Goal: Solve time-dep Schröd eqⁿ $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$

$$\hat{H}(\underline{r},t) = \hat{H}_0(\underline{r}) + \hat{H}'(\underline{r},t)$$

- variational method derivatⁿ
- know how to get singlet or triplet
  - why
  - & how it gets there
- re-derive if a fⁿ is hermitian & orthogonality

TISE $\hat{H}_0|\phi_n\rangle = E_n|\phi_n\rangle$

$$\Psi(\underline{r},t) = \sum_n c_n(t)\,\phi_n(\underline{r})\exp(-iE_nt/\hbar)$$

Probability E_n collapsing into ϕ_n at $t = |c_n(t)|^2$

$$\sum_n c_n(t)(E_n + \hat{H}')\phi_n(\underline{r})\exp(-iE_nt/\hbar)$$

$\downarrow i\hbar\frac{\partial\Psi}{\partial t}$

$$i\hbar\sum_n\left(\frac{-ic_nE_n}{\hbar} + \frac{dc_n}{dt}\right)\phi_n(\underline{r})\exp(-iE_nt/\hbar)$$

$$i\hbar\sum_n \frac{dc_n}{dt}\phi_n(\underline{r})\exp(-iE_nt/\hbar) = \sum_n c_n(t)\,\hat{H}'\phi_n(\underline{r})\exp(-iE_nt/\hbar)$$

$\downarrow$ multiply by $\phi_m^*(\underline{r})$, use orthogonality

$$\frac{dc_m}{dt} = \frac{1}{i\hbar}\sum_n c_n(t)\,H'_{mn}(t)\exp(i\omega_{mn}t)$$

$$H'_{mn}(t) = \iiint \phi_m^*(\underline{r})\,\hat{H}'(\underline{r},t)\,\phi_n(\underline{r})\,d^3r$$

$$\omega_{mn} = \frac{E_m - E_n}{\hbar}$$

we want to solve this for $c_m(t)$

perturbatⁿ "switched on" $t=0$: $c_{n=i}(t=0) = 1$ (initial state)

$$c_{n\neq i}(t=0) = 0$$

Small perturbatⁿ $\rightarrow c_{n\neq i}(t=0) \ll 1$ & $c_{n=i}(t=0) \simeq 1$

$$\therefore \frac{dc_m}{dt} \simeq \frac{1}{i\hbar}H'_{mi}(t)\exp(i\omega_{mi}t)$$

solutⁿ: $c_m(t) = \frac{1}{i\hbar}\int_0^t H'_{mi}(t')\exp(i\omega_{mi}t')\,dt'$

Time-dependent perturbatⁿ causes transitⁿs btw the qntum states

Periodic perturbatⁿ

$\cos x = (e^{ix} + e^{-ix})/2$

sinusoidal perturbatⁿ of angular frequency ω: $\hat{H}'(\underline{r},t) = \hat{H}'(\underline{r})\cos(\omega t)$

$$= \frac{1}{2}\hat{H}'(\underline{r})\,[\exp(i\omega t) + \exp(-i\omega t)]$$

$$H'_{fi}(t) = \iiint d^3r\,\phi_f^*(\underline{r})\,\hat{H}'(\underline{r},t)\,\phi_i(\underline{r})$$

$$= \frac{1}{2}H'_{fi}\,[e^{i\omega t} + e^{-i\omega t}]$$

$$H'_{fi} = \iiint \phi_f^*(\underline{r})\,\hat{H}'(\underline{r})\,\phi_i(\underline{r})\,d^3r$$

time indep

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

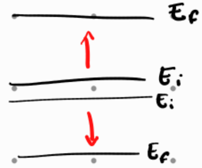
$$c_f(t) = \frac{H'_{fi}}{2i\hbar}\left[\int_0^t \exp(i(-\omega+\omega_{fi})t')\,dt' + \int_0^t \exp(i(\omega+\omega_{fi})t')\,dt'\right]$$

find

$$= \frac{-H'_{fi}}{2\hbar}\left[\overbrace{\frac{\exp(i(-\omega+\omega_{fi})t) - 1}{-\omega+\omega_{fi}}}^{E_f > E_i} + \overbrace{\frac{\exp(i(\omega+\omega_{fi})t) - 1}{\omega+\omega_{fi}}}^{E_f < E_i}\right]$$

1st peak $\omega = \omega_{fi} = \dfrac{E_f - E_i}{\hbar} > 0 \Rightarrow E_f > E_i$

2nd peak $\omega = -\omega_{fi} = -\dfrac{E_f - E_i}{\hbar} > 0 \Rightarrow E_i > E_f$



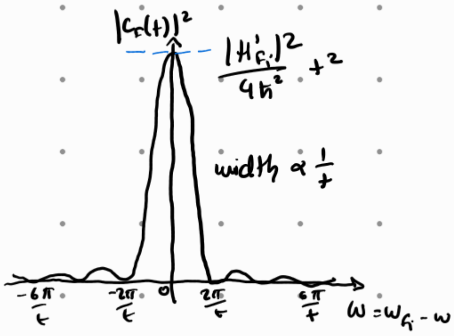
Check energy gain - only 1st term significant

$W = -\omega + \omega_{fi}$

Prob finding system in state ϕ: $|c_f(t)|^2 = \dfrac{|H'_{fi}|}{4\hbar^2} \left| \dfrac{e^{iWt} - 1}{W} \right|^2$

$\sin^2(x) = \frac{1}{2}(1 - \cos(2x))$

$= \dfrac{|H'_{fi}|^2}{4\hbar^2} \dfrac{1}{W^2} 2(1 - \cos Wt)$



$\begin{cases} \text{As } W \to 0, \ \sin\left(\frac{Wt}{2}\right) \to Wt/2 \\ \text{For } W \to 2\pi/t, \ \sin(Wt/2) = \sin\pi = 0 \end{cases}$

As $t \uparrow$: $|c_f(t)|^2$ becomes strongly peaked for $W = \omega_{fi} - \omega = 0$

$\hbar\omega = E_f - E_i$

High % transit° $i \to f$ iff freq perturbat° = ΔE_{if}

perturbat° caused em wave = excitat° qntum system

$|c_f(t)|^2 = \dfrac{|H'_{fi}|^2}{4\hbar^2} \dfrac{1}{W^2} 2(1 - \cos Wt)$ $\xrightarrow{W = -\omega + \omega_{fi}}$ $|c_f(t)|^2 = \dfrac{|H'_{fi}|^2}{4\hbar^2} \left(\dfrac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right)^2$

~ strong if $\omega = -\omega_{fi}$: stimulated emiss°

Perturbat°s aren't fully sinusoidal for all time → perturbat° includes range of frequencies

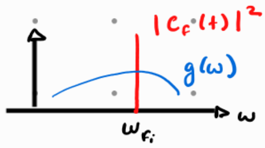
↳ perturbat° includes range frequencies : "density" of freq btw ω & $\omega + d\omega$ is $g(\omega)d\omega$

Total % excitat° $i \to f$ after t : $P(t) = \dfrac{|H'_{fi}|^2}{4\hbar^2} \displaystyle\int_0^\infty \left(\dfrac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right)^2 g(\omega)\, d\omega$

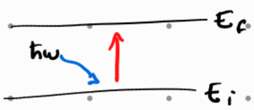
$\text{sinc}(x) = \sin\frac{x}{x}$

$= \dfrac{|H'_{fi}|^2}{4\hbar^2} t^2 \displaystyle\int_0^\infty \text{sinc}^2[(\omega_{fi} - \omega)t/2]\, g(\omega)\, d\omega$

$P(t) = 0$ if $g(\omega) = 0$



$P(t) = \dfrac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})\, t$



Transit° rate $W = \dfrac{dP}{dt} = \dfrac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})$ Fermi's golden rule

Atomic transit°s

Atoms can absorb/emit radiat° by electrons undergoing transit° btw E levels

can be explained in terms of → Time-dep perturbat° theory : basis system = atom, perturbat° due em field

BUT: not good enough → spontaneous emiss°

Stimulated emiss° | Spontaneous emiss° | Absorpt°

electric field $\underline{\mathcal{E}} = \underline{\mathcal{E}}_0 \cos(\underline{k} \cdot \underline{r} - \omega t)$

time & space varying e field; electric field amplitude; wavevector of radiat° $|k| = 2\pi/\lambda$; angular freq of radiat° $\omega = c|\underline{k}|$

(ex) atom at $\underline{r} = 0$

size ~ 1 Å

wavelength visible light $\lambda = 3900 - 7000$ Å

⇓

$\underline{k} \cdot \underline{r}$: very small

Transit° rate $\quad W = \dfrac{\pi |H'_{fi}|^2}{2\hbar} g(\omega_{fi})$

$\cos(A - B) = \cos A \cos B + \sin A \sin B$

$\cos(\underline{k} \cdot \underline{r}) \simeq 1 \qquad \sin(\underline{k} \cdot \underline{r}) \simeq 0$

$$H'_{fi} = e\mathcal{E}_0 \iiint \phi_f^*(\underline{r})\, z\, \phi_i(\underline{r})\, d^3r$$

$\underline{\mathcal{E}} = \underline{\mathcal{E}}_0 \cos(\underline{k} \cdot \underline{r} - \omega t) \simeq \underline{\mathcal{E}}_0 \cos(\omega t)$

$\mathcal{E}$ in z : work done moving an electron by distance z

Spontaneous emiss° rate $\propto |H'_{fi}|^2$

$= e\mathcal{E}z$

$= e\mathcal{E}_0 z \cos(\omega t)$

⇓

Perturbat° $\quad \hat{H}'(\underline{r}, t) = \hat{H}'(\underline{r}) \cos(\omega t)$

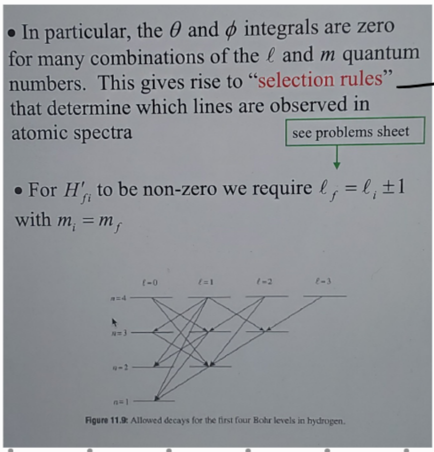
$= e\,\mathcal{E}_0\, z \cos(\omega t)$

magnitude electric field

Spherical polars $z = r\cos\theta$

$$H'_{fi} = e\,\mathcal{E}_0 \int_0^\infty dr\, r^3 R^*_{n_f l_f}(r) R_{n_i l_i}(r) \times \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \cos\theta\, Y^*_{l_f m_f}(\theta,\phi)\, Y_{l_i m_i}(\theta,\phi)$$

determines "strength" spectral lines



electric dipole transit°s

$l_f = l_i \pm 1 \Rightarrow \Delta l = \pm 1$

$m_f = \begin{cases} m_i \\ m_i \pm 1 \end{cases} \Rightarrow \Delta m = \begin{cases} 0 \\ \pm 1 \end{cases}$

no transit° if SR not obeyed!