Interaction of light with atoms: Rate equations

Rate equations: connect wave propagatino to atom dynamics

Einstein A and B coefficients

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 absorption rate W must depend on the intensity and the incident frequency. We'll represent this by the spectral energy density.
- For light at a *specific* frequency, define $W_{12} = B_{12}\rho(v_0)$ 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

$$\frac{dN_2}{dt} = -N_2 A_{21} \to N_2(t) = N_2(0) e^{-A_{21}t}$$
 Lifetime of state:
 $\tau_2 = 1 / A_{21}$

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

ij

$$\frac{dN_i}{dt} = -N_i \sum_j A_{ij} \qquad \qquad \tau_i = 1 / \sum_j A_j$$

• Note this type of process is independent of 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): $\frac{dN_1}{dt} = -N_1 B_{12} \rho(v) + N_2 A_{21} \qquad \frac{dN_2}{dt} = +N_1 B_{12} \rho(v) - N_2 A_{21}$
- In equilibrium with the field, no net change in population densities

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

Thermal equilibrium with BB field

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

$$\frac{N_2^e}{N_1^e} = \frac{g_2}{g_1} e^{-hv_{21}/k_BT} = \frac{B_{12}\rho(v)}{A_{21}} \to \rho(v) = \frac{A_{21}}{B_{12}}\frac{g_2}{g_1} e^{-hv_{21}/k_BT}$$

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

$$\rho_{BB}(v) = 8\pi \frac{v^2}{c^3} \frac{hv}{e^{hv/k_BT} - 1}$$

 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:

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

- Equilibrium: d/dt = 0

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

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

Equilibrium spectral energy density

Solve for the equilibrium spectral energy density

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

$$\frac{g_2}{g_1}e^{-hv_{21}/k_BT}\left(A_{21}+B_{21}\rho(v)\right)=B_{12}\rho(v)$$

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

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

$$\rho_{BB}(v) = 8\pi \frac{v^2}{c^3} \frac{hv}{e^{hv/k_BT} - 1} \qquad \qquad \rho(v) = \frac{A_{21}}{B_{12} \frac{g_1}{g_2} e^{hv_{21}/k_BT} - B_{21}}$$

- The two forms will have the same structure if $B_{12}\frac{g_1}{g_2} = B_{21} \rightarrow \rho(v) = \frac{A_{21}}{B_{21}\left(e^{hv_{21}/k_BT} - 1\right)}$
- So the processes of absorption and stimulated emission are linked.
- Finally, for $\rho_{\scriptscriptstyle BB}(v) = \rho(v)$

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

Physical significance of A/B

• Dimensionally, $B_{21}\rho$ gives a rate, so in the relation between A and B, $8\pi hv^3$ p

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

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

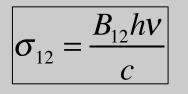
In QED, the E and B energy densities are quantized, and the quanta are the photons.

 $\rho(v) = \frac{8\pi hv^3}{c^3}$ 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 $\frac{dP_a}{dV} = W_{12}N_1hv$
- 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: $\rho c = I$

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



Compare to earlier generalization to account for lineshape of absorption, and bandwidth of source.

Note that the mean free path of photons in the medium is $1/\alpha$

Optical gain

• With population in both levels 1 and 2,

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

$$\frac{dI}{dz} = I \left(N_2 - N_1 \frac{g_2}{g_1} \right) \frac{B_{21}hv_{21}}{c} = I N_{inv} \sigma_{21}$$
Inversion Gain cross-section
$$I(z) = I_0 e^{gz}$$
g: gain coefficient = N_{inv} \sigma_{21}
(opposite sign from absorption coefficient)

For an amplifier of length L,

 $I(L) = I_0 e^{gL} = I_0 \mathbf{G}_0$

G₀: small signal single-pass gain