Time independent Perturbation theory:

Time independent non-degenerate perturbation theory:

Decomposing Hamiltonian into leading and perturbing Hamiltonian.

$$\hat{H} = H_0 + H_1 = H_0 + \lambda H_1$$

$$H_0 |\phi_n^0\rangle = E_n^0 |\phi_n^0\rangle$$

and $H|\psi_n\rangle = E_n|\psi_n\rangle$

$$|\psi_n\rangle = |\phi_n^0\rangle + \lambda|\phi_n^1\rangle + \lambda^2|\phi_n^2\rangle + \cdots\cdots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\cdots$$

$\Rightarrow$ take atmost second order.

$$(H_0 + \lambda H_1)(|\phi_n^0\rangle + \lambda|\phi_n^1\rangle + \lambda^2|\phi_n^2\rangle)$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2)(|\phi_n^0\rangle + \lambda|\phi_n^1\rangle + \lambda^2|\phi_n^2\rangle)$$

$H_0|\phi_n^0\rangle$

$\lambda H_0|\phi_n^1\rangle + \lambda H_1|\phi_n^0\rangle$

$\lambda^2 H_0|\phi_n^2\rangle + \lambda^2 H_1|\phi_n^1\rangle$

$\lambda^3 H_1|\phi_n^2\rangle$ .... (vanishes)

$E_n^0|\phi_n^0\rangle$

$\lambda E_n^0|\phi_n^1\rangle + \lambda E_n^1 |\phi_n^0\rangle$

$\lambda^2 E_n^0|\phi_n^2\rangle + \lambda^2 E_n^1|\phi_n^1\rangle + \lambda^2 E_n^2|\phi_n^0\rangle$

$\lambda^3 E_n^1|\phi_n^2\rangle + \lambda^3|\phi_n^1\rangle$ ..

Zeroth order :-

$$H_0|\phi_n^0\rangle = E_n^0|\phi_n^0\rangle$$

First order :-

$$H_0|\phi_n^1\rangle + H_1|\phi_n^0\rangle = E_n^0|\phi_n^1\rangle + E_n^1|\phi_n^0\rangle$$

Second order

$$H_0|\phi_n^2\rangle + H_1|\phi_n^1\rangle = E_n^0|\phi_n^2\rangle + E_n^1|\phi_n^1\rangle + E_n^2|\phi_n^0\rangle$$

First order :-

$$H_0|\phi_n^1\rangle + H_1|\phi_n^0\rangle = E_n^0|\phi_n^1\rangle + E_n^1|\phi_n^0\rangle$$

$$\Rightarrow \langle\phi_k^0|H_0|\phi_n^1\rangle + \langle\phi_k^0|H_1|\phi_n^0\rangle = E_n^0\langle\phi_k^0|\phi_n^1\rangle + E_n^1\langle\phi_k^0|\phi_n^0\rangle$$

$$\Rightarrow E_k^0\langle\phi_k^0|\phi_n^1\rangle + \langle\phi_k^0|H_1|\phi_n^0\rangle = E_n^0\langle\phi_k^0|\phi_n^1\rangle + E_n^1\delta_{kn}$$

for $k = n$. $\boxed{E_n^1 = \langle\phi_n^0|H_1|\phi_n^0\rangle}$

$$\Rightarrow \cancel{E_k^0}\langle\phi_k^0|\phi_n^1\rangle(E_n^0 - E_k^0) + E_n^1\delta_{kn} = \langle\phi_k^0|H_1|\phi_n^0\rangle$$

$$\Rightarrow \langle\phi_k^0|\phi_n^1\rangle(E_n^0 - E_k^0) = \langle\phi_k^0|H_1|\phi_n^0\rangle - \langle\phi_n^0|H_1|\phi_n^0\rangle\delta_{kn}$$

$$\Rightarrow \langle\phi_k^0|\phi_n^1\rangle = \frac{\langle\phi_k^0|H_1|\phi_n^0\rangle}{E_n^0 - E_k^0} \qquad n \neq k.$$

$$\boxed{\Rightarrow |\phi_n^1\rangle = \sum_{k\neq n}|\phi_k^0\rangle\left(\frac{\langle\phi_k^0|H_1|\phi_n^0\rangle}{E_n^0 - E_k^0}\right)}$$

$$\boxed{\langle\phi_n^0|\phi_n^1\rangle = 0}$$

Second order :-

$$H_0|\phi_n^2\rangle + H_1|\phi_n^1\rangle = E_n^0|\phi_n^2\rangle + E_n^1|\phi_n^1\rangle + E_n^2|\phi_n^0\rangle$$

$$\Rightarrow \langle\phi_k^0|H_0|\phi_n^2\rangle + \langle\phi_k^0|H_1|\phi_n^1\rangle = E_n^0\langle\phi_k^0|\phi_n^2\rangle + E_n^1\langle\phi_k^0|\phi_n^1\rangle + E_n^2\,\delta_{kn}$$

$$\cancel{\Rightarrow E_k^0\langle\phi_k^0|\phi_n^2\rangle + \langle\phi_k^0|H_1|\phi_n^1\rangle = E_n^0\langle\phi_k^0|\phi_n^2\rangle + \langle\phi_n^0|H_1|\phi_n^0\rangle\frac{\langle\phi_k|H_1|\phi_n^0\rangle}{E_n - E_k} + E_n^2\,\delta_{kn}}$$

$$\Rightarrow E_k^0\langle\phi_k^0|\phi_n^2\rangle + \langle\phi_k^0|H_1|\phi_n^1\rangle = E_n^0\langle\phi_k^0|\phi_n^2\rangle + E_n^1\langle\phi_k^0|\phi_n^1\rangle + E_n^2\,\delta_{kn}$$

$k = n$

$$\Rightarrow E_n^2 = \langle\phi_n^0|H_1|\phi_n^1\rangle$$

Writing $|\phi_n^1\rangle$ in $|\phi_k^0\rangle$

$$\Rightarrow \boxed{E_n^2 = \sum_{k\neq n}\frac{|\langle\phi_k^0|H_1|\phi_n^0\rangle|^2}{E_n^0 - E_k^0}}$$

Similiarly

$$\boxed{E_n^m = \langle\phi_n^0|H_1|\phi_n^{m-1}\rangle}$$

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Harmonic oscillator under Electric field:-

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - qE\hat{x} \qquad E>0.$$

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \quad H_1 = -q|E|\hat{x}.$$

$$E_n^0 = \left(n+\frac{1}{2}\right)\hbar\omega. \qquad |\phi_n^0\rangle = |n\rangle.$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^{\dagger})$$

$$\Rightarrow E_n^1 = \langle n|H_1|n\rangle = -q|E|\sqrt{\frac{\hbar}{2m\omega}}\,\langle n|a+a^{\dagger}|n\rangle = 0.$$

$$E_n^2 = \sum_{\substack{k\neq n\\ k=0}} \frac{|\langle k|H_1|n\rangle|^2}{(n-k)\hbar\omega}.$$

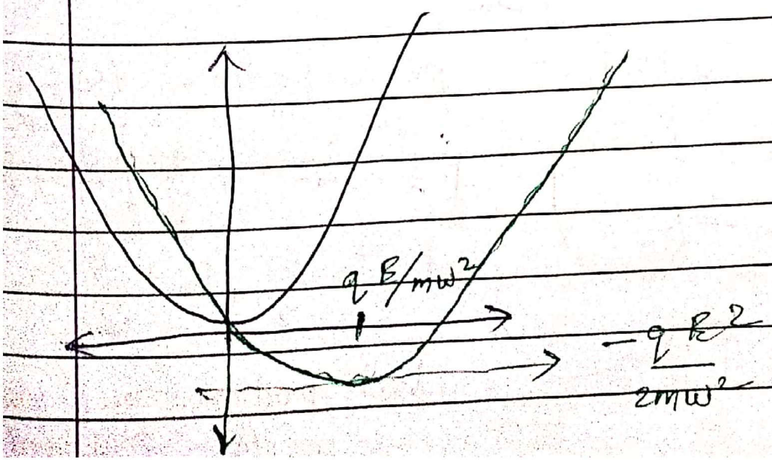
$$\langle k|H_1|n\rangle = -qE\sqrt{\frac{\hbar}{2m\omega}}\,(\langle k|a+a^{\dagger}|n\rangle) = \left(\sqrt{n+1}\,\langle k|n+1\rangle + \sqrt{n}\,\langle k|n-1\rangle\right)$$

$$\Rightarrow E_n^2 = -\frac{q^2|E|^2}{2m\omega^2}$$

So the Hamiltonian can be re-written as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\left(x - \frac{qE}{m\omega^2}\right)^2 - \frac{q^2E^2}{2m\omega^2}$$

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



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17.2.2

Magnetic fied of $B = B_0 \hat{k} + B \hat{i}$

$\cancel{\mu \cdot B_0}$ $H_0 = \mu_0 B_0$

$H_1 = \mu \cdot B$

$\Rightarrow H_0 = -\gamma B_0 S_z$ with eigenstates $|+\rangle, |-\rangle$ in z-basis

$H_1 = -\gamma B S_x$

$E_+^1 = \langle + | \sigma_x | + \rangle = 0$, $E_-^1 = \langle - | \sigma_x | - \rangle = 0$

$$E_+^2 = \frac{|\langle - | H_1 | + \rangle|^2}{E_+^0 - E_-^0} = -\frac{\gamma \hbar B^2}{4 B_0}.$$

$$E_+^0 = -\frac{\gamma B_0 \hbar}{2}, \quad E_-^0 = \frac{\gamma B_0 \hbar}{2}$$

$$E_-^2 = \frac{\gamma \hbar B^2}{4 B_0}$$

$$\Rightarrow |+^1\rangle = |-\rangle \frac{\langle - | H | + \rangle}{E_+^0 - E_-^0} = \frac{B}{2B_0} |-\rangle.$$

$$|-^1\rangle = |+\rangle \frac{\langle + | H | - \rangle}{E_-^0 - E_+^0} = -\frac{B}{2B_0} |+\rangle.$$

$$\Rightarrow |+^{full}\rangle = |+\rangle + \frac{B}{2B_0} |-\rangle$$

$$|-^{full}\rangle = |-\rangle - \frac{B}{2B_0} |+\rangle.$$

For solving without perturbation theory,

$$H = -\frac{\gamma \hbar}{2} \begin{pmatrix} B_0 & B \\ +B & -B_0 \end{pmatrix} \qquad \lambda = \mp \frac{\gamma \hbar}{2} \sqrt{B_0^2 + B^2}$$

$$= \mp \frac{\gamma \hbar}{2} \left(B_0 + \frac{B^2}{2B_0^2} + \cdots \right)$$

Which matches our result for first order.

17.2.3

(i) $\phi(r) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho\, d^3r}{r}$

$$\cancel{\rho = \frac{e}{\left(\frac{4}{3}\pi R^3\right)} \Rightarrow \phi = \frac{\rho}{4\pi\varepsilon_0}\int \frac{4\pi r^2\, dr}{r} = \frac{\rho}{4\pi\varepsilon_0}\int r\, dr = \frac{\rho}{\varepsilon_0}\frac{R^2}{2} = \frac{\rho R^2}{2\varepsilon_0} = \frac{R^2}{2\varepsilon_0}\frac{3e}{\frac{4}{3}\pi R^3} = \frac{3e}{8\varepsilon_0\pi R}}$$

$E = \frac{Q}{R^2}$ at $r = R$. $\Rightarrow \phi(R) = \frac{Q}{R}$.

$$E(r) = Q\frac{r}{R^3}$$

$$\phi(r) = \frac{Q}{R} - \int_R^r \frac{Q}{R^3} r\, dr = \frac{Q}{R} + \frac{Q}{2R^3}(R^2 - r^2)$$

$$= \frac{3Q}{2R} - \frac{Q}{2R^3} r^2$$

$H = H^0 + H'$

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}. \quad = V_0(r)$$

$$H_1 = V(r) - V_0(r) = 0 \quad r \geq R.$$

$$= \frac{3e^2}{2R} + \frac{e^2 r^2}{2R^3} + \frac{e^2}{r} \quad r \leq R.$$

Energy shift for ground state,

$$E_0^1 = \langle 1,0,0 | H_1 | 1,0,0\rangle = -\frac{e^2}{\pi a_0^3}\int_0^R e^{-r/a_0}\left(\frac{3}{2R} - \frac{r^2}{2R^3} - \frac{1}{r}\right) 4\pi r^2 dr.$$

$$\approx \frac{2}{5}\frac{e^2 R^2}{a_0^3}$$

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Thomas - Reiche - Kohn Sum rule :-

$$\sum_{n'} (E_{n'} - E_n) \cdot |\langle n'|\hat{x}|n\rangle|^2 = \frac{\hbar^2}{2m}.$$

$|n\rangle$, $|n'\rangle$ being eigenstates of $H = \frac{p^2}{2m} + V(x)$.

Derivation :-

$$\sum (E_{n'} - E_n) \langle n|\hat{x}|n'\rangle \langle n'|\hat{x}|n\rangle$$

$$= \sum \left(\langle n|XH|n'\rangle \langle n'|X|n\rangle - \langle n|HX|n'\rangle \langle n'|X|n\rangle \right)$$

$$= \sum \langle n| XHX - HX^2|n\rangle$$

$$\langle n|HX^2|n\rangle = E_n \langle n|x^2|n\rangle = \langle n|X^2H|n\rangle$$

$$\Rightarrow \sum (E_{n'} - E_n) |\langle n'|x|n\rangle|^2 = \frac{1}{2}\left(\langle n|2XHX - HX^2 - X^2H|n\rangle\right)$$

$$= \frac{1}{2} \langle n| [X, [H, X]] |n\rangle$$

$$[H, X] = \frac{i\hbar}{m} p, \quad [X, p] = i\hbar$$

$$\Rightarrow \sum (E_{n'} - E_n) |\langle n'|X|n\rangle|^2 = \frac{\hbar^2}{2m}$$

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Selection rules :-

By understanding the symmetries, the new perturbing Hamiltonian can be diagonalised

$$[\Omega, H'] = 0.$$

then H' and Ω ~~are~~ share eigenbasis.

Degenerate perturbation theory :-

$H = H^0 + \lambda \delta H_1$

when H^0 is written in $|\phi_n^0\rangle$ basis.

and if there is an N-fold degeneracy

$$H^0_{\cancel{\ddagger}} = \mathrm{diag}\{E_1^0, E_2^0, \cdots, \underbrace{E_n^0, E_n^0, \cdots, E_n^0}_{N}, \cdots\}$$

with eigenstates $|n^0, 1\rangle, |n^0, 2\rangle, \cdots, |n^0, N\rangle$

$$\langle n^0; p | n^0; l\rangle = \delta_{pl}.$$

$$H^0 |n^0, k\rangle = E_n^0 |n^0; k\rangle \qquad k \in D$$

~~D basis~~

$$D = \mathrm{span}\{|n^0, k\rangle\}_{k=1,2,\cdots N}$$

$$E(\lambda) = E_n^0 + \lambda E_{n,k}^1 + \lambda^2 E_{n,k}^2 + \cdots$$

and $\langle n^0; k | n^p; k\rangle = 0$ ... earlier result :-

~~Zero~~ order $\Rightarrow (H^0 - E_n^0)|n^0; k\rangle = 0.$

First ~~Second~~ $\Rightarrow (H^0 - E_n^0)|n^1; k\rangle = (E_{n,k}^1 - H_1)|n^0, k\rangle$

Second $\Rightarrow (H^0 - E_n^0)|n^2; k\rangle = (E_{n,k}^1 - H_1)|n^1, k\rangle + E_{n,k}^2 |n^0, k\rangle.$

$$\langle n^0; l | E_{n,k}^1 - \cancel{\delta} H_1 | n^0; k\rangle = \langle n^0, l | H^0 - E_n^0 | n^1, k\rangle = 0$$

$$\Rightarrow \boxed{E_{n,k}^1 = \langle n^0; k | H_1 | n^0; k\rangle}$$

This tells us to diagonalise H_1 for 'D' and it's eigenvector are first order corrected $|n^1;\rangle$

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That means

$$|\tilde{\psi}_n\rangle = \sum_{i=1}^{N} c_{n,i} |\phi_i^0\rangle$$

construct ~~$\tilde{\psi}$~~ $|\tilde{\psi}_n\rangle$ to diagonalise H_1.

$$\Rightarrow \langle \tilde{\psi}_p | H' | \tilde{\psi}_n \rangle = H'_{pn} \delta_{pn}$$

then the new basis will be

$$\{ \tilde{\psi}_1, \tilde{\psi}_2, \tilde{\psi}_3, \ldots, \tilde{\psi}_N, \phi^0_{N+1}, \ldots \}$$

H' is diagonalised for $\{ \tilde{\psi}_1 \ldots \tilde{\psi}_N \}$.

$E_n^1 = H'_{nn}$ (in)

~~B~~ Conclusion -

$$\psi_n = \tilde{\psi}_n^0 + \lambda \phi_n^1 + \lambda^2 \ldots \qquad (D)$$

$$\psi_n = \phi_n^0 + \lambda \phi_n^1 + \lambda^2 \phi_n^2 + \ldots \qquad \text{others}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

$$\boxed{E_n^1 = \langle \tilde{\psi}_n^0 | H' | \tilde{\psi}_n^0 \rangle} \qquad D$$

$$E_n^1 = \langle \phi_n^0 | H' | \phi_n^0 \rangle \qquad \text{others}$$

$$\boxed{|\phi_n^1\rangle = \sum_{k \notin D} \frac{\langle k^0 | H' | n^0 \rangle}{E_n^0 - E_k^0} |k^0\rangle}$$

That is, $|k^0\rangle$ ~~is~~ outside the ~~perturbo~~ degenency

2-D Harmonic oscillator :—

$$H_0 = \frac{p_x^2 + p_y^2}{2m} + \frac{K}{2}(x^2+y^2)$$

$$= \hbar\omega_0 (a^\dagger a + b^\dagger b + 1)$$

$$a = \frac{\beta}{\sqrt{2}}\left(x + \frac{i p_x}{m\omega_0}\right), \quad b = \frac{\beta}{\sqrt{2}}\left(y + \frac{i p_y}{m\omega_0}\right)$$

$|n,p\rangle$ be energy eigenstates,

$$E_{n,p} = (n+p+1)\hbar\omega_0$$

Now we shall for $\max\{n,p\} = 1$ ~~max~~

$$E_{01} = E_{10} = 2\hbar\omega_0$$

$H' = Kxy$ ---- Perturbing Hamiltonian.

$$\tilde{\psi}_n = \sum_{i=1}^{2} a_{ni}\,\phi_i^0$$

$$\tilde{\psi}_1 = a|1,0\rangle + b|0,1\rangle, \quad \tilde{\psi}_2 = a'|1,0\rangle + b'|0,1\rangle.$$

$$H' = k\begin{pmatrix} \langle 1,0|xy|1,0\rangle & \langle 1,0|xy|0,1\rangle \\ \langle 0,1|xy|1,0\rangle & \langle 0,1|xy|0,1\rangle \end{pmatrix}$$

$$\langle 10|xy|01\rangle = \frac{1}{2\beta^2}\langle 1,0|\, ab + a^\dagger b + ab^\dagger + a^\dagger b^\dagger\,|0,1\rangle$$

$$= \frac{k}{2\beta^2}$$

$$\Rightarrow H' = \left(E = \frac{k}{2\beta^2}\right)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \lambda_+ = E,\ \lambda_- = -E$$

$\Rightarrow$ ~~$E_{np} = E_{10} + \lambda E,\ E_{np}$~~

$$E_+ = E_{10} + E, \quad E_- = E_{01} - E.$$

$$\frac{1}{\sqrt{2}}(|1,0\rangle + |0,1\rangle), \quad \frac{1}{\sqrt{2}}(|1,0\rangle - |0,1\rangle).$$

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Stark effect, Hydrogen

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \; ; \quad H_1 = \mu . E = er . E$$
$$= e\mathbf{E}\hat{z}.$$

$$E_1^1 = e|E| \langle 1,0,0|z|1,0,0\rangle = 0.$$

$$E_1^2 = \sum \frac{e^2|E|^2 |\langle n,l,m|z|1,0,0\rangle|^2}{E_1^0 - E_n^0}$$

$$\approx -2.25\, a_0^3 \mathcal{E}^2.$$

$\Rightarrow$ Ground State energy; $\Rightarrow$

$$E_0(\lambda) = -13.6 - 2.25 a_0^3 \mathcal{E}^2.$$

But $n = 2$, there is 4-fold degeneracy

$$H_1 = \begin{bmatrix} \langle 2,0,0|H_1|2,0,0\rangle & \langle 2,0,0|H_1|2,1,0\rangle & \cdots \\ \langle 210|H_1|200\rangle & \langle 2,1,0|H_1|2,1,0\rangle & \\ \langle 211|H_1|200\rangle & \langle 2,1,1|H_1|2,1,0\rangle & \\ \langle 21-1|H_1|200\rangle & \langle 2,1,-1|H_1|2,1,0\rangle & \ddots \end{bmatrix}$$

Only non-zero here are

$$\langle 2,0,0|H_1|2,1,0\rangle = e\mathcal{E}\langle 2,0,0|z|2,1,0\rangle.$$
$$= -3e\mathcal{E}a_0$$

$$\Rightarrow H_1 = \begin{bmatrix} 0 & -3e\mathcal{E}a_0 & 0 & 0 \\ -3e\mathcal{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$E_2^1 = 0,\ 0,\ 3e\mathcal{E}a_0,\ -3e\mathcal{E}a_0 \longrightarrow \frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle)$$

$|2,1,1\rangle, |2,1,-1\rangle \quad \frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle)$

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Hydrogen fine structure :-

$$H = \underbrace{\frac{p^2}{2m} + V}_{H_0} - \underbrace{\frac{p^4}{8m^3c^2}}_{H_{relativistic}} + \underbrace{\frac{e^2}{2m^2c^2}\frac{S\cdot L}{r^3}}_{H_{spin\text{-}orbit}} + \underbrace{\frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2}\delta(r)}_{H_{Darwin}}$$

Darwin correction :-

$$E^1_{n,0,0} = \langle n,0,0 | H_{Darwin} | n,0,0 \rangle$$

$$= \frac{\pi}{2}\frac{e^2\hbar^2}{m^2c^2} |\psi_{n00}(0)|^2$$

$$= \alpha^4 mc^2 \cdot \frac{1}{2n^3}.$$

$\delta(r)$ makes $E^1_{n,l,m}$ dissappear until $\psi_{n,l,m}(0)$ exists

$\Rightarrow$ only $l=0$ terms do not vanish at the origin.

Relativistic correction :-

As $[H_K, L_i] = [H_K, L^2] = 0$, H_1 is already diagonal

$$E^1_{n,l,m} = -\langle n,l,m | \frac{p^4}{8m^3c^2} | n,l,m \rangle$$

Now $-\dfrac{p^4}{8m^3c^2} = -\dfrac{1}{2mc^2}\left(H_0 + \dfrac{e^2}{r}\right)$

$$E^1_{n,l,m} = -\frac{1}{2mc^2}\left((E_n^0)^2 + 2E_n^0 \cdot \left\langle \frac{e^2}{r} \right\rangle + \left\langle \frac{e^4}{r^2} \right\rangle \right)$$

From Virial theorem $\langle T \rangle = -\dfrac{\langle V \rangle}{2} \Rightarrow \langle V \rangle = 2E_n^0$

Alternatively one can use the Feynman - Hellmann lemma,

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}.$$

take $\lambda = e$.

$$\left\langle \frac{\partial H}{\partial e} \right\rangle = \frac{\partial E_n}{\partial e} \Rightarrow \left\langle \frac{1}{r} \right\rangle = \frac{m}{\hbar^2} \cdot \frac{e^2}{4\pi\varepsilon_0} \frac{1}{n^2}$$

Now for H energy levels

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

$$E_n = \frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2(N+1+l)^2}$$

where N: highest for Laguerre poly
and $N+l+1 = n$

$$\Rightarrow \frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle$$

$$\frac{\partial H}{\partial l} = \frac{\hbar^2}{2m}\frac{2l+1}{r^2}$$

$$\Rightarrow \left\langle \frac{1}{r^2} \right\rangle = \frac{2m}{\hbar^2(2l+1)} \left\langle \frac{\partial H}{\partial l} \right\rangle = \frac{2m}{\hbar^2(2l+1)} \frac{\partial E_n}{\partial l}$$

$$\Rightarrow E^1_{n,l,m}(\text{rel.}) = -\frac{1}{8}\alpha^4 \frac{mc^2}{n^4}\left(\frac{4n}{l+\frac{1}{2}} - 3\right)$$

Spin-orbit-coupling

$$H_{so} = \frac{e^2}{2m^2c^2} \frac{1}{r^3} S \cdot L$$

$$E^1_{n,l,m}(S\text{-}O) = \frac{e^2}{2m^2c^2} \left\langle \frac{1}{r^3} S \cdot L \right\rangle = \frac{e^2}{4m^2c^2} \hbar^2 \left(j(j+1) - l(l+1) - \frac{3}{4} \right) \left\langle \frac{1}{r^3} \right\rangle$$

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

$$\Rightarrow E^1_{n,l,m}(S\text{-}O) = \frac{e^2\hbar^2}{4m^2c^2} \frac{(j(j+1) - l(l+1) - \frac{3}{4})}{n^3 a_0^3 l (l+\frac{1}{2})(l+1)}$$

Set $j = l + \frac{1}{2}$

$$\Rightarrow E^1_{n,l,m}(S\text{-}O) = \frac{(E_n^0)^2}{mc^2} \frac{n}{(l+\frac{1}{2})(l+1)}$$

Combine relativistic & S-O $\Rightarrow$

$$\langle H_{rel} + H_{S\text{-}O} \rangle = \frac{(E_n^0)^2}{2mc^2} \left\{ 3 + 2n \left[\frac{j(j+1) - 3l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)} \right] \right\}$$

Now for $j = l + \frac{1}{2}$ or $l - \frac{1}{2}$,

$$\Rightarrow E^1_{nlm(fine)} = -\frac{\alpha^4 mc^2}{2n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

as $l \to 0$, S-O term reproduces the Darwin term.

$\therefore$ Total energy

$$E_{n,j,m_j} = \frac{-e^2}{2a_0} \frac{1}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right]$$

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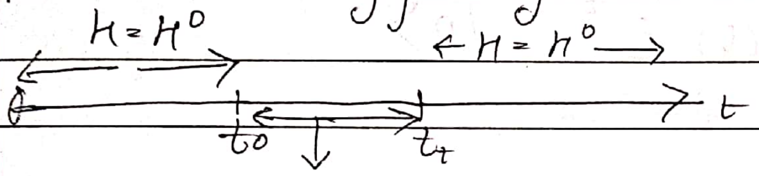
Time dependent Perturbation theory

$H|\psi\rangle = i\hbar|\dot\psi\rangle$ for time independent case.

$H(t) = H^0 + \delta H'(t)$.

No more energy eigenstates:—



$H(t) = H^0 + \delta H(t)$

Interaction picture:— (Dirac picture).

$\langle\psi(t)|\cancel{\psi(t)} A|\psi(t)\rangle = \langle\psi(0)|U^\dagger A\, U|\psi(0)\rangle$

$U^\dagger|\psi(t)\rangle = |\psi(0)\rangle$.

$H^0 \longrightarrow \quad U(t) = e^{-i/\hbar\, H^0 t}$.

for perturbation, let

$|\tilde\psi(t)\rangle = e^{i/\hbar\, H_0 t}|\psi(t)\rangle$.

$\Rightarrow |\psi(t)\rangle = e^{-\frac{i}{\hbar}H_0 t}|\tilde\psi(t)\rangle$.

for no perturbation, $\underline{|\tilde\psi(t)\rangle \Rightarrow |\psi(0)\rangle}$

$i\hbar\frac{\partial}{\partial t}|\tilde\psi\rangle = \cancel{-H^0|\tilde\psi(t)\rangle} + e^{\frac{iH_0 t}{\hbar}}\cdot(\cancel{H^0} + \delta H')e^{-i/\hbar\, H_0 t}|\tilde\psi(t)\rangle$

$\Rightarrow i\hbar\frac{\partial}{\partial t}|\tilde\psi\rangle = \{\underbrace{\exp\left(\frac{iH_0 t}{\hbar}\right)\cdot\delta H\,\exp\left(-\frac{iH_0 t}{\hbar}\right)}_{\delta\tilde H}\}|\tilde\psi(t)\rangle$.

$\Rightarrow i\hbar\frac{\partial}{\partial t}|\tilde\psi\rangle = \delta\tilde H\cdot|\tilde\psi(t)\rangle$

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Unperturbed Hamiltonian with orthonormal basis :—

$$H^0|n\rangle = E_n|n\rangle.$$

$$|\tilde{\psi}(t)\rangle = \sum c_n(t)\,|n\rangle$$

$$\psi(t) = \sum c_n(t)\cdot e^{-\frac{i}{\hbar}E_n t}\,|n\rangle.$$

$$i\hbar\sum \dot{c}_m(t)\,|m\rangle = \sum c_n(t)\cdot \delta\tilde{H}|n\rangle.$$

$$= \sum_m |m\rangle\langle m| \sum_n c_n(t)\,\delta\tilde{H}|n\rangle$$

$$i\hbar\sum \dot{c}_m(t)|m\rangle = \sum_m |m\rangle \sum_n c_n(t)\cdot \underbrace{\langle m|\delta\tilde{H}|n\rangle}_{\delta\tilde{H}_{mn}}.$$

$$i\hbar\,\dot{c}_m(t) = \sum_n c_n(t)\cdot\delta\tilde{H}_{mn}.$$

$$\delta\tilde{H}_{mn} = \langle m|\delta\tilde{H}|n\rangle = \langle m|e^{\frac{iH_0t}{\hbar}}\delta H\cdot e^{-\frac{iH_0t}{\hbar}}|n\rangle.$$

$$= e^{\frac{i(E_m-E_n)t}{\hbar}}\,\underline{\langle m|\delta H|n\rangle}$$

Define $\omega_{mn} = \dfrac{E_m - E_n}{\hbar}$

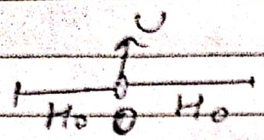
So. $$|\psi(t)\rangle = \sum c_n(t)\cdot e^{-\frac{i}{\hbar}E_n t}\,|n\rangle.$$

$$\underbrace{i\hbar\,\dot{c}_m(t) = \sum_n c_n(t)\cdot e^{i\omega_{mn}t}\,\langle m|\delta H|n\rangle}_{\text{(solving this ODE)}}$$

* Two state evolution, $|a\rangle, |b\rangle$, with E_a, E_b.

$$H^0 = \begin{bmatrix} E_a & 0 \\ 0 & E_a \end{bmatrix} \qquad \delta H' = \begin{bmatrix} 0 & \alpha \\ \alpha^* & 0 \end{bmatrix} \delta(t).$$

(sudden perturbation)



let $|\psi\rangle = |a\rangle$; $t < 0$

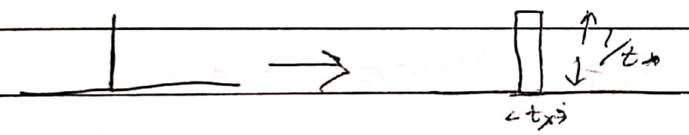
$P(|b\rangle)$ for $t > 0$.

$$i\hbar \dot{c}_a(t) = e^{+i\omega_0 t}\, \delta H_{ab}\, C_b(t).$$
$$i\hbar \dot{c}_b(t) = e^{-i\omega_0 t}\, \delta H_{ba}\, C_a(t).$$

$$\ldots\ldots \omega_0 = \frac{E_a - E_b}{\hbar}.$$

$$i\hbar \dot{c}_a(t) = e^{i\omega_0 t}\, \alpha\, \delta(t) \cdot C_b(t). = \alpha\, \delta(t) \cdot C_b(t)$$
$$i\hbar \dot{c}_b(t) = e^{-i\omega_0 t} \cdot \alpha^* \delta(t) \cdot C_a(t) = \alpha^* \delta(t)\, C_a(t)$$

Approximate $\delta(t) = \frac{1}{t_*}$ for $t \in [0, t_*]$.

$\Rightarrow$ 

$$i\hbar \dot{c}_a = \frac{\alpha}{t_*} C_b \;, \qquad i\hbar \dot{c}_b = \frac{\alpha^*}{t_*} C_a$$

$C_a(0) = 1, \quad C_b(0) = 0.$

Differentiate again,

$$\ddot{C}_a = -\left(\frac{|\alpha|}{\hbar t_*}\right)^2 C_a.$$

$$\Rightarrow C_a = \beta_0 \cos\left(\frac{|\alpha|}{\hbar t_*} t\right) + \beta_1 \sin\left(\frac{|\alpha|}{\hbar t_*} t\right).$$

$$C_b \sim \dot{C}_a \propto \beta_0 \sin\left(\frac{|\alpha| t}{\hbar t_*}\right) + \beta_1 \sin\left(\frac{|\alpha| t}{\hbar t_*}\right).$$

$\beta_1 = 0, \; \beta_0 = 1.$

$$\Rightarrow C_a(t) = \cos\left(\frac{|\alpha| t}{\hbar t_*}\right), \quad C_b(t) = -i\frac{|\alpha|}{\alpha} \sin\left(\frac{|\alpha| t}{\hbar t_*}\right)$$

for $C_a(t > t_x) = C_a(t_x) = \cos\left(\frac{|\alpha|}{\hbar}\right)$

$C_b(t > t_x) = C_b(t_x) = -i\frac{|\alpha|}{\alpha}\cdot\sin\left(\frac{|\alpha|}{\hbar}\right)$

$$\underset{t > t=0}{\psi(t)} = \cos\left(\frac{|\alpha|}{\hbar}\right) e^{-i\frac{E_a t}{\hbar}}\cdot|a\rangle - i\frac{|\alpha|}{\alpha}\sin\left(\frac{|\alpha|}{\hbar}\right) e^{-i\frac{E_b t}{\hbar}}$$

$$P_b(t) = |\langle b|\psi(t)\rangle|^2 = \sin^2\left(\frac{|\alpha|}{\hbar}\right)$$

$$P_a(t) = \cos^2\left(\frac{|\alpha|}{\hbar}\right)$$

* Now perturbation

$$H = H^0 + \lambda\, \delta H$$

$$|\tilde{\psi}(t)\rangle = |\tilde{\psi}^0(t)\rangle + \lambda|\tilde{\psi}^1(t)\rangle + \lambda^2|\tilde{\psi}^2(t)\rangle + \cdots$$

$$i\hbar\frac{\partial}{\partial t}(|\tilde{\psi}(t)\rangle) = \lambda\, \delta\tilde{H}\, |\tilde{\psi}(t)\rangle$$

$$i\hbar\frac{\partial}{\partial t}(|\tilde{\psi}^0\rangle + \lambda|\tilde{\psi}^1\rangle + \lambda^2|\tilde{\psi}^2\rangle) = \lambda\, \delta\tilde{H}\,(\psi^0 + \lambda\psi^1 + \lambda^2\psi^2 \cdots)$$

$i\hbar\frac{\partial}{\partial t}|\psi^0\rangle = 0$; $\Rightarrow$ zeroth order

$i\hbar\frac{\partial}{\partial t}(\psi^1) = \delta H.\psi^0$ $\Rightarrow$ first order.

$i\hbar\frac{\partial}{\partial t}(\psi^2) = \delta H\,\psi^1$ $\Rightarrow$ second order

$\vdots$

$i\hbar\frac{\partial}{\partial t}(\psi^{n+1}) = \delta H\,\psi^n$ $\Rightarrow$ $n+1^{th}$ order

~~Fermi's golden rule~~ :-

if $|\psi(0)\rangle = |\psi_i\rangle$ eigenstate

then ~~t~~ $c_n(0) = \delta_{ni}$

for zeroth order $\dot{c}_f = 0$

$$\dot{c}_f = \frac{1}{i\hbar} \langle f | H' | i \rangle e^{i\omega_{fi}t} \quad \text{for first order}$$

$$d_f(t) = \delta_{fi} + \frac{1}{i\hbar} \int_0^t \langle f | H' | i \rangle e^{\frac{i\omega_{fi}t'}{\hbar}} \, dt'$$

Usual problem structure.

$$H = H_0 + \lambda H_1(t) \qquad \lambda \ll 1.$$

$$|\psi_i\rangle \xrightarrow{t=0} H_1 \xrightarrow{t=t} |\psi_f\rangle.$$

Transition amplitude

$$a_{if} = \langle \psi_i(0) | \psi_f(t) \rangle.$$

$$a_{if} = \frac{1}{i\hbar} \int_0^t d\tau \, \langle \psi_f | H_1 | \psi_i \rangle e^{i\omega_{if}\cancel{t}}$$

$P_{if} = |a_{if}|^2 \rightarrow$ probability of transition from $i \rightarrow f$.

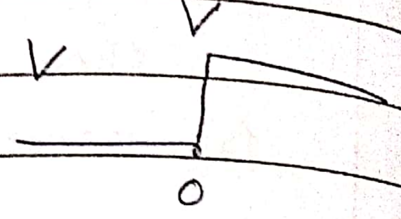
first order

Fermi's golden rule :-

transition from

discrete $\longrightarrow$ continuous

1) constant perturbation $H = H^0 + V$

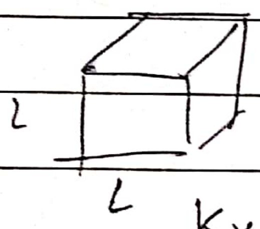


2) Harmonic $H = H^0 + \delta H(t)$

$$\delta H = \begin{cases} 2H' \cos(\omega t) & t \ge 0 \\ 0 & \text{otherwise} \end{cases}$$

Density of states :-

Quantise momentum.



$$\psi = \frac{1}{\sqrt{L^3}} e^{i(k_x x + k_y y + k_z z)}.$$

$k_x L = 2\pi n_x, \quad k_y L = 2\pi n_y, \quad k_z L = 2\pi n_z.$

$$dn = dn_x dn_y dn_z = \frac{L^3}{8\pi^3} d^3k = \rho(E)\, dE$$

$\uparrow$ density of states

no. of states from energy $E \to E + dE$.

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{2m} dk.$$

$d^3k = k\, d\Omega \cdot k\, dk$

$$dn = \left(\frac{L^3}{(2\pi)^3} \frac{m}{\hbar^2} k\, d\Omega \right) . dE = \rho(E)\, dE$$

Constant perturbation :—

$$i \rightarrow f.$$

$$C_m^{(1)}(t_0) = \sum_n \int_0^{t_0} e^{i\omega_{mn} t'} \frac{\delta H_{mn}(t')}{i\hbar} C_n(0)\, dt'$$

$C_n(0) = \delta_{ni}$ at $t=0$, $(|i\rangle)$.

$m = f$.

$$C_f^{1}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} e^{i\omega_{fi} t'} V_{fi}\, dt'$$

$$H = \begin{cases} H_0 & t < 0, \ \cancel{t > t_0} \\ H_0 + V & t > 0. \end{cases}$$

$$C_f^{1}(t_0) = \frac{V_{fi}}{E_f - E_i} e^{\frac{i\omega_{fi} t_0}{2}} \left(-2i \sin\left(\frac{\omega_{fi} t_0}{2}\right)\right)$$

$$P_{i\to f} = |C_f(t_0)|^2 = |V_{fi}|^2 \cdot \frac{4 \cdot \sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{(E_f - E_i)^2}$$

$(a_{if} = C_f)$.

if the perturbation leads to $P_{i\to f} << 1$ then it is correct.

if $E_f \to E_i \Rightarrow P_{i\to f}(t_0) = \frac{|V_{fi}|^2}{\hbar^2} t_0^2$.

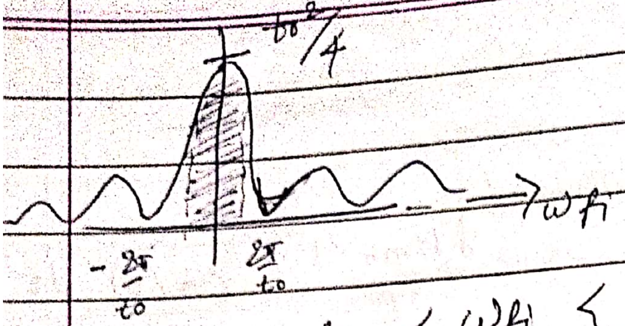
Now total transition probability

$$\Rightarrow \sum_f P_{i\to f}(t_0) = \int P_{i\to f} \cdot \rho(E_f)\, dE_f$$

$$= 4 \int |V_{fi}|^2 \frac{\sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{(E_f - E_i)^2} \rho(E_f)\, dE_f$$

$$\approx \frac{4 |V_{fi}|^2}{\hbar^2} \rho(E_f) \int \frac{\sin^2(\omega_{fi} t_0/2)}{\omega_{fi}^2} dE_f$$

Area $\propto$ $t_0 = \frac{t_0^{2}}{4}\cdot\frac{4\pi}{t_0} = \pi t_0$



$$-\frac{2\pi}{t_0} < \omega_{fi} < \frac{2\pi}{t_0}$$

$$E_i - \frac{2\pi\hbar}{t_0} < E_f < E_i + \frac{2\pi\hbar}{t_0}$$

$$\Rightarrow \int_{E_i - \frac{2\pi\hbar}{t_0}}^{E_i + \frac{2\pi\hbar}{t_0}} dE_f \, \frac{\sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{\omega_{fi}^2} = \frac{\hbar \pi t_0}{2}.$$

$$\Rightarrow \sum_f P^{(1)}_{i\to f}(t_0) = \frac{4|V_{fi}|^2 \cdot \rho(E_i)}{\hbar^2} \cdot \frac{\hbar t_0 \pi}{2}$$

$$\boxed{\Rightarrow \sum_f P_{i\to f}(t) = 2\pi\hbar |V_{fi}|^2 \rho(E_f)\, t.}$$

ω : Transition rate $= \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_i)$

Fermi's Golden rule

Harmonic Perturbations :-

$H(t) = H^0 + \delta H(t)$. (~~H^0 is harmonic~~)

$$\delta H(t) = \begin{cases} 2H' \cos(\omega t) & 0 < t < t_0 \\ 0 & \text{otherwise.} \end{cases}$$

H_1 is Time independent.

$|\tilde{\Psi}\rangle = \sum c_n(t) . |n\rangle$, $c_m^1(t_0) = \sum_n \int_0^{t_0} e^{i\omega_{mn} t'} \frac{\delta H_{mn}(t')}{i\hbar} c_n(0)\, dt'$

$c_n(0) = \delta_{ni}$

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$$c_f^{(1)}(t_0) = \frac{1}{i\hbar}\int_0^{t_0} e^{i\omega_{fi}t'}\, 2H'_{fi}\cos(\omega t')\,dt'$$

$$= \frac{H'_{fi}}{i\hbar}\int_0^{t_0} e^{i\omega_{fi}t'}\, 2\cos(\omega t')\,dt'$$

$$= \frac{H'_{fi}}{i\hbar}\int_0^{t_0}\left(e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}\right)dt'$$

$$= -\frac{H'_{fi}}{\hbar}\left(\frac{e^{i(\omega_{fi}+\omega)t_0}-1}{\omega_{fi}+\omega} + \frac{e^{i(\omega_{fi}-\omega)t_0}-1}{\omega_{fi}-\omega}\right)$$

① $\omega_{fi}+\omega \approx 1 \Rightarrow E_f = E_i - \hbar\omega$.

Stimulated emmission.

② $\omega_{fi}-\omega \approx 1 \Rightarrow E_f = E_i + \hbar\omega$

absorbtion.

Absorbtion

$$c_f^{(1)}(t_0) = \frac{-\frac{H'_{fi}}{\hbar}\, e^{i\frac{(\omega_{fi}-\omega)}{2}t}\, 2i\sin\left(\frac{\omega_{fi}-\omega}{2}t\right)}{\omega_{fi}-\omega}$$

$$P_{i\to f}(t_0) = \frac{4|H'_{fi}|^2}{\hbar^2}\cdot\frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t_0\right)}{\omega_{fi}-\omega}$$

$E_f \approx E_i + \hbar\omega$.

$$\sum P_{i\to f} = \int \rho(E_f)\,dE_f\, P_{i\to}(t_0).$$

$$= \frac{4|H'_{fi}|^2}{\hbar^2}\,\rho(E_f = E_i+\hbar\omega)\int dE_f\,\frac{\sin^2 --}{--^2}$$

$$= \frac{2\pi}{\hbar}|H'_{fi}|^2\,\rho(E_i)\,t_0$$

$$\underline{\omega} = \frac{\sum_f P_{i\to f}}{t_0} = \frac{2\pi}{\hbar}|H'_{fi}|^2\rho(E_f)$$

$E_f = E_i \pm \hbar\omega$.

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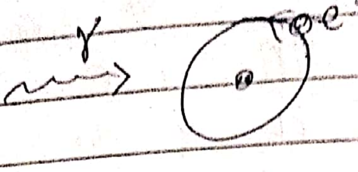
Ionization of Hydrogen :—



for ψ_{1s}.

$E_\gamma = \hbar\omega$.

$E_e = \frac{\hbar^2 k^2}{2m_e} = E_\gamma - E_{ground}$.

① $\lambda_\gamma >> a_0$.

$\Rightarrow \hbar\omega << \cancel{keV}$ 23 keV.

② $E_\gamma >> 13.6 \Rightarrow$ free electron is too far from nucleus.

$\Rightarrow \hbar\omega <$ 2-3 keV

$\hbar\omega > 140$ eV.

$\hat{E}(t) = E(t)\,\hat{z} = 2E_0 \cos(\omega t).\hat{z}$

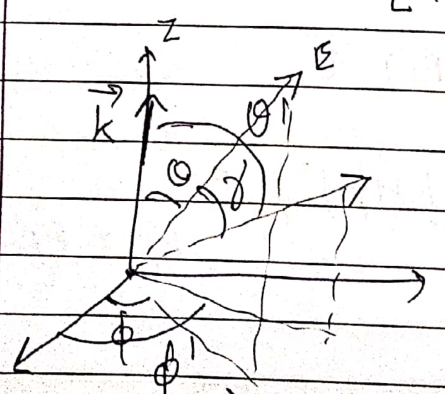
$\delta H = -e\phi = +e\,E(t).z = 2eE_0 \cos(\omega t).r\cos\theta.$

$\therefore \delta H = 2eE_0 r \cos\theta \cos(\omega t).$

$\underline{H' = eEr\cos\theta.}$

$|i\rangle \quad \psi(x)(t=0) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}.$

$|f\rangle \quad \psi(x)(t=t_0) = \frac{1}{L^{3/2}}.e^{ik.x}$ --(free).



$\langle f|H'|i\rangle$

$= \int d^3x.\ \frac{1}{L^{3/2}} e^{-i\vec{k}.\vec{r}}\ eE_0 r\cos(\gamma)$

$\vec{E} = (\theta,\phi) \quad r = (\theta',\phi'), \quad \gamma \angle(E\ \&\ r)$

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$$= \frac{eE_0}{\sqrt{\pi L^3 a_0^3}} \int r^2 dr \, \sin\theta' d\theta' d\phi' \, e^{-ikr\cos\theta'} \, r\cos(\gamma) \, e^{-r/a_0}$$

$$\cos\gamma = n_E \cdot n_r = \sin\theta\cos\phi \cdot \sin\theta'\cos\phi' + \sin\theta\sin\phi\sin\theta'\sin\phi' + \cos\theta\cos\theta'$$

$$\cos\gamma = \underbrace{\sin\theta\sin\theta'\cos(\phi-\phi')}_{\text{this will not contribute.}} + \cos\theta\cos\theta'$$

$$\langle f|H'|i\rangle = \frac{eE_0 \, 2\pi\cos\theta}{\sqrt{\pi L^3 a_0^3}} \int r^3 dr \, e^{-r/a_0} \int d(\cos\theta') \cos\theta' \, e^{-ikr\cos\theta'}$$

$$= -i\, 32\sqrt{\pi}\,(eE_0 a_0) \cdot \frac{k a_0^4}{\sqrt{L^3 a_0^3}} \frac{1}{(1+k^2a_0^2)^3} \cdot \cos\theta$$

$$\rho(E) = \frac{L^3}{8\pi^3} \frac{m}{\hbar^2} k \sin\theta \, d\theta \, d\phi = \frac{L^3}{8\pi^3} \frac{mk}{\hbar^2} d\Omega$$

$$W = \frac{2\pi}{\hbar} d\rho(E) \cdot |H'_{fi}|^2 =$$

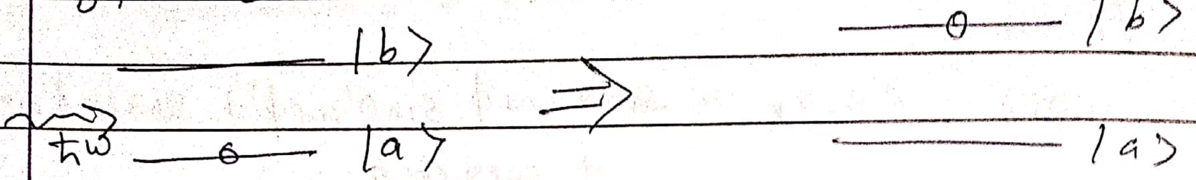
$$\Rightarrow \frac{dw}{d\Omega} = \frac{256}{\pi} \frac{(eE_0 a_0)^2}{\hbar} \frac{m a_0^2}{\hbar^2} \frac{(ka_0)^3}{(1+k^2a_0^2)^6} \cos^2\theta$$

$$W = \int \frac{\partial w}{\partial \Omega} d\Omega = \times \frac{4\pi}{3}$$

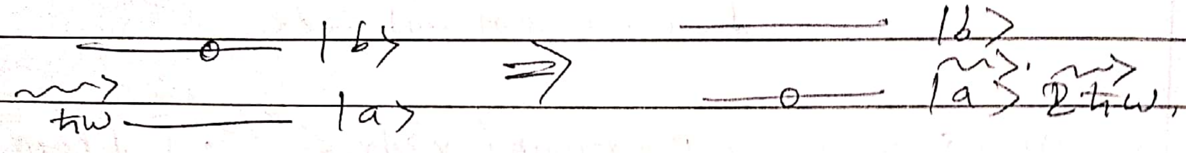
Photon energy has disappeared but remains in by $ka_0 = \sqrt{\frac{\hbar\omega}{13.6}}$.

For 2-states

Stimulated absorbtion.



Stimulated emmision



Example :- $H = H_0 + \delta H_1(t)$

2-level system.

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \quad \delta H_1 = \begin{pmatrix} 0 & \delta e^{i\omega t} \\ \delta e^{-i\omega t} & 0 \end{pmatrix}.$$

$$i\hbar \frac{\partial}{\partial t}(c(t)) = \delta \begin{pmatrix} 0 & e^{i(\omega - \omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix} c(t).$$

$\omega_{21} =$

$\Rightarrow$ ~~$i\hbar\, \dot{c}(t) =$~~

$$i\hbar \begin{bmatrix} \dot{c}_1(t) \\ \dot{c}_2(t) \end{bmatrix} = \delta \begin{pmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}.$$

$c_1(0) = 1, \quad c_2(0) = 0$ be initial conditions.

$$\Rightarrow C_2(t) = \frac{\delta^2}{\delta^2 + \frac{\hbar^2(\omega-\omega_{21})^2}{4}} \sin^2(\Omega t)$$

$$\bullet\ \Omega = \sqrt{\left(\frac{\delta}{\hbar}\right)^2 + \frac{(\omega-\omega_{21})^2}{4}}$$

$\Rightarrow$ Rabi frequency.

$\underbrace{\qquad\qquad\qquad\qquad}_{\text{Strong field limit}}$

$$a_{if} = \frac{1}{i\hbar}\int_0^t d\tau\, \langle b|H|a\rangle\, e^{i\omega_{if}\tau}$$

$$= \frac{1}{i\hbar}\int d\tau\, \delta e^{-i\omega\tau} \cdot e^{i\omega_{if}\tau}$$

$$= \frac{\delta}{i\hbar}\int e^{i(\omega_{if}-\omega)\tau}\, d\tau$$

$$= \frac{-\delta}{\hbar}\, \frac{e^{i(\omega_{if}-\omega)t_0} - 1}{(\omega_{if}-\omega)}$$

$$= \cancel{\frac{\delta}{\hbar} e^{it\omega_i}}$$

$$P_{if} = \frac{\delta^2}{\hbar^2}\, \frac{\left(e^{i(\omega_{if}-\omega)t_0} - 1\right)\left(e^{-i(\omega_{if}-\omega)t_0} - 1\right)}{(\omega_{if}-\omega)^2}$$

$$= \frac{\delta^2}{\hbar^2(\omega_{if}-\omega)^2}\left(2 - \left(e^{i(\omega_{if}-\omega)t_0} + e^{-i(\omega_{if}-\omega)t_0}\right)\right)$$

$$= \frac{2\delta^2}{\hbar^2(\omega_{if}-\omega)^2}\left(1 - \cos((\omega_{if}-\omega)t_0)\right)$$

$$= \underbrace{\frac{4}{\hbar^2}\,\delta^2 \left(\frac{\sin\left(\frac{\omega-\omega_0}{2}t_0\right)}{\omega-\omega_0}\right)^2}_{\text{Weak field}}$$