Transition rates and rate equations

- We have been looking from of the point of view of the photons. What about the atoms?
  - Absorption of a photon induces a transition from level 1 to 2.

$$\frac{dN_1}{dt} = -N_1 W_{12} \qquad \frac{dN_2}{dt} = N_1 W_{12} = -\frac{dN_1}{dt}$$

  - The transition rate W_{12} must depend on the intensity and the incident frequency. We'll represent this by the spectral energy density.
  - For a transition at a *specific* frequency, define

$$W_{12} = B_{12}\rho\left(\nu_0\right)$$ B_{12} = Einstein "B" coefficient

  - Will generalize later for broadband light

Spontaneous emission

- An atom in an excited state can decay to another level through radiation = spontaneous emission

$$\frac{dN_2}{dt} = -N_2 A_{21} \rightarrow N_2(t) = N_2(0)\,e^{-A_{21}t}$$

Lifetime of state:

$$\tau_2 = 1/A_{21}$$

- If there are multiple destination states, **rates** add. Total decay out of level *i* :

$$\frac{dN_i}{dt} = -N_i \sum_j A_{ij}$$

Lifetime of state:

$$\tau_i = 1/\sum_j A_{ij}$$

- Note that spontaneous emission occurs w/o any incident light.

Einstein's treatment of emission and absorption

- Based on thermodynamic principles, Einstein predicted the existence of stimulated emission.
- First suppose we have *only* absorption and spontaneous emission.
- Rate equations for a two-level system (no SE):

$$\frac{dN_1}{dt} = -N_1 B_{12} \rho(\nu) + N_2 A_{21} \qquad \frac{dN_2}{dt} = +N_1 B_{12} \rho(\nu) - N_2 A_{21}$$

- For atoms in dynamic *equilibrium* with the field, there is no net change in population densities

$$0 = -N_1^{(e)} B_{12} \rho(\nu) + N_2^{(e)} A_{21} \rightarrow \frac{N_2^{(e)}}{N_1^{(e)}} = \frac{B_{12} \rho(\nu)}{A_{21}}$$

Thermal equilibrium with BB field

- An atom that is in thermal equilibrium has populations that follow the Boltzmann distribution:

$$\frac{N_2^{(e)}}{N_1^{(e)}} = \frac{g_2}{g_1} e^{-h\nu_{21}/k_B T} = \frac{B_{12}\rho(\nu)}{A_{21}} \rightarrow \rho(\nu) = \frac{A_{21}}{B_{12}} \frac{g_2}{g_1} e^{-h\nu_{21}/k_B T}$$

  – g_1, g_2 = number of degenerate states at levels 1,2
  – If there are more states available, the equilibrium population will be higher.

  – Hydrogen atom: 1s g_1 =2 2p g_2 = 6

  – Molecular rotation: number of states: 2*l*+1

Compare population ratio to blackbody

- If there is only absorption and spontaneous emission, we inferred that the spectral energy density in equilibrium must be:

$$\rho(\nu) = \frac{A_{21}}{B_{12}} \frac{g_2}{g_1} e^{-h\nu_{21}/k_B T}$$

- A field in thermal equilibrium should have the blackbody spectral energy density

$$\rho_{BB}(\nu) = 8\pi \frac{\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

  – What we have is ok in the high frequency limit, but not fully consistent with the BB curve.

Including stimulated emission

- Things make more sense if we allow for another route for transition from 2 to 1
  - Add stimulated emission to rate equations:

$$\frac{dN_1}{dt} = -N_1 B_{12}\rho(\nu) + N_2 B_{21}\rho(\nu) + N_2 A_{21} \qquad \frac{dN_2}{dt} = -\frac{dN_1}{dt}$$

  - Equilibrium: d/dt = 0

$$0 = -N_1^{(e)} B_{12}\rho(\nu) + N_2^{(e)} B_{21}\rho(\nu) + N_2^{(e)} A_{21} \rightarrow \frac{N_2^{(e)}}{N_1^{(e)}} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}$$

$$\frac{N_2^{(e)}}{N_1^{(e)}} = \frac{g_2}{g_1} e^{-h\nu_{21}/k_B T} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}$$

Equilibrium spectral energy density

- Solve for the equilibrium spectral energy density

$$\frac{N_2^{(e)}}{N_1^{(e)}} = \frac{g_2}{g_1} e^{-h\nu_{21}/k_B T} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}$$

$$\frac{g_2}{g_1} e^{-h\nu_{21}/k_B T} \left(A_{21} + B_{21}\rho(\nu)\right) = B_{12}\rho(\nu)$$

$$\rho(\nu) = \frac{A_{21}}{B_{12}\dfrac{g_1}{g_2} e^{h\nu_{21}/k_B T} - B_{21}}$$

- This looks similar in form to the blackbody relation

Einstein's relations between A and B coefficients

- If both the atoms and BB cavity are in thermal equilibrium, the ρ(v)'s that satisfy that constraint must be the same

$$\rho_{BB}(\nu) = 8\pi \frac{\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1} \qquad \rho(\nu) = \frac{A_{21}}{B_{12}\frac{g_1}{g_2} e^{h\nu_{21}/k_B T} - B_{21}}$$

  - The two forms will have the same structure if

$$\boxed{B_{12}\frac{g_1}{g_2} = B_{21}} \rightarrow \rho(\nu) = \frac{A_{21}}{B_{21}\left(e^{h\nu_{21}/k_B T} - 1\right)}$$

  - So the processes of absorption and stimulated emission are linked.
  - Finally, for $\rho_{BB}(\nu) = \rho(\nu)$

$$\boxed{A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21}}$$

Physical significance of A/B

- Dimensionally, $B_{21}\rho$ gives a rate, so in the relation between A and B,

$$\boxed{A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}}$$

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}$$ is a type of spectral energy density.

In QED, the E and B energy densities are quantized, and the quanta are the photons.

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}$$ is effectively the spectral energy density of the vacuum fluctuations of the field.

Connect intensity changes to atomic rates

- In a volume V, absorbed power is $\frac{dP_a}{dV} = W_{12} N_1 h\nu$
- For a beam with area A, $\frac{dP_a}{dV} = \frac{1}{A}\frac{dP}{dz} = -\frac{dI}{dz}$
- Intensity and energy density are related: $\rho c = I$

$$\frac{dP_a}{dV} = -\frac{dI}{dz} = B_{12}\rho N_1 h\nu \qquad \frac{dI}{dz} = -I\, N_1 \frac{B_{12} h\nu}{c} = -I\, N_1 \sigma_{12}$$

$$\boxed{\sigma_{12} = \frac{B_{12} h\nu}{c}}$$

Note that the mean free path of photons in the medium is 1/α

Optical gain

- With population in both levels 1 and 2,

$$\frac{dI}{dz} = I\left(N_2 B_{21} - N_1 B_{12}\right)\frac{h\nu_{21}}{c} \qquad B_{12}\frac{g_1}{g_2} = B_{21}$$

$$\frac{dI}{dz} = I\left(N_2 - N_1\frac{g_2}{g_1}\right)\frac{B_{21}h\nu_{21}}{c} = I\,N_{inv}\sigma_{21}$$

Inversion density

Gain cross-section

$$\boxed{I(z) = I_0 e^{gz}}$$

g: gain coefficient = N_{inv} σ_{21}
(opposite sign from absorption coefficient)

For an amplifier of length L,

$$\boxed{I(L) = I_0 e^{gL} = I_0\, G_0}$$

G_0: small signal single-pass gain