Learning Outcomes

You'll be able to:

- Identify when to apply time-dependent perturbation theory
- Write down time-dependence of coefficients for two-state systems
- Iteratively solve time-dependence of coefficients for two-state systems
- Define the transition probability and transition rate
- Determine the transition probability for a sinusoidal perturbation
- Describe, qualitatively, absorption and stimulated and spontaneous emission
- Calculate the transition rate for stimulated and spontaneous emission
- Write down Fermi's Golden Rule
- Apply your knowledge to simple models of atomic transitions

Time-dependent perturbation theory

Chapter 11

Everything we've done so far with perturbation theory has fallen under the domain of "quantum statics" - we have only considered time independent (static) potentials.

Time independent potentials allow us to use separation of variables to solve the Schrödinger equation and the time dependence of the resulting wavefunction is carried only by the phase factor $e^{-iE_n t/\hbar}$. This ensures all probabilities (e.g. $|\Psi|^2$) and expectation values are time independent.

But, as we all know, time waits for no person (or wavefunction) and we need to account for that in quantum systems, too.

Although the full time-dependent Schrödinger equation can rarely be solved, we can solve it when the time-dependent part of the Hamiltonian is <u>small</u> relative to the time-independent part. In this situation, we can apply <u>time-dependent perturbation theory</u>. This will allow us to treat transitions between energy levels and look at emission and absorption of radiation by atoms.

↑ Think: LASERs!

Two-level systems

We start with an unperturbed system with states ψ_a, ψ_b

← G+S have dropped the superscript "0" on unperturbed states and energies.

$$\hat{H}^0 \psi_{a,b} = E_{a,b} \psi_{a,b} \qquad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$\{i,j\} = \{a,b\}$

Any state can be expressed as

$$\Psi(0) = c_a \psi_a + c_b \psi_b$$

↑ initial state at time $t = 0$

← as usual $|c_a|^2$ gives probability of measuring energy of the system to be E_a.

$\Rightarrow |c_a|^2 + |c_b|^2 = 1$

Without any perturbation, we know the time dependence is given by

$$\Psi(t) = c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar}$$

↑ state at time t

We now turn on a time-dependent perturbation $\hat{H}'(t)$

$$\Psi(t) = c_a(t) \psi_a e^{-iE_a t/\hbar} + c_b(t) \psi_b e^{-iE_b t/\hbar}$$

↑ ψ_a, ψ_b are still an orthonormal basis, so we can still express $\Psi(t)$ in terms of them

↑ we could absorb the exponential into $c_i(t)$, but G+S prefer to keep them separate to remind us of the unperturbed time dependence.

Now our challenge is to solve for $c_a(t), c_b(t)$.

↑ Do this by requiring $\Psi(t)$ satisfy the Schrödinger equation.

If $c_a(0) = 1, c_b(0) = 0$ but $c_a(t) = 0$, $c_b(t) = 1$, then we say the state underwent a transition at some time $0 < t' < t$.

We will show that the solutions are

$$\dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}\right]$$

$$\dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i(E_b - E_a)t/\hbar}\right]$$

If $H'_{aa} = H'_{bb} = 0$ then we find

$$\dot{c}_a = \frac{-i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b$$

$$\dot{c}_b = \frac{-i}{\hbar} H'_{ba} e^{+i\omega_0 t} c_a$$

$$H'_{ij} = \langle \varphi_i | \hat{H}' | \varphi_j \rangle$$

$$\omega_0 = \frac{E_b - E_a}{\hbar} \geq 0$$

To show this, we start from

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t}\Psi$$

$$\hat{H} = \hat{H}^0 + \hat{H}'(t)$$

We then plug in our solution for $\Psi(t)$

$$\Rightarrow \underbrace{c_a(\hat{H}^0\varphi_a)e^{-iE_at/\hbar}}_{(1)} + \underbrace{c_b(\hat{H}^0\varphi_b)e^{-iE_bt/\hbar}}_{(2)} + c_a(\hat{H}'\varphi_a)e^{-iE_at/\hbar} + c_b(\hat{H}'\varphi_b)e^{-iE_bt/\hbar} = i\hbar\left[\dot{c}_a\varphi_a e^{-iE_at/\hbar} + \dot{c}_b\varphi_b e^{-iE_bt/\hbar} + \underbrace{c_a\varphi_a\left(\frac{-iE_a}{\hbar}\right)e^{-iE_at/\hbar}}_{(3)} + \underbrace{c_b\varphi_b\left(\frac{-iE_b}{\hbar}\right)e^{-iE_bt/\hbar}}_{(4)}\right]$$

Let's take term (1):

$$c_a(\hat{H}^0\varphi_a)e^{-iE_at/\hbar} = c_a E_a \varphi_a e^{-iE_at/\hbar}$$

But term (3) is

$$i\hbar\, c_a \psi_a \left(\frac{-iE_a}{\hbar}\right) e^{-iE_a t/\hbar} = c_a \psi_a E_a e^{-iE_a t/\hbar}$$

So term (1) = term (3) and we can cancel them off. And similarly for terms (2) and (4). That leaves us with

$$c_a (\hat{H}'\psi_a) e^{-iE_a t/\hbar} + c_b (\hat{H}'\psi_b) e^{-iE_b t/\hbar} = i\hbar \left[\dot{c}_a \psi_a e^{-iE_a t/\hbar} + \dot{c}_b \psi_b e^{-iE_b t/\hbar}\right]$$

We want to isolate $\dot{c}_a$ (to start with), so we take the inner product with ψ_a

$$\Rightarrow c_a \langle \psi_a | \hat{H}' \psi_a \rangle e^{-iE_a t/\hbar} + c_b \langle \psi_a | \hat{H}' \psi_b \rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a \underbrace{\langle \psi_a | \psi_a \rangle}_{=1} e^{-iE_a t/\hbar} + i\hbar \dot{c}_b \underbrace{\langle \psi_a | \psi_b \rangle}_{=0} e^{-iE_b t/\hbar}$$

We rearrange this as

$$\dot{c}_a = \frac{-i}{\hbar}\left[c_a H'_{aa} e^{-iE_a t/\hbar} + c_b H'_{ab} e^{-iE_b t/\hbar}\right]$$

and multiply by $e^{iE_a t/\hbar}$ to find ← the result we wanted!

$$\dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{-i\omega_0 t}\right] \quad \square$$

If we repeat the trick, but instead take the inner product with ψ_b, we find the other equation we wanted

$$\dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i\omega_0 t}\right]$$

OK, great! Now we have our solutions - but what do we do with them? We still have to solve a differential equation! This may (or may not) be possible in general, but since we are ultimately interested in systems that have more than two states (which will not be solvable in general), let's see how perturbation theory can help us out here.

Let's assume the initial state is

$$\Psi(0) = \psi_a \quad \leftarrow \text{that is, } c_a(0) = 1,\ c_b(0) = 0 \text{ at } t = 0$$

then in the absence of a perturbation, we would have

$$\left.\begin{aligned} c_a^{(0)}(t) &= 1 \\ c_b^{(0)}(t) &= 0 \end{aligned}\right\} \text{ zeroth order solution}$$

↑ this means we're back to quantum statics (no perturbation at all!) and $\Psi(t) = \psi_a$ for all time

We now plug this into our equations

$$\dot{c}_a^{(1)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \underbrace{c_b^{(0)}}_{=0} = 0$$

$$\dot{c}_b^{(1)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \underbrace{c_a^{(0)}}_{=1} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t}$$

Here we're assuming $H'_{aa} = H'_{bb} = 0$ and H'_{ab} small.

$$\Rightarrow \left.\begin{aligned} c_a^{(1)}(t) &= 1 \\ c_b^{(1)}(t) &= -\frac{i}{\hbar}\int_0^t H'_{ba}(t')\, e^{i\omega_0 t'}\, dt' \end{aligned}\right\} \text{ first order solution}$$

We can keep going...

$$\dot{c}_a^{(2)} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b^{(1)}$$

$$= -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{i}{\hbar}\right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'$$

$$\dot{c}_b^{(2)} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a^{(1)}$$

$$\Rightarrow c_a^{(2)}(t) = 1 - \frac{i}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt'' dt'$$

$$c_b^{(2)}(t) = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} dt'$$

↖ N.B. $c_b^{(2)}(t) = c_b^{(1)}(t)$

This process can be carried on indefinitely, with each successive approximation a better estimate of the exact $c_a(t), c_b(t)$.

Note

- the n^{th} order correction has $n-1$ factors of H' in $c_b^{(n)}$
- the exact solutions $c_{a,b}(t)$ obey

$$|c_a(t)|^2 + |c_b(t)|^2 = 1$$

but the approximate solutions do not!

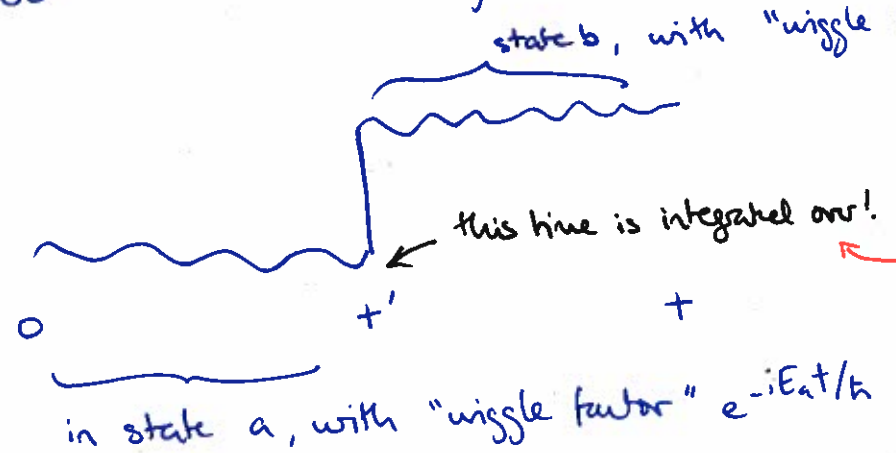
$$|c_a^{(i)}(t)|^2 + |c_b^{(i)}(t)|^2 \neq 1$$ ← the approximate solutions only satisfy this to the appropriate order in H'

If we restore the unperturbed time dependence, our first order solution is

$$c_a^{(1)}(t)\ e^{-iE_a t/\hbar} = e^{-iE_a t/\hbar}$$

$$c_b^{(1)}(t)\ e^{-iE_b t/\hbar} = -\frac{i}{\hbar} \int_0^t e^{-iE_b(t-t')/\hbar} H'_{ba}(t') e^{-iE_a t'/\hbar} dt'$$

This gives us a sort of pictorial representation (but don't read too much into it!)

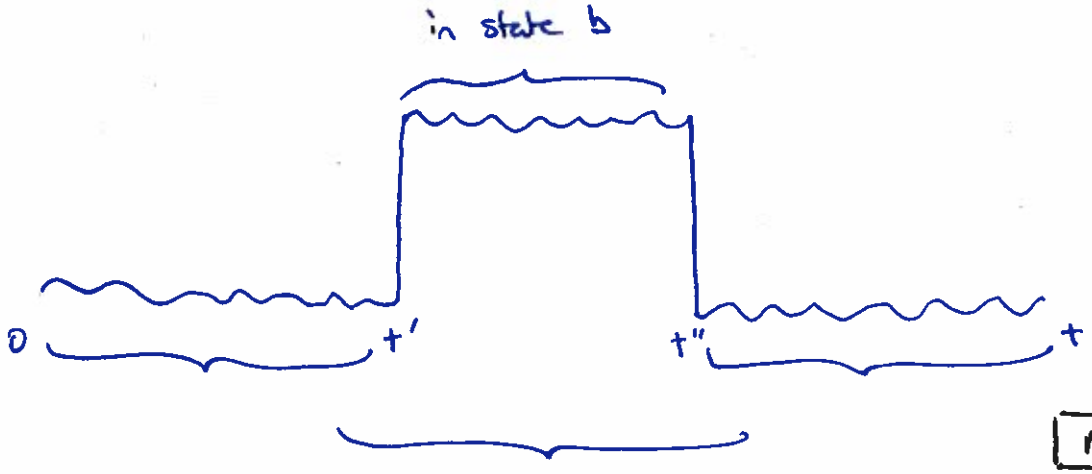


Note: there is no actual sharp transition

We can also play the same game with the second order solution

$$c_a^{(2)}(t)e^{-iE_at/\hbar} = e^{-iE_at/\hbar} + \left(\frac{-i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-iE_a(t-t')/\hbar} \times H'_{ab}(t')e^{-iE_b(t'-t'')/\hbar} H'_{ba}(t'')e^{-iE_at''/\hbar}\, dt''\, dt'$$

which leads to the "picture"



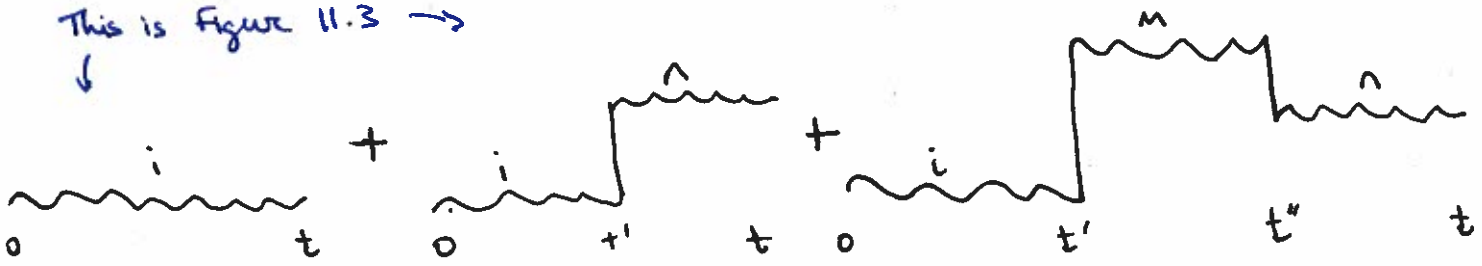
multi level system

Then the general result is

$$c_n^{(2)}(t)e^{-iE_nt/\hbar} = \delta_{ni}e^{-iE_it/\hbar} + \left(\frac{-i}{\hbar}\right)\int_0^t e^{-iE_n(t-t')/\hbar} H_{ni}(t')e^{-iE_it'/\hbar}dt'$$
$$+ \sum_m \left(\frac{-i}{\hbar}\right)^2 \int_0^t \int_0^{t'} e^{-iE_n(t-t')} H_{nm}(t')e^{-iE_m(t'-t'')/\hbar} \times H_{mi}(t'')e^{-iE_it''/\hbar}\, dt''\, dt'$$

Q. Draw the corresponding "picture" for this expression, for $\wedge \neq i$

This is Figure 11.3 →



Let's now consider the case of a specific perturbation
- a sinusoidal time dependence ← i.e. "light" (EM radiation)!

$$\hat{H}'(\bar{r},t) = V(\bar{r})\cos(\omega t)$$

$$\Rightarrow H'_{ab} = V_{ab}\cos\omega t$$

$$V_{ab} \equiv \langle \varphi_a | V(\bar{r}) | \varphi_b \rangle$$

Again we follow C+S and assume $V_{aa} = V_{bb} = 0$

At first order we have

Note, in equations 11.32 to 11.35, C+S drop the superscript "(1)".

$$c_a^{(1)}(t) = 1$$

$$c_b^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H'_{ba}(t')\, e^{i\omega_0 t'}\, dt'$$

$$= -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t')\, e^{i\omega_0 t'}\, dt'$$

$$= -\frac{iV_{ba}}{2\hbar}\int_0^t \left(e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'}\right) dt'$$

$$= -\frac{V_{ba}}{2\hbar}\left(\frac{e^{i(\omega_0+\omega)t}-1}{\omega_0+\omega} + \frac{e^{i(\omega_0-\omega)}-1}{\omega_0-\omega}\right) \qquad (*)$$

We can simplify this result if we consider $\omega \simeq \omega_0$, so that

$$\omega_0 + \omega >> |\omega_0 - \omega|$$

$\Rightarrow$ the second term in (*) will dominate.

This is a reasonable approximations, because perturbations far from ω_0 will have little chance of causing a transition

So

$$c_b(t) \simeq -\frac{V_{ba}}{2\hbar}\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left(e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}\right)$$

$$= -i\frac{V_{ba}}{\hbar}\frac{\sin\left((\omega_0-\omega)t/2\right)}{\omega_0-\omega}e^{i(\omega_0-\omega)t/2}$$

Let's introduce the <u>transition probability</u> - the probability that a particle that started out in the state ψ_a will be found, at time t, in state ψ_b. This is given by

$$\boxed{P^{(1)}_{a\to b}(t) = |c^{(1)}_b(t)|^2}$$

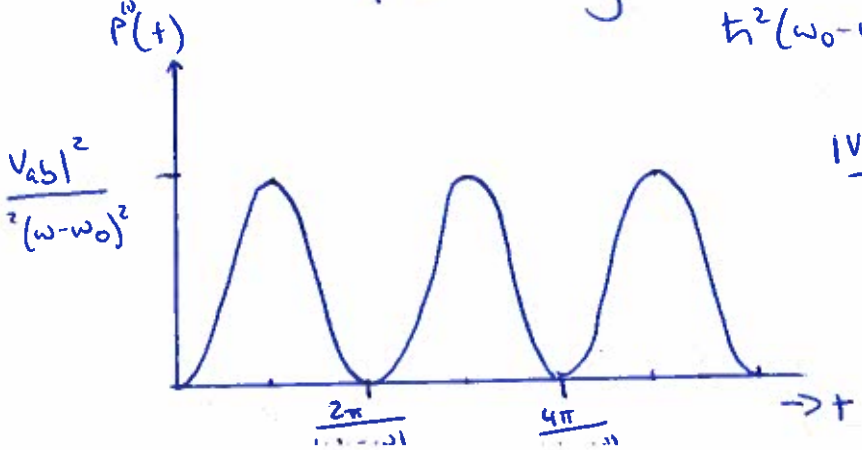
In our case it is

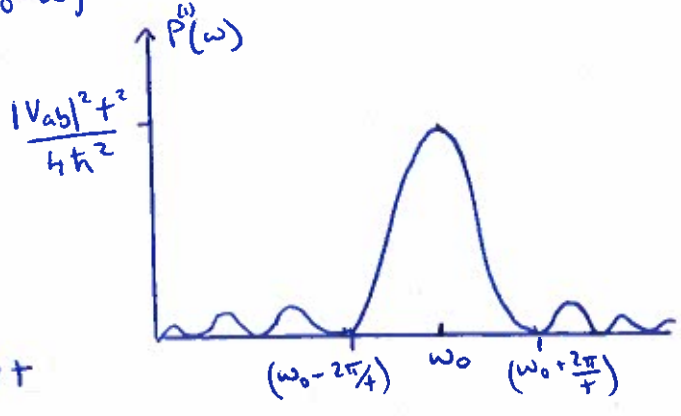
↑ sinusoidal perturbation

$$\boxed{P^{(1)}_{a\to b}(t) \simeq \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2\left[(\omega_0-\omega)t/2\right]}{(\omega_0-\omega)^2}}$$

Some comments:

- transition probability oscillates!
- at times $t_n = \frac{2n\pi}{|\omega_0-\omega|}$ the particle is <u>certain</u> to be in the lower state
- maximum probability is $\frac{|V_{ab}|^2}{\hbar^2(\omega_0-\omega)^2}$ – take to be $\ll 1$ or it is not a "perturbation"





Emission and absorption of radiation

Electromagnetic radiation – which will generically call light – consists of oscillating electric and magnetic fields.

Atoms respond primarily to the oscillating electric field, and for light in the visible spectrum, the wavelength is much longer than the size of an atom, so we can neglect the spatial variation of the electric field.

$\lambda \simeq 500\,nm$ ↑

$r \simeq 0.1\,nm$ ↑

Not true for x-rays!

In other words, incident light is a sinusoidal perturbation on an atom:

$$\bar{E}(\bar{r}) = E_0 \cos(\omega t)\,\hat{k}$$

single frequency ↙

Assuming the light is monochromatic and polarized along $\hat{z}$, we have

$$H' = -qE_0 z \cos(\omega t) \quad \leftarrow q = \text{charge of electron}$$

$$\Rightarrow H'_{ba} = -\wp E_0 \cos(\omega t)$$

$$\wp \equiv q\langle \psi_a | z | \psi_b \rangle \quad \uparrow$$

Since ψ is usually either or odd in $z \leftrightarrow -z$, the diagonal matrix elements generally vanish as then $z|\psi|^2$ is odd.

↑ We can use the tools we developed for sinusoidal oscillations (recall $P^{(1)}_{a\to b}$)!

There are three processes by which light interacts with an atom

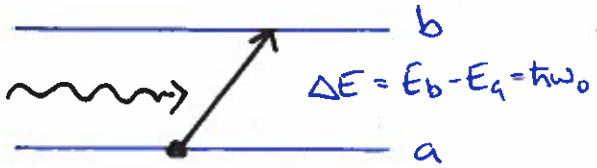
1. Absorption

- atom starts in lower state ψ_a
- incident monochromatic light is a sinusoidal perturbation, so there is a probability of transitioning to state ψ_b given by

$$P^{(1)}_{a\to b} = \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}$$

$$= \frac{|e|^2 E_0^2}{\hbar^2}\frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}$$

- we can represent this as



"absorbs a photon" ← strictly a QED concept

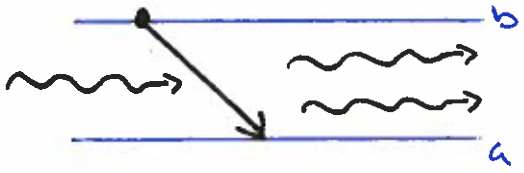
2. Stimulated emission

- atom starts in upper state ψ_b
- repeating the derivation with $c_a(0)=0$ and $c_b(0)=1$ leads to the transition probability

$$P^{(1)}_{b\to a} = \frac{|e|^2 E_0^2}{\hbar^2}\frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2}$$

↑ the <u>same</u> transition probability

- we can represent this as



$\hbar\omega_0 = \Delta E = E_b - E_a$

"emits a photon"

- by repeating this process, we can <u>amplify</u> our light, because the outgoing radication can stimulate more emission.

↖ we call this a LASER!

↗ note we need to start with most atoms in the upper state.

↗ light amplification by stimulated emission of radiation.

3. <u>Spontaneous emission</u>

- atom starts in upper state ψ_b
- <u>without</u> any incident radiation, the atom transitions to state ψ_a
- in the absence of QED this process cannot occur, but the vacuum has nonzero energy even in the ground state in QED => vacuum energy can serve to stimulate "spontaneous" emission

↑ It seems spontaneous to us as we cannot otherwise measure this vacuum or "zero point" energy.

Incoherent perturbations

So far, we've only considered monochromatic radiation. But this is generally not the case - light is frequently a mix of wavelengths

For monochromatic light, recall the transition probability

$$P^{(1)}_{b\to a}(t) = \frac{|e|^2 E_0^2}{\hbar^2} \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

We can reexpress this in terms of the energy density of an electromagnetic wave

$$u = \frac{\epsilon_0}{2} E_0^2$$

$$\Rightarrow P^{(1)}_{b\to a}(t) = \frac{2u}{\epsilon_0 \hbar^2} |e|^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

N.B. for EM fields
$u = \frac{\epsilon_0}{2} E^2 + \frac{1}{2\mu_0} B^2$
But for EM waves $\frac{B^2}{\mu_0} = \epsilon_0 E^2$
$\Rightarrow u = \epsilon_0 E^2 = \epsilon_0 E_0^2 \cos^2\omega t$
Averaging over one cycle $\langle \cos^2\omega t \rangle = 1/2$

But this is for a single value of ω. For a range of frequencies, this becomes

$$P^{(1)}_{b\to a}(t) = \frac{2}{\epsilon_0 \hbar^2} |e|^2 \int_0^\infty \underbrace{\rho(\omega)}_{\uparrow} \left\{ \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2} \right\} d\omega$$

$\uparrow$ $\rho(\omega)d\omega$ = energy density in interval $d\omega$

Since the term in { } is sharply peaked, but $\rho(\omega)$ is quite broad
$\uparrow$ Q+S call this $e(\omega)$.

so let's replace $\rho(\omega) \to \rho(\omega_0)$

$$\Rightarrow P^{(1)}_{b\to a}(t) \simeq \frac{2}{\epsilon_0 \hbar^2} |e|^2 \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2} d\omega$$

Now let $x \equiv \frac{(\omega_0-\omega)t}{2}$ and extending the lower limit of integration to $-\infty$ (which is fine, because the integrand $\simeq 0$ there), we have

$$P^{(1)}_{b\to a}(t) \simeq \frac{2|e|^2}{\epsilon_0 \hbar^2}\eta(\omega_0)\int_{-\infty}^{\infty}\frac{\sin^2 x}{\left(\frac{2x}{t}\right)^2}\frac{2}{t}dx$$

$$= \frac{|e|^2}{\epsilon_0\hbar^2}\eta(\omega_0)\,t\underbrace{\int_{-\infty}^{\infty}\frac{\sin^2 x}{x}dx}_{=\pi}$$

$$= \frac{\pi|e|^2}{\epsilon_0\hbar^2}\eta(\omega_0)\,t$$

Note that we've now "washed out" the sinusoidal variation in this probability. In fact, the <u>transition rate</u>

$$\boxed{R^{(1)}_{b\to a} \equiv \frac{d}{dt}P^{(1)}_{b\to a}(t)}$$

is now constant!

$$R^{(1)}_{b\to a} = \frac{\pi}{\epsilon_0\hbar^2}|e|^2\eta(\omega_0)$$

This is the transition rate for a wave incident along the y direction, polarised in the z direction. But what about the case where light is incident from many directions? Then, in that case, we need the average of $|\bar{e}\cdot\hat{n}|^2$, where $\bar{e} = q\langle\psi_b|\bar{r}|\psi_a\rangle$, and the average is over all polarisations and incident directions. We can always choose our axes such that

$$\bar{e}\cdot\hat{n} = e\cos\vartheta \quad\Rightarrow\quad |\bar{e}\cdot\hat{n}|^2_{ave} = \frac{1}{4\pi}\int|\bar{e}|^2\cos^2\vartheta\sin\theta\,d\theta\,d\phi$$

$\hat{n}$: direction of polarisation

$$= \frac{|\bar{e}|^2}{3}$$

This leads us to the transition rate for stimulated emission from state b to state a, under the influence of incoherent, unpolarised light incident from all directions

$$R_{b\to a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\bar{e}|^2 \eta(\omega_0)$$

N.B. $\bar{e} \equiv q\langle \psi_b | \bar{r} | \psi_a \rangle$ is called p in G+S and is a generalisation of the electric dipole moment

$\eta(\omega_0)$ is the energy density in the fields, per unit frequency, evaluated at $\omega_0 = (E_b - E_a)/\hbar$. It is called $\rho(\omega_0)$ in G+S.

Spontaneous emission

Chapter 11.3

We've been considering stimulated emission so far, so let's now look at spontaneous emission. Assume that we have N_a atoms in a lower state ψ_a and N_b in upper state N_b. Let the spontaneous emission rate be A. The stimulated emission rate is proportional to

$$\frac{\pi |\bar{e}|^2}{3\epsilon_0 \hbar^2} \eta(\omega_0) \equiv B_{ba}\eta(\omega) \Rightarrow$$ number of particles leaving upper state is $N_b B_{a}(\omega_0)$

If we assume the absorption rate is $B_{ab}(\omega_0)$ we have

$$\frac{dN_b}{dt} = \underbrace{-N_b A}_{\text{\# of atoms leaving state b because of spontaneous emission}} \underbrace{- N_b B_{ba}\eta(\omega_0)}_{\text{number of particles leaving state b because of stimulated emission}} + \underbrace{N_a B_{ab}\eta(\omega_0)}_{\text{\# of particles joining state b through (stimulated) absorption}}$$

If we assume that the atoms are in statistical equilibrium with the thermal radiation field, then the number of atoms in each state is constant $\Rightarrow \frac{dN_b}{dt} = 0$

$$\Rightarrow \rho(\omega_0) = \frac{A}{\frac{N_a}{N_b} B_{ab} - B_{ba}}$$

Statistical mechanics tells us that the number of particles with a specific energy E, at temperature T, is given by

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_B T}}{e^{-E_b/k_B T}} = e^{\hbar\omega_0/k_B T}$$

$e^{-E/k_B T}$ is the "Boltzmann factor"

$$\Rightarrow \rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_B T} B_{ab} - B_{ba}}$$

The energy density of thermal radiation is given by

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

← Blackbody radiation formula

Equating these two gives us

$$B_{ab} = B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |\bar{e}|^2$$

$$A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba} = \frac{\omega_0^3 |\bar{e}|^2}{3\pi\epsilon_0 \hbar c^3}$$

transition rate for stimulated emission = rate for absorption [we knew that already!]

rate for spontaneous emission [which we didn't know!]

Now that we have the transition rate for spontaneous emission, we can calculate the <u>lifetime</u> of the excited state.

The decay rate is given by

$$\frac{d}{dt} N_b = -A N_b \quad \Rightarrow \quad N_b(t) = N_b(0) e^{-At}$$

Then the lifetime is

$$\tau = \frac{1}{A} \qquad \leftarrow \text{for one decay mode}$$

If there are many excited states and the atoms start in a highly excited states, then there are many decay modes (or decay channels) and the rates simply add, so

$$\tau = \frac{1}{A_1 + A_2 + \ldots + A_n} \qquad \leftarrow \text{for } n \text{ decay modes}$$

Selection rules

Hidden in our discussion has been the matrix elements $\langle \psi_b | \hat{r} | \psi_a \rangle$ – in fact, calculating these is the main challenge when calculating spontaneous emission rates. Often these matrix elements are <u>zero</u>, however (see Chapter 6 for more details).

For example, for spherically symmetric Hamiltonians we can use the states ψ_{nlm}, so our matrix elements become $\langle n'l'm' | \hat{r} | nlm \rangle$

In this case, angular momentum conservation requires

$$\Delta l = l' - l = \pm 1$$
$$\Delta m = m' - m = 0 \text{ or } \pm 1$$

These "selection rules" follow just from the symmetry of the system. If they are not met then the matrix elements are zero and the transitions are called "forbidden".

Note:

- this does not mean they cannot occur, because we have assumed an electric dipole form for our electromagnetic wave – magnetic dipole and higher multipole operators are possible – it means they are not possible in this approximation and therefore their decay rates are much suppressed (magnetic transitions are much slower than electric ones)

- if $m' = m \Rightarrow \langle n'l'm'|x|nlm\rangle = \langle n'l'm'|y|nlm\rangle = 0$
  if $m' = m \pm 1 \Rightarrow \langle n'l'm'|x|nlm\rangle = \pm i\langle n'l'm'|y|nlm\rangle$
  $\langle n'l'm'|z|nlm\rangle = 0$

Fermi's Golden rule

Chapter 11.4

Our final discussion of radiation and atoms will generalise our discrete energy level systems (considered so far) to the case where there is a continuum of final state energies – this is what happens with the photoelectric effect, in which we excite an electron from a bound state (discrete) to a scattering state (continuous).

Since we can no longer assign a precise final state, we must consider a range ΔE around E_f. First we recall our expression for the transition probability

$$P_{a\to b}(t) = |c_b(t)|^2 \simeq \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}.$$

Now we integrate over the possible final state energies

(initial state i; possible final states n; "density of states")

$$P(t) = \int_{E_f-\Delta E/2}^{E_f+\Delta E/2} \frac{|V_{in}|^2}{\hbar^2} \left\{ \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2} \right\} \rho(E_n)\, dE_n$$

$$\omega_0 = \frac{E_n - E_i}{\hbar}$$

the density of states × the interval dE_n gives the number of states with energy in range E_n to $E_n + dE_n$

For short times we can expand the sine function and our probability $\propto t^2$, as it was for the discrete case.

But at long times, the sine function (divided by $(\omega_0-\omega)^2$) is strongly peaked at $E_f = E_i + \hbar\omega$ and has a width $\frac{4\pi\hbar}{t}$.

see p. 414

$$P(t) = \frac{|V_{if}|}{\hbar^2} \rho(E_f) \int_{-\infty}^{\infty} \frac{\sin^2((\omega_0-\omega)t/2)}{(\omega_0-\omega)^2} dE_n = \frac{2\pi}{\hbar} \left|\frac{V_{if}}{2}\right|^2 \rho(E_f)\, t$$

The transition rate in this case is called Fermi's Golden Rule

$$R = \frac{2\pi}{\hbar} \left|\frac{V_{if}}{2}\right|^2 \rho(E_f)$$

the transition rate is proportional to the square of the matrix element (which tells us about the dynamics) times the density of states (which tells us how many states are accessible).

We will skip section 11.5