More on Time Dependent PT and Selection Rules

Let's look at a system we've studied before — an charged particle in an SHO potential with an electric field applied. But this time we'll consider an oscillating field so that

Pulse of frequency $\sim\Omega$

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2}_{H_0} - \underbrace{q\mathcal{E}\, x \cos\Omega t\, e^{-t^2/\tau^2}}_{h(x,t)}$$

At $t=-\infty$ the particle will just be in an eigenstate of H_0 and as usual we'll suppose that it's in the ground state for simplicity. Thus

$$a_0(t=-\infty) = 1$$

$$a_n(t=-\infty) = 0 \qquad n>0$$

Making the approximation that $a_n(t)$ remains small (ie doing first order PT) we have

$$i\hbar \frac{da_n}{dt} = e^{-i(E_0-E_n)t/\hbar}\, e^{-t^2/\tau^2} \cos\Omega t$$
$$\times -q\mathcal{E} \langle n|x|0\rangle$$

integrating

$$a_n(t) = \frac{-q\mathcal{E}}{2i\hbar}\langle n|x|0\rangle \int_{-\infty}^{t} dt\, \left(e^{i\Omega t} + e^{-i\Omega t}\right) e^{+in\omega t - \frac{t^2}{\tau^2}}$$

We cannot do this integral in terms of elementary functions but we can answer the question "what is the amplitude at $t = +\infty$". Then

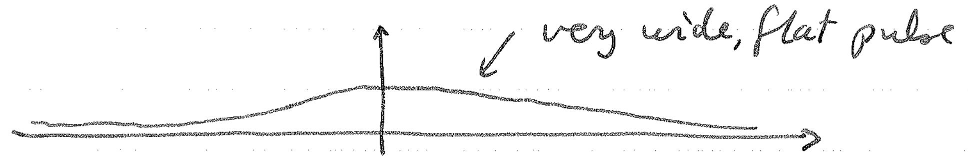
$$a_n(t) = -\frac{q\mathcal{E}}{2i\hbar} \langle n|x|0\rangle \int_{-\infty}^{\infty} dt \; e^{-t^2/\tau^2 + it(n\omega+\Omega)} + e^{-t^2/\tau^2 + it(n\omega-\Omega)}$$

The gaussian integrals can be done (complete the square) and we get

$$a_n(\infty) = \frac{-q\mathcal{E}}{2i\hbar} \langle n|x|0\rangle \, \tau\sqrt{\pi} \; \times \left\{ e^{-(n\omega+\Omega)^2\tau^2/4} + e^{-(n\omega-\Omega)^2\tau^2/4} \right\}$$

This expression tells us many things:

1. Set $\Omega = 0$. Then as $\tau \to \infty$



$$a_n(\infty) \to 0$$

ie no transitions are induced. This is exactly what we expect in the adiabatic approximation.

2. If $\langle n|x|0\rangle = 0$

then $a_n(\infty) = 0$. In fact we know that this matrix element is non-zero only for $n=1$. This is an example of a <u>selection rule</u>. Particular perturbation can only induce transitions between certain states.

3. If $\Omega = n\omega$

then $$a_n(\infty) = -\frac{q\,\mathcal{E}}{2i\hbar}\langle n|x|0\rangle\,\tau\sqrt{\pi}$$

and is not suppressed at large τ. This is the resonance effect we have met before; when

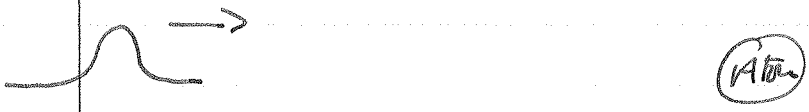
$$\hbar\Omega = E_1 - E_0$$

transitions are induced easily. Of course we can't actually take $\tau \to \infty$ in this formula because ~~[illegible]~~ $a_n(t)$ would get too big and invalidate our approximation.

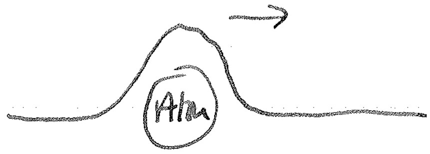
B. Hydrogen atom + the EM field

Now we'll go one step further and look at what happens when a pulse of e.m. radiation hits an atom in the ground state

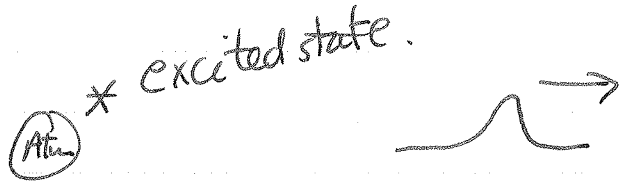
$t = -\infty$



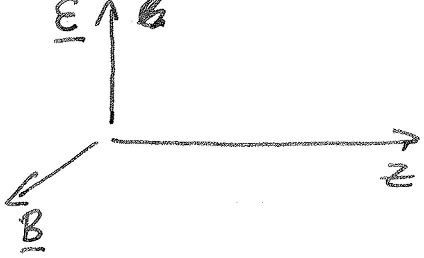
$t \simeq 0$



$t = +\infty$



You know that radiation has a $\underline{E}$ and $\underline{B}$ field perpendicular to the direction of propagation (which we'll take to be along the z-axis)



A pure plane wave would have

$$\underline{E} = \underline{\varepsilon} \quad \cos\omega\left(\frac{z}{c} - t\right)$$

constant polarization vector

with $\underline{\varepsilon}$ lying in the x-y plane. We want a wavepacket so choose

$$\underline{E} = \frac{\tau}{\sqrt{\pi}} \int_{-\infty}^{\infty} d\omega \, e^{-(\omega-\omega_0)^2 \tau^2} \, \underline{\varepsilon} \cos\omega\left(\frac{z}{c} - t\right)$$

$$= \underline{\varepsilon} \quad \cos\omega_0\left(\frac{z}{c} - t\right) e^{-\left(\frac{z}{c} - t\right)^2 / 4\tau^2}$$

This describes a wavepacket which passes the origin $z = 0$, where an atom is, at $t = 0$, and has duration $\sim \tau$

The $\underline{E}$ field interacts with the electron in the atom through the Hamiltonian

$$h = + e \, \underline{E}(\underline{r}, t) \cdot \underline{r}$$

provided the wavelength of the light $\gg$ atomic size which typically it is. So now, just copying what we've done before

$$i\hbar \frac{da_n}{dt} = \langle n | e \, \underline{\varepsilon} \cdot \underline{r} \qquad \times$$

$$\frac{\tau}{\sqrt{\pi}} \int_{-\infty}^{\infty} d\omega \, e^{-(\omega-\omega_0)^2\tau^2} \times e^{-i(E_0-E_n)t/\hbar} \cos\omega\left(\frac{z}{c}-t\right)|0\rangle$$

so

$$i\hbar\, a_n(+\infty) = \langle n| e\, \underline{\varepsilon}.\underline{r} \quad \times$$

$$\frac{1}{2}\frac{\tau}{\sqrt{\pi}} \int_{-\infty}^{\infty} d\omega \, e^{-(\omega-\omega_0)^2\tau^2} \int_{-\infty}^{\infty} dt \; e^{-i(E_0-E_n)t/\hbar} \times\left(e^{i\omega z/c} e^{-i\omega t} + e^{-i\omega z/c} e^{i\omega t}\right)|0\rangle$$

$$= \langle n| e\, \underline{\varepsilon}.\underline{r}|0\rangle \times \frac{\tau}{2\sqrt{\pi}} \int_{-\infty}^{\infty} d\omega \, e^{-(\omega-\omega_0)^2\tau^2} \times 2\pi \left\{ e^{\frac{i\omega z}{c}}\,\delta\!\left(\frac{E_0-E_n}{\hbar}+\omega\right) + e^{-\frac{i\omega z}{c}}\,\delta\!\left(\frac{E_0-E_n}{\hbar}-\omega\right)\right\}|0\rangle$$

amount of frequency ω in wavepacket

energy conserving δ-functions.

$$= \langle n| e\, \underline{\varepsilon}.\underline{r}\, e^{\frac{i\omega z}{c}}|0\rangle\, \tau \sqrt{\pi}\, e^{-(\omega-\omega_0)^2\tau^2}$$

with $\omega = \dfrac{E_n-E_0}{\hbar}$

+ (similar term with $\omega = -\dfrac{E_n-E_0}{\hbar}$, which is suppressed for large τ – it gives no $n \to 0$ transition)

In optical transitions $\lambda \sim 10^3 \times$ atomic size so the $e^{i\frac{\omega z}{c}} - e^{i z/\lambda}$

factor is going to be $\sim e^{i 10^{-3}}$

as the wavefunctions are dropping off exponentially fast for $r >$ atomic size. So the selection rules are determined by the matrix element

$$\langle n | e \underline{\varepsilon} . \underline{r} | 0 \rangle$$

where $\underline{\varepsilon}$ lives in the x-y plane for radiation in the z-dirn.

<u>Examples:</u>

We'll calculate a couple of matrix elements for x-polarized radiation.

Let's look at the "selection rules" a little.

Note that i) $n=1, l=0 \longrightarrow n=2, l=0$ is forbidden

ii) $n=1, l=0 \longrightarrow n=2, l=1$ is allowed

In the second process the angular momentum of our H atom at $t=-\infty$ is 0 whereas at $t=+\infty$ it is 1. How can this be?

1. Perhaps conservation of angular momentum is violated. Not a nice prospect.

2. If angular momentum is conserved, the extra ang. mom. of the atom must have come from somewhere. <u>It can only have come from the e.m. field.</u> We conclude that the absorbed photon must have angular momentum (spin) 1 !!
This is correct — photons have spin 1.

So we have showed that a photon incident on ~~the~~ a hydrogen atom in its ground state can excite the electron, provided that

$$\hbar\omega = E_m - E_0, \quad \text{selection rules satisfied.}$$

Now, if you look carefully at the mathematics we have gone through you'll see that the opposite process can occur as well. A photon of energy $\hbar\omega$ incident on the atom in its excited state can cause the atom to decay to its ground state and emit another photon of energy $\hbar\omega$. This is called stimulated emission of radiation; it is crucial to the operation of lasers.

In addition, of course, an atom in an excited state can decay by emission of a photon to a state of lower energy. This is called spontaneous emission, and we don't have time to go into the details now.

a) Transition from ground state to $n=2,\ \ell=0$ state

$$M = e\mathcal{E}\int_0^\infty r^2 dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta$$

$$\times\ r\sin\theta\cos\phi \times \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

$$\times \frac{1}{4\sqrt{2\pi a_0^3}}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$$

$= 0$ because of the ϕ integral

This transition is said to be "forbidden".

b) to $n=2,\ \ell=1,\ m=\pm1$ state

$$M = e\mathcal{E}\int_0^\infty r^2 dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta$$

$$\times\ r\sin\theta\cos\phi \times \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

$$\times \frac{1}{8\sqrt{\pi a_0^3}}\ \frac{r}{a_0}\ e^{-r/2a_0}\sin\theta\,(\cos\phi \pm i\sin\phi)$$

$$= e\mathcal{E}\cdot \underset{\phi}{\pi}\cdot \underset{\theta}{\frac{4}{3}}\cdot \frac{1}{8\pi a_0^3}$$

$$\times \int_0^\infty dr\ r^4\, e^{-3r/2a_0}$$

$$= e\mathcal{E}\ \frac{4\pi}{3}\cdot\frac{1}{8\pi a_0^3}\left(\frac{2a_0}{3}\right)^5 4!$$

This transition is "allowed". We have discovered <u>selection rules</u> — you will learn lots more about them in the months to come. For now, why don't you work out what happens for $n=2,\ \ell=1,\ m=0$?

Transition to a continuum; Fermi's Golden Rule

Sometimes there is not just one possible final state of a given energy. For example consider an isolated atom in an excited state. eg

Hydrogen $n=2$, $l=1$

$*$

This atom will eventually decay to the ground state by emitting a photon;

Hydrogen
$n=1$, $l=0$ g.s

photon

energy $E_2 - E_1$

Now, although the energy of the photon is fixed by the energy difference between the two atomic states the direction in which it is emitted is not. Thus to get the total decay ~~rate~~ probability we need to sum over all the possible final states.

We derived a formula for the transition amplitude to a single state m from 0; for going from m to 0 we'd get

$$a_m(\infty) = \frac{-i}{\hbar} \tau \sqrt{\pi}\, e^{-\left(\frac{\Delta E}{\hbar} - \omega_0\right)^2 \tau^2} \langle 0 | e\, \underline{\varepsilon} . \underline{r} | m \rangle$$

note that this amplitude is for ~~incident radiation~~ a disturbance (ie perturbation) of frequency ω_0 and duration τ. You should have noticed by now that we always get an expression which looks something like this no matter what the details of the process. So to decay spontaneously and create a ~~pho~~ wavepacket of duration τ and central frequency ω_0 we expect to find

$$a_m(\infty) = \frac{-i}{\hbar} \tau \times \text{const} \times e^{-\left(\Delta E/\hbar - \omega_0\right)^2 \tau^2} \langle 0 | e\, \underline{\varepsilon} . \underline{r} | m \rangle$$

without doing a full calculation with a quantized radiation field we cannot determine this constant.

In fact this is essentially what we get from a full calculation.

So the probability for transition to this state is

$$|a_m(\infty)|^2$$

Now, if our system can actually make a transition to many different states then the total probability of decay is

$$P(\tau) = \sum_m |a_m(\infty)|^2$$

where we've emphasised that this probability depends on τ – remember τ is the duration of the disturbance

In our decay example the possible final states are labelled not by a discrete variable but by an continuous variable so really we should write

$$P(\tau) = \int dN \, |a_N(\infty)|^2$$

Let $E = \hbar\omega_0$ be the energy of the photon in the final state; then the number of photon states in a given energy range depends on the energy ie N is a function of E so

$$P(\tau) = \int dE \, \frac{dN}{dE} \, |a_N(\infty)|^2 .$$

$$= \frac{\text{const}}{\hbar^2} \tau^2 \, |\langle 0| e \underline{\varepsilon} . \underline{r} |m\rangle|^2$$

$$\times \int \hbar \, d\omega_0 \, \frac{dN}{dE} \, e^{-2(\Delta E/\hbar - \omega_0)^2 \tau^2}$$

Compared to the exponential $\frac{dN}{dE}$ turns out to be a slowly varying function of E so we can approximate it by its value at $E = \Delta E = E_m - E_0$ (ie where $\omega_0 = \frac{E_m - E_0}{\hbar}$ and there is no exponential suppression). Now we can do the ω_0 integral to get

$$P(\tau) = \text{const} \, \frac{\tau}{\hbar} \, \left.\frac{dN}{dE}\right|_{E = E_m - E_0} |\langle 0| e \underline{\varepsilon} . \underline{r} |m\rangle|^2$$

"density of states" – we'll calculate it next

Finally we observe that this decay probability is proportional to the duration of the perturbation; it gives us a decay probability per unit time

$$\frac{dP(t)}{dt} = \frac{\text{const}}{\hbar} \left.\frac{dN}{dE}\right|_{E=E_m-E_0} \left|\langle 0|e\,\underline{\varepsilon}.\underline{r}|m\rangle\right|^2.$$

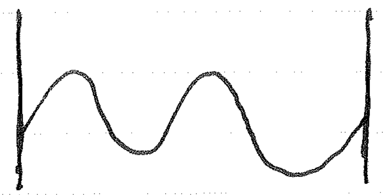
This is <u>Fermi's Golden Rule</u>; if we'd done it properly ~~&~~ we'd have got that the constant is 2π. The most important thing to notice from this formula at the moment is that the <u>selection</u> rules are determined by the same matrix element as for the case of excitation by the e.m. field.

Density of States for a Free Particle.

There is a problem in Set 5 on this that you must do.

Here is a different way of doing it.....

To count states we must work in a finite size system so consider a plane wave in a periodic box



$$\psi = \frac{1}{\sqrt{L}} e^{i(px - Et)/\hbar}$$

$$\psi(x+L, t) = \psi(x, t).$$

$$\therefore \quad e^{ipL/\hbar} = 1 \quad \text{so} \quad \frac{pL}{\hbar} = 2n\pi$$

n - integer.

or $$n = \frac{L}{h} p$$

Suppose n varies from n_0 to $n_0 + \Delta n$; the number of states is just Δn, therefore

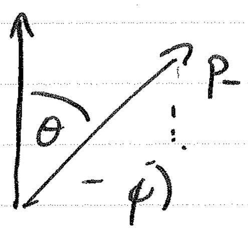
$$\Delta N = \Delta n = \frac{L}{h} \Delta p$$

In three dimensions we'd just have

$$\Delta N = \Delta n_x \, \Delta n_y \, \Delta n_z = \frac{L^3}{h^3} \Delta p_x \, \Delta p_y \, \Delta p_z$$

$$= \frac{V}{h^3} \Delta p_x \, \Delta p_y \, \Delta p_z$$

If we're looking for the number of states with momentum $p = \sqrt{p_x^2 + p_y^2 + p_z^2}$ between p and $p + \Delta p$ its best to work in spherical polar coordinates



$$\Delta N = \frac{V}{h^3} \quad p^2 \Delta p \, \Delta\phi \, \sin\theta \, \Delta\theta$$

Integrate over the angles

$$\Delta N = \frac{V}{h^3} \quad 4\pi p^2 \Delta p$$

but $\quad E = p^2/2m \qquad p = \sqrt{2mE}.$

$$\therefore \; \Delta p = \frac{\sqrt{2m}}{2} \frac{\Delta E}{E^{1/2}}.$$

so $$\Delta N = \frac{V}{h^3} \, 4\pi \, 2mE \, \frac{\sqrt{2m}}{2} \frac{\Delta E}{E^{1/2}}.$$

or $$\frac{\Delta N}{\Delta E} = \frac{4\pi V}{h^3} \, m\sqrt{2m} \, E^{1/2}$$