\rangle = \langle n|a\sqrt{m}\,|m-1\rangle$$
$$= \sqrt{m}\sqrt{m-1}\,\langle n|m-2\rangle$$

from the orthogonality condition, $\langle n|m\rangle = \delta_{n,m}$

[Harmonic oscillator wavefunctions are orthogonal]

thus, $\langle n|a^2|m\rangle = \sqrt{m}\sqrt{m-1}\,\langle n|m-2\rangle$
$$= \sqrt{m(m-1)}\,\delta_{n,m-2}$$

we can calculate the other terms.

⇒ We can calculate the matrix elements of H by

$$\langle n|H|m\rangle = \begin{pmatrix} H_{00} & H_{01} & H_{02} & \cdots \\ H_{10} & H_{11} & H_{12} & \cdots \\ \vdots & & \ddots & \end{pmatrix}$$

Since Hamiltonian is diagonal in this basis, only the diagonal elements survive.

⇒ Matrix elements of position operator:

$$\langle n|x|m\rangle = \frac{a_0}{\sqrt{2}}\langle n|(a + a^\dagger)|m\rangle$$

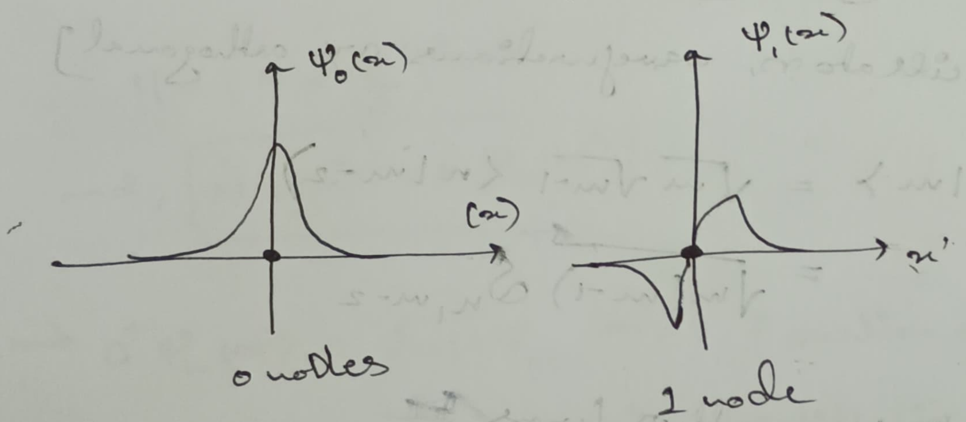
$\Rightarrow$ Matrix element of ~~position operator,~~ momentum operator

$$\langle n|p_x|m\rangle = \frac{i p_0}{\sqrt{2}}\langle n|(a-a^\dagger)|m\rangle$$

$\Rightarrow$ Consider T = expectation value of KE,

$$T = -\frac{\hbar^2}{2M}\int \psi^* \frac{d^2}{dx^2}\psi\, dx = \frac{\hbar^2}{2M}\int\left|\frac{d\psi}{dx}\right|^2 dx$$

thus, as the number of nodes increases, the KE also increases. [prove!]



$\longrightarrow$ KE increases.

Hamiltonian in Magnetic field

consider,

$Q = -e$ [electron]

$\bar{B} = B\hat{z}$ [magnetic field in xy plane]

then,

$$\boxed{H = \frac{(\bar{p} + e\bar{A})^2}{2M}}$$

where $\bar{A}$ = vector potential of $\bar{B}$

By convention, we usually take $\bar{A} = Bx\hat{y}$ or

$\bar{A} = -By\hat{x}$

thus; $H = \frac{p_x^2}{2M} + \frac{(p_y + eBx)^2}{2M}$

[Note: if two operators commute, then they have a common eigen function]

then, $[p_y, H] = 0 \Rightarrow p_y = -i\hbar \frac{\partial}{\partial y}$

thus, $\boxed{p_y e^{ik_y y} = (\hbar k_y) e^{ik_y y}}$

Consider,

$$H\psi(x,y) = E\psi(x,y) \quad (1) \text{ then,}$$

(2) – $\psi(x,y) = e^{ik_y y}\phi(x)$ [separation of var]

substituting (2) in (1), and separating variables,

$$\left[\frac{p_x^2}{2M} + \frac{(\hbar k_y + eBx)^2}{2M}\right]\phi(x) = E\phi(x)$$

$$\Rightarrow \left[\frac{-\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega_c^2\left(x + k_y\frac{\hbar}{eB}\right)^2\right]\phi(x) = E\phi(x)$$

where $\omega_c = \frac{eB}{M}$ [cyclotron frequency]

$\sqrt{\frac{\hbar}{eB}} = l_0$ [magnetic length scale], which is similar to momentum length scale $a_0 = \sqrt{\frac{\hbar}{M\omega}}$

$$\Rightarrow \left[\frac{-\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega_c^2\left(x + k_y l_0^2\right)^2\right]\phi(x) = E\phi(x)$$

this looks like a shifted HO. Thus magnetic field produces a HO type wave equation

$$\Rightarrow \left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2} M\omega_c^2 \left(x + k_y l_0^2\right)^2 \right] \phi(x) = E\phi(x)$$

consider, $\xi = \dfrac{x + k_y l_0^2}{l_0}$, then,

perturbation.

$$\boxed{\hbar\omega_c \left[-\frac{1}{2}\frac{d^2}{d\xi^2} + \frac{1}{2}\xi^2 \right] \phi(\xi) = E\phi(\xi)}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c$$

Hermite polynomials in ξ

$$\Phi_n(x,y) = N_n e^{ik_y y} H_n(\xi) e^{-\xi^2/2}$$

[solved by Landau & thus called Landau levels]

[check out : Born interpretation of Quantum mechanics.

Stern-Gerlach Experiment

$\Rightarrow$ inhomogeneous magnetic field [why?]

$$\Rightarrow \vec{M_s} = -g_s \frac{e}{2m_e}\vec{S}$$

spin magnetic moment

spin gyromatic ratio.

$\Rightarrow$ Addition of angular momentum, $\vec{S_1}$, $\vec{S_2}$ is given by

$$\vec{S} = \vec{S_1} + \vec{S_2} : 0 \text{ to } 1$$

where both $\bar{S_1}$ & $\bar{S_2}$ are spin-$\frac{1}{2}$ systems.

$$|S, M_s\rangle = a|S_1, M_{s_1}\rangle + b|S_2, M_{s_2}\rangle \equiv |S_1, S_2, M_{s_1}, M_{s_2}\rangle$$

total spin

z-component of total spin

since S_1 & S_2 are $\frac{1}{2}$ systems

we can also write,

$$|S, M_s\rangle \equiv |M_{s_1}, M_{s_2}\rangle$$

consider, $|S, M_S\rangle = |1, +1\rangle = |M_{S_1}, M_{S_2}\rangle = |\uparrow\uparrow\rangle$

and $|S, M_S\rangle = |1, 0\rangle = |M_{S_1}, M_{S_2}\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right]$

where $|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$; $|\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$

[Clebsch-gordon coefficients]

$\Rightarrow$ Consider, $\bar{l}$ and $\bar{s}$ then $\bar{J}$ (total angular momentum)

goes from $\bar{J}$: $|l+s|$ to $|l-s|$, from QM-1,

$$\boxed{|j = l+\tfrac{1}{2}, m_j\rangle} = \sqrt{\frac{l+m_j+\frac{1}{2}}{(2l+1)}}\,|l, m_j - \tfrac{1}{2}\rangle \otimes |\uparrow\rangle$$

$$+ \sqrt{\frac{l-m_j+\frac{1}{2}}{(2l+1)}}\,|l, m_j + \tfrac{1}{2}\rangle \otimes |\downarrow\rangle$$

Hydrogen atom.

$\Rightarrow$ This is a two-body problem

$$H = \frac{-\hbar^2}{2m_e}\nabla^2 + V(r)$$

$$H\psi(\bar{r}) = E\psi(\bar{r})$$

thus we use spherical Harmonics,

$$\boxed{\psi(\bar{r}) \sim R(r)\, Y^m_l(\theta, \phi)}$$

then the ground state wavefunction,

$$\psi_{100}(\bar{r}) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$ where a_0 = Bohr radius.

→ Consider $1e^{\ominus}$ system: 8/1/26

$$H_0 = \frac{-\hbar^2}{2m_e}\nabla^2_{\bar r} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \longrightarrow$$ unperturbe Hamiltonian.

we know, for H-atom,

$$E_n = \frac{-13.6}{n^2}\, eV, \quad n = 1, 2, \ldots$$

$$H_0\psi(\bar r) = E_n\psi(\bar r)$$

consider, $H = H_0 + H'$

$H' = -\bar p \cdot \bar E$ where $\bar p \equiv$ dipole moment $= -e\bar r$

if, $\bar E = E_0\hat x$, then,

$$H' = +eE_0 x = eE_0 r\sin\theta\cos\phi$$

consider, $E_0 = 1V/mm = 10^3 V/m$.

$$\left.\begin{aligned} &\text{and } \varepsilon_0 \sim 10eV = 10^{-18} J \\ &\text{whereas, } \varepsilon' = eE_0 a_0 = 10^{-26} J \end{aligned}\right\}$$

since $\varepsilon' \ll \varepsilon_0$ we can take H' as a perturbati term.

then,

$H = H_0 + H'$,

where $H' = \lambda V(x)$ such that the energy associated with H' ($E_{H'}$) is very very less than the energy associated with H_0.

$$E_{(H')} \ll E_{(H_0)}$$

we know that,

$$H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$$

and $\langle\psi_n^{(0)}|\psi_l^{(0)}\rangle = \delta_{nl}$; where n: quantum numbers.

Now,

$$H|\psi_n\rangle = E_n|\psi_n\rangle, \quad -(3)$$

$E_n \equiv E_n(\lambda)$; $|\psi_n\rangle \equiv |\psi_n(\lambda)\rangle$; where λ = free parameter.

upon expanding,

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad -(1)$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \quad -(2)$$

substituting (1) & (2) in (3), where $H = H_0 + \lambda V(x)$

$$H\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \dots\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots\right)$$

comparing λ^0 coefficients,

$$\boxed{H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle} \quad -(a)$$

comparing λ^1 coefficients,

$$H_0|\psi_n^{(1)}\rangle + V(x)|\psi_n^{(0)}\rangle - E_n^{(0)}|\psi_n^{(1)}\rangle - E_n^{(1)}|\psi_n^{(0)}\rangle = 0$$

$$\Rightarrow \boxed{(H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (V(x) - E_n^{(1)})|\psi_n^{(0)}\rangle = 0} \quad -(b)$$

comparing λ^2 coefficients,

$$\Rightarrow \boxed{(H_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (V(x) - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0} \quad (c)$$

Taking same phase for unperturbed eigenket $|\psi_n^{(0)}\rangle$ and the perturbed eigenket $|\psi_n\rangle$

then, $\langle\psi_n^{(0)}|\psi_n\rangle \Rightarrow$ real.

$$\Rightarrow \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \dots \Rightarrow \text{Real}$$

$\Downarrow$

for this to be true

$$\Rightarrow \boxed{\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = \langle\psi_n^{(1)}|\psi_n^{(0)}\rangle}$$

Normalizing $|\psi_n\rangle \Rightarrow \langle\psi_n|\psi_n\rangle = 1$

$$\Rightarrow \langle\psi_n|\psi_n\rangle = \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda\left[\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(1)}|\psi_n^{(0)}\rangle\right]$$
$$+ \lambda^2[\ldots] + \cdots$$

$$\Rightarrow 1 = 1 + \underbrace{\lambda\left[2\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle\right]}$$
$$+ \underbrace{\lambda^2\left[2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \langle\psi_n^{(1)}|\psi_n^{(1)}\rangle\right]} + \cdots$$

each of the terms should be zero,

$$\therefore \boxed{\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0} \text{ and,}$$

$$\cancel{2\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(1)}|\psi_n^{(1)}\rangle = 0}$$

$$\cancel{\Rightarrow \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = -1}$$

$$\boxed{\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = -\frac{1}{2}\langle\psi_n^{(1)}|\psi_n^{(1)}\rangle}$$

Taking equation (b), and multiplying, $\langle\psi_l^{(0)}|$

$$(H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (V - E_n^{(1)})|\psi_n^{(0)}\rangle = 0,$$

$$\Rightarrow \langle\psi_l^{(0)}|(H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + \langle\psi_l^{(0)}|V|\psi_n^{(0)}\rangle$$
$$- \langle\psi_l^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle = 0$$

$$\Rightarrow [E_l^{(0)} - E_n^{(0)}]\langle\psi_l^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_l^{(0)}|V|\psi_n^{(0)}\rangle$$
$$- E_n^{(1)}\langle\psi_l^{(0)}|\psi_n^{(0)}\rangle = 0$$

$$\langle\psi_l^{(0)}|\psi_n^{(0)}\rangle = \delta_{ln}$$

$$\Rightarrow \boxed{[E_l^{(0)} - E_n^{(0)}]\langle\psi_l^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_l^{(0)}|V|\psi_n^{(0)}\rangle - E_n^{(1)}\delta_{ln} = 0}$$

case (1) : $l = n$,

$$\boxed{\lambda E_n^{(1)} = \lambda \langle \psi_n^{(0)} | V(x) | \psi_n^{(0)} \rangle} \quad (1) \longrightarrow \text{1st order energy correction.}$$

case (2) : $l \neq n$;

$$\boxed{\langle \psi_l^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_l^{(0)} | V(x) | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}}}$$

then,

$$\lambda | \psi_n^{(1)} \rangle = \lambda \sum_l | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle$$

$$= \lambda \sum_{l \neq n} \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle | \psi_l^{(0)} \rangle$$

$$+ \lambda \cancelto{0}{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle} | \psi_n^{(0)} \rangle$$

$$\boxed{\lambda | \psi_n^{(1)} \rangle = \sum_{l \neq n} \frac{\lambda \langle \psi_l^{(0)} | V(x) | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}} | \psi_l^{(0)} \rangle} \quad (2)$$

$\Longrightarrow$ from (1),

$$\lambda E_n^{(1)} = \langle \psi_n^{(0)} | \lambda V(x) | \psi_n^{(0)} \rangle$$

$$= \boxed{\langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle}$$

$\Longrightarrow$ from (2),

$$\boxed{\lambda | \psi_n^{(1)} \rangle = \sum_{l \neq n} \frac{\langle \psi_l^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}} | \psi_l^{(0)} \rangle}$$

Taking equation (c),

$$(H_0 - E_n^{(0)}) | \psi_n^{(2)} \rangle + (V - E_n^{(1)}) | \psi_n^{(1)} \rangle - E_n^{(2)} | \psi_n^{(0)} \rangle = 0$$

and multipling it with $\langle \psi_l^{(0)}|$

$$\Rightarrow \langle \psi_l^{(0)} | (H_0 - E_n^{(0)}) | \psi_n^{(2)} \rangle + \langle \psi_l^{(0)} | V | \psi_n^{(1)} \rangle$$

$$+ (-E_n^{(1)}) \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle - E_n^{(2)} \langle \psi_l^{(0)} | \psi_n^{(0)} \rangle = 0$$

$$\Rightarrow (E_l^{(0)} - E_n^{(0)}) \langle \psi_l^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_l^{(0)} | V | \psi_n^{(1)} \rangle$$

$$- E_n^{(1)} \langle \psi_l^{(0)} | \psi_n^{(1)} \rangle = E_n^{(2)} \delta_{ln}$$

case ①: $l = n$,

$$E_n^{(2)} = \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle$$

substituting for $|\psi_n^{(1)}\rangle$,

$$E_n^{(2)} = \sum_{l \neq n} \frac{\langle \psi_n^{(0)} | V | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}}$$

$$\boxed{E_n^{(2)} = \sum_{l \neq n}' \frac{|\langle \psi_l^{(0)} | V(x) | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_l^{(0)}}}$$

→ 2nd order energy correction term.

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⟹ Consider a positively charged particle in

$$H_0 = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2.$$

$$E_n^{(0)} = \left(n + \frac{1}{2}\right) \frac{\hbar\omega}{1}$$

$$\psi_n^{(0)}(x) \sim \phi_n\left(\frac{x}{a_0}\right) e^{-x^2/2a_0^2} \quad \text{where } a_0 = \sqrt{\frac{\hbar}{m\omega}}.$$

$\Rightarrow \langle x | \psi_n^{(0)} \rangle = \psi_n^{(0)}(x)$

Given, $Q = +e$,

$\Rightarrow \bar{E} = E_x \hat{x}$ then $H' = -\bar{P}\cdot\bar{E}$, $\bar{P} = ex\hat{x}$

~~$H' = -eE_x \hat{x}$~~ $H' = -eE_x x$

and $H = H_0 - eE_x x = H_0 - bx$

where $b = eE_x$

the complete Hamiltonian is given by,

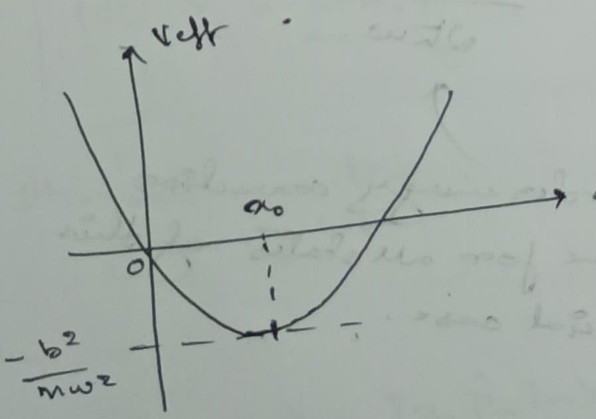
$\Rightarrow H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 - bx \Rightarrow$ to solve, we complete the square

$\Rightarrow H|\psi_n\rangle = E|\psi_n\rangle$

$V_{eff}(x)$

$\Rightarrow H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \left(\frac{1}{2}m\omega^2(x-x_0)^2 - \frac{b^2}{2m\omega^2}\right)$

where $x_0 = \frac{b}{m\omega^2}$



we know that,

$\Rightarrow E_n = (n+\frac{1}{2})\hbar\omega - \frac{b^2}{2m\omega^2}$

and

$\Rightarrow \psi_n^{(0)}\left(\frac{x-x_0}{a_0}\right)$

$\Rightarrow$ Since, $E_n = (n+\frac{1}{2})\hbar\omega - \frac{b^2}{2m\omega^2}$, $b = eE_x$.

the first order energy correction is zero, i.e,

$E_n^{(1)} = \langle \psi_n^{(0)} | x | \psi_n^{(0)} \rangle = \langle n | x | n \rangle$

$= \frac{a_0}{\sqrt{2}} \langle n | (a + a^\dagger) | n \rangle$

⇒ taking the matrix element,

$$\langle l|x|n\rangle = \frac{a_0}{\sqrt{2}}\left[\langle l|(a+a^{\dagger})|n\rangle\right]$$

$$= \frac{a_0}{\sqrt{2}}\left[\sqrt{n}\,\delta_{l,n-1} + \sqrt{n+1}\,\delta_{l,n+1}\right]$$

⇒ $a|n\rangle = \sqrt{n}|n-1\rangle$; $\langle l|n-1\rangle = \delta_{l,n-1}$

and $\langle n|x|n\rangle = 0$.

⇒ calculating the 2nd order energy correction,

$$E_n^{(2)} = \frac{b^2 a_0^2}{2}\sum_{l\neq n}\frac{|\sqrt{n}\,\delta_{l,n-1} + \sqrt{n+1}\,\delta_{l,n+1}|^2}{E_n^{(0)} - E_l^{(0)}}$$

$$E_n^{(2)} = \frac{b^2 a_0^2}{2}\left[\frac{n}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{(n+1)}{E_n^{(0)} - E_{n+1}^{(0)}}\right]$$

$$E_n^{(2)} = \frac{b^2 a_0^2}{2}\left[-\frac{1}{\hbar\omega}\right] = -\frac{(eE_x)^2 a_0^2}{2\hbar\omega}.$$

2nd order energy correction is negative for all states of this special case.

⇒ Calculating $|\psi_n^{(1)}\rangle$,

$$|\psi_n^{(1)}\rangle = \sum_{l\neq n}{}' \frac{\langle l|H'|n\rangle}{E_n^{(0)} - E_l^{(0)}}|l\rangle$$

from the matrix element, $\langle l|x|n\rangle$,

$$|\psi_n^{(1)}\rangle = \sum_{l\neq n}{}' \frac{\langle l|-bx|n\rangle}{E_n^{(0)} - E_l^{(0)}}|l\rangle$$

we know that $x = \frac{a_0}{\sqrt{2}}(a+a^+)$, substituting, we get,

$$|\psi_n^{(1)}\rangle = -\frac{b a_0}{\sqrt{2}} \sum_{l \neq n} \frac{\langle l | a + a^+ | n\rangle}{E_n^{(0)} - E_l^{(0)}} |l\rangle$$

$$= -\frac{b a_0}{\sqrt{2}} \sum_{l \neq n}' \left[\frac{\sqrt{n}\,\delta_{l,n-1} + \sqrt{n+1}\,\delta_{l,n+1}}{E_n^{(0)} - E_l^{(0)}}\right] |l\rangle$$

$$= -\frac{b a_0}{\sqrt{2}} \left[\frac{\sqrt{n}\,|n-1\rangle}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{\sqrt{n+1}\,|n+1\rangle}{E_n^{(0)} - E_{n+1}^{(0)}}\right]$$

$$|\psi_n^{(1)}\rangle = \left(-\frac{b a_0}{\sqrt{2}}\right)\left(\frac{1}{\hbar\omega}\right)\left[\frac{\sqrt{n}\,|n-1\rangle}{1} - \frac{\sqrt{n+1}\,|n+1\rangle}{1}\right]$$

$$= \frac{-b a_0}{\sqrt{2}\,\hbar\omega}\left[(a - a^+)|n\rangle\right]$$

we know that, $\hat{p}_x = -i\frac{\sqrt{\hbar m\omega}}{\sqrt{2}}(a - a^+)$

$$\boxed{|\psi_n^{(1)}\rangle = \frac{-i x_0 \hat{p}_x |n\rangle}{\hbar}}, \quad \text{where } x_0 = \frac{b}{m\omega^2}$$

1st order correction of nth eigenket.

thus,

$$|\psi_n\rangle = |n\rangle - \frac{i x_0 \hat{p}_x |n\rangle}{\hbar}$$

$$= \left(1 - \frac{i x_0 p_x}{\hbar}\right)|n\rangle \simeq \left(e^{-\frac{i x_0 p_x}{\hbar}}\right)|n\rangle$$

$$\cancel{= \left(1 - x_0 \frac{d}{dx}\right.} = \left(1 - x_0\frac{d}{dx}\right)|n\rangle \simeq \left(e^{-x_0\frac{d}{dx}}\right)|n\rangle$$

we know that,

$$\langle x|\hat{p}_x|u\rangle = \hat{P}_x \langle x|u\rangle$$

where $\langle x|u\rangle = \psi_u(x)$, $|u\rangle \Rightarrow \psi_u^{(0)}$ which is the unperturbed state

thus;

$$\cancel{\psi_u(x) = \langle x|\psi_u(x)\rangle = e^{-x_0\frac{d}{dx}}\langle u|x\rangle}$$

$$\cancel{= e^{-x_0\frac{d}{dx}}\psi_u^{(0)}(x)}$$

$$\psi_u(x) = \langle x|\psi_u\rangle = e^{-x_0\frac{d}{dx}}\langle x|u\rangle$$

$$= e^{-x_0\frac{d}{dx}}\psi_u^{(0)}(x)$$

$$= \left(1 - x_0\frac{d}{dx}\right)\psi_u^{(0)}(x)$$

$$\psi_u^{exact}(x-x_0) = \psi_u^{(0)}(x) - x_0\frac{d}{dx}\psi_n^{(0)}(x)$$

$$\Updownarrow$$

$$H_n\left(\frac{x-x_0}{a_0}\right)e^{-\frac{(x-x_0)^2}{2a_0^2}}$$

$\Rightarrow$ Perturbed energy levels & perturbed functions for H' of form $H' \sim x^4$, $H' \sim x^3$:

for diatomic molecules, we take,

$$H_0 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$$

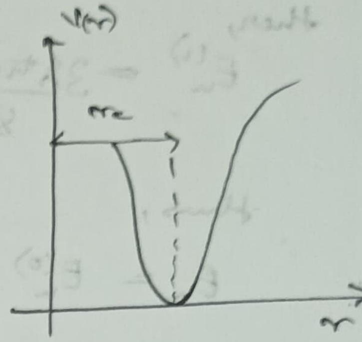
but, ~~this is no~~ the energy levels are not similar to the ones obtained experimentally.

We use Morse potential for ~~more~~ better accepted values

Morse potential : $V(r) = D_e\left[1-e^{-\beta(r-r_e)}\right]^2 - D_e$

$$V(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2 - D_e$$

$$= D_e\left(e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)}\right)$$



upon Taylor series expansion about r_e.

$$\Rightarrow V(r) \approx D_e\beta^2(r-r_e)^2 - D_e\beta^3(r-r_e)^3 + \frac{7}{12}D_e\beta^4(r-r_e)^4 - \cdots$$

consider,

$x = r - r_e$, $\quad D_e\beta^2 = \frac{1}{2}\mu\omega^2 \Rightarrow \omega^2 = \frac{2D_e\beta^2}{\mu}$,

then for a diatomic molecule following Morse's potential,

$$H = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(r)$$

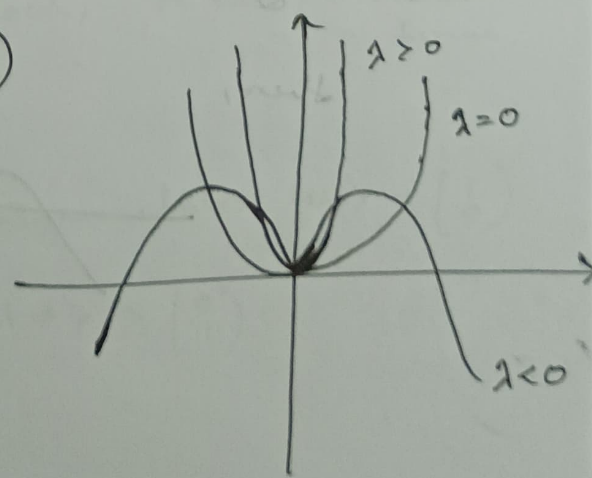
reduced mass.

$$H = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}\mu\omega^2x^2 - \underbrace{(\ )x^3}_{\text{cubic term}} + \underbrace{(\ )x^4}_{\text{quartic term.}}$$

$$H = \hbar\omega\left[-\frac{1}{2}\frac{d^2}{d\eta^2} + \frac{1}{2}\eta^2 + \frac{\lambda}{2}\eta^4\right]$$

where $\eta = \frac{x}{a_0}$

then $V(\eta) = \hbar\omega\left(\frac{1}{2}\eta^2 + \frac{\lambda}{2}\eta^4\right)$



thus for $\lambda > 0$ & $\lambda = 0$,

infinite bound states,

for $\lambda < 0$,

finite bound states.

then,

$$E_n^{(1)} = \frac{3\lambda\hbar\omega}{8}(2n^2+2n+1)$$ ← first order energy correction.

Thus,

$$E_n = E_n^{(0)} + E_n^{(1)}$$

for $\lambda > 0$, the energy levels will be higher

for $\lambda < 0$, the energy levels will be lower

upon calculating $\Delta E_n = E_{n+1} - E_n$

we see that the energy levels are not evenly distributed.

⇒ calculating 2nd order correction for ground state:

$$E_0^{(2)} = -\lambda^2\hbar\omega\left(\frac{21}{32}\right)$$

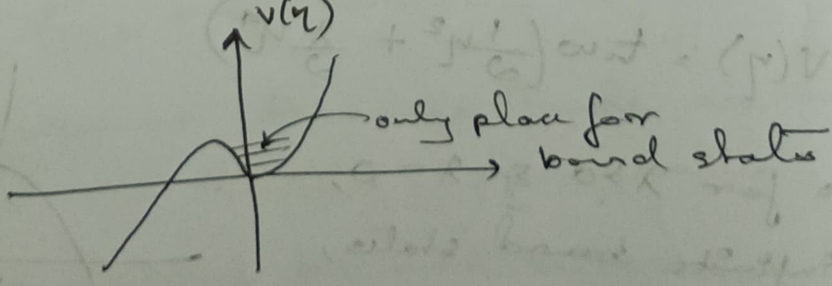
⇒ Consider,

$$H_0 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$$

$$H' = \frac{\lambda\hbar\omega\eta^3}{2}$$

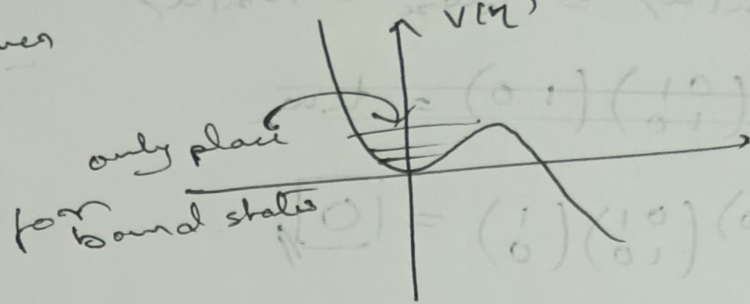
$$V(\eta) = \frac{\hbar\omega}{2}[\eta^2 + \lambda\eta^3], \quad \lambda > 0$$

then,



$$V(x) = \frac{\hbar\omega}{2}\left[x^2 + \lambda x^3\right], \quad \lambda < 0$$

then



⟹ Consider we apply magnetic field such that,

$$\bar{B} = B_x \hat{x} + B_z \hat{z} \qquad \omega_x = \frac{eB_x}{m}$$

then, $$H = -\bar{\mu}_s \cdot \bar{B} = \hbar\omega_x \sigma_x + \hbar\omega_z \sigma_z \qquad \omega_z = \frac{eB_z}{m}.$$

where σ_x & σ_z are Pauli matrices,

then,

$$E_{\pm} = \pm\hbar\sqrt{\omega_x^2 + \omega_z^2}$$

$$|+\gamma\rangle = \begin{bmatrix} \cos\left(\frac{\theta}{2}\right) \\ \sin(\theta/2) \end{bmatrix} \; ; \quad |-\gamma\rangle = \begin{bmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{bmatrix}$$

where $\theta = \tan^{-1}\left(\frac{\omega_x}{\omega_z}\right)$

take, $H_0 = \hbar\omega_z \sigma_z$; $H' = \hbar\omega_x \sigma_z$, $\omega_z \gg \omega_x$.

applying perturbation method, $H' \rightarrow$ perturbative term.

$$E_{\pm}^{(0)} = \pm\hbar\omega_z$$

for $+\hbar\omega_z$, the ~~eigenvalue~~ eigenvector $|u\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

and $-\hbar\omega_z$, the eigenvector $|d\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

thus, the first order energy correction is,

$$E_+^{(1)} = \langle u|\hbar\omega_x\sigma_x|u\rangle = \hbar\omega_x \langle u|\sigma_x|u\rangle$$

$$\cancel{= \hbar\omega_x \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1&0\end{pmatrix} = \hbar\omega_x}$$

$$= \hbar\omega_x \begin{pmatrix}1&0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \boxed{0}$$

and

$$E_-^{(1)} = \langle d|\hbar\omega_x\sigma_x|d\rangle = \hbar\omega_x\langle d|\sigma_x|d\rangle$$

$$= \hbar\omega_x \begin{pmatrix}0&1\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \boxed{0}$$

the 2nd order energy correction is,

$$E_+^{(2)} = \frac{|\langle d|\hbar\omega_x\sigma_x|u\rangle|^2}{E_+^{(0)} - E_-^{(0)}} = \frac{(\hbar\omega_x)^2}{2\hbar\omega_z}|\langle d|\sigma_x|u\rangle|^2$$

$$\boxed{E_+^{(2)} = \frac{(\hbar\omega_x)^2}{2\hbar\omega_z}} = \frac{1}{2}\frac{\hbar\omega_x^2}{\omega_z} \longrightarrow (1)$$

we know, $E_+ = \hbar\sqrt{\omega_x^2 + \omega_z^2} = \hbar\omega_z\sqrt{1 + \left(\frac{\omega_x}{\omega_z}\right)^2}$

$$E_+ \approx \hbar\omega_z\left(1 + \frac{1}{2}\left(\frac{\omega_x}{\omega_z}\right)^2 + \cdots\right)$$

$$\approx \hbar\omega_z + \underbrace{\frac{1}{2}\frac{\hbar\omega_x^2}{\omega_z}}_{(2)} + \cdots$$

we see that (1) & (2) are the same. & thus satisfied.

first order function corrections,

$$|u^{(1)}\rangle = \frac{\langle d|\hbar\omega_x \sigma_x|u\rangle}{E_+^{(0)} - E_-^{(0)}} |d\rangle = \frac{\omega_x}{2\omega_z}|d\rangle = \begin{pmatrix} 0 \\ \frac{\omega_x}{2\omega_z} \end{pmatrix}$$

~~$|u\rangle =$~~ when $\omega_z >> \omega_x$, from $\tan^{-1}$ expansion,

$$\theta \simeq x - \frac{x^3}{3} + \frac{x^5}{5} - + \cdots \simeq \left(\frac{\omega_x}{\omega_z}\right)$$

thus,

$$|u\rangle = |u^{(0)}\rangle + |u^{(1)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{\omega_x}{2\omega_z} \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{\omega_x}{2\omega_z} \end{pmatrix}$$

15/1/2026

Degenerate Perturbation Theory

Degenerate Harmonic Oscillator

$\Rightarrow$ Consider isotropic 2D - Harmonic Oscillator

$$H_0 = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\Omega^2(x^2+y^2)$$

$$H_0\psi(x,y) = \mathcal{E}_{n_x, n_y}\psi(x,y)$$

then, $\mathcal{E}_{n_x n_y} = (n_x + n_y + 1)\hbar\Omega$; $n_x = 0, 1, 2, \ldots$ and $n_y = 0, 1, 2, \ldots$

$$\psi^{(0)}_{n_x, n_y}(x,y) = N\phi_{n_x}\left(\frac{x}{a_0}\right)\phi_{n_y}\left(\frac{y}{a_0}\right), \quad a_0 = \sqrt{\frac{\hbar}{m\Omega}}$$

the ground state is:

$$\mathcal{E}_{0,0} = \hbar\Omega, \quad \psi_{0,0}(x,y) = N_0\,\phi_0\left(\frac{x}{a_0}\right)\phi_0\left(\frac{y}{a_0}\right)$$

First excited state:

$$\mathcal{E}_{0,1} = 2\hbar\Omega, \quad \psi_{0,1}(x,y) = N_1\,\phi_0\left(\frac{x}{a_0}\right)\phi_1\left(\frac{y}{a_0}\right)$$

Same energy degeneracy

$$\mathcal{E}_{1,0} = 2\hbar\Omega, \quad \psi_{1,0}(x,y) = N_2\,\phi_1\left(\frac{x}{a_0}\right)\phi_0\left(\frac{y}{a_0}\right)$$

⇒ Since the 1st excited state has the same eigenvalue but different eigenfunctions, ~~they are~~ the energy level is said to be doubly - degenerate

To solve this we need to build the Degenerate Perturbation theory.

$\psi_1(x,y)$ & $\psi_2(x,y)$ are orthogonal to each other.

⇒ Consider,

$H = H_0 + H'$ and $H' = \lambda V$

for a doubly - degenerate system,

$$H_0|\psi_{01}^{(0)}\rangle = E^{(0)}|\psi_{01}^{(0)}\rangle$$
$$H_0|\psi_{10}^{(0)}\rangle = E^{(0)}|\psi_{10}^{(0)}\rangle$$

taking $\psi_{01}(x,y) = \psi_1(x,y)$
$\psi_{10}(x,y) = \psi_2(x,y)$

then we take the linear combination,

$$|\psi^{(0)}\rangle = a|\psi_1^{(0)}\rangle + b|\psi_2^{(0)}\rangle$$

$$\Rightarrow |\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$H|\psi_n\rangle = E_n|\psi_n\rangle$, where $n = \{n_x, n_y\}$

Looking at coefficients of λ,

$$H_0|\psi^{(1)}\rangle + V|\psi^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle + E^{(1)}|\psi^{(0)}\rangle$$

multiply by $\langle\psi_1^{(0)}|$,

$$\cancel{\langle\psi_1^{(0)}|H|\psi^{(1)}\rangle} + \langle\psi_1^{(0)}|V|\psi^{(0)}\rangle = \cancel{E^0\langle\psi_1^{(0)}|\psi^{(1)}\rangle} + E^{(1)}\langle\psi_1^{(0)}|\psi^{(0)}\rangle$$

(1)

and,

$$\langle \psi_2^{(0)} | H_0 | \psi^{(1)} \rangle + \langle \psi_2^{(0)} | V | \psi^{(0)} \rangle = E^{(0)} \langle \psi_2^{(0)} | \psi^{(1)} \rangle + E^{(1)} \langle \psi_2^{(0)} | \psi^{(0)} \rangle$$

(2)

upon solving (1) & (2)

$$\Rightarrow a \langle \psi_1^{(0)} | V | \psi_1^{(0)} \rangle + b \langle \psi_1^{(0)} | V | \psi_2^{(0)} \rangle = E^{(1)} a$$

$$\boxed{a V_{11} + b V_{12} = E^{(1)} a.}$$

and $a \langle \psi_2^{(0)} | V | \psi_1^{(0)} \rangle + b \langle \psi_2^{(0)} | V | \psi_2^{(0)} \rangle = E^{(1)} b$

$$\boxed{a V_{21} + b V_{22} = E^{(1)} b.}$$

since

$V_{ij} = \langle \psi_i^{(0)} | V | \psi_j^{(0)} \rangle$, $i, j = 1, 2,$

then $V_{12} = V_{21}^*$, then,

$$\begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E^{(1)} \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\Rightarrow \boxed{E_\pm^{(1)} = \frac{1}{2}(V_{11} + V_{22}) \pm \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}}$$

$$E_\pm = E^{(0)} + \lambda E_\pm^{(1)}$$

then, $E_+^{(1)} = a_+, b_+$ and $E_-^{(1)} = a_0, b_0.$

We get the solutions as :

$$|\psi_+\rangle = a_+ |\psi_1^{(0)}\rangle + b_+ |\psi_2^{(0)}\rangle$$

$$|\psi_-\rangle = a_- (|\psi_1^{(0)}\rangle) + (b_- |\psi_2^{(0)}\rangle)$$

and $\langle \psi_\pm | \psi_\mp \rangle = 0$ //

N-fold degeneracy

$$\Rightarrow H_0 |\psi_j^{(0)}\rangle = E_0 |\psi_j^{(0)}\rangle \quad ; \quad j = 1, 2, \ldots N$$

$$|\psi\rangle = \sum_{k=1}^{N} c_k |\psi_k^{(0)}\rangle$$

then,

$$\begin{pmatrix} V_{11} & V_{12} & V_{13} & \cdots & V_{1M} \\ V_{21} & V_{22} & V_{23} & \cdots & V_{2M} \\ \vdots \\ V_{M1} & V_{M2} & V_{M3} & \cdots & V_{MM} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_M \end{pmatrix} = E^{(1)} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_M \end{pmatrix}$$

here the Energy eigenvalues are the same but there exists N - energy eigenfunctions.

Hence we say there is N-fold degeneracy.

Case : Rotation

$$H_0 = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2} m \Omega^2 (x^2 + y^2)$$

$$H' = m\omega^2 xy \quad ; \quad \Omega \gg \omega.$$

$$H = H_0 + H'$$

Rotation matrix:

$$\begin{pmatrix} X_+ \\ X_- \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

$$X_+ = \frac{1}{\sqrt{2}}(x+y) \quad ; \quad X_- = \frac{1}{\sqrt{2}}(-x+y)$$

thus,

$$x = \frac{(x_+) - (x_-)}{\sqrt{2}} \quad ; \quad y = \frac{(x_+) + (x_-)}{\sqrt{2}}$$

transforming,

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \longrightarrow \frac{\partial^2}{\partial x_+^2} + \frac{\partial^2}{\partial x_-^2}$$

thus, $(x^2+y^2) \longrightarrow (x_+^2 + x_-^2)$

$2xy \longrightarrow (x_+^2 - x_-^2)$

thus we can transform the Hamiltonian as,

$$H_0 = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial X_+^2} + \frac{\partial^2}{\partial X_-^2}\right) + \frac{1}{2} m \Omega^2 (x_+^2 + x_-^2)$$

$$H' = \frac{1}{2} m\omega^2 (x_+^2 - x_-^2)$$

$$H = H_0 + H'$$

thus,

$$H = \left(\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial X_+^2} + \frac{\partial^2}{\partial X_-^2}\right)\right) + \frac{1}{2} m (\Omega^2 + \omega^2) x_+^2$$

$$+ \frac{1}{2} m (\Omega^2 - \omega^2) x_-^2$$

$$V(x_+, x_-) = \frac{1}{2} m \left(\Omega^2 \gamma_+^2 x_+^2 + \Omega^2 \gamma_-^2 x_-^2\right)$$

where $\gamma_\pm = \sqrt{1 \pm \frac{\omega^2}{\Omega^2}}$

then,

$$E_{n_x n_y} = \left(n_x + \frac{1}{2}\right)\hbar \Omega \gamma_+ + \left(n_y + \frac{1}{2}\right)\hbar \Omega \gamma_-$$

where $n_x = 0, 1, 2, \ldots$

$n_y = 0, 1, 2, \ldots$

we get the exact result to be,

$$\psi_{n_x n_y}(x_+, x_-) = N_{n_x n_y}\, \phi_{n_x}\left(\frac{x_+}{a_+}\right) \phi_{n_y}\left(\frac{x_-}{a_-}\right)$$

where,

$$a_\pm = \gamma_\pm a_0 \,;$$

$$a_0 = \sqrt{\frac{\hbar}{m\Omega}}$$

where ϕ_{n_x} & ϕ_{n_y} are oscillatory wave function, which is (Hermite) $\times$ (Gaussian)

19/1/2026

$\Rightarrow$ Consider,

$$H_0 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2} m\Omega^2 (x^2 + y^2)$$

where $\Omega \gg \omega$, $H' = m\omega^2 xy$,

$$\varepsilon_{n_x n_y} = (n_x + n_y + 1)\hbar\Omega.$$

and $\psi_{n_x, n_y}(x, y) = \phi_{n_x}\left(\frac{x}{a_0}\right) \phi_{n_y}\left(\frac{y}{a_0}\right)$

for $n_x = 0$, $n_y = 0$,

$\varepsilon_{0,0} = \hbar\Omega$ and $\psi_{0,0}(x, y) = \phi_0\left(\frac{x}{a_0}\right) \phi_0\left(\frac{y}{a_0}\right)$

$$E^{(1)}_{0,0} = \langle \phi_0 \phi_0 | m\omega^2 xy | \phi_0 \phi_0 \rangle$$

~~taking~~ defining operators : $a = \left(\frac{i\hat{p}_x}{p_0} + \frac{\hat{x}}{x_0}\right)\frac{1}{\sqrt{2}}$

and $a^+ = \left(\frac{-i\hat{p}_x}{p_0} + \frac{\hat{x}}{x_0}\right)\frac{1}{\sqrt{2}}$

thus, $p_0 = \sqrt{\hbar m\Omega}$, $a_0 = \sqrt{\frac{\hbar}{m\Omega}}$

similarly, defining operators for y-coordinate,

$$b = \left(\frac{i\hat{P}_y}{p_0} + \frac{y}{a_0}\right)\frac{1}{\sqrt{2}} \quad , \quad b^+ = \left(\frac{-i\hat{P}_y}{p_0} + \frac{y}{a_0}\right)\frac{1}{\sqrt{2}}$$

then, $x = \frac{a_0}{\sqrt{2}}(a + a^+)$ and $y = \frac{a_0}{\sqrt{2}}(b + b^+)$

$$E_0^{(1)} = \frac{m\omega^2}{2}\langle \phi_0 \phi_0 |(a + a^+)(b + b^+)| \phi_0 \phi_0 \rangle = 0$$

thus, $$E_0^{(2)} = \sum_{n_x \neq 0}\sum_{n_y \neq 0} \frac{|\langle n_x n_y | m\omega^2 xy | 0,0\rangle|^2}{\varepsilon_{(0,0)} - \varepsilon_{(n_x, n_y)}} = \frac{-\hbar\omega^4}{8\Omega^3}$$

[from the previous rotation example,

$$E_{n_x, n_y} = \hbar\Omega\gamma_+\left(n_x + \frac{1}{2}\right) + \hbar\Omega\gamma_-\left(n_y + \frac{1}{2}\right)$$

for $E_0^{(2)} = \frac{-\hbar\omega^4}{8\Omega^3}$]

$\Longrightarrow$ From doubly-degenerate system, we saw that,

$\varepsilon_{0,1} = \varepsilon_{1,0}$ but the eigenfunctions are different.

$$\varepsilon_{0,1} : \phi_0\left(\frac{x}{a_0}\right)\phi_1\left(\frac{y}{a_0}\right) \equiv \psi_1(x,y)$$

$$\varepsilon_{1,0} : \phi_1\left(\frac{x}{a_0}\right)\phi_0\left(\frac{y}{a_0}\right) \equiv \psi_2(x,y)$$

then ψ_1 & ψ_2 are orthogonal, thus we can choose them to our basis vectors.

then,
$$\begin{pmatrix} H_{11}^{(1)} & H_{12}^{(1)} \\ H_{21}^{(1)} & H_{22}^{(1)} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

where the matrix elements are.

$$H'_{jk} = \langle \psi_j | H' | \psi_k \rangle \quad ; \quad j,k = 1,2$$

$\Rightarrow H'_{11} = 0 \; ; \; H'_{22} = 0$

$$H'_{12} = \frac{\hbar w^2}{2\Omega} = \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right) = H'_{21}$$

solving for,

$$\begin{pmatrix} 0 & \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right) \\ \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right) & 0 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E^{(1)}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

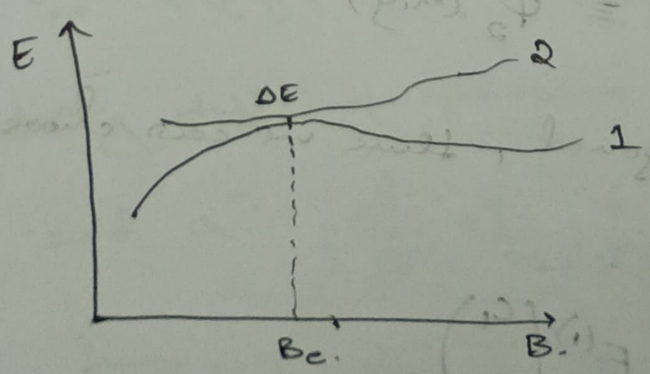
we get $E^{(1)} = \pm \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right)$

$$2\hbar\Omega \;\; \frac{|0,1\rangle}{|1,0\rangle} \xrightarrow{H'} \begin{array}{l} |0,1\rangle \Rightarrow 2\hbar\Omega + \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right) \\ |1,0\rangle \Rightarrow 2\hbar\Omega - \hbar\Omega\left(\frac{w^2}{2\Omega^2}\right) \end{array}$$

Quasi-degenerate Systems.

[/Avoided level crossings/Nearly degenerate]

$\Rightarrow$ Consider, two bands.



If E' (perturbation) is greater than ΔE,

$E' > \Delta E$,

then the perturbation mixes the 2 & 1 states.

$\Rightarrow$ we solve using a numerical tech. $\rightarrow$ exact diagonalization consider,

$$H = H_0 + H' \quad , \quad H_0 |\psi_k^{(0)}\rangle = E_k^{(0)} |\psi_k^{(0)}\rangle \quad , \quad k = 1, 2, \ldots$$

we know that,

$$|\psi\rangle = \sum_{k=1} c_k |\psi_k^{(0)}\rangle \quad \text{and} \quad H|\psi\rangle = E|\psi\rangle$$

thus,

$$(H_0 + H') \sum_k c_k |\psi_k^{(0)}\rangle = E \sum_k c_k |\psi_k^{(0)}\rangle$$

multiplying with $\langle\psi_j^{(0)}|$,

$$\Rightarrow \langle\psi_j^{(0)}| (H_0 + H') \sum_k c_k |\psi_k^{(0)}\rangle = E \sum_k c_k \langle\psi_j^{(0)}|\psi_k^{(0)}\rangle$$

$$\Rightarrow \sum_k c_k \left[E_k^{(0)} \delta_{jk} + H'_{jk} \right] = E \sum_k c_k \delta_{jk}$$

$$\Rightarrow \boxed{(E_j^{(0)} - E) c_j + \sum_k c_k H'_{jk} = 0}$$

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$\Rightarrow$ case : H-atom.

$H = H_0 + H'$ where $H_0 \rightarrow$ Hamiltonian for H atom.

& H' is perturbation due to $\vec{E}$ or $\vec{B}$.

	$\|100\rangle$	$\|200\rangle$	$\|210\rangle$	$\|211\rangle$	$\|21{-1}\rangle$
$\langle 100\|$	( )	( )	( )	( )	( )
$\langle 200\|$	( )	( )	( )	( )	( )
$\langle 210\|$	( )	( )	( )	( )	( )
$\langle 211\|$	( )	( )	( )	( )	( )
$\langle 21{-1}\|$	( )	( )	( )	( )	( )

If $H = H_0$, then the matrix is diagonal.

If $H = H_0 + H'$, the off-diagonal elements are non-zero.

→ Exact degenerate terms.

Stark - Effect

$\Rightarrow$ H-atom, is subjected to uniform $\bar{E} = E_0 \hat{z}$

then the dipole moment, $\bar{d} = -e\bar{r}$

thus $H' = -\bar{d}\cdot\bar{E} = eE_0 z = eE_0 r\cos\theta$

calculating the energy scale,

$$E_n^{(0)} = \frac{-13.6}{n^2}\ eV$$

the energy associated with H' is very less than $E_n^{(0)}$ $\Rightarrow$ thus, H' can be taken as the perturbative term.

$$\Rightarrow \psi_{100}(\bar{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$E_1^{(1)} = \langle \psi_{100} | eE_0 z | \psi_{100} \rangle = 0$$

from this, we can say that the ground state does not have permanent / intrinsic dipole moment $\bar{d}$.

$\Rightarrow$ dipole moment for a charged distribution is :

$$\bar{d} = \int \rho(\bar{r})\bar{r}\, d^3 r$$

we know $\rho(\bar{r}) = -e|\psi_{100}(\bar{r})|^2$

substituting, $\bar{d} = \frac{-e}{\pi a_0^3}\int e^{-2r/a_0}\bar{r}\, d^3 r = 0$

$\therefore$ $\bar{d} = 0$ for ground state H-atom.

$\Rightarrow$ to calculate the 2nd order correction for ground state

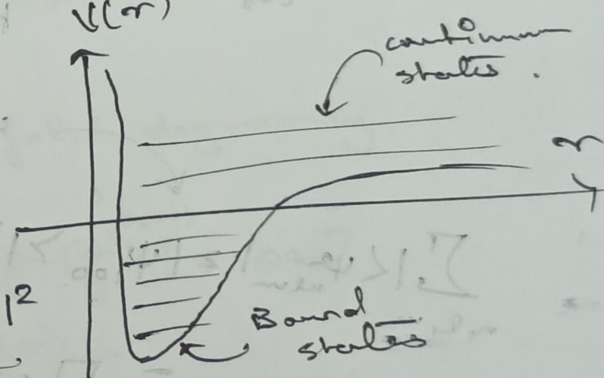
$$E_{100}^{(2)} = \underbrace{\sum_{n\neq 1,l,m}' \frac{|\langle \psi_{n,l,m}| eE_0 z|\psi_{100}\rangle|^2}{E_1^{(0)} - E_n^{(0)}}}_{\text{contri from boundstates.}} + \underbrace{\sum_{\vec{k}} \frac{|\langle \psi_k | eE_0 z|\psi_{100}\rangle|^2}{E_1^{(0)} - \frac{\hbar^2 k^2}{2m}}}_{\text{contribution from the continuum states}}$$

$\Rightarrow$ here, the contribution from the continuum states are very less & thus can be ignored

thus,

$$E_{100}^{(2)} = \sum_{n\neq 1,l,m} \frac{|\langle \psi_{n,l,m}| eE_0 z|\psi_{100}\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

$$= -e^2E_0^2 \sum_{n\neq 1,l,m}' \frac{|\langle \psi_{n,l,m}|z|\psi_{100}\rangle|^2}{E_n^{(0)} - E_1^{(0)}}$$



we know that,

$$E_2^{(0)} - E_1^{(0)} < E_3^{(0)} - E_1^{(0)} \Longrightarrow \frac{1}{E_2^{(0)} - E_1^{(0)}} > \frac{1}{E_3^{(0)} - E_1^{(0)}}$$

summation over n,

$$E_{100}^{(2)} = \sum_{l,m}' (-e^2E_0^2)\left[\frac{|\langle \psi_{2,l,m}|z|\psi_{100}\rangle|^2}{E_2^{(0)} - E_1^{(0)}} + \frac{|\langle \psi_{3,l,m}|z|\psi_{100}\rangle|^2}{E_3^{(0)} - E_1^{(0)}} + \dots\right]$$

replacing, $E_3^{(0)} - E_1^{(0)} \longrightarrow E_2^{(0)} - E_1^{(0)}$

$E_4^{(0)} - E_1^{(0)} \longrightarrow E_2^{(0)} - E_1^{(0)}$ ...

and so on, we can write.

$$\frac{}{(E_2^{(0)} - E_1^{(0)})} \sum_{n \neq 1, l, m}$$

removing the condition, $n \neq 1$, since no extra term will be added if $n = 1$. because

$$eE_0 \langle \psi_{100} | z | \psi_{100} \rangle = 0$$

$$\Rightarrow E_{100}^{(2)} > \frac{-e^2 E_0^2}{(E_2^{(0)} - E_1^{(0)})} \sum_{n,l,m} |\langle \psi_{n,l,m} | z | \psi_{100} \rangle|^2$$

taking this term,

$$\sum_{n,l,m} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 = \sum \langle \psi_{nlm} | z | \psi_{100} \rangle^* \langle \psi_{nlm} | z | \psi_{100} \rangle$$

$$= \sum \langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle$$

using the completeness theorem,

$$\sum_{nlm} | \psi_{nlm} \rangle \langle \psi_{nlm} | = \mathbb{1}$$

$$\Rightarrow \sum_{nlm} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 = \langle \psi_{100} | z^2 | \psi_{100} \rangle = \frac{\langle r^2 \rangle_{100}}{3} = a_0^2$$

thus, $E_{100}^{(2)} > -\frac{e^2 E_0^2 a_0^2}{(E_2^{(0)} - E_1^{(0)})} \approx \boxed{-2.66\, 4\pi \varepsilon_0 a_0^3 E_0^2}$

we can calculate $E_{100}^{(2)}$ exact by taking the contribution by the continuum states,

$$E_{100}^{(2)}\Big|_{\text{exact}} = -2.25 (4\pi \varepsilon_0 a_0^3) E_0^2$$

Magnitude of induced dipole moment:

$$D_{ind} = -\frac{\partial E^{(2)}_{100}}{\partial E_0} = -\frac{2(2.25\, 4\pi\varepsilon_0 a_0^3)E_0^2}{\partial E_0}$$

$$D_{ind} = (4.5)(4\pi\varepsilon_0 a_0^3)E_0 = \alpha_{100} E_0$$

where $\alpha_{100} = (4.5)(4\pi\varepsilon_0 a_0^3)$ = polarizability of the atom.

Linear Stark Effect

Considering $n=2$; $E_2^{(0)} = \frac{-13.6}{4}$ eV

the 1st excited state has 4-fold degeneracy.

s-orbital $\rightarrow \psi_1(\bar{r}) = \langle \bar{r} | \psi_{200} \rangle = \sqrt{2} f(r)[r-2a_0]$

p-orbitals:

$\psi_2(\bar{r}) = \langle \bar{r} | \psi_{210} \rangle = \sqrt{2} f(r) z$

$\psi_3(\bar{r}) = \langle \bar{r} | \psi_{21,+1} \rangle = -f(r)(x+iy)$

$\psi_4(\bar{r}) = \langle \bar{r} | \psi_{2,1,-1} \rangle = f(r)(x-iy)$

where $f(r) = \frac{1}{\sqrt{64\pi a_0^3}} e^{-r/2a_0}$

we use the degenerate perturbation theory,

taking $\langle \psi_j | \psi_k \rangle = \delta_{jk}$ where $j,k = 1,2,3,4$

$\Rightarrow$ the perturbation matrix:

$$\begin{pmatrix} H'_{11} & H'_{12} & H'_{13} & H'_{14} \\ H'_{21} & H'_{22} & H'_{23} & H'_{24} \\ H'_{31} & H'_{32} & H'_{33} & H'_{34} \\ H'_{41} & H'_{42} & H'_{43} & H'_{44} \end{pmatrix}$$

$\Rightarrow H'_{jk} = eE_0 \langle \psi_j | z | \psi_k \rangle$

$H'_{12} = H'_{21} = -3eE_0 a_0$

& all others $= 0$

$$\Rightarrow \begin{bmatrix} 0 & -3ea_0E_0 & 0 & 0 \\ -3ea_0E_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \Leftrightarrow \begin{bmatrix} 0 & -3ea_0E_0 \\ -3ea_0E_0 & 0 \end{bmatrix}$$

Thus ψ_1 & ψ_2 states are mixed with each other.

$$|\phi_+\rangle \quad E_2^{(0)} + 3ea_0E_0$$

$$\underset{|200\rangle;\ |210\rangle;\ |21{+}1\rangle;\ |21{-}1\rangle}{n=2} \xrightarrow{H'} \quad |21{+}1\rangle\ \&\ |21{-}1\rangle \quad E_2^{(0)} \text{ (degenerate)}$$

$$|\phi_-\rangle \quad E_2^{(0)} - 3ea_0E_0$$

$$E' = \pm 3ea_0E_0$$

$$\left.\begin{aligned} \text{where } |\phi_+\rangle &= \frac{1}{\sqrt{2}}\left[|\psi_{200}\rangle - |\psi_{210}\rangle\right] \\ |\phi_-\rangle &= \frac{1}{\sqrt{2}}\left[|\psi_{200}\rangle + |\psi_{210}\rangle\right] \end{aligned}\right\} \text{ —(1)}$$

and $\rho_\pm = -e|\phi_\pm(\vec{r})|^2$

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$\Rightarrow$ We saw linear stark effect for $n = 2$,

$$H' = eE_0 z$$

$$\psi = c_1|\psi_{200}\rangle + c_2|\psi_{210}\rangle + c_3|\psi_{211}\rangle + c_4|\psi_{21-1}\rangle$$

$$\begin{pmatrix} 0 & -3ea_0E_0 & 0 & 0 \\ -3ea_0E_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E'\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

considering the block-diagonal matrices,

$$\begin{pmatrix} 0 & -3ea_0E_0 \\ -3ea_0E_0 & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\Rightarrow -3ea_0E_0 \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\sigma_x}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$\Rightarrow E^{(1)}_{\pm} = \pm 3ea_0E_0$, we know $c_3 = c_4 = 0$

taking $E^{(1)}_{+} = +3ea_0E_0$,

$$-3ea_0E_0\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 3ea_0E_0\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \Rightarrow c_1 = -c_2$$

Say $c_1 = -c_2 = N \Rightarrow \Psi_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

thus,

$E^{(1)}_{+} = +3ea_0E_0 \; : \; \psi = \frac{1}{\sqrt{2}}\left[|\psi_{200}\rangle - |\psi_{210}\rangle\right]$

Similarly, for

$E^{(1)}_{-} = -3ea_0E_0 \; : \; \psi = \frac{1}{\sqrt{2}}\left[|\psi_{200}\rangle + |\psi_{210}\rangle\right]$

as seen in eqn. (1)

Fine Structure Corrections to Energy levels.

→ 1 electron - atom:

In the case of spherical symmetry, $\bar{r}$ is just a func of r, i.e., $\bar{r} = R(r)$, then,

$$H_0 = \frac{-\hbar^2}{2m}\nabla^2 + V(\bar{r})$$

$$V(\bar{r}) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

$E_n = \frac{-m_0 e^2}{2n^2}\alpha^2$, $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$

fine structure constant

$\Rightarrow$ Relativistic correction to KE : H_k

Spin-orbital ~~correct~~ coupling : H_{SO}

$\sim (\bar{L}\cdot\bar{S})$

Darwin's correction : H_D

$\Rightarrow$ Relativistic correction to KE : H_k

We know that, relativistic KE is given by,

$$T = \sqrt{(\bar{p}c)^2 + m_0^2 c^4} - m_0 c^2$$

non-relativistic approximation $\Rightarrow p \ll m_0 c$

$$T = m_0 c^2 \sqrt{1 + \frac{\bar{p}^2 c^2}{m_0^2 c^4}} - m_0 c^2$$

$$= m_0 c^2 \left(1 + \frac{p^2}{m_0^2 c^2}\right)^{1/2} - m_0 c^2$$

$$T = \frac{\bar{p}^2}{2m_0} - \frac{\bar{p}^4}{8m_0^3 c^2} + \cdots$$

relativistic correction to kinetic energy

Classical $\Longrightarrow$ convert to Quantum.

taking $p = \frac{\hbar}{a_0}$

$$\boxed{\hat{T} = \frac{-\hbar^2 \nabla^2}{2m_0} - \frac{\hbar^4 \nabla^4}{8m_0^3 c^2}}$$

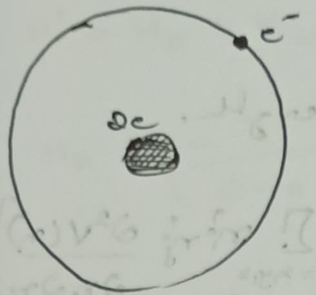
$H_k \sim m_0 c^2 \alpha^4$

fine structure constant

$$\boxed{H_k' = -\frac{1}{2m_0 c^2}\left(\frac{\bar{p}^2}{2m}\right)^2}$$

$H_k \ll H_0$ & thus can be treated as a perturbation term and we can solve it.

⟹ Spin-orbit Coupling : H_{so}



electron velocity : $\bar{v}$

$\bar{E}$ produced by the nucleus,

$$\bar{E} = \frac{Ze}{4\pi\varepsilon_0}\left(\frac{\bar{r}}{r^3}\right)$$

from the electron's frame of reference ⟹

$$\bar{B} = \frac{-\bar{v}\times\bar{E}}{c^2} \quad ; \quad \bar{\mu}_s = -g\,\mu_B \frac{\bar{S}}{\hbar}$$

where $\mu_B = \frac{e\hbar}{2m_0}$, $\bar{S} = \frac{\hbar}{2}\bar{\sigma}$, $g = 2$

$$H_{so} = -\bar{\mu}_s \cdot \bar{B}$$

$$B = \frac{-\bar{v}\times\bar{E}}{c^2} = \frac{\bar{E}\times\bar{v}}{c^2}$$

$$= \left(\frac{-g\,\mu_B}{4\pi\varepsilon_0\hbar}\right)\left(\frac{Ze}{m_0c^2 r^3}\right)\bar{S}\cdot\bar{L}$$

$$= \frac{1}{m_0c^2}\,\frac{Ze}{4\pi\varepsilon_0}\,\frac{1}{r^3}(\vec{L})$$

$$H_{so} = \left(\frac{1}{2m_0^2c^2}\right)\boxed{\left(\frac{Ze^2}{4\pi\varepsilon_0}\,\frac{1}{r^3}\right)}(\bar{L}\cdot\bar{S}) \rightarrow \frac{1}{r}\frac{dV(r)}{dr}$$

$$\bar{B} = \frac{-\bar{v}\times\bar{E}}{c^2} = (2) \rightarrow$$

only applicable to linear motion

taking,

$r \sim a_0$, $L \sim \hbar$, $S \sim \hbar$,

then,

$$\boxed{H_{so} = \left(\frac{1}{2m_0^2c^2}\right)\left(\frac{Ze^2}{4\pi\varepsilon_0}\,\frac{1}{r^3}\right) \sim m_0c^2\alpha^4}$$

We see that the spin-orbital coupling has the same degree of α as the H_K.

⟹ Darwin's Correction : H_D

$$\langle x(t)\rangle = \langle x(t=0)\rangle + V_{av}t + \lambda_c\cos(\omega t),\ \text{where}$$

for a free relativistic particle.

$$\rightarrow \lambda_c = \frac{\hbar}{m_0c},\quad \hbar\omega = 2m_0c^2$$

$$\bar{V}(\bar{r}) = \frac{1}{V_c} \int_{V_c} V(\bar{r} + \bar{r}') \, d^3 r'$$

where $V_c = \frac{4}{3}\pi \lambda_c^3$ $\longrightarrow$ compton wavelength.

$$\bar{V}(\bar{r}) = \frac{1}{V_c} \int_{V_c} \left[V(\bar{r}) + \sum_{i=x,y,z} r_i' \frac{\partial V(r)}{\partial r_i} + \frac{1}{2} \sum_{\substack{i=x,y,z \\ j=x,y,z}} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j} \right]$$

1st terms : $V(\bar{r}) \rightarrow V(\bar{r})$

2nd term :

$$\sum_{i=x,y,z} r_i' \frac{\partial V(r)}{\partial r_i} \longrightarrow 0$$

3rd term :

$$\frac{1}{2} \sum_{\substack{i=x,y,z \\ j=x,y,z}} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j}$$

$$\Rightarrow \frac{1}{V_c} \int d^3 r' r_i' r_j' = \frac{\lambda_c^2}{5} \delta_{ij}$$

$$\frac{1}{V_c} \int_{V_c} \left(\frac{1}{2} \sum_{i,j} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j} \right) d^3 r \longrightarrow \frac{\lambda_c^2}{10} \nabla^2 V(r)$$

$$\therefore \bar{V}(\bar{r}) = V(\bar{r}) + \frac{\lambda_c^2}{10} \nabla^2 V(\bar{r})$$

$\longrightarrow$ relativistic correction term.

Here the order of magnitude of

$$\frac{\lambda_c^2}{10} \nabla^2 V(\bar{r}) \sim m_0 c^2 \alpha^4$$

Thus is taken as a perturbative term

after further correction.

$$\frac{\lambda_c^2}{8} \nabla^2 V(\bar{r})$$

$$\bar{V}(\bar{r}) = \frac{1}{V_c}\int_{V_c} V(\bar{r}+\bar{r}')\, d^3r'$$

where $V_c = \frac{4\pi}{3}\lambda_c^3 \longrightarrow$ compton wavelength.

$$\bar{V}(\bar{r}) = \frac{1}{V_c}\int_{V_c}\left[V(\bar{r}) + \sum_{i=x,y,z} r_i' \frac{\partial V(r)}{\partial r_i} + \frac{1}{2}\sum_{\substack{i=x,y,z\\ j=x,y,z}} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j}\right] d^3r'$$

1st terms : $V(\bar{r}) \rightarrow V(\bar{r})$

2nd term : $\sum_{i=x,y,z} r_i' \frac{\partial V(r)}{\partial r_i} \longrightarrow 0$

3rd term : $\frac{1}{2}\sum_{\substack{i=x,y,z\\ j=x,y,z}} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j}$

$$\Rightarrow \frac{1}{V_c}\int d^3r' r_i' r_j' = \frac{\lambda_c^2}{5}\delta_{ij}$$

$$\frac{1}{V_c}\int_{V_c}\left(\frac{1}{2}\sum_{i,j} r_i' r_j' \frac{\partial^2 V(r)}{\partial r_i \partial r_j}\right) d^3r \longrightarrow \frac{\lambda_c^2}{10}\nabla^2 V(r)$$

$$\therefore \bar{V}(\bar{r}) = V(\bar{r}) + \frac{\lambda_c^2}{10}\nabla^2 V(\bar{r})$$

$\longrightarrow$ relativistic correction term.

Here the order of magnitude of

$$\frac{\lambda_c^2}{10}\nabla^2 V(\bar{r}) \sim m_0 c^2 \alpha^4$$

Thus is taken as a perturbative term

after further correction.

$$\frac{\lambda_c^2}{8}\nabla^2 V(\bar{r})$$

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$\Rightarrow$ we get the total correction term to be

$$H' = H_k + H_{so} + H_D$$

$$H_k = \left(\frac{-1}{2m_0c^2}\right)\left(\frac{\bar{P}^2}{2m}\right)^2$$

$$H_{so} = \left(\frac{1}{2m_0^2c^2}\right)\left(\frac{1}{r}\right)\frac{dV(r)}{dr}\,\bar{L}\cdot\bar{S} = \left(\xi(r)\right)\left(\bar{L}\cdot\bar{S}\right)$$

$$H_D = \frac{\hbar^2}{8}\nabla_r^2 V(\bar{r})$$

where $V(\bar{r})$ is any potential.

the unperturbed energy is:

$$E_n \equiv E_n^{(0)} = -\frac{1}{2}m_0c^2\frac{(Z\alpha)^2}{n^2}.$$

and the perturbed energy is:

$$E' = \frac{1}{2}m_0c^2\alpha^4 \Rightarrow E' \ll E_n \text{ ∴ }$$ thus perturbation theory can be applied.

space dependent spin dependent

$$\Rightarrow |n\,l\,s\,m_l\,m_s\rangle = |n\,l\,m_l\rangle \otimes |s\,m_s\rangle$$

for the 1st energy level, $E_1 = \frac{m_0c^2}{2}(Z\alpha)^2$

the states are $\Rightarrow$

1. $|100\rangle \otimes |\tfrac{1}{2}\,\tfrac{1}{2}\rangle$
2. $|100\rangle \otimes |\tfrac{1}{2}\,\tfrac{-1}{2}\rangle$

$\Rightarrow$ <u>Degeneracy of the nth level</u> : $2n^2$

the uncoupled basis : $|n\,l\,m_l\,m_s\rangle$

⇒ CSCO : the observables, H_0, $\bar{L}^2$, $\bar{S}^2$, L_z, S_z (complete set of commuting observables)
are commutative.

⇒ for the matrix elements,

$$\langle n l' m_l' m_s' | H' | n l m_l m_s \rangle$$

taking $[L_z, H'] = 0$, then,

$$\Rightarrow \langle l' m_l' m_s' | \cancel{\hbar} L_z H' - H' L_z | l m_l m_s \rangle = 0$$

$$(m_l' - m_l) \langle l' m_l' m_s' | H' | l m_l m_s \rangle = 0$$

If $m_l' \neq m_l$, then,

$$\langle l' m_l' m_s' | H' | l m_l m_s \rangle = 0$$

⇒ table of commutations b/w ~~commutati~~ operators :

taking $\bar{J} = \bar{L} + \bar{S}$ (for the time being)

	$\bar{L}$	$\bar{L}^2$	$\bar{S}^2$	$\bar{S}$	$\bar{\delta}$	$\bar{J}^2$
H_K	y	y	y	y	y	y
H_{SO}	N	y	y	N	y	y
H_D	y	y	y	y	y	y

⇒ first order energy correction

$$E_K^{(1)} = \frac{-1}{2m_0c^2} \langle n l m_l | \left(\frac{p^2}{2m}\right) | n l m_l \rangle$$

consider,

$$H_0 = -\frac{p^2}{2m_0} - \frac{e}{r} \; ; \; \text{eff} \; c = \frac{Ze^2}{4\pi\varepsilon_0}$$

then,

$$\frac{\bar{p}^2}{2m_0} = H_0 + \frac{c}{r}$$

$$\Rightarrow \left(\frac{p^2}{2m_0}\right) = \left(H_0' + \frac{c}{r}\right)\left(H_0' + \frac{c}{r}\right) = H_0^2 + c\left(H_0\frac{1}{r} + \frac{1}{r}H_0\right) + c_0^2\frac{1}{r^2}$$

Substituting,

$$E_k^{(1)} = \frac{-1}{2m_0c^2}\langle nlm | H_0^2 + c_0\left(H_0\frac{1}{r} + \frac{1}{r}H_0\right) + \frac{c^2}{r^2} | nlm_l\rangle$$

$$= \frac{-1}{2m_0c^2}\left[E_n^2 + c_0\right]$$

$$= \frac{-1}{2m_0c^2}\left[E_n^2 + 2c_0 E_n\langle|\tfrac{1}{r}|\rangle + c_0^2\langle\tfrac{1}{r^2}\rangle\right.$$

$$= \frac{-1}{2m_0c^2}\left[E_n^2 - 2E_n\langle|V(r)|\rangle + c_0^2\left\langle\left|\frac{1}{r^2}\right|^2\right\rangle\right.$$

$\frac{1}{\cancel{E_{max}}} = R_{max}$,

~~are you in~~

then $l_{max} = n-1$

$\Rightarrow E_k^{(1)} < 0$.

where $\langle V(r)\rangle = 2E_n$

then, $$E_k^{(1)} = \frac{-E_0^2}{2m_0c^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right]$$

Runge-Lenz vector

$\Rightarrow$ We can check that,

$$[l_k, H_{n-1}] = -i\hbar\, \xi(r)(\bar{L}\times\bar{S})_k, \quad k = x, y, z \quad -①$$

Similarly, $$[S_k, H_{so}] = +i\hbar\, \xi(r)(\bar{L}\times\bar{S})_k. \quad -②$$

from ① & ②,

$[\cancel{L_k, S_k, H_{SO}}, \cancel{L_k, S_k, H_{SO}},$

$[\underbrace{L_k + S_k}_{\vec{J}}, H_{SO}] = 0$

here we take $L_k + S_k = \vec{J}$, thus

$[\vec{J}, H_{SO}] = 0 \; ; \; [\vec{J}^2, H_{SO}] = 0.$

→ Say we have the CSCO:

CSCO ⇒ $\vec{L}^2, \vec{S}^2, \vec{J}^2, J_z,$

~~for a given~~ L, ~~if L is not~~

~~⇒ $|nljm_l\rangle$~~

writing it differently,

$$|l, \tfrac{1}{2}, j = l \pm \tfrac{1}{2}, m_j\rangle = \pm\sqrt{\frac{l \pm m_j + \frac{1}{2}}{(2l+1)}}\, Y_l^{m_j - \frac{1}{2}}\, \chi_{\frac{1}{2}, \frac{1}{2}}$$

$$+ \sqrt{\frac{l \mp m_j + \frac{1}{2}}{(2l+1)}}\, Y_l^{m_j + \frac{1}{2}}\, \chi_{\frac{1}{2}, -\frac{1}{2}}$$

→ finding the matrix elements for J & $\hat{J}$ (operator)

~~$\langle nljm_j|L^2|nljm_j\rangle$~~ = $\langle n l j m_j | L^2 | n l j m_j\rangle = \hbar^2 l(l+1)$

$\langle|\vec{S}^2|\rangle = \hbar^2 s(s+1) = \frac{3\hbar^2}{4}.$

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

$\langle n l j m_j | H_{SO} | n l j m_j\rangle = \langle nl | S(r) | nl\rangle$

then,

$$\langle \bar{L}\cdot\bar{S}\rangle = \frac{\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\hbar^2}{2}.$$

case ① : $l \neq 0$

when $j = l + \frac{1}{2}$ then,

$$E_{so} = -E_n \frac{(Z\alpha)^2}{2n(l+\frac{1}{2})(l+1)}$$

when $j = l - \frac{1}{2}$ then,

$$E_{so} = +E_n \frac{(Z\alpha)^2}{2nl(l+\frac{1}{2})}$$

case ② : $l = 0$,

then $E_{so} = 0$.

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$\Rightarrow$ We saw that,

$H_{so} : |j m_j\rangle \Rightarrow [\bar{L}, H_{so}] \neq 0, \; [\bar{S}, H_{so}] \neq 0$

[coupled basis because L & S are coupled]

and $[\bar{J}, H_{so}] = 0$

If we take the uncoupled basis $|l, s, m_l, m_s\rangle$ we will have to calculate all the off-diagonal elements as well.

$$\langle l', s', m_l', m_s' | H_{so} | l, s, m_l, m_s\rangle$$

and $H_{so} = \xi(r)\,\bar{L}\cdot\bar{S}$

$$= \xi(r)\left[\frac{(L_+S_-) + (L_-S_+)}{2}\right] + L_z S_z$$

where $\left.\begin{array}{l} L_\pm = L_x \pm iL_y \\ S_\pm = S_x \pm iS_y \end{array}\right\}$ are the ladder operators.

$\Rightarrow$ consider the Darwin term,

$$H_D = \frac{\lambda_c^2}{8} \nabla^2 v(\bar{r})$$

for spherical symmetric potential,

$$v(r) = \frac{-Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right) \Rightarrow \nabla^2 v(r) = \frac{Ze^2}{\varepsilon_0}\delta^3(\bar{r})$$

$$= \frac{Ze^2}{\varepsilon_0}\frac{\delta(\bar{r})}{4\pi r^2}$$

we see that,

$$[\bar{L}, H_D] = 0, \quad [L^2, H_D] = 0$$

$$R_{nl}(r) \sim r^l \longrightarrow l=0, \; R_{nl} \xrightarrow{r\to 0} \text{constant}$$

$$l \neq 0, \; R_{nl} \xrightarrow{r\to 0} 0$$

for the energy correction,

$$E_D = \langle n'l'm_l'm_s' | H_D | n l m_l m_s \rangle$$

$$E_D = \left(\frac{\lambda_c^2}{8}\right)\left(\frac{Ze^2}{\varepsilon_0}\right) |\psi_{n00}(\bar{r}=0)|^2 \longrightarrow \frac{Z^3}{\pi n^3 a_0^3}$$

$$E_D = \begin{cases} -E_n \dfrac{(Z\alpha)^2}{n}, & l=0 \\ 0, & l \neq 0 \end{cases}$$

$\Rightarrow$ We see that the energy corrections for all three terms are of the same order & thus all of them should be considered.

$$\boxed{E' \sim m_0 c^2 \alpha^4}$$

$\Rightarrow$ For $l=0$: $\Delta E_{nj} = E_K^{(1)} + E_D$

For $l \neq 0$: $\Delta E_{nj} = E_K^{(1)} + E_{SO}$

$$\boxed{\Delta E_{nj}(\text{total}) = E_K^{(1)} + E_{SO} + E_D = E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]}$$

where $j = l \pm s$. $\Rightarrow$ $\boxed{\text{Range of } j : \frac{1}{2}, \frac{3}{2}, \ldots, n - \frac{1}{2}}$

for given j, we get m_j states. Total number of m_j states $\Rightarrow (2j+1)$

$\therefore$ for $l = 0$,

$$\Delta E_{nj} = E_n\left(\frac{Z\alpha}{n}\right)^2\left[n - \frac{3}{4}\right]$$

$\Rightarrow$ Thus,

$$\boxed{E_{nj} = E_n + \underbrace{\Delta E_{nj}}_{\text{energy correction}}}$$

$\Rightarrow$ For a given j ; there are two possible values of $l = j \pm \frac{1}{2}$, except for j_{max}, i.e,

j_{max} : $l = j_{max} - \frac{1}{2} = \left(n - \frac{1}{2}\right) - \frac{1}{2} = (n-1)$

$l \neq j_{max} + \frac{1}{2} = \left(n - \frac{1}{2}\right) + \frac{1}{2} = n \Rightarrow l \neq n.$

$\Rightarrow$ Due to relativistic correction, the nth level is split into n-sublevels (multiplets).

$\Rightarrow$ For ground state, $\Rightarrow$ notation : $1S_{1/2}$

$n = 1$, $E = E_1$, $l = 0$, $j = \frac{1}{2}$

$$E_{1,\frac{1}{2}} = E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right] = E_1\left[1 + \left(\frac{Z\alpha}{2}\right)^2\right]$$

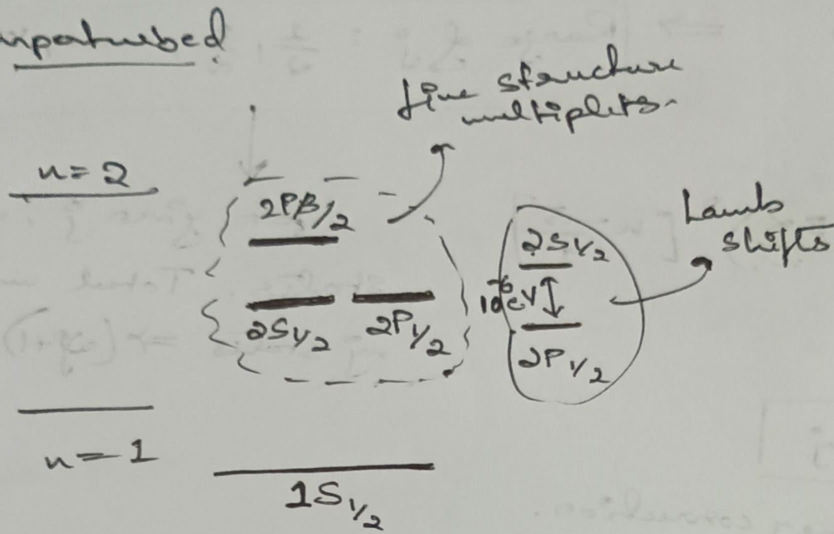
$\Rightarrow$ for $n = 2$, $\Rightarrow$ notation : $2S_{1/2}$, $2P_{1/2}$, $2P_{3/2}$

$E = E_2$, $l = \{0, 1\}$, $j = \{\frac{1}{2}, \frac{3}{2}\}$

when $j = \frac{1}{2}$, $l = \{0, 1\}$; when $j = \frac{3}{2}$, $l = \{1\}$

$$E_{2,\frac{1}{2}} = E_2\left[1 + 5\left(\frac{Z\alpha}{4}\right)^2\right] \quad ; \quad E_{2,\frac{3}{2}} = E_2\left[1 + \left(\frac{Z\alpha}{2}\right)^2\right]$$

→ Hydrogen atom energy levels :



⟹ Eigenvectors of $2P_{3/2}$:

Clebsch-Gordon coefficients

$$|l\,s\,j\,m_j\rangle = \left(\pm\sqrt{\frac{l \pm m_j + \frac{1}{2}}{(2l+1)}}\; Y_l^{m_l = m_j - \frac{1}{2}}\; \chi_{\frac{1}{2},+\frac{1}{2}}\right) +$$

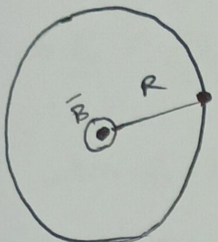
$$\left(+\sqrt{\frac{l \mp m_j + \frac{1}{2}}{(2l+1)}}\; Y_l^{m_l = m_j - \frac{1}{2}}\; \chi_{\frac{1}{2},-\frac{1}{2}}\right)$$

where $\chi_{\frac{1}{2},+\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix} = |\tfrac{1}{2}, +\tfrac{1}{2}\rangle$

solving for, $|1, \frac{1}{2}, \frac{3}{2}, +\frac{3}{2}\rangle$, $|1, \frac{1}{2}, \frac{3}{2}, +\frac{1}{2}\rangle$, $|1, \frac{1}{2}, \frac{3}{2}, -\frac{1}{2}\rangle$ & $|1, \frac{1}{2}, \frac{3}{2}, -\frac{3}{2}\rangle$, we get,

Aharonov - Bohm Effect

→ Consider a +ve charged particle that is restricted to move in a circular path of radius R.



$Q = +e$, mass $= M$

$$H_0 = \frac{-\hbar^2}{2MR^2}\frac{d^2}{d\phi^2}$$

applying magnetic field, $\bar{B} = B\hat{z}$

$$\bar{A} = \frac{1}{2}\bar{B}\times\bar{r} = \frac{1}{2}Br\hat{\phi}$$

then $H = \frac{1}{2M}(\hat{P}_\phi - eA_\phi)^2$

where, $\hat{P}_\phi = \frac{-i\hbar}{R}\frac{d}{d\phi}$

$$H_0 = \frac{\hbar^2}{2MR^2}\left[i\frac{d}{d\phi} + \frac{\Phi}{\Phi_0}\right]^2$$ where $\Phi = B\pi R^2$ and $\Phi_0 = \frac{h}{e}$ not $\hbar$

then,

$$E_m^{(0)} = \underbrace{\left(\frac{\hbar^2}{2MR^2}\right)}_{\mathcal{E}_0}\left(m - \frac{\Phi}{\Phi_0}\right)^2, \quad m = 0, \pm1, \pm2, \ldots$$

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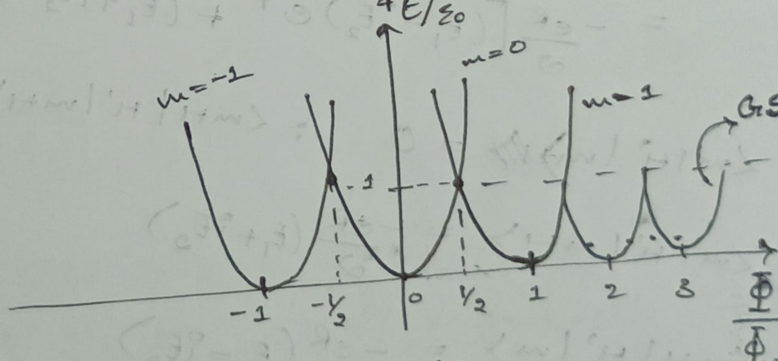
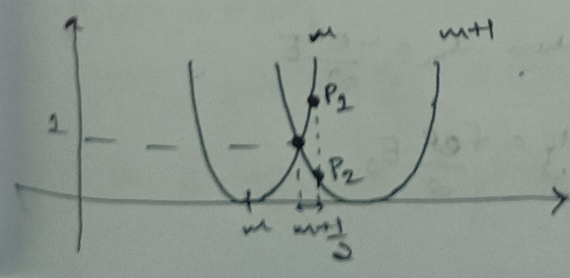
$$\psi_m(\Phi) = \langle\phi|m\rangle = \frac{1}{\sqrt{2\pi}}e^{im\Phi}$$



there is crossing between $|m\rangle$ & $|m+1\rangle$ state

at $\frac{\Phi}{\Phi_0} = (m + \frac{1}{2})$



At $m+\frac{1}{2}$, the levels are degenerate

& for $\frac{\Phi}{\Phi_0} = (m+\frac{1}{2}) + \delta$ where $\delta \ll 1$

we call it Quasi-degenerate

then,

$$E_m^{(0)}(P_1) = \varepsilon_0\left(\frac{1}{2}+\delta\right)^2 \quad ; \quad \langle\phi|m\rangle = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$E_{m+1}^{(0)}(P_2) = \varepsilon_0\left(\frac{1}{2}-\delta\right)^2 \quad ; \quad \langle\phi|m+1\rangle = \frac{1}{\sqrt{2\pi}}e^{i(m+1)\phi}$$

thus,

$$H_0 = \begin{array}{c|cc} & |m\rangle & |m+1\rangle \\ \hline \langle m| & \varepsilon_0\left(\frac{1}{2}+\delta\right)^2 & 0 \\ \langle m+1| & 0 & \varepsilon_0\left(\frac{1}{2}-\delta\right)^2 \end{array} = a_0\sigma_0 + a_z\sigma_z$$

where,

$$a_0 = \frac{\varepsilon_0}{4} + \delta^2\varepsilon_0$$

$$a_z = \varepsilon_0\delta$$

$\Rightarrow$ Now if we apply,

$$\bar{E} = E_1\hat{i} + E_2\hat{j}$$

Dipolar energy $\Rightarrow H' = -e\bar{E}\cdot\bar{r}\Big|_{r=R}$

$$H' = -eR\left[E_1\cos\phi + E_2\sin\phi\right]$$

$$= -\frac{eR}{2}\left[(E_1 - iE_2)e^{i\phi} + (E_1+iE_2)e^{-i\phi}\right]$$

$$\langle m|H'|m\rangle = 0 \quad ; \quad \langle m+1|H'|m+1\rangle = 0$$

$$\langle m|H'|m+1\rangle = -\frac{eR}{2}(E_1+iE_2)$$

$$\langle m+1|H'|m\rangle = -\frac{eR}{2}(E_1-iE_2)$$

$$H' = \begin{pmatrix} 0 & -\frac{eR}{2}(E_1+iE_2) \\ -\frac{eR}{2}(E_1-iE_2) & 0 \end{pmatrix} = a_x\sigma_x + a_y\sigma_y$$

where $a_x = -\frac{eR}{2}E_1$

$$a_y = +\frac{eR}{2}E_2$$

then, $H = H_0 + H' = a_0\sigma_0 + a_x\sigma_x + a_y\sigma_y + a_z\sigma_z$

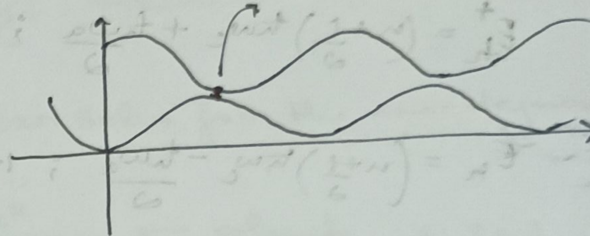
parametrizing, $a_x = a\sin\theta\cos\beta$, $a_y = a\sin\theta\sin\beta$

and $a_z = a\cos\theta$, $a = \sqrt{a_x^2 + a_y^2 + a_z^2}$

$$\Rightarrow E_{\pm} = \frac{\varepsilon_0}{4} + \delta^2\varepsilon_0 \pm \sqrt{(\varepsilon_0\delta)^2 + \left(\frac{eR}{2}\right)^2 (E_1^2 + E_2^2)}$$

when $\delta = 0$, we get,

$$E_{\pm} = \frac{\varepsilon_0}{4} \pm \frac{eR}{2}\sqrt{E_1^2 + E_2^2}$$



Jayens – Cummings Effect

$$H_0 = \left[\underbrace{\left(a^\dagger a + \frac{1}{2}\right)\hbar\omega_c \mathbb{1}_{2\times 2}}_{\text{Quantized EM}} + \left(\frac{\hbar}{2}\omega_a\sigma_z\right)\right]$$

← Hamiltonian for two ~~State system~~ energy level system.

with $\Delta E = \hbar\omega_a$

photonic wavefunction ← Quantized EM

coupling term = H_{int}

$$H_{interaction} = \left[\frac{\hbar g}{2}\left(a\sigma_+ + a^\dagger\sigma_-\right)\right]$$

where $\sigma_{\pm} = \frac{\sigma_x \pm i\sigma_y}{2}$, thus.

$$\sigma_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} ; \sigma_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$\frac{\hbar\omega_a}{2} ; \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$\hbar\omega_a$

$-\frac{\hbar\omega_a}{2} ; \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$H_0 = \begin{pmatrix} \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega_c + \left(+\frac{\hbar\omega_a}{2}\right) & 0 \\ 0 & \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega_c - \left(+\frac{\hbar\omega_a}{2}\right) \end{pmatrix}$$

we know that,

$a^\dagger|n\rangle = \sqrt{(n+1)}|n+1\rangle$

$a|n\rangle = \sqrt{n}|n-1\rangle$

$a^\dagger a|n\rangle = n|n\rangle$

$H_0|\Psi\rangle = E|\Psi\rangle$

$$|\Psi\rangle = |n\rangle \otimes \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} |n\rangle c_1 \\ |n\rangle c_2 \end{pmatrix}$$

are the eigenvectors of H_0

Thus,

$$\begin{bmatrix} \left(n+\frac{1}{2}\right)\hbar\omega_c + \frac{\hbar\omega_a}{2} & 0 \\ 0 & \left(n+\frac{1}{2}\right)\hbar\omega_c \mp \frac{\hbar\omega_a}{2} \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$E_n^+ = \left(n+\frac{1}{2}\right)\hbar\omega_c + \frac{\hbar\omega_a}{2}$; $|n\rangle \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} |n\rangle \\ 0 \end{pmatrix}$

$E_n^- = \left(n+\frac{1}{2}\right)\hbar\omega_c - \frac{\hbar\omega_a}{2}$; $|n\rangle \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ |n\rangle \end{pmatrix}$

for ground state, $n=0$

$E_0^- = \frac{\hbar\omega_c}{2} - \frac{\hbar\omega_a}{2}$; $|0\rangle \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ |0\rangle \end{pmatrix} = |\chi_0^-\rangle$

$E_0^+ = \frac{\hbar\omega_c}{2} + \frac{\hbar\omega_a}{2}$; $|0\rangle \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} |0\rangle \\ 0 \end{pmatrix} = |\chi_0^+\rangle$

$n=1$

$E_1^- = \frac{3\hbar\omega_c}{2} - \frac{\hbar\omega_a}{2}$; $|1\rangle \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ |1\rangle \end{pmatrix} = |\chi_1^-\rangle$

$E_1^+ = \frac{3\hbar\omega_c}{2} + \frac{\hbar\omega_a}{2}$; $|1\rangle \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} |1\rangle \\ 0 \end{pmatrix} = |\chi_1^+\rangle$

for $n=2$

$E_2^- = \frac{5\hbar\omega_c}{2} - \frac{\hbar\omega_a}{2}$; $|2\rangle \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ |2\rangle \end{pmatrix} = |\chi_2^-\rangle$

when $\omega_c = \omega_a$, we get,

$E_0^- = 0$; $\begin{pmatrix} 0 \\ |0\rangle \end{pmatrix}$

$E_0^+ = E_1^- = \hbar\omega$; $\begin{pmatrix} |0\rangle \\ 0 \end{pmatrix}$ & $\begin{pmatrix} 0 \\ |1\rangle \end{pmatrix}$

$E_1^+ = E_2^- = 2\hbar\omega$; $\begin{pmatrix} |1\rangle \\ 0 \end{pmatrix}$ & $\begin{pmatrix} 0 \\ |2\rangle \end{pmatrix}$

$\vdots$

We see that except for the ground state, all the other states are doubly degenerate.

$$\boxed{\mathcal{E}_n = (n+1)\hbar\omega \; ; \; n = 0,1,2,\ldots \; ; \; \underbrace{\begin{pmatrix} |n\rangle \\ 0 \end{pmatrix} \text{ \& } \begin{pmatrix} 0 \\ |n+1\rangle \end{pmatrix}}_{\text{eigenvectors}}}$$

where $\omega = \omega_c = \omega_a$

for $\omega_c \neq \omega_a$, we don't see degeneracy.

Once we include $H_{interaction}$, we see that the energy ~~from~~ difference increases $\Longrightarrow$ Non-degeneracy increases.

$\delta = \omega_a - \omega_c \rightarrow$ Detuning frequency.

$\rightarrow \delta > 0$, then its said to be on-resonant

$\delta = 0$, then its said to be off-resonant

$\Longrightarrow$ including $H_{interaction}$, we ~~get~~ can solve for the non-degenera

Zemann Effect

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r^2} \leftarrow \text{coloumb potential}$$

$$H = \frac{(\bar{P} + e\bar{A})^2}{2m_e} + V(r) \quad \text{and} \quad \bar{B} = \bar{\nabla} \times \bar{A}$$

where $\bar{A}$ is a vector potential.

We expand the square term of the Hamiltonian by operating it on a dummy function.

$$H = \frac{+\bar{P}^2}{2m_e} + \frac{e}{m_e}\bar{A}\cdot\bar{P} + \frac{e^2\bar{A}^2}{2m_e} + V(r)$$

$$H_L' = \frac{e}{m_e}\bar{A}\cdot\bar{P} = \frac{e}{m_e}\left(\frac{1}{2}\bar{B}\times\bar{r}\right)\cdot\bar{P}, \quad \text{taking } \bar{L} = \bar{r}\times\bar{P}$$

$$H_L' = \frac{e}{2m_e}\bar{L}\cdot\bar{B} \qquad \varepsilon_1 \quad \bar{\mu}_L = \frac{-e}{2m_e}\bar{L} = -\mu_B\frac{\bar{L}}{\hbar}$$

where $\mu_B = \frac{e\hbar}{2m_e} \rightarrow$ Bohr magneton.

$$\bar{\mu}_s = -g_s\mu_B\frac{\bar{S}}{\hbar} \quad ; \quad \bar{S} = \frac{\hbar}{2}\bar{\sigma} \qquad \text{where } g_s = 2$$

$$\bar{\mu} = \bar{\mu}_l + \bar{\mu}_s = -\frac{\mu_B}{\hbar}(\bar{L} + 2\bar{S}) = -\frac{\mu_B}{\hbar}(\bar{J} + \bar{S})$$

$\Longrightarrow$ Consider the results of Quantum Projection theorem:

Given any vector operator $\bar{V}$, in a particular basis $|j\,m_j\rangle$

can be written as,

$$\langle j m_j | \bar{V} | j m_j \rangle = \frac{\langle j m_j | \bar{V} \cdot \bar{J} | j m_j \rangle \langle j m_j | \bar{J} | j m_j \rangle}{j(j+1)\hbar^2}$$

using this result,

$$\bar{\mu} = -g_e \frac{\mu_B}{\hbar} \bar{J}, \text{ where,}$$

$$g_e = 1 + \left(\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right)$$

$\downarrow$

Lande g-factor.

$H_0 \Rightarrow$ unperturbed Hamiltonian. fine structure correction

$$\Rightarrow H = \frac{\bar{P}^2}{2m_e} + V(r) + \frac{\mu_B}{\hbar}(\bar{L} + 2\bar{S}) \cdot \bar{B} + \frac{e^2 \bar{A}^2}{2m_e} + H_{fs}$$

$$\bar{B} = B\hat{z}$$

$$H = H_0 + \underbrace{\frac{\mu_B}{\hbar}(L_z + 2S_z)B}_{\text{Paramagnetic term}} + \underbrace{\frac{e^2 B^2 r^2}{8m_e}}_{\text{Diamagnetic term}} + H_{fs}$$

$H_Z \Leftarrow$ Paramagnetic term. Diamagnetic term $\Rightarrow H_D$

Order of magnitude for Paramagnetic & Diamagnetic terms

Diamagnetic term <<< Paramagnetic term.

10/02/26

$$\frac{E_d}{E_z} = \frac{\text{energy associated with diamagnetic term.}}{\text{energy associated with paramagnetic term}}$$

$$\frac{E_d}{E_z} = \left(\frac{e^2 B^2 \langle r^2 \rangle}{8m_e} \right) \left(\frac{1}{\mu_B B} \right) \approx \frac{e a_0^2 n^4 B}{4\hbar Z^2} \sim \frac{n^4}{Z^2} B \times 10^{-6}$$

using for $l = 0$, $\langle r^2 \rangle = \frac{a_0^2 n^4}{Z^2}$

thus, $\frac{E_d}{E_z} \approx \frac{n^4}{Z^2} B \times 10^{-6}$

therefore, $B \ll \frac{Z^2 \times 10^6}{n^4}$, diamagnetism $\longrightarrow 0$.

$\Rightarrow H = H_0 + H_{FS} + \frac{\mu_B}{\hbar}(L_z + 2S_z)B_z$.

case ①:

If weak magnetic field, then,

$H_0 : m_e e^2 \alpha^2$

where $\alpha \Rightarrow$ Fine structure constant $= \frac{e^2}{4\pi\varepsilon_0 \hbar c}$

$E_{FS} = m_e e^2 \alpha^4 \approx 10^{-22} J$

$E_z : \mu_B B \sim B \times 10^{-23} J$

If $B < 1$ Tesla, then $E_z \ll E_{FS}$. ⟵ Here we can treat Zeeman term as perturbative term.

case ②:

If strong magnetic field, then,

$B > 10$ Tesla, then $E_z \gg E_{FS}$. ⟵ Here we can treat the fine structure correction as perturbative term

※ [Zeeman-effect → Midsem]

$\Rightarrow$ Weak $\bar{B} \rightarrow \bar{B} < 1$ Tesla;

$H_{unperturbed} = (H_0 + H_{FS})$; $H' = H_z$

thus $H_{SO} \rightarrow \bar{L}\cdot\bar{S}$

~~$\bar{J}\cdot\bar{J}^2 : |n l s m_j\rangle$~~ $\bar{J}\cdot\bar{J}^2 : |n l s j m_j\rangle \equiv |j m_j\rangle$

for a given 'j', $\langle m_j | H | m_j' \rangle = 0$; $m_j \neq m_j'$

~~for all $m_j \neq m_z$~~.

~~we know for unperturbed~~ ~~$H_{unperturbed} = (H_0 + H_{FS})$~~,

~~$E_{nj} = E_n + \Delta E_{nj}$~~

$$E_{nj} = E_n + \Delta E_{nj}$$

then, $E_z = \langle j m_j | \frac{\mu_B B}{\hbar}(L_z + 2S_z) | j m_j \rangle$

$$= \frac{\mu_B B}{\hbar} \langle j m_j | (J_z + S_z) | j m_j \rangle$$

we know that, $J_z | j m_j \rangle = \hbar m_j | j m_j \rangle$

$$E_z = \frac{\mu_B B}{\hbar} \left[\hbar m_j + \langle j m_j | S_z | j m_j \rangle \right]$$

from Clebsch - Gordan coefficients,

$$| l, s, j = l \pm \tfrac{1}{2}, m_j \rangle = \pm \sqrt{\frac{l \pm m_j + \frac{1}{2}}{(2l+1)}}\, Y_l^{m_l = m_j - 1/2} \chi_{1/2}^{+1/2}$$

$$+ \sqrt{\frac{l \mp m_j + \frac{1}{2}}{(2l+1)}}\, Y_l^{m_l = m_j + 1/2} \chi_{1/2}^{-1/2}$$

then,

$$\langle j = l \pm \tfrac{1}{2}, m_j | S_z | j = l \pm \tfrac{1}{2}, m_j \rangle = \pm \frac{m_j \hbar}{(2l+1)}$$

$$E_z^{\pm} = \frac{\mu_B B}{\hbar} \left[\hbar m_j \pm \frac{m_j \hbar}{(2l+1)} \right] = \mu_B B m_j \left[1 \pm \frac{1}{2l+1} \right]$$

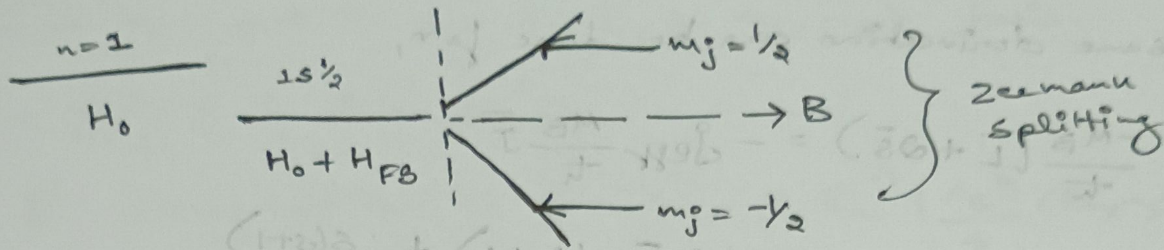
$E_z^+ : j = l + \frac{1}{2}$ & $E_z^- : j = l - \frac{1}{2}$

$$\boxed{E_z^{\pm} = \mu_B B m_j \left[1 \pm \frac{1}{2l+1} \right]}$$

for $l = 0$, we take E_z^+, $j = 1/2$

$$E_z^+ = \mu_B B \left(\pm \frac{1}{2}\right) \left[1 + \frac{1}{1} \right] = \mu_B B \left(\pm \frac{1}{2}\right)(2)$$

$E_z^+ = \pm \mu_B B$ for $l = 0$,



Here $\boxed{E_{1,1/2} = E_1\left(1+\frac{\alpha^2}{4}\right) \pm \mu_B B}$ ← for $\bar{B} < 1$ Tesla.

for $n=2$,

$2P_{3/2}$: $l = 1$, $j = 3/2$

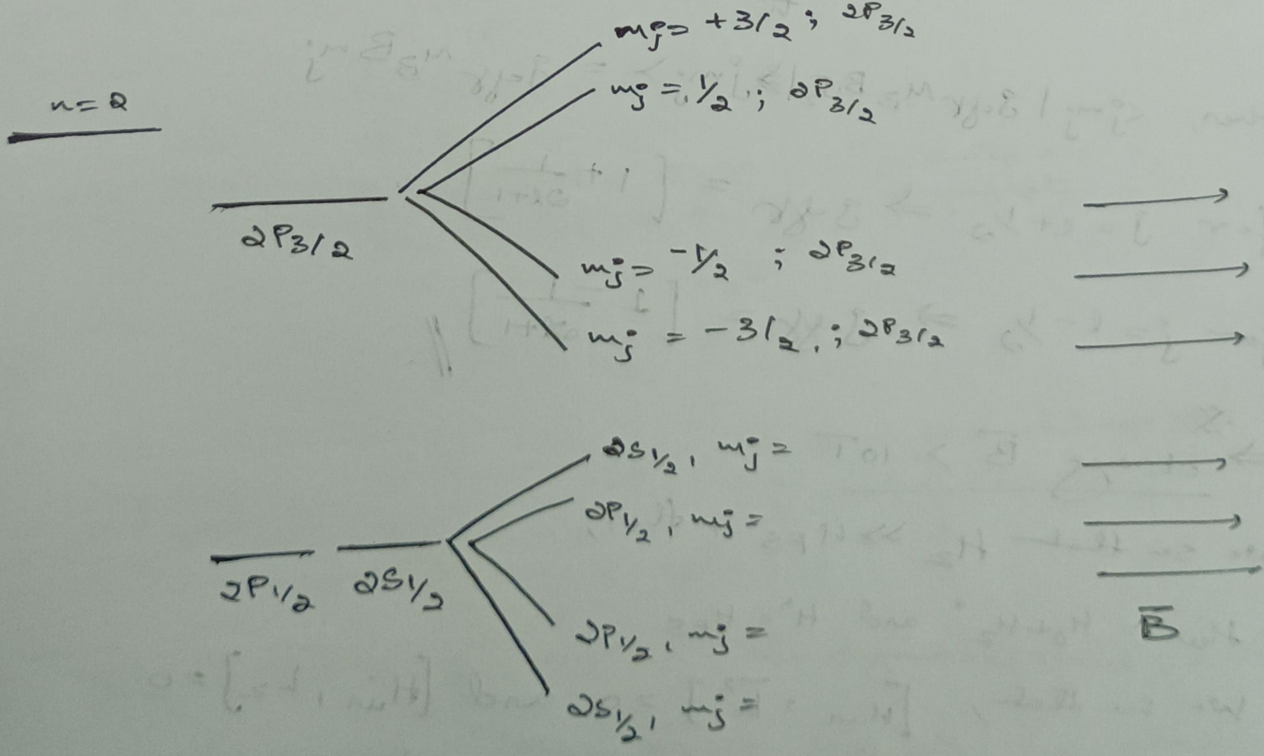
~~2s~~ $E_Z = \mu_B B m_j \left(\frac{4}{3}\right)$ where $m_j = \left\{\pm 3/2, \pm\frac{1}{2}\right\}$

$2P_{1/2}$: $l = 1$, $j = 1/2$.

$E_Z = \mu_B B m_j \left(\frac{2}{3}\right)$ where $m_j = \left\{\pm\frac{1}{2}\right\}$.

$2S_{1/2}$: $l = 0$, $j = 1/2$

$E_Z = \mu_B B m_j (2)$ where $m_j = \left\{\pm\frac{1}{2}\right\}$.



the same derivation can be done for,

$$\bar{\mu} = \frac{-\mu_B}{\hbar}(\bar{L} + 2\bar{S}) = -g_{eff}\frac{\mu_B}{\hbar}\bar{J}$$

$$\text{where } g_{eff} = 1 + \frac{j(j+1) \mp l(l+1) + s(s+1)}{2j(j+1)}$$

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⇒ We saw that, for $B < 1T$

$H_{un} = H_0 + H_{FS}$; $H' = \frac{\mu_B(L_z + 2S_z)B}{\hbar}$

$E_z = \langle j m_j | H' | j m_j \rangle$

$E_z^{\pm} = \mu_B B m_j \left(1 \pm \frac{1}{2l+1}\right)$

$E_z^+ : j = l + 1/2$; $E_z^- : j = l - 1/2$

$\bar{\mu} = -g_{eff}\frac{\mu_B}{\hbar}\bar{J}$

$g_{eff} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$

$H' = -\bar{\mu}\cdot\bar{B} = g_{eff}\frac{\mu_B B J_z}{\hbar}$

then, $\langle j m_j | g_{eff}\mu_B B J_z | j m_j \rangle = g_{eff}\mu_B B m_j$

for $j = l + 1/2 \Rightarrow g_{eff} = \left[1 + \frac{1}{2l+1}\right]$

for $j = l - 1/2 \Rightarrow g_{eff} = \left[1 - \frac{1}{2l+1}\right]$ //.

※

⇒ Strong $\bar{B} > 10T$:

We see that $H_Z \gg H_{FS}$, then,

$H_{un} = H_0 + H_Z$ and $H' = H_{FS}$

We see that, $[H_{un}, \bar{L}^2] = 0$ and $[H_{un}, L_z] = 0$

$[H_{un}, S_z] = 0$; $[H_{un}, \bar{S}^2] = 0$; $[\bar{J}^2, H_Z] \neq 0$

thus we can work in the $|n, l, s, m_l, m_s\rangle$ basis.

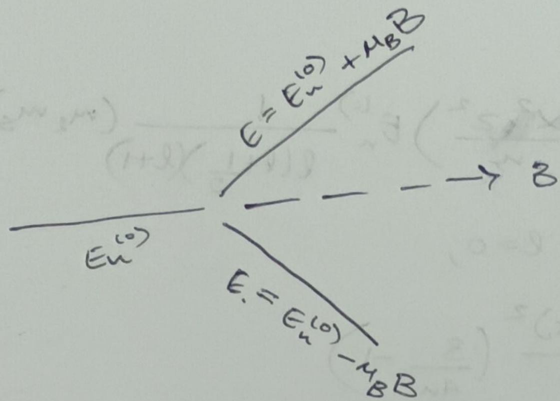
for a given n & since $s = 1/2$

$$E = \langle l m_l m_s | H_0 + H_2 | l m_l m_s \rangle = E_n^{(0)} + \frac{\mu_B B}{\hbar} \langle l m_l m_s | L_z + 2S_z | \rangle$$

$$= E_n^{(0)} + \frac{\mu_B B}{\cancel{\hbar}} (m_l + 2m_s) \cancel{\hbar}$$

thus for unperturbed $\Rightarrow$ $E_{un} = E_n^{(0)} + \mu_B B (m_l + 2m_s)$

for $n = 1$, $l = 0$, $m_s = \pm\frac{1}{2}$ $\Rightarrow E_{un} = E_n^{(0)} + 2\mu_B B (\pm \frac{1}{2})$

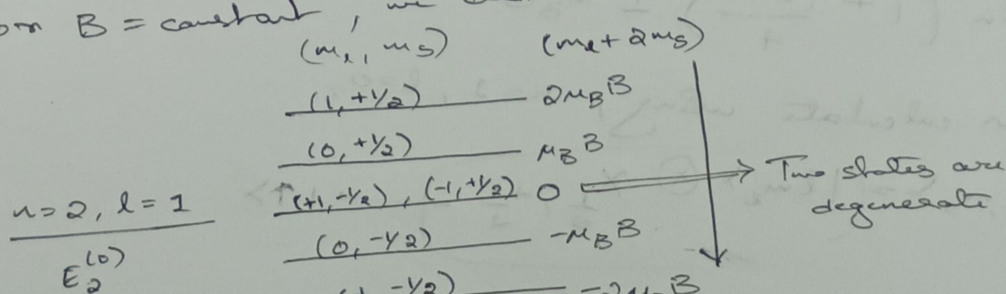


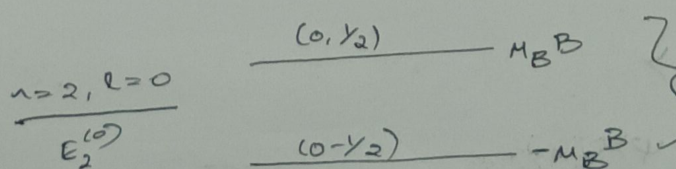
Thus, even for unperturbed ~~then~~, we see the splitting.

for $n = 2$, $l = \{0, 1\}$, $\Rightarrow$ consider $n = 2$ & $l = 1$

we can show the energy levels to be:

for B = constant,





these two ~~add up~~ line up along with the other states.

Thus, $\{|2,1,0,+1/2\rangle$ & $|2,0,0,+1/2\rangle\}$ are degenerate states, similarly $\{|2,1,0,-1/2\rangle$ & $|2,0,0,-1/2\rangle\}$ & $\{|2,1,1,-1/2\rangle$ & $|2,1,-1,1/2\rangle\}$ are also individually degenerate.

for the perturbation term: $H_{FS} = H_K + H_{SO} + H_D$

H_K & H_D are spin independent,

$$H_{SO} = \frac{1}{2m_0^2c^2}\left(\frac{1}{r}\frac{dV(r)}{dr}\right)\vec{L}\cdot\vec{S}$$

$$= \left(\frac{1}{2m_0^2c^2}\right)\left(\frac{Ze^2}{4\pi\varepsilon_0 r^3}\right)\left[L_zS_z + \frac{1}{2}(L_+S_- + L_-S_+)\right]$$

We know that, $\langle l, m_l | L_\pm | l, m_l\rangle = 0$

$$\langle s, m_s | S_\pm | s, m_s\rangle = 0$$

solving this,

$$\langle l m_l m_s | H_{SO} | l m_l m_s\rangle = \left(-\frac{\alpha^2 Z^2}{n}\right)E_n^{(0)}\frac{1}{l(l+\frac{1}{2})(l+1)}(m_l m_s)$$

We know that for any n & $l=0$,

$$E_{FS} = E_K + E_D = -E_n^{(0)}\frac{(Z\alpha)^2}{n}\left(\frac{3}{4n} - 1\right)$$

for $n=1$, $l=0$, $E_{FS} = \dfrac{E_n^{(0)}(Z\alpha)^2}{4}$

$$E_1^\pm = E_n^{(0)}\left(1 + \frac{(Z\alpha)^2}{4}\right) \pm \mu_B B$$

we can calculate using, $n=1$, $l=0$,

$$|l, m_l, m_s\rangle = \boxed{|l m_l\rangle \otimes \chi_{\frac{1}{2}, +\frac{1}{2}}} \longrightarrow |\uparrow\rangle$$

$$|l, m_l, m_s\rangle = \boxed{|l m_l\rangle \otimes \chi_{\frac{1}{2}, -\frac{1}{2}}} \longrightarrow |\downarrow\rangle$$

$$|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle$$

solving $H|\psi\rangle = E|\psi\rangle$

for $H = H_0 + H_K + H_D + \dfrac{\mu_B B}{\hbar}2S_z$

we get $E_1^\pm = E_n^{(0)}\left(1 + \dfrac{(Z\alpha)^2}{4}\right) \pm \mu_B B$

[We can also solve for

→ Intermediate B :

*

→ Intermediate B :

⇒ Intermediate B :

Time dependent Perturbation theory

We know time dependent Schrodinger equation to be:

$$i\hbar \frac{\partial \psi}{\partial t}(\bar{r},t) = H_0 \psi(\bar{r},t)$$

where H_0 is time independent.

$$\psi(\bar{r},t) = \psi_E(t)\psi(\bar{r})$$

after separation of variables,

$$\frac{i\hbar}{\psi_E(t)} \frac{d}{dt}\psi_E(t) = \frac{1}{\psi(\bar{r})} H_0 \psi(\bar{r}) = E$$

$$\boxed{\psi_E(t) = e^{-i/\hbar\, Et}}$$

Say $U(t) = e^{\frac{i}{\hbar}E_n(t)}$ then, $e^{-\frac{i}{\hbar}H_0 t}|n\rangle = e^{-\frac{i}{\hbar}E_n t}|n\rangle$

$H_0|n\rangle = E_n|n\rangle \Rightarrow$ stationary states.

thus,

$$|\psi(t)\rangle = \sum_n C_n e^{-\frac{iE_n t}{\hbar}}|n\rangle$$

$$\langle\psi(t)|\psi(t)\rangle = \sum_n |C_n|^2$$

~~Probability $|C_n|^2$~~ Probability $|C_n|^2$ is independent of time.

$\Rightarrow$ If $H = H_0 + V(t)$, then we get Non-stationary states.

We know, $|\psi(t)\rangle = U(t)|n\rangle$

We can draw two different pictures:

Schrodinger Picture	Heisenberg Picture
States : $\lvert n(t)\rangle$	States : $\lvert n(t=0)\rangle = \lvert n\rangle$
operator: A_S	operator : $A_H(t) = U^\dagger(t) A_S U(t)$
$\Rightarrow i\hbar\frac{d}{dt}\lvert\psi(t)\rangle_S = H\lvert\psi(t)\rangle_S$	$\Rightarrow U^\dagger(t)\lvert\psi(t)\rangle = U^\dagger(t)[U\lvert\psi(t=0)\rangle]$
	$= \lvert\psi(t=0)\rangle$
$i\hbar\frac{d}{dt}A_S = 0$	

Time dependent Perturbation theory

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$$\psi(\bar{r},t) = \psi_E(t)\psi(\bar{r})$$

after separation of variables,

$$\frac{i\hbar}{\psi_E(t)} \frac{d\psi_E(t)}{dt} = \frac{1}{\psi(\bar{r})} H_0 \psi(\bar{r}) = E$$

$$\boxed{\psi_E(t) = e^{-i/\hbar Et}}$$

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$\Rightarrow i\hbar \frac{d}{dt}\lvert\psi(t)\rangle_S = H\lvert\psi(t)\rangle_S$	$\Rightarrow U^{+}(t)\lvert\psi(t)\rangle = U^{+}(t)[U\lvert\psi(t=0)\rangle]$
	$= \lvert\psi(t=0)\rangle$
$i\hbar \frac{d}{dt} A_S = 0$	

Interaction Picture :

$$\boxed{|\psi(t)\rangle_I = e^{iH_0t/\hbar}|\psi(t)\rangle_s}$$

$$i\hbar\frac{d}{dt}|\psi(t)\rangle_I = i\hbar\frac{d}{dt}\left[e^{iH_0t/\hbar}|\psi(t)\rangle_s\right]$$

$$\boxed{|\psi(t=0)\rangle_I = |\psi(t=0)\rangle_s}$$

$$i\hbar\frac{d}{dt}|\psi(t)\rangle_I = i\hbar\left[\frac{iH_0}{\hbar}e^{iH_0t/\hbar}|\psi(t)\rangle_s + e^{iH_0t}\frac{d}{dt}|\psi(t)\rangle_s\right]$$

$$i\hbar\frac{d}{dt}|\psi(t)\rangle_I = -H_0e^{iH_0t/\hbar}|\psi(t)\rangle_s + e^{iH_0t/\hbar}(H_0+V(t))|\psi(t)\rangle_s$$

$$= e^{iH_0t/\hbar}V(t)|\psi(t)\rangle_s$$

then,

$$i\hbar\frac{d}{dt}|\psi(t)\rangle_I = \underbrace{\left(e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}\right)}_{V_I(t)}\underbrace{\left(e^{iH_0t}|\psi(t)\rangle_s\right)}_{|\psi(t)\rangle_I}$$

$$\boxed{i\hbar\frac{d}{dt}|\psi(t)\rangle_I = V_I(t)|\psi(t)\rangle_I}$$

where $\boxed{V_I(t) = e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}} \Longleftrightarrow V_I(t) = U^+(t)V(t)U(t)$

$$A_I(t) = e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}$$

-※ Quiz / Midsem.

then,

$$\boxed{i\hbar\frac{d}{dt}A_I(t) = [A_I(t), H_0] + i\hbar\left[\frac{\partial A_s}{\partial t}\right]_I}$$

$$|\psi(t)\rangle_I = \sum_n c_n(t)|n\rangle$$ ← eigenstates of the unperturbed state, H_0

$$i\hbar\frac{d}{dt}\sum_n c_n(t)|n\rangle = e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}\sum_n c_n(t)|n\rangle$$

$$= \sum_n c_n(t)e^{iH_0t/\hbar}V(t)e^{-iE_nt/\hbar}|n\rangle$$

$$i\hbar \frac{d}{dt}\sum_n c_n(t)|n\rangle = \sum_n c_n(t)\, e^{iH_0 t/\hbar}\, V(t)\, e^{-iE_n t/\hbar}|n\rangle$$

multiply ~~from~~ $\langle m|$ on both sides,

$$i\hbar \frac{d}{dt}\sum_n c_n(t)\underbrace{\langle m|n\rangle}_{\delta_{mn}} = \sum_n c_n(t)\langle m|e^{iH_0 t/\hbar}\, V(t)\, e^{-iE_n t/\hbar}|n\rangle$$

$$= \sum_n c_n(t) e^{i(E_m - E_n)t/\hbar} \langle m|V|n\rangle$$

take $\omega_{mn} = \frac{(E_m - E_n)}{\hbar}$ and $\langle m|V|n\rangle = V_{mn}$

then,

$$i\hbar \frac{d}{dt}\sum_n c_n(t)\,\delta_{mn} = \sum_n c_n(t)\, V_{mn}(t)\, e^{i\omega_{mn}t/\hbar}$$

$$\Rightarrow \boxed{i\hbar \frac{d}{dt} c_m(t) = \sum_n c_n(t)\, V_{mn}(t)\, e^{i\omega_{mn}t/\hbar}} \quad (1)$$

where $\boxed{V_{mn}(t) = \langle m|V(t)|n\rangle}$

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whereas $m,n = \{1,2,\dots\}$ for infinite well

$m,n = \{0,1,2,\dots\}$ for HO

from (1), we get,

$$i\hbar \frac{d}{dt} c_1(t) = c_1(t) V_{11}(t) \cancel{e^{i(0)t/\hbar}}^{1} + c_2(t) V_{12}(t) e^{i\omega_{12}t/\hbar} + \dots$$

$$i\hbar \frac{d}{dt} c_2(t) = c_1(t) V_{21}(t) e^{i\omega_{21}t/\hbar} + c_2(t) V_{22}(t) \cancel{e^{i(0)t/\hbar}}^{1} + \dots$$

$\vdots$

In matrix representation, we see the set of equations to be :

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & V_{13}e^{i\omega_{13}t} & \cdots \\ V_{21}e^{i\omega_{21}t} & V_{22} & V_{23}e^{i\omega_{23}t} & \cdots \\ \vdots & \vdots & & \vdots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

Now, taking $V(t) \longrightarrow \lambda H'(t)$

where $H'(t)$ is the perturbative term,

and expanding $C_n(t)$ to be,

$$C_n(t) = C_n^{(0)}(t) + \lambda C_n^{(1)}(t) + \lambda^2 C_n^{(2)}(t) + \cdots \quad -(2)$$

then, upon substituting (2) & equating equal powers of λ,

$$\dot{C}_m^{(0)}(t) = 0 \implies C_m^{(0)}(t) = \text{constant}$$

$$\dot{C}_m^{(1)}(t) = \frac{1}{i\hbar}\sum_n H'_{mn}(t)\, e^{i\omega_{mn}t}\, C_n^{(0)}(t) \quad -(4)$$

$$\dot{C}_m^{(2)}(t) = \frac{1}{i\hbar}\sum_n H'_{mn}(t)\, e^{i\omega_{mn}t}\, C_n^{(1)}(t)$$

$\vdots$

Take the initial condition to be, $C_n^{(0)}(t) = \delta_{ni} \quad -(3)$

Substituting (3) in (4),

$$\dot{C}_m^{(1)}(t) = \frac{1}{i\hbar}\sum_n H'_{mn}(t)\, e^{i\omega_{mn}t}\, \delta_{ni}$$

$i \rightarrow$ initial state

$f \rightarrow$ final state.

$$\dot{C}_m^{(1)}(t) = \frac{1}{i\hbar} H'_{mi}(t)\, e^{i\omega_{mi}t}$$

thus

$$\boxed{C_m^{(1)}(t) = \frac{1}{i\hbar}\int H'_{mi}(t')\, e^{i\omega_{mi}t'}\, dt'}$$

$$\boxed{C_f^{(1)}(t) = \frac{1}{i\hbar}\int H'_{fi}(t')\, e^{i\omega_{fi}t'}\, dt'}$$

thus the transition probability,

$$\boxed{P_{fi}(t) = |C_f^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left[\int H'_{fi}(t') e^{i\omega_{fi}t'} dt'\right]^2}$$

⇒ Example: [Kicked oscillator]

Consider, $H_0 = \hbar\omega(a^\dagger a + \frac{1}{2}) \Rightarrow$ SHO

$$\vec{E}(t) = \mathcal{E}_x e^{-t^2/\tau^2}\hat{x} \quad , \quad Q = +e$$

$$V(t) = -e\mathcal{E}_x x e^{-t^2/\tau^2} \; ; -\infty < t < \infty$$

$$H_0 = (a^\dagger a + \frac{1}{2})\hbar\omega$$

If initial state ⇒ $|i\rangle = |n\rangle$

from perturbation theory, time dependent,

$$C_{fn}^{(1)} = \frac{1}{i\hbar}\int_{-\infty}^{\infty} \langle f|V(t')|n\rangle e^{i\omega_{fn}t'} dt'$$

calculating the matrix element,

$$\langle f|V(t)|n\rangle = -e\mathcal{E}_x e^{-t^2/\tau^2}\langle f|x|n\rangle$$

from ladder operator representation for x,

$$\langle f|V(t)|n\rangle = -e\mathcal{E}_x e^{-t^2/\tau^2}\frac{a_0}{\sqrt{2}}\left[\delta_{f,n-1}\sqrt{n} + \delta_{f,n+1}\sqrt{n+1}\right]$$

$$C_{f=(n+1),n}^{(1)}(t\to\infty) = -\frac{e\mathcal{E}_x}{i\hbar}\frac{a_0}{\sqrt{2}}\sqrt{n+1}\int_{-\infty}^{\infty} e^{(-t')^2/\tau^2} e^{i\omega t'} dt'$$

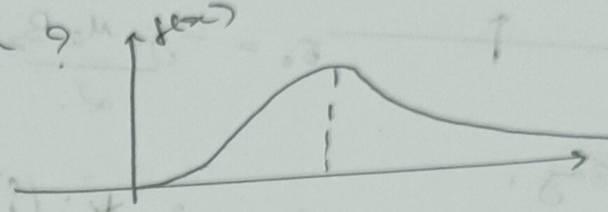
$$\int_{-\infty}^{\infty} e^{(-t')^2/\tau^2} e^{i\omega t'} dt' = \sqrt{\pi}\,\tau e^{-\omega^2\tau^2/4}$$

$$C_{(n+1),n}^{(1)}(t\to\infty) = -\frac{e\mathcal{E}_x}{i\hbar}\frac{a_0}{\sqrt{2}}\sqrt{n+1}\sqrt{\pi}\,\tau e^{-\omega^2\tau^2/4}$$

then,

$$P_{(n+1),n} = |C^{(1)}_{(n+1),n}|^2 = \boxed{\left(-\frac{eE_x a_0}{\hbar\sqrt{2}}\right)^2 \pi\tau^2 (n+1)\, e^{-\omega^2\tau^2/2}}$$

At what ω will P be maximum?



$$\frac{\partial P}{\partial \tau} = 0 \Rightarrow \tau = \frac{\sqrt{2}}{\omega}$$

As $\tau \to 0 \Rightarrow P \to 0$

as $\tau \to \infty \Rightarrow P \to 0$.

[One-dimensional representation of δ-function,

$$\delta(t) = \frac{1}{\sqrt{\pi\tau^2}} e^{-t^2/\tau^2} \quad \text{for } \tau \to 0 \;]$$

→ Example:

$$\bar{F} = \frac{F_0}{\pi}\left(\frac{\tau/\omega}{t^2+\tau^2}\right)\hat{x}$$

then $x(t) = \frac{F_0}{\pi} x \left(\frac{\tau/\omega}{t^2+\tau^2}\right)$

[δ-function Lorentz-ian representation,

$$\delta(t) = \frac{\tau/\pi}{t^2+\tau^2} \quad \text{for } \tau \to 0.]$$

We can solve the similar way as the last example.

→ Consider, [Midsem]

$\bar{B} = B_z \hat{z}$

$q = +e$

$\cancel{H_0 = -g_s g_1}$ $H_0 = -\frac{g_s \mu_B B_z}{\hbar} \sigma_z$

then,

$$\downarrow \qquad E_1 = +\frac{g_s \mu_B B_z}{2}$$

$$\uparrow \qquad E_0 = -\frac{g_s \mu_B B_z}{2}$$

say,

$\uparrow : \begin{pmatrix}1\\0\end{pmatrix} = |0\rangle$; $\downarrow : \begin{pmatrix}0\\1\end{pmatrix} = |1\rangle$

$$H_0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix}$$

to flip the ~~sping~~ of spin of the particle at ground state $\Rightarrow$ the particle should jump to the excited state E_1.

Applying magnetic field,

$$\bar{B}(t) = B_0 \left(\cos(\omega t + \phi)\,\hat{x} - \sin(\omega t + \phi)\right)\hat{y}$$

$$V(t) = -\frac{g_s \mu_B (\bar{\sigma} \cdot \bar{B}(t))}{2} = \begin{pmatrix} 0 & \delta e^{i\omega t} \\ \delta^* e^{-i\omega t} & 0 \end{pmatrix}$$

where $\delta = \frac{g \mu_B B_0}{2} e^{i(\phi + \pi)}$

$$H = H_0 + V(t) = \begin{pmatrix} E_0 & \delta e^{i\omega t} \\ \delta^* e^{-i\omega t} & E_1 \end{pmatrix} \leftarrow \text{2D-Hilbert space.}$$

we know that,

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn}(t)\, e^{i\omega_{mn} t}\, c_n(t)$$

$n = \{0, 1\}$

$m = \{0, 1\}$

then,

$$i\hbar \dot{C}_0 = V_{00} C_0(t) + V_{01}(t) e^{i\omega_{01} t} C_1(t)$$

$$\langle 0|V(t)|0\rangle = 0 \quad ; \quad \langle 0|V(t)|1\rangle = \delta e^{i\omega t}$$

$\omega_{01} = -\omega_{10}$ then,

$$i\hbar \dot{C}_0 = 0\,C_0(t) + \delta e^{i\omega t} e^{i\omega_{01} t} C_1(t)$$

$$\boxed{i\hbar \dot{C}_0 = \delta e^{i(\omega-\omega_{10})t} C_1(t)} \quad (2)$$

$\cancel{i\hbar \dot{C}_0 = V_{10} C_1(t)}$ $\cancel{i\hbar \dot{C}_0 = V_{10} C_1(t)}$

$$i\hbar \dot{C}_1 = V_{10} C_0(t) e^{i\omega_{10} t} + \cancel{V_{11} C_1(t)} \to 0$$

$$\boxed{i\hbar \dot{C}_1 = \delta^* e^{-i(\omega-\omega_{10})t} C_0(t)} \quad (1)$$

Solving for (1) & (2), with initial conditions given by,

$t=0$, $C_0(t=0) = 1$, $C_1(t=0) = 0$, then,

$$\ddot{C}_1(t) + i(\omega-\omega_{10})\dot{C}_1(t) + \frac{|\delta|^2}{\hbar^2} C_1(t) = 0. \qquad [\delta \to \text{Dim of energy}]$$

$$C_1(t) \sim e^{i\lambda t}$$

$$\lambda_\pm = \frac{-(\omega-\omega_{10})}{2} \pm \left(\sqrt{\frac{(\omega-\omega_{10})^2}{4} + \frac{|\delta|^2}{\hbar^2}}\right)$$

General solution :

$$C_1(t) = A e^{i\lambda_+ t} + B e^{i\lambda_- t}$$

Rabi oscillation frequency

$$C_1(t) = \frac{-i\delta^*}{\hbar\Omega} \sin(\Omega t) , \quad \text{where} \quad \boxed{\Omega = \sqrt{\frac{(\omega-\omega_{10})^2}{4} + \frac{|\delta|^2}{\hbar^2}}}$$

then,

$$\boxed{|C_1(t)|^2 = \frac{|\delta|^2}{\frac{\hbar^2(\omega-\omega_{10})^2}{4} + |\delta|^2} \sin^2(\Omega t)} \quad \text{Transition probability}$$

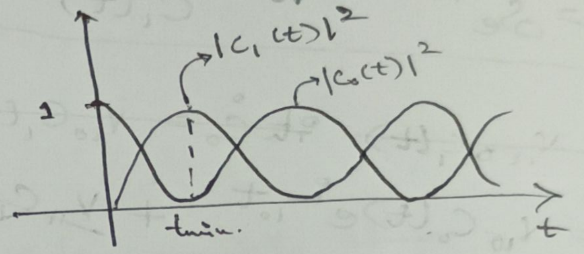
And $|C_0(t)|^2 = 1 - |C_1(t)|^2$

for resonance condition, $\omega = \omega_{10}$

$$|C_1(t)|^2 = \sin^2\left(\frac{|\delta| t}{\hbar}\right)$$

$$\frac{|\delta| t}{\hbar} = \left(n + \frac{1}{2}\right)\pi \; ; \; n = 0, 1, 2, \ldots$$

then $t_{min} = \dfrac{\hbar \pi}{2|\delta|}$



for $\omega = \omega_{10}$

$$|\delta| = \frac{g_s \mu_B B_0}{2}$$

$B_0 = 10^{-6}\,T$

then $t_{min} = \dfrac{\hbar \pi}{2|\delta|} \sim 10^{-5}\,s$

———X———

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for off-resonance condition, $\omega \neq \omega_{10}$

$$|C_1(t)|^2 = \frac{|\delta|^2}{|\delta|^2 + \frac{\hbar^2(\omega - \omega_{10})^2}{4}} \sin^2(\Omega t)$$

Say $\text{Amp} = \dfrac{|\delta|^2}{|\delta|^2 + \frac{\hbar^2(\omega-\omega_{10})^2}{4}}$

$\Rightarrow$ for $\omega \neq \omega_{10} \Rightarrow \text{Amp} < 1$

thus $|C_1(t)|^2 < 1$

$\rightarrow$ Say $B_z = 1T$, order of $\omega_{10} = \dfrac{\mu_B B_z}{\hbar} \sim 10^{10}$ rad/s

for resonance $\Rightarrow \omega \sim 10^{10}$ rad/s.

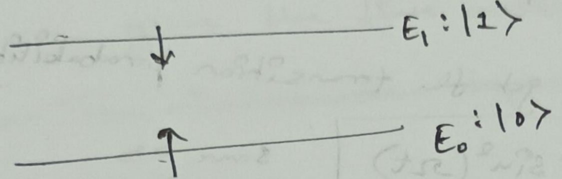
If we use $\vec{B}(t) = B_x(\cos(\omega t + \phi))$?

can be considered as a superposition of clockwise & anti-clockwise circularly polarized fields thus, $\bar{B}(t) = \dfrac{B_x\left[e^{i(\omega t+\phi)} + e^{-i(\omega t+\phi)}\right]}{2}\hat{i} = B_x(t)\,\hat{i}$

$$V(t) = -\frac{g_s \mu_B B_x(t)}{2}\sigma_x$$

where $|0\rangle = \begin{pmatrix}1\\0\end{pmatrix}$

$|1\rangle = \begin{pmatrix}0\\1\end{pmatrix}$



expressing $V(t)$ as matrix & substituting in

$H = H_0 + V(t)$.

We know that,

$$i\hbar \frac{dC_m}{dt} = \sum_n V_{mn}(t)\, e^{i\omega_{mn}t}\, C_n(t)$$

We get the equations of motion to be,

$$\Rightarrow i\hbar\, \dot{C}_0(t) = \left[\delta e^{i(\omega-\omega_{10})t} + \delta^* e^{-i(\omega+\omega_{10})t}\right] C_1(t)$$

where $\delta = \dfrac{g_s \mu_B B_x e^{i(\phi+\pi)}}{4}$

$$i\hbar\, \dot{C}_1(t) = \left[\delta e^{i(\omega+\omega_{10})t} + \delta^* e^{-i(\omega-\omega_{10})t}\right] C_0(t)$$

with the initial conditions, $t=0$

$C_0(t=0) = 1$, $C_1(t=0) = 0$

for $\omega \simeq \omega_{10} \Rightarrow (\omega-\omega_0) << (\omega+\omega_0)$

$e^{\pm i(\omega+\omega_{10})t}$: highly oscillating term & upon integrating it vanishes to zero. $\Longrightarrow$ "Rotating Wave Approximation"

After neglecting the highly oscillating terms, we get the coupled equations to be the same as in the case of $\bar{B}(t) = B_0(\cos(\omega t+\phi)\,\hat{x} - \sin(\omega t+\phi))\,\hat{y}$

#

$$i\hbar \dot{C}_0(t) = \delta e^{i(\omega-\omega_{10})t} C_1(t)$$

$$i\hbar \dot{C}_1(t) = \delta^* e^{-i(\omega-\omega_{10})t} C_0(t)$$

Solving for the initial conditions,

$$\ddot{C}_1(t) + i(\omega-\omega_{10})\dot{C}_1(t) + \frac{|\delta|^2}{\hbar^2} C_1(t) = 0$$

Solving the general solution, we get the transition probability to

$$\boxed{|C_1(t)|^2 = \frac{|\delta|^2}{|\delta|^2 + \frac{\hbar^2(\omega-\omega_{10})^2}{4}} \sin^2(\Omega t)}$$

same as previous case.

$$\Omega = \sqrt{\frac{(\omega-\omega_{10})^2}{4} + \frac{|\delta|^2}{\hbar^2}} \qquad \text{where } \delta = \frac{g_s \mu_B B_x e^{i(\phi+\pi)}}{4}$$

$\Rightarrow$ We calculate $C_0(t)$ & $C_1(t)$, then,

$$|\psi(t)\rangle_I = \begin{pmatrix} C_0(t) \\ C_1(t) \end{pmatrix} = C_0(t)\begin{pmatrix}1\\0\end{pmatrix} + C_1(t)\begin{pmatrix}0\\1\end{pmatrix}$$

$$|\psi(t)\rangle_I = e^{iH_0 t/\hbar}|\psi(t)\rangle_S$$

$$|\psi(t)\rangle_S = e^{-iH_0 t/\hbar}|\psi(t)\rangle_I = \begin{pmatrix} e^{-iE_0 t/\hbar} & 0 \\ 0 & e^{-iE_1 t/\hbar}\end{pmatrix}\begin{pmatrix} C_0(t) \\ C_1(t)\end{pmatrix}$$

We know,

$$H_0 = -\frac{g_s \mu_B B_z \sigma_z}{2}$$

$$\langle\psi(t)|\sigma|\psi(t)\rangle_I = \langle\psi(t)|\sigma|\psi(t)\rangle_S$$

At $t=0$, $\langle\sigma_z\rangle = 1$, $\langle\sigma_x\rangle = \langle\sigma_y\rangle = 0$

for $t>0$, $\langle\sigma_z\rangle \neq 1$, $\langle\sigma_x\rangle, \langle\sigma_y\rangle \neq 0$

for $t = t_0$ (on resonance),

$$\langle\sigma_z\rangle = -1, \langle\sigma_x\rangle = \langle\sigma_y\rangle = 0.$$

⟹ We know for Schrodinger picture,

$$|\psi(t)\rangle_S = e^{-iH_0 t/\hbar}\,|\psi(t=0)\rangle_S$$

$U_S(t) \equiv$ time evolution operator → H_0 (time independent)

⟹ Dyson gave the time evolution operator for the ~~Inter Time Independent dependent theory~~ Interaction picture

Dyson Series

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