Modern Physics

Unit 6: Hydrogen Atom - Radiation
Lecture 6.5: Optical Absorption

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We now have a simple quantum model for how light is emitted. How is light absorbed?

(August Beer; 1825-1863)

Classically we know from measurements that:

\[ I_0(\omega) = \frac{1}{2} c \varepsilon_0 E_0^2 \left[ \frac{J/s}{m^2} \right] \]

\[ \Delta I(x) = I(x + \Delta x) - I(x) \Rightarrow \Delta I(x) = -\alpha I(x) \Delta x \]

\[ \therefore \frac{1}{I(\lambda)} \frac{dI(\lambda)}{dx} = -\alpha(\lambda) \]

\[ \text{Transmission} \equiv \frac{I}{I_0} = e^{-\alpha x} \bigg|_{x=L} \]
Typical results

http://www.pveducation.org/pvcdrom/pn-junction/absorption-coefficient
What is absorbing the light?
The absorption problem including atomic quantum states

EM radiation at frequency $\omega$

$I_0$  \hspace{2cm} I

$I(x)$  \hspace{2cm} $I(x+\Delta x)$

$\Delta x$

$\Delta I(x) = I(x+\Delta x) - I(x) \Rightarrow \Delta I(x) = -\alpha I(x) \Delta x$

$\therefore \frac{1}{I(\omega)} \frac{dI(\omega)}{dx} = -\alpha(\omega)$

What are atomic contributions to $\alpha$?

Collection of atoms: $\Delta x$

Model as a two-state system:

$E_2$

$N_2$, $g_2$

$E_1$

$N_1$, $g_1$
Einstein: Three fundamental ATOMIC Optical Processes

Spontaneous Emission Rate
probability per unit time to go from $2 \to 1$

Absorption Rate
probability per unit time to go from $1 \to 2$

Stimulated Emission Rate*
probability per unit time to go from $2 \to 1$ in the presence of another photon

*A 'new' process invented by Einstein in 1917. Required to derive Planck's blackbody law. The 'new' process needed to:

i) be proportional to the intensity of the incident radiation field and

ii) cause emission of a photon.
What to calculate?
Focus on relative populations

1. How many transitions per second to go from $2 \rightarrow 1$ by spontaneous emission?
   • proportional to number of atoms $N_2$ in state $E_2$

2. How many transitions per second to go from $1 \rightarrow 2$?
   • proportional to the energy density of the radiation field $u(f)$ - how many photons are there?
   • proportional to number of atoms $N_1$ in state $E_1$
Defining the Transition Probabilities (assume $g_1=g_2$)

I. Spontaneous Emission

![Diagram of energy levels $E_1$, $E_2$, and transitions $N_1$, $N_2$]

$$f = \frac{E_2 - E_1}{h}$$

$$\left[ \text{Rate}_{2\rightarrow1} \right]_{\text{spontaneous}} \equiv A_{21}$$

*Number of photons of energy $E_2 - E_1$ emitted per second by spontaneous emission* $= N_2 A_{21}$

*Change in $N_2$ over a time interval $dt$ due to spontaneous emission* :

$$dN_2 = -A_{21}N_2 dt$$
II. Absorption

\[ f = \frac{E_2 - E_1}{h} \]

\[ \left[ \text{Rate}_{1\rightarrow2} \right]_{\text{absorption}} = B_{12} u(f) \]

\( u(f) \) is the energy density of the radiation field at frequency \( f \)

Number of photons with energy \( E_2 - E_1 \) absorbed per second

\[ = N_1 B_{12} u(f) \]

Change in \( N_1 \) over a time interval \( dt \) due to absorption:

\[ dN_1 = -B_{12} u(f) N_1 dt \]

Units: \([u(f)] = \text{J} \cdot \text{s/m}^3\)

\([u_{\text{tot}}=u(f)df] = \text{J/m}^3\)
III. Stimulated (Induced) Emission

\[
\left[ \text{Rate}_{2 \rightarrow 1} \right]_{\text{stimulated emission}} \equiv B_{21} u(f)
\]

\(u(f)\) is the energy density of the radiation field at frequency \(f\).

Number of photons of energy \(E_2 - E_1\) emitted per second by stimulated emission = \(N_2 B_{21} u(f)\)

Change in \(N_2\) over a time interval \(dt\) due to stimulated emission:

\[
dN_2 = -B_{21} u(f) N_2 dt
\]
How does the number of electrons in the two levels change with time?

In equilibrium (describes Blackbody radiation)

\[ 1 \rightarrow 2 = 2 \rightarrow 1 \]

\[ \frac{dN_1}{dt} \bigg|_{\text{absorption}} = \frac{dN_2}{dt} \bigg|_{\text{spontaneous emission}} + \frac{dN_2}{dt} \bigg|_{\text{stimulated emission}} \]

\[ -N_1 B_{12} u(f) = -N_2 A_{21} - N_2 B_{21} u(f) \]

Solve for \( u(f) \)

\[ u(f) = \frac{A_{21}}{B_{21}} \left( \frac{1}{\left( \frac{N_1}{N_2} \frac{B_{12}}{B_{21}} - 1 \right)} \right) \]
The Boltzmann factor

For a system with a large number of atoms in thermal equilibrium at some temperature $T$, how are the atoms distributed as a function of energy?

For a system with two energy states:

$$N_1 \propto e^{-\left(\frac{E_1}{k_B T}\right)} \quad N_2 \propto e^{-\left(\frac{E_2}{k_B T}\right)}$$

$$\frac{N_1}{N_2} = e^{\left(\frac{E_2 - E_1}{k_B T}\right)} = e^{\left(\frac{hf}{k_B T}\right)}$$

$$u(f) = \frac{A_{21}}{B_{21}} \frac{1}{\left(\frac{hf}{k_B T} B_{12} - 1\right)}$$

$k_B = 1.38 \times 10^{-23}$ J/K
But......from first week of course: Planck - Blackbody Radiation

\[ u(f) \, df = \frac{8\pi f^2}{c^3} \frac{hf}{\left(e^{hf/k_B T} - 1\right)} \, df; \quad \text{units:} \left[ u(f) = \frac{Js}{m^3} \right] \]

\[ u(f) = \frac{A_{21}}{B_{21}} \left( \frac{1}{e^{hf/k_B T} B_{12} - 1} \right) \]

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evidently, by direct comparison (Einstein, 1917):

\[ B_{12} = B_{21}, \quad \frac{A_{21}}{B_{21}} = \frac{8\pi h f^3}{c^3} \]

Find one, the other two are determined
How to measure?
consider only two states in H atom
If \( N_2 \) is the number of atoms in the state \( E_2 \), how does \( N_2 \) change with time in the absence of radiation?

\[
f = \frac{E_2 - E_1}{h}
\]

\[
\frac{dN_1}{dt}_{\text{absorption}} = \frac{dN_2}{dt}_{\text{spontaneous}} + \frac{dN_2}{dt}_{\text{stimulated emission}}
\]

\[-N_1 B_{12} u(f) = -N_2 A_{21} - N_2 B_{21} u(f) \]

\[u(f) = 0\]

\[
\frac{dN_2}{dt} = -N_2 A_{21}
\]

\[N_2(t) = N_2(t = 0) e^{-A_{21} t}\]

Change in \( N_2 \) with \( t \) is fundamental quantity of interest; typically \( A_{21} \) ranges between \( 10^{-3} \) s\(^{-1}\) (microwaves) to \( 10^{15} \) s\(^{-1}\) (X-rays).
Let's say $A_{21}$ is measured to be $2 \times 10^8 \text{ s}^{-1}$ ($\tau=5 \text{ ns}$) for the $3p \rightarrow 2s$ transition in atomic H. What is $B_{21}$?

\[ f = \frac{E_2 - E_1}{\hbar} = \frac{-(3)^2 \text{-} (2)^2}{h} = \frac{-1.51 \text{ eV} + 3.4 \text{ eV}}{h} \]

\[ = \frac{1.89 \text{ eV}}{6.626 \times 10^{-34} \text{ Js}} \cdot \frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} = 4.6 \times 10^{14} \text{ Hz} \]

\[ \frac{A_{21}}{B_{21}} = \frac{8\pi \hbar f^3}{c^3} \]

\[ B_{21} = \frac{1}{8\pi \hbar} \left( \frac{c^3}{f^3} \right) A_{21} = \frac{1}{8\pi \left( 6.626 \times 10^{-34} \text{ Js} \right)} \left( \frac{3.0 \times 10^8 \text{ m} / \text{s}}{4.6 \times 10^{14} \text{ s}^{-1}} \right)^3 2 \times 10^8 \text{ s}^{-1} \]

\[ = 3.3 \times 10^{21} \text{ J}^{-1} \text{m}^3 \text{s}^{-1} \]

Can now calculate rate of stimulated emission $= B_{21} u(f)$
u(f) depends on conditions. If H gas atoms are in thermal equilibrium at some temperature T, then

$$u(f) = \frac{8\pi f^2}{c^3} \frac{hf}{(e^{hf/k_B T} - 1)}$$

Suppose the H is in a gas cloud at say T=750 K. Then

**Rate for stimulated emission =**

$$B_{21} u(f) = \frac{c^3}{8\pi h f^3} A_{21} \cdot \frac{8\pi f^2}{c^3} \frac{hf}{(e^{hf/k_B T} - 1)} = \frac{A_{21}}{(e^{hf/k_B T} - 1)}$$

$$A_{21} = 2 \times 10^8 \text{s}^{-1} \quad hf = \left(6.626 \times 10^{-34} \text{ J s}\right)\left(4.6 \times 10^{14} \text{ s}^{-1}\right) = 3.05 \times 10^{-19} \text{ J}$$

$$k_B T = \left(1.38 \times 10^{-23} \text{ J K}^{-1}\right)(750 \text{ K}) = 1.04 \times 10^{-20} \text{ J}$$

$$\frac{hf}{k_B T} = \frac{3.05 \times 10^{-19} \text{ J}}{1.04 \times 10^{-20} \text{ J}} = 29.5 \quad e^{29.5} \approx 2\pi \times 10^{12}$$

$$B_{21} u(f) = \frac{2 \times 10^8 \text{s}^{-1}}{2\pi \times 10^{12}} = 3.2 \times 10^{-5} \text{s}^{-1}$$

**CONCLUSION:**
Rate of spontaneous emission is $2 \times 10^8 / \text{s}$
Rate of stimulated emission at 750 K is $3 \times 10^{-5} / \text{s}$
Up next: Allowed Transitions, Selection Rules and Lasers