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 Sch. eqn.

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

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

$$\phi_n(x,t) = e^{-iE_nt/\hbar}\,\phi_n(x)$$

Now lets turn on the perturbation:

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

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

$$\psi(x,t) = \sum_n a_n(t)\, e^{-iE_nt/\hbar}\,\phi_n(x)$$

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 $\psi(x,t)$

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

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

$$= \cancel{E_n\psi}$$

$\int dx\, \phi_f^*$

$$\Rightarrow\; i\hbar \sum_n \dot a_n\, e^{-iE_nt/\hbar} = \lambda \sum_n a_n\, H^{(1)}\, e^{-iE_nt/\hbar}$$

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

we can introduce two new variables

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

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.

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

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

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

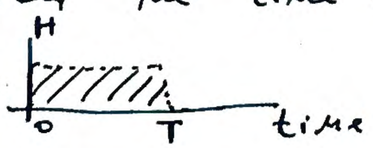
$\lambda^{(1)}$: $\quad i\hbar\, \dot{a}_f^{(1)} = \sum_n a_n^{(0)} e^{i\omega_{fn} t} H_{fn}^{(1)}$

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

and $\quad \boxed{i\hbar\, \dot{a}_f^{(s+1)} = \sum a_n^{(s)} e^{i\omega_{fn} t} H_{fn}^{(1)}}$

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 ~~switch~~ fall off into say ϕ_f. So the question we ask: WHAT IS THE PROBABILITY TO TRANSITION FROM $a_i \to a_f$ during T?

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

from ℓ': $\dot{a}_f^{(1)} = \frac{1}{i\hbar} e^{i\omega_{fi}/t} H_{fi}^{(1)} \Rightarrow$

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

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

→ Lets study several important cases:

$H^{(1)}(t) = W(x)$ no t-dep.

$H^{(1)}(t) = W(x)\, e^{-i\omega t}$

Ⓐ CONSTANT PERTURBATION

For the constant perturbation

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

$\dot{a}_f^{(1)} = \frac{1}{i\hbar} e^{i\omega_{fi}t} H_{fi}$ where $H_{fi} = \int_{-\infty}^{\infty} dx\, \phi_f^* H(x) \phi_i$

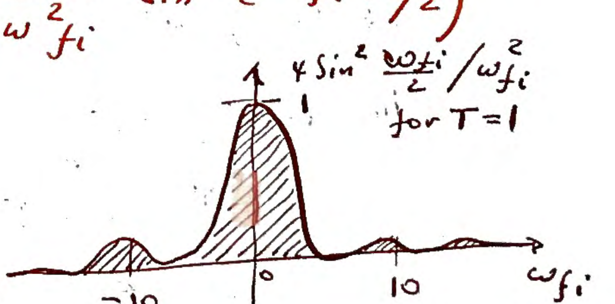
So the solution is

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

Thus at the 1^{st} order perturbation:

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

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



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

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

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

1. Recall we just calculated the transition from the state $|i\rangle \to |f\rangle$

2. <u>SELECTION RULE</u>: if $H_{fi} = 0$ no transition

3. The transition is strongest when $\omega_{if} = 0$

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

and the <u>probability per unit of time</u> $\equiv$

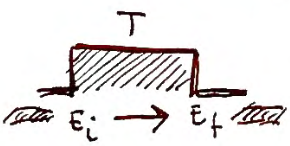
$\equiv$ <u>transition rate</u> $\sim T$

4. if $\frac{E_f - E_i}{\hbar} = \omega_{fi}$ is large $P_{fi} \to 0$!

(make sense – hard to move between the high energy states.)

5. Also if $\sin^2 \omega_{fi} T/2 = 0 \Rightarrow \omega_{fi} = \frac{2\pi}{T} \cdot n$ $n = 1, 2, \dots$

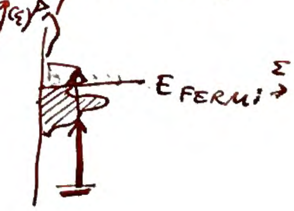
no transition



$$\frac{E_f - E_n}{\hbar} = \frac{2\pi n}{T} \Rightarrow \omega_f - \omega_i = \frac{2\pi}{T} n$$ ⇐ 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:

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

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

$\rho_f dE$ is the density of final states

if $\rho \equiv$ constant

$$= \frac{2\pi}{\hbar} \rho_f |H_{fi}^{(1)}|^2 T$$

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

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

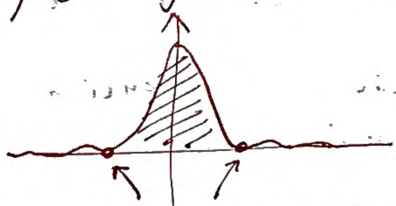
This equation is also knows as <u>fermi golden rule</u>

often it's written as

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

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



$\omega_{fi} \le \frac{2\pi}{T}$

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

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

$\Delta E \cdot T \sim h$. The longe 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 <u>monochromatic</u> light, lasers etc.

$$H^{(1)}(t) = W(x)\, e^{-i\omega t}$$

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

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

integrate $0 \to T$

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

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

As you see the result is about the same as $W(x)$ except for $\omega_{if} \to \omega_{if} - \omega$

few notes

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

$$\omega_{if} - \omega = 0 \quad \text{or} \quad E_f - E_i = \hbar\omega$$

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

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

• $\rho(\omega)\,d\omega$ ⇒ 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. $i = n$ $f \equiv m$ $E_m > E_n$

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

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

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

pay attention - not mn

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

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 alrédy solved: $W(x) e^{-i\omega t}$

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

and by integration the equation from 0 to T we get

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

and

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

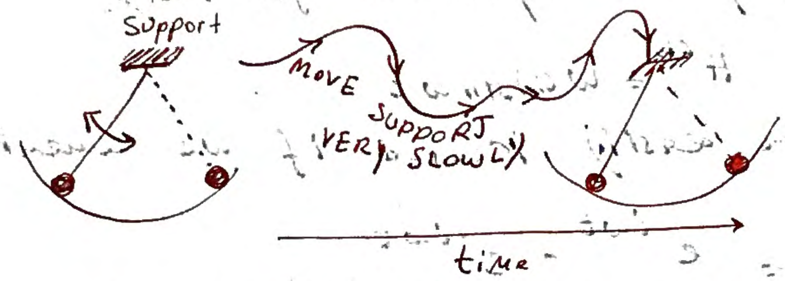
This means that we only get the largest amplitude when $\omega_{fi} \mp \omega = 0 \Rightarrow$

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

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.

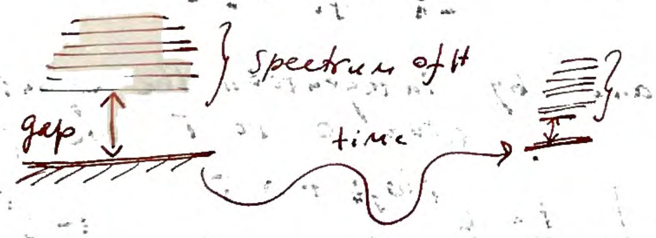
ADIABATIC VS. SUDDEN PERTURBATION



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 ~~insulating~~ 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 calutate P_{fi} for this case:

$$H^{(1)}(t) = W(x)\,V(t) \qquad \text{e.g. } V(t)\, e^{\eta t} \quad 0<\eta \ll 1$$

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?

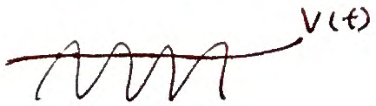
As before:

$$\dot{a}_f(t) = \frac{1}{i\hbar} H_{fi}^{(1)} V(t)\, e^{i\omega_{fi} t}$$

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

since $V(t)$ is almost constant within dt

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



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. $V(t) = e^{\eta t} \Rightarrow$

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

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

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

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

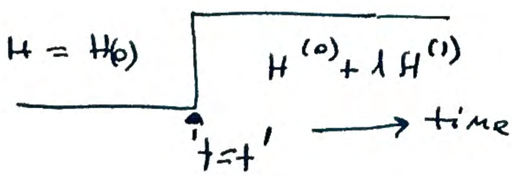
for small η they are the same.

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 ~~in~~ of high energy collisions with neutral targets
- laser ablation process
- core-hole ionization
- multi electron 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 $t < t'$ and $t > t'$:

$$\begin{cases} H^{(0)} \phi_n^< = E_n^< \phi_n^< & t<0 \\ H \phi_n^> = E_n^> \phi_n^> & t>0 \end{cases}$$

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

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.

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

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

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

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

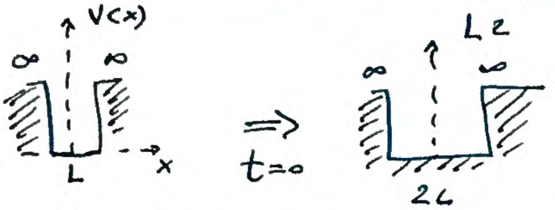
$$a_f^> = \sum_n \cancel{a_n^<} \, \delta_{ni} \langle \phi_f^> | \phi_n^< \rangle =$$

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

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.

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

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

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 $P_1 = a_1^* a_1 = \frac{32}{9\pi^2} \cong 0.36 = 36\%$

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

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

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

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

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

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

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

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

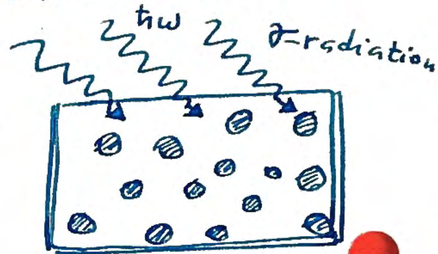
NB! in other words the system never can be found in moving from $|1\rangle \to |2\rangle$! $|4\rangle$

$\boxed{\text{Sudden Perturbation introduce new selection rules!!}}$

As the high point of non-quantum field theory of atoms interacting with light we consider <u>Einstein theory of an atom interacting with EM wave</u>.

But 1^{st} lets recap the theory of radiation.

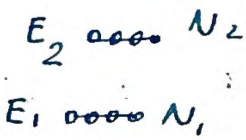
<u>Einstein postulate:</u> Ratio of probabilities of spontaneous emmission / to stimulated emission B is a constant:



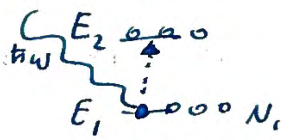
$$\frac{A}{B} = \frac{\hbar\omega^3}{\pi^2 c^3}$$

One of Einshtein's main achievements was in the calculation of A and B.

For simplicity we consider a two-state model

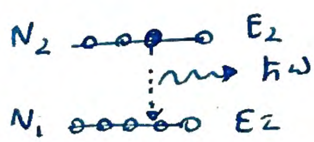


ABSORPTION



$$N_{ab} \sim N_1 \cdot \rho(\omega) = N_1 \rho(\omega) \cdot C$$

EMISSION



spontaneous emission

$\sim N_2$

$= AN_2$

Stimmulated emmision

$\sim N_2 \rho(\omega)$

$= BN_2 \rho(\omega)$

A, B, C are known as the Einshtein coeff.s.

At equilibrium: $\quad C N_1 \rho(\omega) = B N_2 \rho(\omega) + A N_2 \Rightarrow$

$$\rho(\omega) = \frac{A}{B\left(\frac{CN_1}{BN_2} - 1\right)}$$

. From stat. physics $N \sim e^{-E/k_BT} \Rightarrow$

$$\frac{N_1}{N_2} = e^{(E_2 - E_1)/k_BT} = e^{\hbar\omega/k_BT}$$

$$\Rightarrow \rho(\omega) = \frac{A}{B\left(\frac{C}{B} e^{\hbar\omega/k_BT} - 1\right)} = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/k_BT} - 1\right)}$$

↑ Plank formula for Black body radiation

Now we will have a kind of "boundary" condition set up by time $t=0$

$$i\hbar\, \dot{a}_f = \frac{1}{2}\,\varepsilon_0\, \bar{D}_{fi} \left[e^{i(\omega_{fi}+\omega)t} + e^{+i(\omega_{fi}-\omega)t} \right]$$

which we can easily integrate

$$a_f(t) = -\frac{i\varepsilon_0}{2\hbar}\bar{D}_{fi}\left[\frac{e^{i(\omega_{if}+\omega)t}}{(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)}}{(\omega_{fi}-\omega)}\right]_0^T$$

The transition we are to derive can be absorption or emission.

ABS: $E_i < E_f$ $\omega_{fi} > 0$

Since $\omega_{fi}-\omega < \omega < \omega_{fi}+\omega$ the term

$$\omega_{fi}-\omega < \omega \qquad \frac{e^{-i(\omega_{fi}-\omega)t}}{(\omega_{fi}-\omega)} < \frac{e^{-i\omega t}}{\omega}\Big|_0^T \uparrow^{\infty}$$

This means the 2d term is very large or we can call it the resonance term.

And now we neglect the 1st non-resonant term.

This approximation is called $\boxed{\text{the rotating wave APPROXIMATION.}}$

This approximation is used in the NMR and laser theories.

NB!! However, for the <u>EMMISION</u> process this consideration <u>is OPPOSITE</u>, i.e. the 1st term dominates.

→ So lets consider emission.

By comparing the values in $\rho(\omega)$ we can get:

$$\boxed{B = C \text{ and } \frac{A}{B} = \frac{\hbar\omega^3}{\pi^2 c^3}}$$

This is nice but lets try the same exercise from the time-dependent perturbation point of view: lets approximate the effect of the external field by $E(t) = \hat{e}\, \mathcal{E}_0 \cos \omega t$ $\quad \hat{e}$ is the polarization of light.

We swith the light on at $t = T$.
Then the interaction of the external field with an electron: $\quad H^{(1)}(t, \vec{r}) = q\, \vec{\mathcal{E}} \cdot \vec{r} = q\, \mathcal{E}_0 (\hat{e} \cdot \vec{r}) \cos \omega t$

$H^{(0)}$ is the unpertutbed hamiltonian with ϕ_n and E_n. After we turn on the laser:

$$\Psi(\vec{r}, t) = \sum \underbrace{a_n(t)\, e^{-i\omega_n t}}_{\text{time evolution is here}} \phi_n(r)$$ we know those

In the 1^{st} order we can write down the evolution of $\dot{a}_n(t)$ as:

$$i\hbar\, \dot{a}_f = \sum_n a_n(t)\, H^{(1)}_{fn}(t)\, e^{i\omega_{fn} t}$$

where $H^{(1)}_{fn} = \int \phi_f^* H^{(1)} \phi_n \, dr = q\, \mathcal{E}_0\, \hat{e} \cdot \underbrace{\tfrac{1}{2}(e^{i\omega t} + e^{-i\omega t})}_{= \cos \omega t} \cdot$

$\int dr\, \phi_f^* \vec{r}\, \phi_n \, d\vec{r}$. Lets introduce new

NB! | variables: $D_{fn} \equiv \underbrace{q \int \phi_f^* \vec{r}\, \phi_n \, dr}_{\text{dipole matrix element}} \equiv \rho_{fn}(\omega)$ and $\bar{D}_{fn} = \hat{e} \cdot D_{fn}$

We rewrite our equation for $\dot{a}_f(t)$ as:

$$i\hbar\, \dot{a}_f = \frac{1}{2} \mathcal{E}_0 \sum_n \bar{D}_{fn}\, a_n(t) \left[e^{i(\omega_{fn} + \omega)t} + e^{i(\omega_{fn} - \omega)t} \right]$$

we assume that at $t=0$ the system is in the well defined state ϕ_i and $a_i(0) = 1$ $\quad a_n = 0$ if $n \neq i$

Let's assume that at time $t=0$ the system is in the state 2; $\omega_{21} = (E_2 - E_1)/\hbar$.

$$a_2(t) = -i \frac{\mathcal{E}_0}{2\hbar} \bar{D}_{21} \frac{e^{i(\omega_{21}-\omega)t}}{(\omega_{21}-\omega)} \Rightarrow$$

$$P_{21} = |a_2|^2 = \frac{\mathcal{E}_0^2}{4\hbar^2} \frac{|\bar{D}_{21}|^2}{(\omega_{21}-\omega)^2} \sin^2\left((\omega_{21}-\omega)t/2\right)$$

To make the case more specific; let's assume that we are dealing with H_2 atoms:

then $\bar{D}_{21} = \langle 2 | D_z | 1 \rangle =$

here for simplicity assume the light is polarized along $\vec{z}$

$$= \langle n, \ell, m_\ell | \hat{z} | 1, 0, 0 \rangle = \iiint_V d\bar{r}\, \psi^*_{nlm}(r) \hat{z}\, \psi_{100}(r)$$

In spherical coordinates $z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}\, Y_\ell^0(\theta,\varphi)$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, Y_\ell^{*m_\ell}(\theta,\varphi) \left[\sqrt{\frac{4\pi}{3}} Y_1^0(\theta,\varphi)\right]\left(\frac{1}{\sqrt{4\pi}}\right) =$$

$$= \frac{1}{\sqrt{3}} \delta_{\ell,1} \delta_{m,0}$$

Notice if $\bar{D}_z = 0$ then the transition is $= 0$ so for z-polarized light hydrogen can make the transition to the states with $\ell = 1$ and $m_\ell = 0$.

NB! More generally the atom can make an electric-dipole transition from $|n\rangle \to |m\rangle$ if

dipole SELECTION RULES

$$\boxed{\begin{aligned} &\ell_2 - \ell_1 = \Delta l = \pm 1 \text{ and} \\ &m_{\ell_2} - m_{\ell_1} = \Delta m_\ell = 0 \text{ or } \pm 1 \end{aligned}}$$

Practically all spectroscopic and neutron scattering probes can "only" excite a system based on the dipole selection rules.

So if you want to study quadrupole, and multipole excitations, try some probes which break the dipole selection rules.