Approximation Methods II

Time-dependent Perturbations.

The most simple way to describe the time-dependent perturbations is to consider how our system interacts with an external source of EM radiation.

① TRANSITION PROBABILITY.

What we need to do is to solve our t-dependent Sh. eqn.

$$i\hbar \frac{\partial \psi}{\partial t} = (H^{(0)} + \lambda \overbrace{H^{(1)}}^{H^{(1)}(r,t)})\psi = H\psi.$$

We assume that we know the solution of the stationary state (E_n, ϕ_n) and the only time-evolution is in the phase:

$$H_0: \; \phi_n(x,t) = e^{-iE_n t/\hbar}\, \phi_n^{(0)}(x)$$

Now lets turn on the perturbation:

$t=0$ at this time the system H is very close to $H^{(0)}$

so $\{\psi_n(x,t)\}$ should be a pretty good approximation for the whole hamiltonian as well.

$$\boxed{\psi(x,t) = \sum_n a_n(t)\, e^{-iE_n t/\hbar}\, \phi_n(x)} \quad \lambda \ll 1$$

So our task is to determine $a_n(t)$, so our amplitudes will evolve as a function of (t).

Note if pert. is $=0$ then $a_n(t) = a_n(0)$.

▸ To obtain the solution we plug in $\psi(x,t)$

$$i\hbar \sum_n \dot{a}_n(t) e^{-iE_n t/\hbar}\phi_n + = \lambda \sum_n a_n(t)\, e^{-iE_n t/\hbar} H^{(1)}\phi_n +$$

$$+ \sum_n \left(-\frac{i}{\hbar} i\hbar\, E_n\, a_n(t)\, e^{-iE_n t/\hbar}\right)\phi_n(x) \quad + \cancel{H_0\psi}$$

$$= E_n\psi \qquad = E_0\phi_0$$

$$\int d\tau\, \phi_f^* \;\Big|\; \Rightarrow i\hbar \sum_n \dot{a}_n e^{-iE_n t/\hbar} = \lambda \sum_n a_n H^{(1)} e^{-iE_n t/\hbar}$$

$$\dot{a} = \frac{da}{dt}$$

$$\boxed{i\hbar\, \dot{a}_f(t) = \lambda \sum_n a_n\, e^{i\overbrace{(E_f - E_n)}^{}t/\hbar} \cdot H^{(1)}_{fn}(r,t)}$$

$$\longrightarrow \omega_{fn}$$

we can introduce two new variables

$$\omega_{fn} \equiv (E_f - E_n)/\hbar, \quad \text{and} \quad H^{(1)}_{fn} \equiv \int_{-\infty}^{\infty} \phi_f^* H^{(1)}(t)\, \phi_n \, d\tau$$

Next step is to expand the amplitudes in terms of λ: $a_f(t) = a_f^{(0)} + \lambda a_f^{(1)} + \lambda^2 a_f^{(2)} + \dots$

the criteria for this would be: $\lambda : \underline{H}$

$$a_f^{(1)} \ll a_f^{(0)}$$

$$i\hbar \frac{d}{dt}\left(a_f^{(0)} + \lambda a_f^{(1)} + \dots \right) \dot{a}_f = \left[\sum_n a_n(t)\, e^{i\omega_{fn} t} H_{fn}^{(1)} \right] \lambda$$

Collect λ terms:

$\lambda^{(0)}$: $i\hbar \dfrac{d a_f^{(0)}}{dt} = 0$, no λ on the left side

$\lambda^{(1)}$: $i\hbar\, \dot{a}_f^{(1)} = \sum_n a_n^{(0)} e^{i\omega_{fn} t} H_{fn}^{(1)}$ $\quad \langle f | H^{(1)} | n \rangle$ ↳ (t)

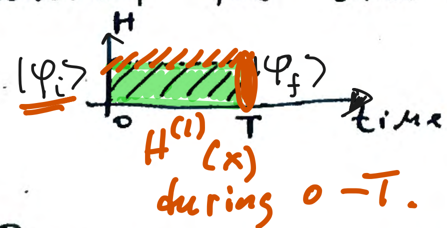
$\lambda^{(2)}$: $i\hbar\, \dot{a}_f^{(2)} = \sum a_n^{(1)} e^{i\omega_{fn} t} H_{fn}^{(1)}$

and

$$\boxed{i\hbar\, \dot{a}_f^{(s+1)} = \sum_n a_n^{(s)} e^{i\omega_{fn} t} H_{fn}^{(1)}} \quad \int_{-\infty}^{\infty} \langle \varphi_f | H^{(1)} | \varphi_n \rangle d\tau$$

This is a set of integro-differential equations which are difficult to solve analytically.

→ One of the ways to simplify the problem is to consider the time-dependent perturbation like this:



Assume that the system is initially at ϕ_i

then $a_n^{(0)} = \delta_{ni}$ at $t=0$

Once we turn off the perturbation the system will fall off into say $|\phi_f\rangle$. So the question we ask: WHAT IS THE PROBABILITY TO TRANSITION FROM $a_i \to a_f$ during T?

i.e $P_{fi} = \langle f | i \rangle = a_f^* a_i$

from λ^1: $\dot{a}_f^{(1)} = \frac{1}{i\hbar} e^{i\omega_{fi}t} H_{fi}^{(1)} \Rightarrow$

$$\boxed{a_f^{(1)} = \frac{1}{i\hbar}\int_0^T e^{i\omega_{fi}t/\hbar} H_{fi}^{(1)} dt} \Rightarrow$$

$$P_{fi} = |a_f^{(1)}|^2$$

→ Lets study several important cases; for example

$H^{(1)}(t) = W(x)$ no t-dep. (e.g. dc magnetic field)

and $H^{(1)}(t) = W(x) e^{-i\omega t}$ (e.g laser ligh with ω)

Ⓐ CONSTANT PERTURBATION

For the constant perturbation $H^{(1)}(t) = W(x)$, so we get

$$\boxed{\dot{a}_f^{(1)} = \frac{1}{i\hbar} e^{i\omega_{fi}t} H_{fi}} \quad \text{where } H_{fi} = \int_{-\infty}^{\infty} dx\, \phi_f^* \underbrace{H(x)\phi_i}_{} \quad \langle f | H | i \rangle$$

So the solution is

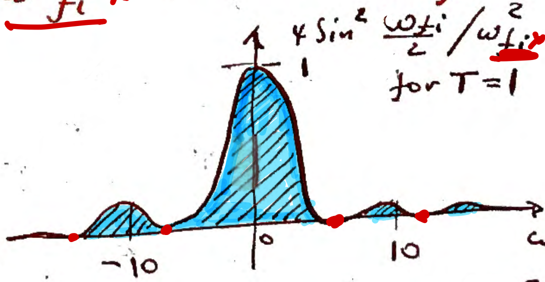
$$a_f^{(1)} = \frac{1}{i\hbar} H_{fi}^{(x)} \underbrace{\int_0^T e^{i\omega_{fi}t} dt}_{} \Big|_0^T = \frac{H_{fi}^{(1)(x)}}{\hbar\omega_{fi}} \left(1 - e^{i\omega_{fi}T}\right)$$

$\omega_f - \omega_i$

Thus at the 1st order perturbation:

$$P_{fi} = \underbrace{a_f^{(1)*} a_i^{(1)}}_{} = \frac{4|H_{fi}^{(x)}|^2}{\hbar^2 \underline{\omega_{fi}^2}} \boxed{\sin^2(\omega_{fi}T/2)} = 0$$

we used $\left\{ \begin{array}{l} \cos x = 1 - 2\sin^2\frac{x}{2} \\ \frac{e^{i\omega} + e^{-i\omega}}{2} \equiv \cos x \end{array} \right\}$



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

! { This is a very interesting result since even for the independent of time perturbation $W(x)$ we get a rather non-trivial frequency dependence.

Specific features of the 1^{st} order transition:

1. Recall we just calculated the transition from the state $\underline{|i\rangle \rightarrow |f\rangle}$

2. SELECTION RULE: if $\boxed{H^{(1)}_{fi} = 0}$ no transition

3. The transition is strongest when $\underline{\omega_{if} = 0}$ $\Rightarrow$ if $\underline{E_f = E_i}$

for small ω_{fi} $\boxed{\sin x \simeq x}$ $\Rightarrow$ $\boxed{P_{fi} \sim T^2}$ ← T

and the probability per unit of time $\equiv \dfrac{P_{if}}{T} \sim T$

$\equiv$ transition rate $\sim T$. The longer you expose system the higher chance.

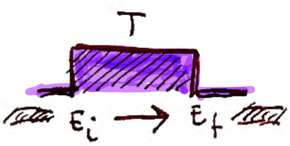
4. if $\dfrac{E_f - E_i}{\hbar} = \omega_{fi}$ is large $\underline{P_{fi} \rightarrow 0}$!

(make sense $\rightarrow$ hard to move between the high energy states.)

$\omega_f - \omega_i = \dfrac{2\pi}{T} \cdot n$

5. Also if $\underline{\sin^2 \omega_{fi} T/2 = 0}$ $\Rightarrow$ $\boxed{\omega_{fi} = \dfrac{2\pi}{T} \cdot n}$ or $n = 1, 2, \ldots$

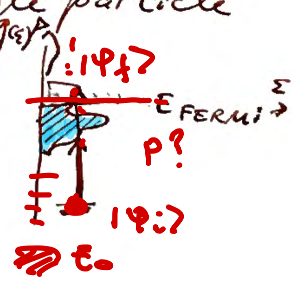
no transition



$\dfrac{E_f - E_n}{\hbar} = \dfrac{2\pi n}{T} \Rightarrow \omega_f - \omega_i = \dfrac{2\pi}{T} n$ ⇐ what is the physical meaning?

6. The most interesting feature it oscillates!

7. What if we transition not into a single particle state, but into a band of states



in this case:

$$P_{fi} = \int_{-\infty}^{\infty} |a_f|^2 \rho_f(E_f)\, dE_f =$$

$4 H_{fi}/\hbar^2 \omega_{fi}^2 \sin^2(\omega_{fi} T/2)$

$\underline{\rho_f\, dE \text{ is the density of final states}}$

if $\rho \equiv$ constant

$$= \frac{2\pi}{\hbar} \rho_f\, |H^{(1)}_{fi}|^2 \cdot T$$

$$\int_{-\infty}^{\infty} \frac{\sin^2}{\xi^2}\, d\xi = \pi$$

FERMI GOLDEN RULE:

8. The transition rate: $\boxed{\dfrac{dP_{fi}}{dT} = \Gamma_{fi} = \dfrac{2\pi}{\hbar} \rho_f |H_{fi}|^2}$

This equation is also knows as fermi golden rule

often it's written as

$$\boxed{\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|\langle f | H^{(1)(+)} | i\rangle\right|^2 \rho_f(\varepsilon)}$$

The F.G.R is the foundation of spectroscopy.

4. For large T the area or the transition rate is largest for the central peak. In this case

$w(x) \neq \boxed{t}$

If we measure ω_{fi} from P_{fi} we end up with the uncertainty of $\Delta\omega \sim \frac{2\pi}{T}$ or $\hbar\Delta\omega \sim \frac{2\pi\hbar}{T} \Rightarrow$

$\Delta E \sim \frac{2\pi\hbar}{T}$ or $\boxed{\Delta E \sim \frac{h}{T}}$ (not $\hbar$!) or

$\Delta E \cdot T \sim h$ The longer we perform our measurement the less certain or definition of ω_{if} !

Larges transition rate corresponds brighten line or highest intensity in an experiment.

B. HARMONIC PERTURBATION

Occurs expementally most often, as we use the external EM radiation e.g monochromatic light, lasers etc.

$$H^{(1)}(t) = w(x)\, e^{-i\omega t} \leftarrow \text{laser}$$

400nm

Again we assume the perturbation is switched on and off for the time T.

laser ON OFF 0 T

$$\dot{a}_f = \frac{1}{i\hbar} e^{i(\omega_{fi}-\omega)t} \int_{-\infty \to 0}^{\infty \to T} \underbrace{\phi_f^* \, w(x)\, \phi_i \, dt}_{= H^{(1)}_{fi}}$$

$\to$ integrate $0 \to T$

$$\to \boxed{a_f(T) = \frac{H^{(1)}_{fi}}{\hbar(\omega_{fi}-\omega)}\left(1 - e^{i(\omega_{fi}-\omega)T}\right)}$$

and $P_{fi} = a_f^* a_f = \dfrac{4|H_{fi}|^2}{\hbar^2} \dfrac{\sin^2[(\omega_{fi}-\omega)T/2]}{(\omega_{fi}-\omega)^2}$

L2

$\frac{\sin^2 \omega_{if}}{\omega_{if}^2}$ W(x) 6

As you see the result is about the same as W(x) except for $\boxed{\omega_{if} \to \omega_{if} - \omega}$ $P \sim \frac{\sin\alpha^2}{\alpha^2}$, $\alpha \to (\omega_{if} - \omega)$

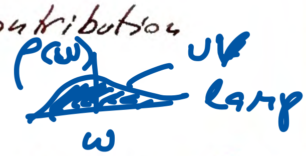
few notes

→ for a harmonic perturbation P_{fi} is maxed at

$\omega_{if} - \omega = 0$ or $\underline{E_f - E_i = \hbar\omega}$ → $E_f = E_i + \hbar\omega$

This means that we need to shine light with the frequency ω to match the transition energy. $E_f - E_i$.

→ For harmonic perturbation we have contribution from all frequencies ω.



(c) Consider the case when it's not a laser but a lamp which delivers all frequencies ω

What's the $P_{i \to f}$ in this case? simple:

We will return to this in 2 pages.

$$\underline{P_{f-i}} = \int |a_f|^2 \rho(\omega) d\omega = \frac{4}{\hbar^2} \int |H_{fi}^{(\omega)}|^2 \frac{\sin^2(\omega_{fi} - \omega) T/2)}{(\omega_{fi} - \omega)^2} \cdot \rho(\omega) d\omega$$

⇒ the function under the integral $\sim \frac{\sin^2(\omega_{fi} - \omega)}{(\omega_{fi} - \omega)}$ selects the frequencies $\omega_{if} \sim \omega$

$$\boxed{P_{i \to f} = \frac{4\pi}{\hbar^2} |H_{fi}^{(\omega)}(\omega_{if})|^2 \rho(\omega_{if})}$$

Notice the external stimuli can cause the system to go upward and downward.

→ i.e $i \equiv n$ $f \equiv m$ $E_m > E_n$

$$\Gamma_{mn} = \frac{2\pi}{\hbar^2} |H_{mn}(\omega_{mn})|^2 \rho(\omega_{mn})$$

and if $i = m$ and $f = n$ $E_m < E_n$

$$\Gamma_{mn} = \frac{2\pi}{\hbar^2} |H_{nm}|^2 \rho(\omega_{nm}) = \frac{2\pi}{\hbar^2} |H_{nm}(-\omega_{mn})|^2 \rho(\omega_{mn})$$

↑ pay attention – not mn

Since $\rho(\omega)$ and $\rho(-\omega)$ the same $H(-\omega) = (H(\omega))^+$ ⇒ $\Gamma_{nm} = \Gamma_{mn}$

Lets apply those general equations for the simpler case of $H^{(1)} = W(x) \sin \omega t$

This case can be easily treated if we remember that

$$\sin \omega t = \frac{e^{i\omega t} - e^{-i\omega t}}{2i} \quad \text{and}$$

$$\cos \omega t = \frac{e^{i\omega t} + e^{i\omega t}}{2}$$

So we can convert either case into the problem which we alredy solved: $W(x) e^{-i\omega t}$

$$\dot{a}_f = \frac{1}{i\hbar} H_{fi}^{(1)} e^{i\omega_{fi} t} = \frac{1}{2\hbar} H_{fi}^{(1)} \cdot [e^{i(\omega_{fi}-\omega)t} - e^{i(\omega_{fi}+\omega)t}]$$

and by integration the equation from 0 to T we get

$$a_f = -\frac{i}{2\hbar} H_{fi} \left[\frac{1-e^{i(\omega_{fi}+\omega)T}}{\omega_{fi}+\omega} - \frac{1-e^{i(\omega_{fi}-\omega)T}}{\omega_{fi}-\omega} \right]$$

$$\text{and } P_{fi} = |a_f|^2 = \frac{|H_{fi}|^2}{4\hbar^2} \left[\frac{1-e^{i(\omega_{fi}+\omega)T}}{\omega_{fi}+\omega} - \frac{1-e^{i(\omega_{fi}-\omega)T}}{\omega_{fi}-\omega} \right]$$

This means that we only get the largest amplitude when $\omega_{fi} \mp \omega = 0 \Rightarrow$

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

This means that if the transition occurs the system MUST emmit or absorb a quanta of energy $\hbar\omega$.

NB! READ pages 367-368 for Solved Problems 3 and 4.

Few extra points about the validity of pert. treatment.

+ Surprizingly the approx. is Not valid if T becomes long:

going back to $P(t,\omega) = \dfrac{|H^{(1)}_{fi}|^2}{4\hbar^2} \cdot \underline{F(t, \omega-\omega_{if})}$ pert. laser

$$F \equiv \left\{ \frac{\sin[(\omega_{if}-\omega)T/2]}{(\omega_{if}-\omega)/2} \right\}^2 \qquad \underbrace{(\omega_{if}-\omega)\frac{T}{2}}\equiv x$$

$$= \left\{ \underbrace{\frac{\sin x}{x}}_{\substack{\to 1 \\ x\to 0}} \cdot \underbrace{T}_{\to\infty} \right\}^2 \Rightarrow x \to 0 \quad F \to T^2 \to \infty \text{ if } T\to\infty$$

$P(T\to\infty)\to\infty$ $\omega_{if} \to \omega_{laser}$

but any probability must be ≤ 1.

so we get $\underbrace{T \ll \dfrac{\hbar}{|H^{(1)}_{if}|}}_{i\to f}$

which only works for the 1st approx

for the 2d and 3d we get $H^{(1)}_{kn}$ terms which must be constrained too.

$i \to k \to n \to f$

+ Another point is about coupling to the states with continious spectrum

Let's start with a simple example:
A scattering of a spinless particle of mass m off the potential $W(\bar{r})$

$W(r)$ $|p\rangle$

The state of the particle at time t is $|\psi(t)\rangle$ and can be span over the states of a definitive momentum $\bar{p}$ and E

$$E = \frac{p^2}{2m} \rightarrow \langle \bar{r} | \bar{p} \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\bar{p}\cdot\bar{r}/\hbar}$$

$|\langle p | \psi(t)\rangle|^2$ is the probality density associated with measurement of momentum $\bar{p}$

!: The detector will detect a signal if

- the particle scatters with momentum $\bar{p}_f$ within a solid angle $\delta\Omega_f$ around $\bar{p}_f$ and $E_f = p_f^2/2m$

$$\Rightarrow \quad \delta P(p_f, t) = \int_{\substack{p \in p_f \\ E \in E_f = \frac{p_f^2}{2m}}} d\bar{p}\, |\langle p | \psi(t)\rangle|^2$$

$d\bar{p} \rightarrow p^2\, dp\, d\Omega$

$\Rightarrow p^2 = E \cdot 2m$

$\cancel{2} p\, dp = dE\, \cancel{2}m$

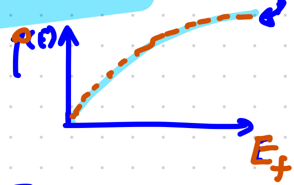
?

$$d\bar{p} = \rho(E)\, dE\, d\Omega$$

$$\boxed{\rho(E) = p^2\, dp/dE}$$

Thus we have $E = p^2/2m$ in 3D

DENSITY OF STATES → $\rho(E) = p^2 \frac{dp}{dE} = p^2 \frac{m}{p} = m\sqrt{2mE} \sim \sqrt{E}$



So going back to the $\delta P(\bar{p}_f, t) =$

$$= \int_{\substack{\Omega \in \Omega_f \\ E \in \epsilon_f \\ p \in p_f}} d\Omega\, dE\, \rho(E) |\langle p | \psi(t) \rangle|^2 \leftarrow \text{the Scattering case}$$

Now we can generalize this eqn:

Lets assume that our $H^{(0)}$ has a spectrum of eigenstates $|\alpha\rangle$ with $\langle \alpha | \alpha' \rangle = \delta(\alpha - \alpha')$

the system at time t is $|\psi(t)\rangle$

Q: What is a probability of finding a system in a group of final states after a measurement.

We characterize the group by the set of parameters or conditions α centered around α_f and the energy is continious.

$$\delta P(\alpha_f, t) = \int_{\alpha \in} d\alpha\, |\langle \alpha | \psi(t) \rangle|^2$$

now we can change variables and introduce the density of final states

The main point: we replace α by E and the set of some other parameters β

$p \to E$
$d\Omega_f \downarrow \beta$

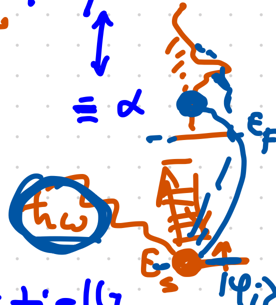
Such that $\boxed{d\alpha = \underbrace{\rho}_{\text{generalized density of final states}}(\beta, E)\, d\beta\, dE}$

then

$$\delta P(\alpha_f, t) = \int_{\substack{\beta \in \beta_f \\ E \in E_f}} d\beta\, dE\, \rho(\beta, E)\, |\langle \beta, E | \psi(t)\rangle|^2$$

$\equiv \alpha$

Now we can formulate the **FERMI GOLDEN RULE**



Let's consider that our system is initially in the eigenstate $|\varphi_i\rangle$ of $H^{(0)}|\varphi_i\rangle$ and belongs to the descrete spectrum of $H^{(0)}$

+ consider the case as before that $H^{(1)}$ is Constant in time t, recal we had

$$a(t) = |\langle \beta, E | \psi(t)\rangle|^2 = \frac{1}{\hbar^2} |\langle \beta, E_f | H^{(1)}(x) | \varphi_i\rangle|^2 \cdot F\left(t, \frac{E - E_i}{\hbar}\right)$$

$d\Omega_i$ $\quad E \quad |H_{if}|^2 \quad E_i \quad \omega - \omega_i$

$$= \left[\frac{\sin(\omega_{fi} t/2)}{\omega_{fi}/2}\right]^2$$

if $H^{(1)}(x)$ not t

Finally we have:

e.g. $d\Omega_f$

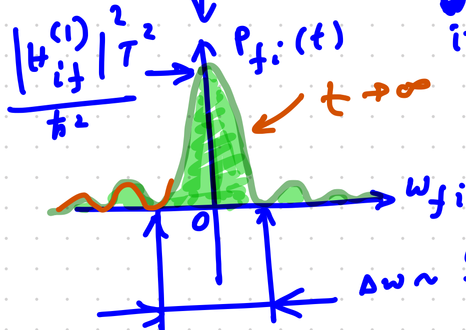
$$\delta P(\varphi_i, \alpha_f, t) = \frac{1}{\hbar^2} \int d\beta \, dE \, \rho(\beta, E) \cdot$$

$\beta, E \in$ domain of final states

$$\cdot \left| \langle \beta, E | H^{(1)} | \varphi_i \rangle \right|^2 F\left(t, \frac{E - E_f}{\hbar}\right)$$

$$\sim \int d\beta \otimes F(E) \otimes \rho(E)\, dE$$

↳ may depend on E



it varies rapidly around "0" or $E \sim E_i$ $\omega \sim \omega_i$

We can approximate this function by

$$\underline{t \to \infty} \quad F\left(t, \boxed{\frac{E - E_i}{\hbar}}\right) = 2\pi t\, \delta\left(\frac{E - E_i}{2\hbar}\right) \overset{t\to\infty}{=}$$

$$\frac{\sin^2 \alpha t}{\alpha^2} \quad \alpha$$

$$= 2\pi\hbar t\, \delta(E - E_i)$$

On the other hand

✓ $\rho(E, \beta) |\langle \ldots \rangle|^2$ varies slower with E

varies slow with E

$$\Rightarrow \delta \boxed{P}(\varphi_i, \alpha_f, t) = \frac{2\pi\hbar t}{\hbar^2} \int \delta\beta \, dE \, \delta(E - E_i)$$

$$\cdot \rho(\beta, E) |\langle \ldots \rangle|^2 = \delta\beta_f \frac{2\pi}{\hbar} t \cdot$$

$$|\langle \beta_f, E_f = E_i | H^{(1)} | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i)$$

Recall, a constant pert $H^{(1)}(x)$ can only move the system if $E_i = E_f$

Also the probability increases with t and the transition rate: $\leftarrow dP/dt$

$$\Gamma_{i \to f} \equiv \frac{d}{dt}\,\delta P(\varphi_i, \alpha_f, t)$$

is time independent

$$\frac{d^2\sigma}{dE\,d\Omega_\beta}$$

We can introduce a transition probability density per unit interval of parameter β_f

$\Gamma = \frac{P}{t}$

$\frac{dP}{dt\,d\beta \leftarrow \Omega}$

$$w(\varphi_i, \alpha_f) = \frac{d\Gamma(\varphi_i, \alpha_f)}{d\beta_f \leftarrow d\Omega_f}$$

which is finally gives us:

$$\boxed{w(\varphi_i, \underbrace{\alpha_f}_{\Omega}) = \frac{2\pi}{\hbar}\left|\langle \beta_f, E_f = E_i | H^{(1)} | \varphi_i \rangle\right|^2 \cdot \rho(\beta_f, E_f = E_i)}$$

often written $\rho(\beta_f)\cdot\delta(E_f - E_i)$ $\quad \delta(\varphi_f, \theta)$

FERMI GOLDEN RULE

Now go back to our 2 problems:

1) oscillator with sin-like perturbation:

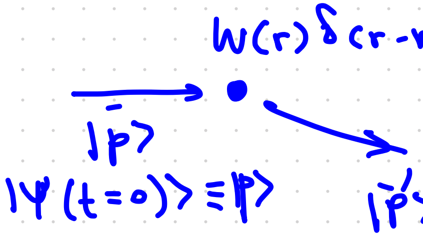
$E_i \to E_f + \hbar\omega$

$$w(\varphi_i, \alpha_f) = \frac{\pi}{2\hbar} \left| \langle \beta_f, E_f = E_i + \hbar\omega | H^{(1)} | \varphi_i \rangle \right|^2 \rho(\beta_f)\, \delta(E_f - E_i - \hbar\omega)$$

$E_f = E_i + \hbar\omega$

2) and scattering of the massless particle

recal the potential $W(\bar{r})$ with a matrix $\langle r | W | r' \rangle = W(r)\,\delta(r - r')$



← what's the probality? we salter into the state p centered around p_f and such as $p_i = p_f$

$$w(p_i, p_f) = \frac{2\pi}{\hbar} \left| \langle p_f | \bar{W}(r) | p_i \rangle \right|^2 \rho(E_i = E_f) \quad \text{or} \int \rho(E)\,\delta(E_f - E_i)$$

recal $\rho(E) = m\sqrt{2mE}$ and $\langle r | p \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i p \cdot r / \hbar}$

$$w(p_i, p_f) = \frac{2\pi}{\hbar} m\sqrt{2mE_i} \cdot \left(\frac{1}{2\pi\hbar}\right)^6$$

$$\cdot \left| \int d\bar{r}\, e^{i(p_i - p_f)\cdot r/\hbar} \bar{W}(r) \right|^2$$

this is just a Fourier transform of the $W(r)$

Since here $|p_i\rangle$ is not normalized we can devide w by the probability current

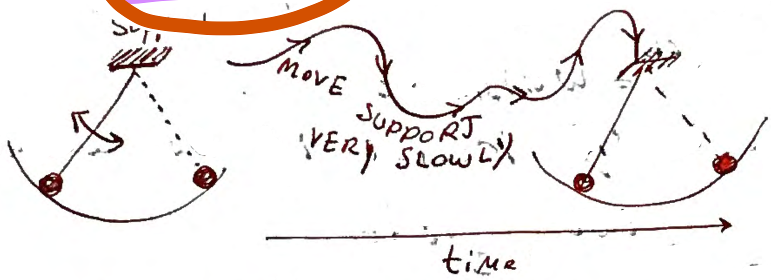
$$j_i = \left(\frac{1}{2\pi\hbar}\right)^3 \frac{\hbar k_i}{m} = \left(\frac{1}{2\pi\hbar}\right)^3 \sqrt{\frac{2E_i}{m}}$$

$$\sim (q \cdot n \cdot \bar{v})$$

$$\Rightarrow \left[\frac{w(p_i, p_f)}{j_i} = \frac{m^2}{4\pi^2\hbar^4} \left| \int d^3\bar{r}\, e^{i(\bar{p}_i - \bar{p}_f)\cdot r/\hbar} \cdot \bar{W}(r) \right|^2 \right.$$

This is scatt. cross section in the Born approximation!

ADIABATIC vs. SUDDEN PERTURBATION



The system will NOT notice the the support has moved.

this kind of process we call - addiabatic process.

def. More rigorously: A physical system remains in its state if a given perturbation acts slow enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian spectrum.

Lets calulate P_{fi} for this case

$\underline{H^{(1)}(t) = W(x) \cdot V(t)}$ e.g. $V(t) = e^{\eta t}$ $0 < \eta << 1$ ← real function

so the function is almost linear in t.

We also assume that perturbation was on for the long time e.g. $-\infty$ and the system was in ϕ_i

Question: what is the probably to find the system at ϕ_f at time t?

As before: $\frac{da^{(1)}_f}{dt}(t) = \frac{1}{i\hbar} H_{fi}^{(1)} V(t) e^{i\omega_{fi} t}$

$$a_f(t) = \frac{H_{fi}^{(1)}}{i\hbar} W(x) \int_{-\infty}^{t} V(t)\, \underbrace{e^{i\omega_{fi} t}}_{\text{fast oscillating}}\, dt$$

Lets try to solve as approximation: since $V(t)$ is almost constant within dt

$V(t)\ e^{\eta t}$ ... $\underbrace{\quad}_{dt}$ $\rightarrow a_f(t) \approx \frac{H_{fi}^{(1)}}{i\hbar} \frac{V(t)}{i\omega_{fi}} e^{i\omega_{fi} t} =$

$$= - \frac{H_{fi}^{(1)}}{\hbar\omega_{fi}} \cdot e^{i\omega_{fi} t} \cdot V(t) \rightarrow |a_f|^2$$

Since the perturbation is small we conclude that $|a_f| \ll 1$ or $|H_{if}^{(1)}| \ll \hbar\omega_{if}$

and $P_{fi} = \dfrac{|H_{fi}^{(1)}|^2 \cdot V^2(t)}{\hbar^2 \omega_{fi}^2}$ e.g. $\underline{V(t) = e^{\eta t}} \Rightarrow$ $\eta \ll 1$

W(x)

$$\boxed{P_{fi} = \frac{|H_{fi}^{(1)}|^2}{\hbar^2 \omega_{fi}^2} e^{2\eta t}}$$

W(x) V(t)

On the other hand if we plug in V(t) into the exact integral

$$\rightarrow a_f(t) = \frac{H_{fi}^{(1)}}{i\hbar} \int_{-\infty}^{t} e^{\eta t} e^{i\omega_{fi} t}\, dt \Rightarrow$$

$$= \frac{H_{fi}^{(1)}\, e^{i(\omega_{fi} - i\eta)t}}{\hbar(\omega_{fi} - i\eta)} \quad \xrightarrow{|a_f|^2}$$

EXACT integral:

$$\boxed{P_f(t) = \frac{|H_{fi}^{(1)}|^2 e^{2\eta t}}{\hbar^2(\omega_{fi}^2 + \eta^2)}}$$

$\ll 1$

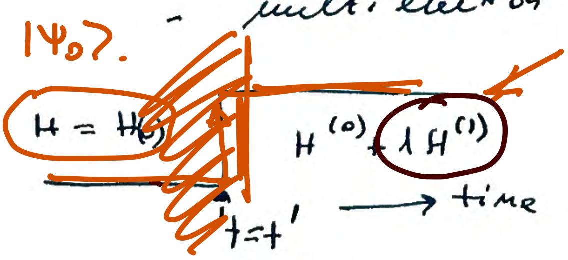
for small η they are the same.

Go over Problem 5 p. 370

SUDDEN APPROXIMATION

Assume we applied an ult-ra fast pulse by switching at $t = t'$. Examples include

- electron losses of high energy collisions with neutral targets
- laser ablation process
- core-hole ionization
- multielectron transitions of complex atoms



We assume the eigenstates for $H^{(0)}$ and $H^{(0)} + \lambda H^{(1)}$ are known

So what happens to $\psi(t)$?

For $t < t'$ $\quad H^{(0)}\phi_n^< = E_n^< \phi_n^<$ $\quad t<0$

$t > t'$ $\quad H\phi_n^> = E_n^> \phi_n^>$ $\quad t>0$

assume how to solve it

$\rightarrow \Psi^< = \sum_n a_n^< \phi_n^< e^{-iE_n^< t/\hbar}$ $\quad \rightarrow \Psi^> = \sum_m a_m^> \phi_m^> e^{-iE_m^> t/\hbar}$

here $\phi_m^>$ and $E_m^>$ are for the perturbed system.

How to define $a_m^>$? Use the continuity of the amplitude of probability at $t=0$, i.e.

$\phi_f^{>*}$ $\Big|$ $\sum_n a_n^< \phi_n^< = \sum_m a_m^> \phi_m$ at $t=0$.

$$\sum_n a_n^< \langle \phi_f^> | \phi_n^< \rangle = \sum_m a_m^> \langle \phi_f^> | \phi_m^> \rangle = \sum_m \delta_{fm} a_m^>$$

$$a_f^> = \sum_n a_n^< \langle \phi_f^> | \phi_n^< \rangle$$

$\rightarrow$ if we assume that for $t<0$ the system is in the state i $\Rightarrow a_i^< = 1$

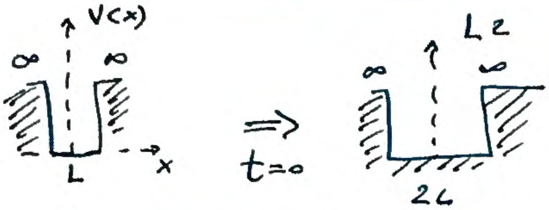
$$a_f^> = \sum_n \delta_{ni} \langle \phi_f^> | \phi_n^< \rangle =$$

$$\boxed{a_f^> = \langle \phi_f^> | \phi_i^< \rangle}$$

this kind of trivial is not it?

One peculiar observation: to get $a_f^>$ we need eigenstates for the initial and final state of the system.
But there can be a situation when $f = i = n$ however those are identical quantum numbers or the same eigenstates BUT for different energies or eigenvalues $E_n^<$ and $E_n^>$ and $E_n^< \neq E_n^>$!

Let me illustrate this:



The question is when we suddenly enlarged the well what is the probability to find the particle in the same ground state. [So the quantum numbers are the same]

Recall: for $t<0$ $\phi_n^< = \sqrt{\frac{2}{L}} \sin \frac{\pi x n}{L}$ $E_n^< = \frac{\pi^2 \hbar^2}{2mL^2} n^2$

for $t>0$ $\phi_n^> = \sqrt{\frac{1}{L}} \sin \frac{\pi x}{2L} n$ $E_n^> = \frac{\pi^2 \hbar^2 n^2}{2m(2L)^2}$

The transition amplitude

$$a_1 = \langle \phi_1^> | \phi_1^< \rangle = \int_0^{2L} \phi_1^{>*} \phi_1^< dx$$

Since $\phi_1^< = 0$ when $x > L$ we can simplify

$$a_1 = \int_0^L \phi_1^{>*} \phi_1^< dx = \frac{\sqrt{2}}{L} \int_0^L \sin\left(\frac{\pi x}{2L}\right) \sin\left(\frac{\pi x}{L}\right) dx$$

$= \frac{4\sqrt{2}}{3\pi}$ the probability $P_1 = a_1^* a_1 = \frac{32}{9\pi^2} = 0.36 = 36\%$

Next lets calculate the probability that we end up at one of the excited states n.

$$a_n = \langle \phi_n^> | \phi_1^< \rangle =$$

$$= \frac{\sqrt{2}}{L} \int_0^L \sin \frac{\pi x n}{2L} \cdot \sin \frac{\pi x n}{L} dx = \frac{\sqrt{2}}{\pi} \left[\frac{(-1)^{(n+1)/2}}{n-2} - \frac{(-1)^{(n+1)/2}}{n+2} \right]$$

(proof this)

$$a_n = \frac{4\sqrt{2}}{\pi} \frac{(-1)^{(n+1)/2}}{n^2-4}$$

hint: $\sin \frac{\pi}{2} m = (-1)^{(m+3)/2}$ for odd m and 0 for even m.

Finally the probability $P_{if} = P_n =$

$$= a_n^* a_n = \begin{cases} 32/(\pi^2 (n^2-4)^2) \sim \frac{1}{n^4} & \text{for odd } n = 2k+1 \\ 0 & \text{for even } n = 2k \end{cases}$$

$k = 0, 1, 2, 3, \ldots$

NB! in other words the system never can be found in moving from $|1\rangle \to |2\rangle$, $|4\rangle$!

[Sudden Perturbation introduce new selection rules!!]

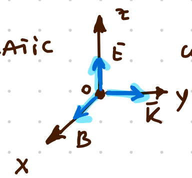
HOW ATOM INTERACTS WITH LIGHT?

Recall we already considered the case of

$H^{(1)} \sim \sin \omega t$ and ended up with a resonance $\omega_{fi} = (E_f - E_i)/\hbar$

+ Fields and potentials associated with EM field.

e.g. MONOCHROMATIC LIGHT



$\omega = ck$

The vector potential is given by

$$A(r, t) = A_0 \bar{e}_z e^{iky - \omega t} + A_0^* \bar{e}_z e^{-i(ky - \omega t)}$$

Recall from EM $\begin{cases} \bar{E}(\bar{r}, t) = -\frac{\partial}{\partial t} \bar{A}(r, t) \\ \bar{B}(\bar{r}, t) = \nabla \times A(r, t) \end{cases} \Rightarrow$

$$E(\bar{r}, t) = i\omega A_0 \bar{e}_z e^{i(ky - \omega t)} + c.c.$$

$$B(\bar{r}, t) = ik A_0 \bar{e}_x e^{i(ky - \omega t)} + c.c.$$

Lets choose the time origin such that A_0 is pure imaginary $\Rightarrow \begin{cases} i\omega A_0 = \mathcal{E}/2 \\ ik A_0 = B/2 \end{cases}$ and $\frac{\mathcal{E}}{B} = \omega/k = c$

Then we obtain:

$$\begin{cases} \bar{E}(\bar{r}, t) = \mathcal{E} e_z \cos(ky - \omega t) \\ \bar{B}(\bar{r}, t) = B e_x \cos(ky - \omega t) \end{cases}$$

and pointing vector $\bar{G} = \varepsilon_0 c^2 \bar{E} \times \bar{B}$

HAMILTONIAN

interaction of spin $\bar{S}$ with B from light.

$$H = \frac{1}{2m} [\bar{p} - q\bar{A}(\bar{R}, t)]^2 + V(\bar{R}) - q/m \, \bar{S} \cdot \bar{B}(R, t)$$

$$H = H_0 + W(t), \quad H_0 \equiv \frac{p^2}{2m} + V(R)$$

$$H^{(1)} \equiv W(t) = -q/m \, \bar{P} \cdot \bar{A}(R, t) - \frac{q}{m} S \cdot B(R, t) + \frac{q^2}{2m} [A(R, t)]^2$$

Notice if $A(R, t) \to 0$ $\quad W(t) \to 0$

if the intensity of light is low

$\frac{q^2}{2m}[A(R,t)]^2$ can be neglected. compared to A

$\Rightarrow W(t) \simeq W_I(t) + W_{II}(t)$

$W_I \rightarrow -\frac{q}{m}\bar{P}\cdot\bar{A}(R,t)$

$W_{II} \rightarrow -\frac{q}{m}\bar{S}\cdot\bar{B}(R,t)$

By the way it's interesting to compare W_I / W_{II}

For example since $S \sim \hbar$ and $B \sim k_0 A_0$ since ($B = \underline{ikA_0} e_x e^{i(ky-\omega t)}$ + c.c)

$$\frac{W_{II}}{W_I} \simeq \frac{q/m\, \hbar k A_0}{q/m\, p A_0} = \frac{\hbar k}{p}$$

but $h/p \sim$ atom size $a_0 \sim 0.5 Å$

and $k = 2\pi/\lambda \Rightarrow$

$\boxed{\frac{W_{II}}{W_I} \sim \frac{a_0}{\lambda} \ll 1 \text{ for the optical spectrum! but not for x-rays}}$

ELECTRIC DIPOLE HAMILTONIAN

Start with $A(r) \rightarrow$ put into $W_I = -\frac{q}{m}P.[\frac{A_0}{2} e^{iky} e^{-i\omega t}$ $+ c.c.]$, expand $e^{\pm iky} \simeq 1 + \pm iky - \frac{1}{2}k^2y^2 + ..$

b/c $y \sim a_0 \rightarrow ky \sim \frac{a_0}{\lambda} \ll 1$ for optical interaction range

Thus $e^{\pm iky} \sim 1$ hmmm....

$$W \cong -\frac{q}{m} p_z \left[A_0 \cdot 1 \cdot e^{-i\omega t} + c.c\right] =$$

$$= \text{since } i\omega A_0 = \frac{\mathcal{E}}{2} =$$

$$= -\frac{q}{m} p_z A_0 \cdot \frac{i\omega}{i\omega} \left[e^{-i\omega t} + e^{+i\omega t} \right]$$

$$= -\frac{q}{m} p_z \frac{\mathcal{E}}{2} \cdot \frac{1}{i\omega} \cdot \left[e^{-i\omega t} + e^{i\omega t} \right]$$

$$= \frac{q\mathcal{E}}{m\omega} p_z \sin \omega t \equiv W_{DE}$$ ← famous electric dipole hamiltonian

1st approx. ignore W_{II} :

$$W(t) \propto W_{DE}(t)$$

MatRix ELEMENT OF WDE

Lets assume we know $|\varphi_i\rangle$ and $|\varphi_f\rangle$ of H^0
E_i E_f

$$\langle \varphi_f | W_{DE} | \varphi_i \rangle = \frac{q\mathcal{E}}{m\omega} \sin \omega t \langle \varphi_f | P_z | \varphi_i \rangle$$

if we forget about magnetic part of Hamiltonian

$$[z, H_0] = i\hbar \frac{\partial H_0}{\partial p_z} = i\hbar \frac{P_z}{m} \Rightarrow$$

$$\langle \varphi_f | [z, H_0] | \varphi_f \rangle = \langle \varphi_f | z H_0 - H_0 z | \varphi_i \rangle =$$

$$= -(E_f - E_i)(\langle \varphi_f | z | \varphi_i \rangle) = -\frac{i\hbar}{m} \langle \varphi_f | P_z | \varphi_i \rangle$$

if we introduce $\underline{\underline{\omega_{if}}} = \frac{E_i - E_f}{\hbar}$ $\Rightarrow$ $\boxed{\langle \varphi_f | P_z | \varphi_i \rangle = i m \underline{\underline{\omega_{fi}}} \langle \varphi_f | Z | \varphi_i \rangle}$

NB! if you choose a frame xyz not related to the light polarization but to symmetry of φ_i and φ_f you will have to replace it by the combination of X, Y, Z operators ⇐

↑ this matrix element is b/c $\bar{E}$ ↑z along $\bar{e}_z$

ELECTRIC DIPOLE TRANSITION RULES

if $\langle \varphi_f | z | \varphi_i \rangle \neq$ the transition $|\varphi_i\rangle \to |\varphi_f\rangle$
is called DIPOLE ALLOWED.
if it's $= 0$ then go to the further expansion in $W(t)$.
e.g. quadrupole transition, magnetic dipole
but since dipole $\gg$ all other terms
they are small.

e.g. all optical emissions are dipole allowed.

For hydrogen atom:

$$\begin{cases} \varphi_{n \ell m_i}(r) = R_{n_i \ell_i}(r)\, Y_{\ell_i}^{m_i}(\theta \varphi) \\ \varphi_{n \ell m_f}(r) = \cdots \end{cases}$$

since $z = r \cdot \cos\varphi = r \cdot \sqrt{\frac{4\pi}{3}}\, Y_1^0(\theta) \Rightarrow$

$$\langle \varphi_i | z | \varphi_i \rangle \propto \int d\Omega\, Y_{\ell_f}^{m_f *}(\theta,\varphi)\, Y_1^0(\theta)\, Y_{\ell_i}^{m_i}(\theta,\varphi)$$

$\neq 0$ if $\boxed{\ell_f = \ell_i \pm 1}$ and $\boxed{m_f = m_i}$

or more generally $\boxed{m_f = m_i \pm 1}$ if E is not along $\hat{z}$.

1. Comments: z odd operator $z \to -z$ $\Rightarrow$ it connect only states of DIFFERENT PARITIES
b/c parity of the states are those of ℓ_i, ℓ_f
$\Rightarrow \Delta \ell = \ell_i - \ell_f = \text{odd}!$

2. IF there is a SPIN-ORBIT term
$\xi(r) L \cdot S$ we should label
the electron is classified as: ℓ, s, J, m with $J = L + S$
we should demand $\neq 0$ matrix element of $\bar{R}$ (w.r.t. z)

in the $|\ell, s, j, m_j\rangle$ basis $\Rightarrow$

we can show that in this case the selection rules:

$$\begin{cases} \Delta J = \pm 1, 0 \\ \Delta \ell = \pm 1 \\ \Delta m_j = \pm 1, 0 \end{cases}$$

$\Rightarrow$ note $\Delta J = 0$ is not forbiden!

NON RESONANT EXCITATIONS

Let's assume the atom is excited by the non-resonant ω.

What happens is that atom will acquire an electric dipole moment $\langle D\rangle(t)$ which oscillate with forced ω and $\sim \mathcal{E}$. This model is fundamental for the optical properties of solids.

With this model we can calculate the polarization induced by light.

Let's begin. the goal is to calculate $|\psi(t)\rangle$ as a function of $\mathcal{E}$ in the 1^{st} order.

We also assume that at $t=0$ $|\psi(t=0)\rangle = |\varphi_0\rangle$ is known.

Thus in the 1^{st} approx. we use the perturbation

$$H^{(1)} \equiv W \equiv \frac{q\mathcal{E}}{m\omega} \langle \varphi_n | P_z | \varphi_i \rangle$$

in the problem we solved for $H^{(1)} \propto e^{i\omega t} \cdot W(x)$

where we got

$$P_{i\to f}(t,\omega) = \frac{|H^{(1)}_{fi}|^2}{4\hbar^2} \left| \frac{1-e^{i(\omega_{fi}+\omega)t}}{\omega_{fi}+\omega} - \frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega} \right|^2$$

and $|\psi(t)\rangle = e^{-i\varepsilon_0 t/\hbar} |\varphi_0\rangle + \sum_{n\neq 0} \lambda\, a_n^{(1)}(t)\, e^{-i\varepsilon_n t/\hbar} |\varphi_n\rangle$

where $a_n^{(1)}(t) = \frac{|H^{(1)}_{ni}|}{2i\hbar} \left[\qquad \right] \Rightarrow$ multiply by $e^{+i\varepsilon_0 t/\hbar}$

Thus we can write down:

$$|\psi(t)\rangle = |\varphi_0\rangle + \sum_{n\neq 0} \frac{q\mathcal{E}}{2mi\hbar\omega} \langle\varphi_n|P_z|\varphi_0\rangle \cdot$$

$$\cdot \left\{ \frac{e^{-i\omega_{no}t} - e^{i\omega t}}{\omega_{no} + \omega} - \frac{e^{-i\omega_{no}t} - e^{-i\omega t}}{\omega_{no} - \omega} \right\}$$

From this we find

part of home work!

$\langle P_z(t)\rangle = \langle\psi(t|\,qZ\,|\psi(t)\rangle$ = retain only terms in 1^s order $\mathcal{E}$ and ignoring the terms which oscillate with the natural frequencies $\pm\,\omega_{no}$, and replacing $\langle\varphi_n|P_z|\varphi_0\rangle$ by $\ldots \propto \langle\varphi_n|Z|\varphi_0\rangle =$
$= im\omega_{fi}\langle\varphi_f|Z|\varphi_i\rangle$

We end up!

$$\boxed{\langle D_z\rangle(t) = \frac{2q^2}{\hbar}\,\mathcal{E}\cos\omega t \sum_n \frac{\omega_{no}\,|\langle\varphi_n|Z|\varphi_0\rangle|^2}{\omega_{no}^2 - \omega^2}}$$

Some discussion is due: Oscillator STRENGTH.

Let's define $2m\cdot\omega_{no}\cdot|\langle\varphi_n|Z|\varphi_0\rangle|^2/\hbar \equiv f_{no}$

is a real dimensionless characterizing $|\varphi_0\rangle \longleftrightarrow |\varphi_n\rangle$

Show that: $\boxed{\sum_n f_{no} = 1}$ (Thomas-Reiche-Kuhn sum rule)

RESONANT EXCITATIONS

Resonant Excitations

Consider $\omega_{fi} \sim \omega$ of light

a Bohr atom

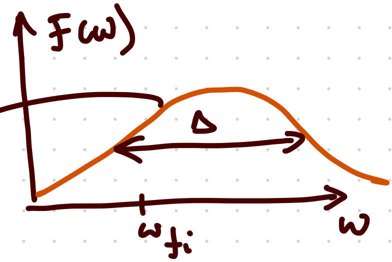
Recall that for the dipole approximation

$$P_{i\to f}(t,\omega) = \frac{q^2}{2\hbar^2}\left(\frac{\omega_{fi}}{\omega}\right)^2 \left|\langle\varphi_f|Z|\varphi_i\rangle\right|^2 \cdot \varepsilon^2 \cdot F(t, \omega-\omega_{fi})$$

where $F(t, \omega-\omega_{f}) \equiv \dfrac{\sin^2\left[(\omega_{fi}-\omega)\frac{t}{2}\right]}{(\omega_{fi}-\omega)^2}$

Broad-Band radiation

In reality the radiation is rarely mono chromatic. Let's denote the incident flux within $[\omega \pm d\omega]$ per unit surface as $F(\omega)d\omega$



the excitation linewidth

if Δ is finite we say we deal with a "WHITE SPECTRUM"

The incident radiation is generally incoherent, without well-defined phase relation.

$$P_{total} \equiv \bar{P}_{i\to f} = \text{SUM of transitions for each wave}$$

Recall the Pointing vector

$$\bar{G} = \varepsilon_0 c \frac{\varepsilon^2}{2} \bar{e}_y \Rightarrow \varepsilon^2 = \frac{2\bar{G}\cdot\bar{e}_y}{\varepsilon_0 c}$$

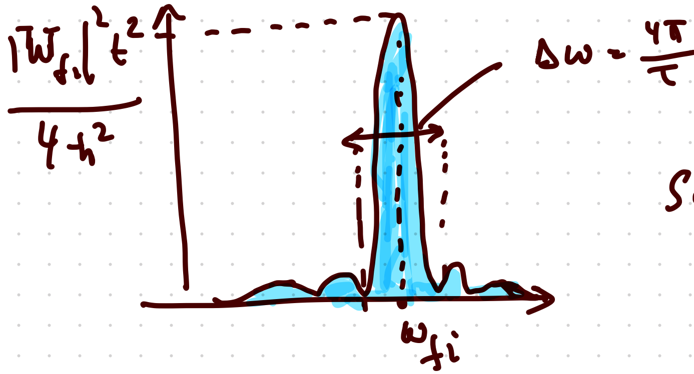
$$\varepsilon^2 \to \text{by} \qquad \to \int \text{over } \omega$$

$$\bar{P}_{if}(t) = \frac{q^2}{2\varepsilon_0 c} \cdot \frac{1}{\hbar^2} \left|\langle \varphi_f | z | \varphi_i \rangle\right|^2 \times$$

$$\times \int d\omega \left(\frac{\omega_{fi}}{\omega}\right)^2 \mathcal{F}(\omega)\, F(t, \omega-\omega_{fi})$$

How to evaluate the integral?

1) compared to $\frac{4\pi}{t}$ $F(t, \omega-\omega_{fi})$



So $\dfrac{\sin^2(\dots)}{(\dots)^2}$ behaves as $\delta(\omega - \omega_{if})$

if t is large so $\dfrac{4\pi}{t} \ll \Delta$

$\uparrow$ excitation line width

$$F(t, \omega - \omega_{if}) \simeq 2\pi t\, \delta(\omega - \omega_{fi})$$

$$\Rightarrow \bar{P}_{if} \simeq \frac{q^2}{2\varepsilon_0 c \hbar^2} |\langle \varphi_f | z | \varphi_i \rangle|^2 \cdot 2\pi t \underbrace{\int d\omega\, \delta(\omega - \omega_{if}) \cdot \mathcal{J}(\omega)}_{\mathcal{J}(\omega_{fi})}$$

$$\bar{P}_{if} = C_{if}\, \mathcal{J}(\omega_{fi})\, t$$

$$C_{if} \downarrow \; \frac{4\pi^2}{\hbar} |\langle \varphi_f | z | \varphi_i \rangle|^2 \alpha$$

where $\alpha = \dfrac{q^2}{4\pi\varepsilon_0} \cdot \dfrac{1}{\hbar c} = \dfrac{e^2}{\hbar c} \simeq \dfrac{1}{137}$

$\Rightarrow \bar{P}_{if} \uparrow$ as $t \uparrow$

The transition probability per unit time

$$\bar{W}_{if} = C_{if} \mathcal{F}(\omega_{fi})$$

Note: in all those derivations we assume that radiation is in a well-defined polarization state and it propagates along a well defined direction.

if we average C_{if} over all directions and all polarizations

we obtain B_{if} which is exactly the Einshtein coefficients to describe the absorption and induced emission.
And this is a quantum mech. version!