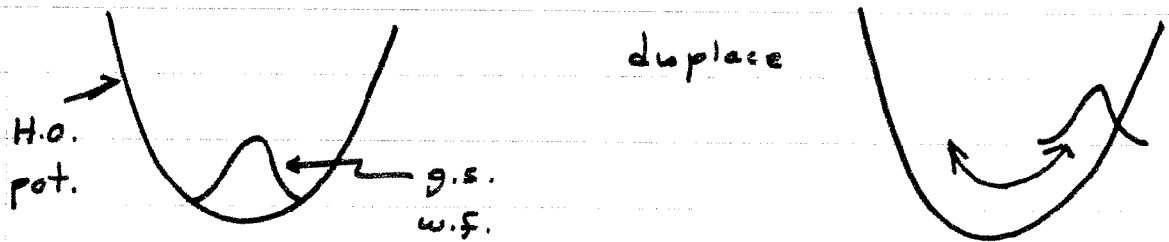


Coherent states (from last lecture)



a displaced ground-state w.f. oscillates as an undistorted wavepacket, much like a classical particle. this coherent state is

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n e^{-\frac{|\alpha|^2}{2}}}{\sqrt{n!}} |n\rangle$$

α is a complex number whose amplitude + phase are related to the amplitude + phase of oscillation

$$P_n = |\langle n|\alpha\rangle|^2 = \frac{(|\alpha|^2)^n e^{-|\alpha|^2}}{n!},$$

which is identical to the Poisson distribution

$$P_{\bar{n}}(n) = \frac{\bar{n}^n e^{-\bar{n}}}{n!} \quad \text{with } |\alpha|^2 = \bar{n}$$

①

Physics 721 Lecture #3 8 Sept. 2005

Topics: review of Fermi's "Golden Rule"
Einstein A+B coefficients
on-resonant cross section

take $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ $\mathcal{H}_0, \mathcal{H}_1$ are hermitian

assume $\mathcal{H}_0 |i\rangle = E_i |i\rangle$, the eigenvalue problem,
has 2 solutions:

$$\mathcal{H}_0 |g\rangle = E_g |g\rangle$$

E_i s are real

$$\mathcal{H}_0 |e\rangle = E_e |e\rangle$$

this is a "two-level" (really, two-state) system

$$\text{let } E_g = 0, E_e = \hbar \omega_0$$

any state of this system (atom) can be written:

$$\psi = c_g |g\rangle + c_e |e\rangle$$

now, add the perturbation:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t) \quad \text{where } \mathcal{H}_1(t) = 0 \text{ for } t < 0$$

②

the system obeys:

$$\mathcal{H}|\psi\rangle = i\hbar \frac{d}{dt} |\psi\rangle$$

we want to calculate, for $|\psi\rangle_{\text{initial}} = |g\rangle$,

$$P_{g \rightarrow e} = |\langle e | \psi(t) \rangle|^2.$$

$$\text{With } |\psi(t)\rangle = \underbrace{c_g(t)|g\rangle + c_e(t)|e\rangle}_{\downarrow}$$

$$(\mathcal{H}_0 + \mathcal{H}_1(t))|\psi\rangle = i\hbar \frac{d}{dt} [\quad]$$

$$0 + c_g(t)\mathcal{H}_1|g\rangle + \hbar\omega_0 c_e(t)|e\rangle + c_e(t)\mathcal{H}_1|e\rangle =$$

$$i\hbar \frac{d}{dt} (c_g(t)|g\rangle + c_e(t)|e\rangle)$$

multiplying by $\langle g|$ and $\langle e|$:

$$i\hbar \frac{d}{dt} c_g(t) = c_e(t) \langle g | \mathcal{H}_1 | e \rangle + 0$$

$$i\hbar \frac{d}{dt} c_e(t) = c_g(t) \langle e | \mathcal{H}_1 | g \rangle + \hbar\omega_0 c_e(t)$$

these 2 eqns. are coupled by

$$\langle g | \mathcal{H}_1 | e \rangle = \langle e | \mathcal{H}_1 | g \rangle^*$$

we assume $\langle e | \mathcal{H}_1 | e \rangle = \langle g | \mathcal{H}_1 | g \rangle = 0$ no loss of generality

③

note that whenever $\partial_1(t) = 0$

$$c_g(t) = b_g, \text{ and } c_e(t) = b_e e^{-i\omega_0 t}$$

where b_g, b_e are constants

If ∂_1 is "small" in the sense that its matrix elements are small compared to those of ∂_0 , it is convenient (but general) to write

$$c_g(t) = b_g(t); \quad c_e(t) = b_e(t) e^{-i\omega_0 t}$$

substituting these into the equations for $c_i(t)$:

$$i\hbar \frac{d}{dt} b_g(t) = b_e(t) e^{-i\omega_0 t} \langle g | \partial_1 | e \rangle$$

$$i\hbar \frac{d}{dt} b_e(t) e^{-i\omega_0 t} + \hbar\omega_0 b_e(t) e^{-i\omega_0 t} = \hbar\omega_0 b_e(t) e^{-i\omega_0 t} + b_g(t) \langle e | \partial_1 | g \rangle$$

simplifying and multiplying the 2nd eq. by $E^{i\omega_0 t}$

$$i\hbar \dot{b}_g(t) = b_e(t) e^{-i\omega_0 t} \langle g | \partial_1 | e \rangle$$

$$i\hbar \dot{b}_e(t) = b_g(t) e^{i\omega_0 t} \langle e | \partial_1 | g \rangle$$

(still exact; now make some approximations)

(4)

let $b_g(0) = 1$, $b_e(0) = 0$. let t be small enough that $|b_e(t)| \ll 1$. Then $b_g(t) \approx 1$ and we have

$$i\hbar \dot{b}_e(t) = e^{i\omega_0 t} \langle e | \mathcal{H} | g \rangle \quad \text{for small } t$$

integrating

$$b_e(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_0 t'} \langle e | \mathcal{H} | g \rangle dt'$$

Note: this is like the F.T. of the perturbation

or

$$P_{g \rightarrow e} \equiv |b_e(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_0 t'} \langle e | \mathcal{H} | g \rangle dt' \right|^2$$

Now we go to a case of particular interest in atomic physics, where $\mathcal{H}(t)$ is sinusoidal:

$$\mathcal{H}(t) = \hat{V} \sin \omega t = \frac{\hat{V}}{2i} (e^{i\omega t} - e^{-i\omega t}) \quad \omega \gg 0$$

where \hat{V} is time independent, hermitian operator with only off diagonal matrix elements

$$\langle e | \hat{V} | g \rangle = V_{eg} = V_{ge}^*$$

(5)

substituting this form of \mathcal{A}_1 into $P_{g \rightarrow e}$:

$$P_{g \rightarrow e} = \frac{|V_{eg}|^2}{4\hbar^2} \left| \int_0^t \left[e^{i(\omega_0 + \omega)t} - e^{i(\omega_0 - \omega)t} \right] dt \right|^2 =$$

$$\frac{|V_{eg}|^2}{4\hbar^2} \left[\left(\frac{e^{i(\omega_0 + \omega)t}}{i(\omega_0 + \omega)} - \frac{e^{i(\omega_0 - \omega)t}}{i(\omega_0 - \omega)} \right) \Big|_0^t \right]^2 =$$

$$\frac{|V_{eg}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_0 + \omega)t}}{i(\omega_0 + \omega)} - \frac{1 - e^{i(\omega_0 - \omega)t}}{i(\omega_0 - \omega)} \right|^2$$

if we take $|\omega_0 - \omega| \ll \omega_0, \omega_0 + \omega$
(the resonant, or rotating wave approximation)
we can neglect the first term above.

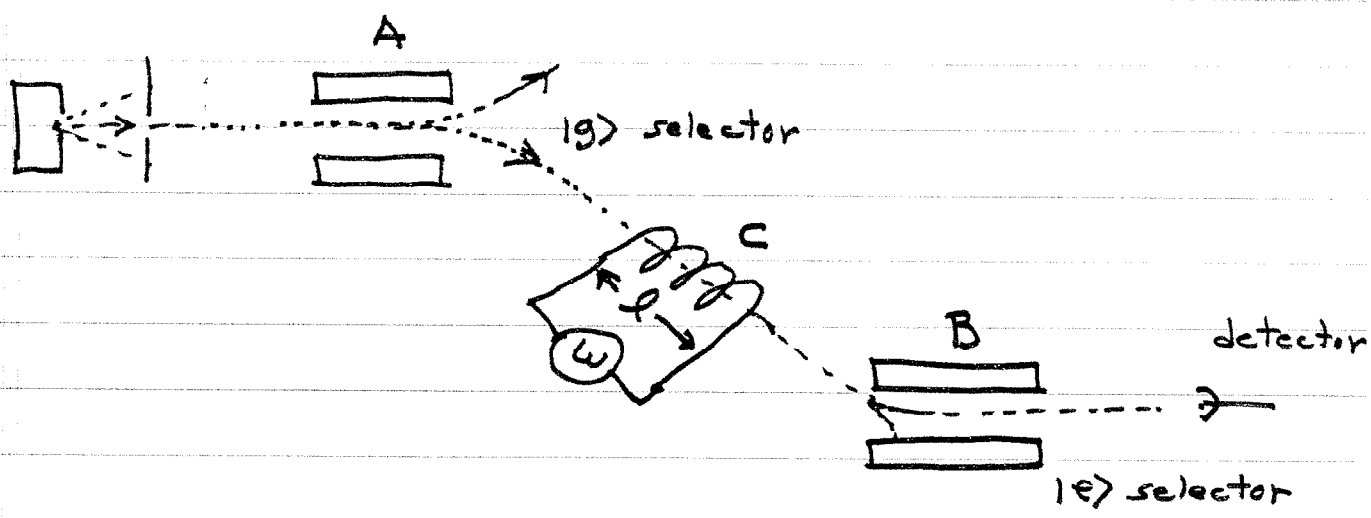
re-writing $\frac{1 - e^{i(\omega_0 - \omega)t}}{\omega_0 - \omega} = -ie^{i(\omega_0 - \omega)t/2} \frac{\sin(\omega_0 - \omega)t/2}{(\omega_0 - \omega)/2}$

we have:

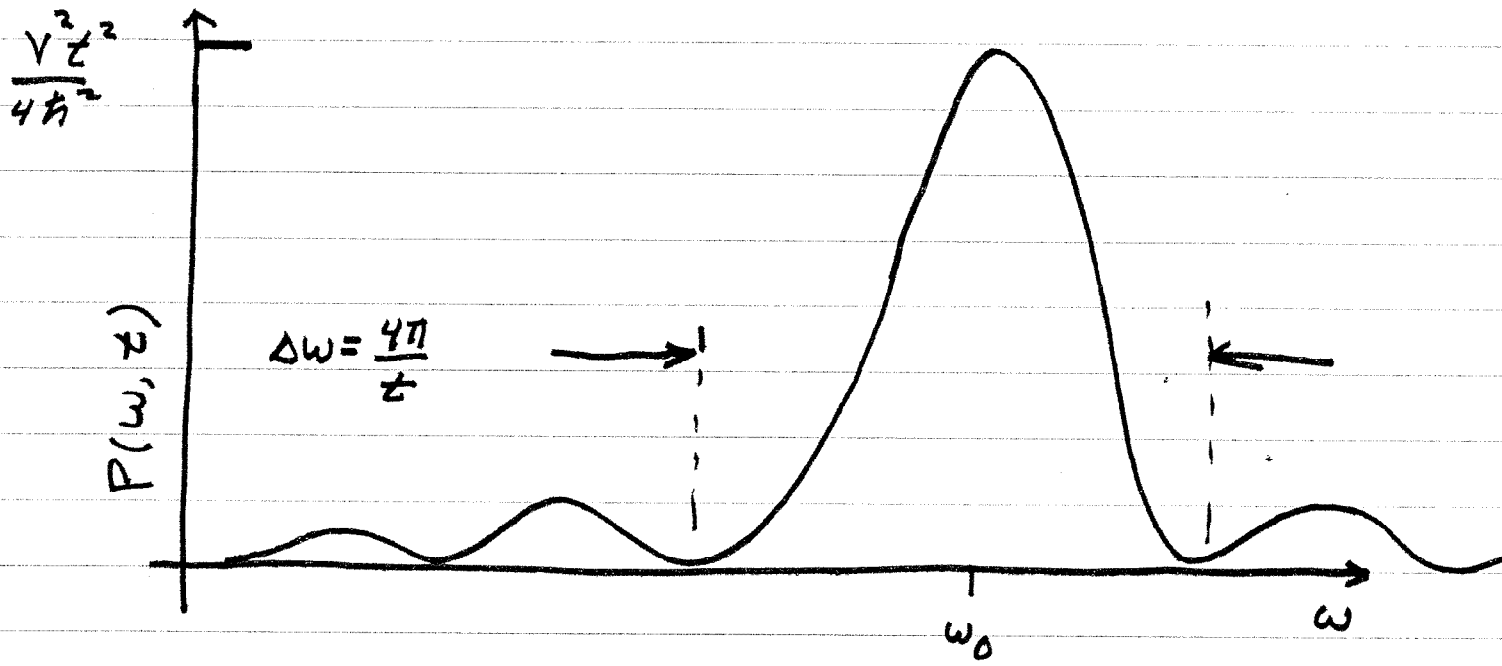
$$P_{g \rightarrow e}(t) = \frac{|V_{eg}|^2}{4\hbar^2} \frac{\sin^2(\omega_0 - \omega)t/2}{[(\omega_0 - \omega)/2]^2}$$

6

This is called the Rabi resonance formula
(I.I. Rabi invented magnetic resonance
for atomic beams, Columbia University)



interaction time $t = l/v$



width goes like $1/t$, as in $\Delta E \Delta t \sim \hbar$

as $t \rightarrow \infty$, $\Delta\omega \rightarrow 0$, (but with $\frac{V^2 t^2}{4\hbar^2} \ll 1$) (7)

recall the relation:

$$\lim_{\epsilon \rightarrow 0^+} \frac{\epsilon}{\pi} \frac{\sin^2 x/\epsilon}{x^2} = \delta(x)$$

with $x = (\omega_0 - \omega)/2$ and $\epsilon = 1/\epsilon$ we have

$$\begin{aligned} \lim_{t \rightarrow \infty} \frac{\sin^2 [(\omega_0 - \omega)t/2]}{[(\omega_0 - \omega)/2]^2} &= \pi t \delta[(\omega_0 - \omega)/2] \\ &= 2\pi t \delta(\omega_0 - \omega) \end{aligned}$$

so, substituting into $P_{g \rightarrow e}(t)$ from page (5):

$$P_{g \rightarrow e}(t) = \frac{\pi}{2\hbar^2} |V_{eg}|^2 \delta(\omega_0 - \omega) t$$

that is, the probability of having made a transition grows linearly with time — it is a rate process with

$$\mathcal{R} = \frac{\pi}{2\hbar^2} |V_{eg}|^2 \delta(\omega_0 - \omega) \quad \text{Fermi's Golden Rule}$$

If we write this in terms of energy: $E = \hbar\omega$, we will have:

$$\mathcal{R} = \frac{\pi}{2\hbar} |V_{eg}|^2 \delta(E_0 - E) \quad \text{But Fermi's golden rule is often}$$

written as: $\mathcal{R} = \frac{2\pi}{\hbar} |V_{eg}|^2 \delta(E_0 - E)$ — why? If the perturbation is static ($\omega=0$) both resonant and non-resonant terms contribute, giving a factor of 2 in the matrix element, a factor of 4 in the rate. Some people define $\mathcal{R}(t) = 2\hat{V} \sin \omega t$, and the extra factor of 2 recovers the familiar, static form of F.G.R.

see Cohen-Tannoudji et al, Quant. Mech. p 1301 for a careful treatment

(8)

Discussion:

How did a process going as t^2 on resonance become a rate process going as t ?

What is the meaning of $t \rightarrow \infty$ while $\frac{|V_{eg}|^2 t^2}{4\hbar^2} \ll 1$?

note that $\frac{\sin^2(\omega_0 - \omega)t/2}{[(\omega_0 - \omega)/2]^2}$ gets higher as t^{+2} but narrower as t^{-1}

so the area goes like t .

If the perturbation is truly monochromatic - a single value of $(\omega_0 - \omega)$ - then the population grows as t^2 for short times.

But, if there is a spread of $(\omega_0 - \omega)$, and if we can think of the different $(\omega_0 - \omega)$ components contributing incoherently (with random phases) to the transition probability, we will need to sum (integrate) over all $(\omega_0 - \omega)$.

If the breadth of $P_{g \rightarrow e}(\omega, t)$ is wider than the spread of $(\omega_0 - \omega)$, then the integral gives as t and it is a rate!

9

The spread in $(\omega_0 - \omega)$ can come from a spread in ω (broad-band source) or in ω_0 (excited state not a true eigenstate)

If the excitation time is longer than $1/\Delta\omega$ and if during $1/\Delta\omega$ the excitation probability is low, we have a rate process

Otherwise, we may need to treat the problem coherently, which we will do later

Now, having reviewed the Q.M. approach to rate processes, we will look at Einstein's 1917 treatment of radiative processes including absorption ($|g\rangle \rightarrow |e\rangle$) and emission ($|e\rangle \rightarrow |g\rangle$) both spontaneous and stimulated.

In reviewing Fermi's G.R. we saw the rate was governed by matrix elements $V_{ge} = \langle g | \hat{V} | e \rangle$.

We shall see that ~~for~~ ~~for~~ ^{for optical}, electric dipole transitions

$\hat{V} = \vec{E} \cdot \hat{d}$ where \vec{E} is the classical electric field of the light and \hat{d} is the dipole moment operator, $e\hat{r}$.

Einstein considered a 2-level (2-state) atom and a thermal (i.e., broad-band) radiation field. For a broad excitation

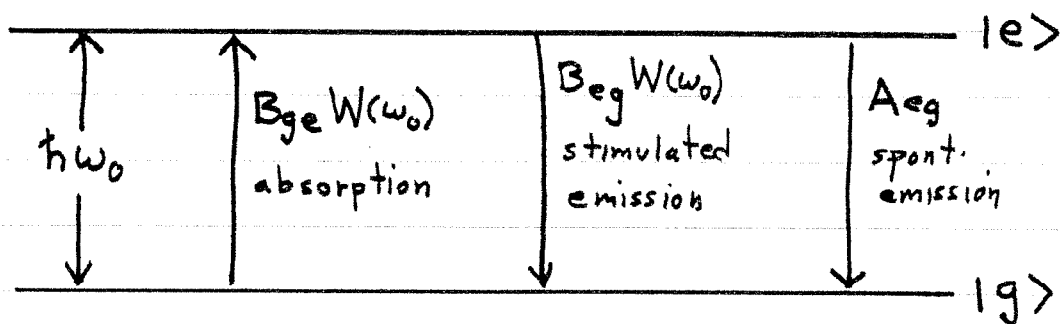
$$\begin{aligned} R_{\text{FGR}} &= \frac{\pi}{2\hbar^2} |\text{deg}|^2 \int E^2(\omega) \delta(\omega_0 - \omega) d\omega \\ &= \frac{\pi}{2\hbar^2} |\text{deg}|^2 E^2(\omega_0) \end{aligned}$$

where ~~the~~ $E^2(\omega_0)$ is the proportional to the E-M energy density (energy per unit volume, per unit frequency interval).

Without having this quantum result, Einstein wrote

$$R_{ge} = B_{ge} W(\omega) \quad \text{where } W(\omega) \text{ is the energy density per unit } dV d\omega.$$

In addition, Einstein considered spontaneous emission (emission in the absence of light) and stimulated emission - induced by the presence of light. These latter two are $e \rightarrow g$ processes.



Each of these terms: $B_{ge} W(\omega_0)$, $B_{eg} W(\omega_0)$, and A_{eg} are rates per unit population in the state from which the transition starts.

Here, we place no restriction on the populations

$$N_e + N_g = 1$$

$$\dot{N}_g = -N_g B_{ge} W(\omega_0) + N_e B_{eg} W(\omega_0) + N_e A_{eg} = -\dot{N}_e$$

in equilibrium $\dot{N}_g = \dot{N}_e = 0$

so $N_e A_{eg} = (N_g B_{ge} - N_e B_{eg}) W(\omega_0)$

$$\text{solve for } W(\omega_0) = \frac{N_e A_{eg}}{N_g B_{ge} - N_e B_{eg}} = \frac{A_{eg}}{\frac{N_g}{N_e} B_{ge} - B_{eg}}$$

Now, let us assume that $W(\omega_0)$ is the thermal or "blackbody" or Planck distribution.

Then, we expect the atomic level populations to be in thermal equilibrium, according to the Boltzmann distribution:

$$\frac{N_g}{N_e} = e^{\hbar\omega_0/kT}, \quad \text{so}$$

$$W_{\text{thermal}}(\omega_0) = \frac{A_{eg}}{(e^{\hbar\omega_0/kT})B_{ge} - B_{eg}}$$

But, we know the Planck distribution to be:

$$W_{\text{Planck}}(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$

equating $W_{\text{thermal}}(\omega_0) = W_{\text{Planck}}(\omega_0)$:

$$\frac{A_{eg}}{e^{\hbar\omega_0/kT} B_{ge} - B_{eg}} = \frac{\hbar\omega^3/\pi^2 c^3}{e^{\hbar\omega_0/kT} - 1}$$

This will be true only if: $B_{eg} = B_{ge}$ and

$$A_{eg} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{eg}$$

(13)

Discussion:

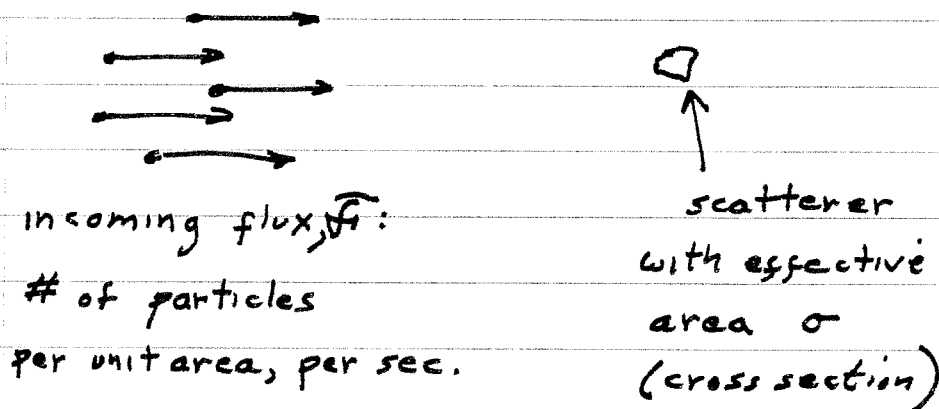
- We expected $B_{eg} = B_{ge}$ because Fermi's golden rule would work either direction and $|V_{ag}| = |V_{ge}|$ - but Einstein deduced this from statistical thermodynamics.
- We will calculate A_{eg}/B_{eg} from Q.M., but Einstein got it from thermal physics.
- Stimulated emission was unknown before Einstein; thermodynamics demands it; it is very important
- Why is there spontaneous emission? Einstein knew it happened, but without field quantization it appears not to exist.

Note: • many derivations of Einstein $A+B$ coefficients include degeneracy factors for ground and excited ~~the~~ levels - a common situation, but one we have ignored.

- the derivation depends on very little. It does not depend on the dipole approx, e.g.

Resonant Absorption Cross-Section

From the Einstein relationship of A+B, we can determine the cross section for absorption of light by a 2-level atom.



absorption rate = $\tilde{I} \cdot \sigma$ but we also know that

rate = $B_{ge} W(\omega_0)$ by combining these, we will get σ .

\tilde{I} = number of photons / area-seconds
(we will assume monochromatic at ω_0)

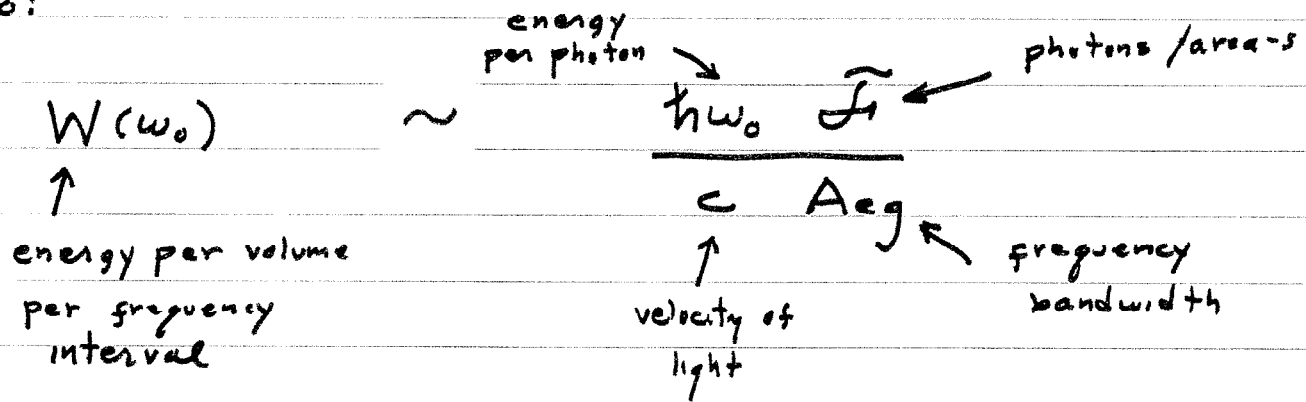
$W(\omega_0)$ = energy / volume - frequency interval
(assumed broadband)

we need to convert \tilde{I} into a $W(\omega_0)$.

A major difficulty is converting a monochromatic, beam-like flux to a broad-band isotropic thermal-like field as in Einstein's treatment.

Note that for a 2-state system with spontaneous emission from $|e\rangle \rightarrow |g\rangle$ as the only relaxation of $|e\rangle$, the width of the state $|e\rangle$ is A_{eg} . (More on this later in the course.)

So:



and $\tilde{J} \sim \frac{WcA_{eg}}{h\omega_0}$; $R_{g \rightarrow e} = \tilde{J}\sigma = B_{ge}W$

$$\sigma = \frac{BW}{\tilde{J}} = \frac{BW h\omega_0}{WA_{eg}c} = \frac{B}{A} \frac{h\omega_0}{c} = \frac{\pi^2 c^2}{\omega_0^2} = \frac{\lambda^2}{4}$$

the details will depend on polarization and angular momentum, and we can do an exact QM calculation, but σ , on resonance is dependent only on λ^2 .

(16)

Appendix: the Planck radiation formula
(following Loudon)

Consider a single mode, freq. ω , of the E-M field in thermal equilibrium. The probability that it is excited to the n^{th} excited state is:

$$P(n) = \frac{e^{-n\hbar\omega/kT}}{\sum_{m=0}^{\infty} e^{-m\hbar\omega/kT}}$$

here we set
the energy of $n=0$ to 0.

think of this as the probability of finding n photons
in the mode if you measured

changing variables to define $U = e^{-\hbar\omega/kT}$,

$$P(n) = \frac{U^n}{\sum_{m=0}^{\infty} U^m}, \quad \text{but } \sum_{m=0}^{\infty} U^m = \frac{1}{1-U}$$

$$\text{so } P(n) = U^n (1-U)$$

$$\langle n \rangle \equiv \sum_m P(m) m = (1-U) \sum_m m U^m = (1-U) U \frac{\partial}{\partial U} \sum_m U^m$$

$$\langle n \rangle = \frac{U}{1-U} = \frac{e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}} = \frac{1}{e^{\hbar\omega/kT} - 1}$$

multiplying by the mode density: $\omega^2/\pi^2 c^3$ and the energy $\hbar\omega$

$$\text{gives } W_{\text{Planck}} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$