Two ways of emission

(a) Absorption

(b) Spontaneous emission

(c) Stimulated emission

Before

\( h \nu \rightarrow E_x \)

\( E_0 \)

After

\( E_x \)

None

\( E_0 \)

\( h \nu \rightarrow E_0 \)

\( h \nu \rightarrow E_0 \)

Radiation

Matter

Matter

Radiation
Light-matter interaction

- Basic equation: Schroedinger equation:
  \[ \psi(x, t) = -\frac{i\hbar}{\hbar^2} \nabla^2 + V(x) \psi(x, t) = -i\hbar \frac{\partial \psi(x, t)}{\partial t} \]

  Hamilton-Operator $H_0$

- Ansatz: $\psi(x, t) = \psi(x)e^{i(E/\hbar)t}$

- Light represents a perturbation to the (atomic) system

- Perturbation theory: $V = V_0 + V'(t)$ \hspace{1cm} $H = H_0 + H'(t)$

- $H'_{mn} := \int \psi_m^* H' \psi_n \, dV$ is an element of the perturbation matrix

- Represents the effect of $H'$ on the states $m$ and $n$
Golden rule of Fermi

- Harmonic oscillating perturbation potential
  \[ H_{mn}'(t) = H_{mn}'^0 \cos \omega t = \frac{1}{2} H_{mn}'^0 \left[ e^{i\omega t} + e^{-i\omega t} \right] \]

- Transition rate (or transition probability for one atom) from state i (initial) to state f (final):
  \[ W_{i,f} = \frac{|c_f(t)|^2}{t} = \frac{\pi |H_{fi}'^0|^2}{2\hbar^2} \delta(\Delta \omega). \]

- **Golden rule of Fermi**:
  - A transition is possible only if \( \omega_{perturbation} = (E_f - E_i) / \hbar \)
  - The probability for a transition to occur is \( \propto |H_{fi}'^0|^2 \)
  - The probability for a transition to occur from i \( \rightarrow \) f is EQUAL to the probability for a transition to occur from f \( \rightarrow \) i
Lineshape function

• Transition frequencies in atoms are not arbitrarily narrow
• Various mechanisms broaden the transitions
• Dirac delta function is replaced by the lineshape function:

\[ \int g(\Delta \omega) d\omega = 1 \]

• Thus the transition rate becomes

\[ W_{if} = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\Delta \omega). \]
Dipole interaction

• The light field interacts with the atom via dipole interaction

• Perturbation potential: $\mathcal{H}' = e \mathbf{E} \cdot \mathbf{x}$,

• The material specific part of $W_{if}$ is represented by the Dipole-Matrix-Element

  $$\mu := \mu_{mn} = \mu_{nm} = e \int \psi_m^* \mathbf{x} \psi_n \, dV$$

• The transition rate thus becomes

  $$W = W_{if} = W_{fi} = \frac{\pi}{6\hbar^2} \frac{E_0^2}{\mu^2} g(\Delta\omega).$$
Transition cross section

- We can not measure $E$ but only the Fluence (energy flux) or Intensity [W/cm$^2$] :

$$I = \sqrt{\varepsilon \varepsilon_0 / \mu_0 E_0^2 / 2}$$

- Thus $W$ becomes

$$W = \frac{\pi}{3 n \varepsilon_0 c_0 \hbar^2} |\mu|^2 g(\Delta \omega) I$$

- The Intensity $I$ corresponds to the Photon flux [s$^{-1}$cm$^{-2}$]

$$F = \frac{I}{\hbar \omega}$$

- Thus

$$W = \frac{\pi \omega}{3 n \varepsilon_0 c_0 \hbar} |\mu|^2 g(\Delta \omega) F =: \sigma F = \sigma \frac{I}{\hbar \omega}$$

with

$$\sigma(\Delta \omega) = \frac{\pi \omega}{3 n \varepsilon_0 c_0 \hbar} |\mu|^2 g(\Delta \omega)$$

......Transition cross section [cm$^2$]
Energy- Photon density

• q photons in a volume V:
  \[ \rho_{ph} = \frac{q}{V} \quad \text{and} \quad \rho_{em} = \frac{\hbar \omega q}{V} \]
  
  Photon density \hspace{1cm} \text{Energy density}

• Photons move with velocity \( c = \frac{c_0}{n} \)
  \[ F = c \rho_{ph} \]

• Thus
  \[ W = \sigma c \rho_{ph} = \frac{\sigma c \rho_{em}}{\hbar \omega} \]
2-level system

• Stimulated processes: Transition rates are given by the transition probability for one atom: $W=W_{12}=W_{21}$

• Spontaneous process: Average lifetime $\tau_{sp}$ → transition rate = $1/\tau_{sp}$

• Total transition rates are calculated by multiplying the individual transition rates with the number of atoms that are available for that process:

$$\frac{dN_2}{dt} = N_1 W_{12} - N_2 W_{21} - \frac{N_2}{\tau_{sp}}$$

$$\frac{d\rho_{ph}}{dt} = -N_1 W_{12} + N_2 W_{21} = W(N_2 - N_1)$$

Rate equations
2-level system cont’d.

- The photon density and the photon flux are related via
  \[ F = c \rho_{ph} \]

- Because \( dz = c \, dt \) we have \( d\rho_{ph} / dt = dF / dz \) and thus
  \[ \frac{dF}{dz} = (N_2 - N_1) \sigma F \]

- The rate of change in photon flux or intensity thus becomes
  \[ \frac{dF}{F} = \frac{dI}{I} = (N_2 - N_1) \sigma dz \]

- Integration gives
  \[ \frac{F(z)}{F(0)} = \frac{I(z)}{I(0)} = e^{(N_2 - N_1)\sigma z} = e^{-\alpha z} \]

- Absorption coefficient: \( \alpha = -(N_2 - N_1) \sigma = (N_1 - N_2) \sigma \)
Spontaneous emission

- Can be regarded as being stimulated by vacuum fluctuations
- QED needed to explain this phenomenon
- Consider a black body in thermal equilibrium instead:
  - Spectral energy density is $\rho_{em}(\omega)$
  - Spontaneous emission rate is $A(\omega) N_2$
  - Stimulated emission rate is $B_{21}(\omega) \rho_{em}(\omega) N_2$
  - Absorption rate is $B_{12}(\omega) \rho_{em}(\omega) N_1$
- In thermal equilibrium, for every $\omega$ it must be
  $$B_{21}(\omega) \rho_{em}(\omega) N_2 + A(\omega) N_2 = B_{12}(\omega) \rho_{em}(\omega) N_1$$
- In thermal equilibrium, the Boltzmann distribution is valid:
  $$N_2 / N_1 = e^{-(E_2 - E_1) / k_B T} = e^{-\hbar \omega / k_B T}$$
- Thus

$$\rho_{em}(\omega) = \frac{A(\omega)}{B_{12}(\omega) e^{\hbar \omega / k_B T} - B_{21}(\omega) / B_{12}(\omega)}$$
Thus:

\[ B_{21}(\omega) = B_{12}(\omega) \quad \text{Same probability for absorption and stimulated emission} \]

and

\[ A(\omega) = \frac{\hbar \omega^3 n^3}{\pi^2 c_0^3} B_{21}(\omega) \quad \text{Probability for spontaneous emission becomes higher for higher frequencies.} \]
Lineshape

- “Natural broadening” results from the finite lifetime of excited states
- Spontaneous emission is equivalent with an exponential decaying radiation field with frequency \( \omega_0 = (E_2 - E_1)/\hbar \)

- The power spectrum of the emitted light is the Fourier transform of

\[
e^{-t/2\tau_{sp}} e^{j\omega_0 t}
\]

and is thus

\[
g(\Delta\omega) = \frac{1}{\pi} \frac{2\tau_{sp}}{1 + (2\tau_{sp} \Delta\omega)^2}
\]

- FWHM linewidth is

\[
\Delta\omega_{FWHM} = \frac{1}{\tau_{sp}}
\]
Homogeneous broadening

Natural broadening

Impact broadening

\[ g(\Delta \omega) = \frac{1}{\pi} \frac{T_2}{1 + (\Delta \omega T_2)^2} \]
Inhomogeneous broadening

• The increase in the linewidth of is caused by effects which cause different radiating or absorbing atoms (or ions) to interact with different wavelength components.

• The absorption and emission cross sections have different spectral shapes for different atoms.

• The fluorescence spectrum is broader than of a single atoms, since it shows an average over many differently emitting atoms.

In a solid medium, there can be different lattice locations e.g. of laser-active ions, where the ions experience different local electric and magnetic fields. This is particularly the case for glasses, but can also occur in crystalline materials (particularly in disordered crystals).
Transition frequency of a stationary atom: \( \omega_0 \)

Transition frequency of an atom moving with velocity \( v \):

\[
\omega' = \omega_0 \sqrt{\frac{1 + v/c_0}{1 - v/c_0}}
\]
Linewidth broadening

The same active ion (Nd)

- Lineshapes in most solid state materials (and dyes) are the result of the existence of a manifold of many closely separated energy levels as every electronic state is split into many vibronic and rotational states.
- Neither homogeneous nor inhomogeneous broadening
- As all atoms have the same manifold of states, the behaviour is similar to a homogeneously broadened system
Saturation of Absorption

• Consider a 2-level system at optical frequencies
• At room temperature $N_2 \approx 0$, thus $N = N_1 + N_2 \approx N_1$
• Absorption coefficient: $\alpha = \alpha_0 = N \sigma$
• But: Absorption is changing $N_2 \rightarrow \alpha = \alpha(I)$

$$\frac{dN_2}{dt} = -W(N_2 - N_1) - \frac{N_2}{\tau_{sp}}$$

$$\Delta N := N_2 - N_1$$

$$N_1 = \frac{N - \Delta N}{2}$$

$$N_2 = \frac{N + \Delta N}{2}$$

$$\frac{d\Delta N}{dt} = -\Delta N \left(2W + \frac{1}{\tau_{sp}}\right) - \frac{N}{\tau_{sp}}$$

and stationary

$$-\frac{\Delta N}{N} = \frac{1}{1 + 2W \tau_{sp}}$$
Saturation of Absorption II

- Using the known relation between $W$ and $I$
  \[ W = \sigma F = \sigma \frac{I}{\hbar \omega} \]
- we obtain
  \[
  \frac{-\Delta N}{N} = \frac{1}{1 + I(2\sigma \tau_{sp}/\hbar \omega)} := \frac{1}{1 + I/I_s}
  \]

\[ \alpha = -\sigma \Delta N \]

\[ \Rightarrow \frac{\alpha(I)}{\alpha_0} = \frac{1}{1 + I/I_s} \]

Saturation Intensity $I_s$
Saturation of the lineshape

Homogeneously broadened medium

Inhomogeneously broadened medium

Spectral hole burning
Two-, three-, four level systems

- No inversion

- Inversion

- Easy inversion
Two-level system: Rate equation

\[ W_{21}^{\text{ind}} = W_{12}^{\text{ind}} = W^{\text{ind}} = B I \]

Absorption \hspace{1cm} \text{Stimulated emission} \hspace{1cm} \text{Spontaneous emission}

\[ \frac{dN_2}{dt} = BI(N_1 - N_2) - AN_2 \]

Pump intensity

\[ \frac{dN_1}{dt} = BI(N_2 - N_1) + AN_2 \]

If the total number of molecules is \( N \):

\[ N \equiv N_1 + N_2 \]

\[ \Delta N \equiv N_1 - N_2 \]

\[ 2N_2 = (N_1 + N_2) - (N_1 - N_2) \]

\[ = N - \Delta N \]

\[ \Rightarrow \frac{d\Delta N}{dt} = -2BI\Delta N + 2AN_2 \]

\[ \Rightarrow \frac{d\Delta N}{dt} = -2BI\Delta N + AN - A\Delta N \]
Two-level system: no inversion

\[
\frac{d\Delta N}{dt} = -2BI \Delta N + AN - A\Delta N
\]

In steady-state: \[0 = -2BI \Delta N + AN - A\Delta N\]
\[\Rightarrow (A + 2BI)\Delta N = AN\]
\[\Rightarrow \Delta N = AN / (A + 2BI)\]
\[\Rightarrow \Delta N = N / (1 + 2BI / A)\]

\[
\Delta N = \frac{N}{I + I_s / I_{sat}}
\]

\[I_{sat} = A / 2B\]

saturation intensity

\[N_1 > N_2\] always
Three-level system: Rate equation

\[
\frac{dN_2}{dt} = BIN_1 - AN_2
\]

Absorption

\[
\frac{dN_1}{dt} = -BIN_1 + AN_2
\]

Spontaneous emission

The total number of molecules is \( N \):

\[
N \equiv N_1 + N_2
\]

\[
\Delta N \equiv N_1 - N_2
\]

Level 3 decays fast: \( N_3 = 0 \)

\[
\frac{d\Delta N}{dt} = -2BIN_1 + 2AN_2
\]

\[
2N_2 = N - \Delta N
\]

\[
2N_1 = N + \Delta N
\]

\[
\Rightarrow \frac{d\Delta N}{dt} = -BIN - BI \Delta N + AN - A \Delta N
\]
Three-level system: inversion

\[ \frac{d\Delta N}{dt} = -B \Delta N - BI \Delta N + AN - A \Delta N \]

In steady-state:
\[ 0 = -B \Delta N - BI \Delta N + AN - A \Delta N \]
\[ \Rightarrow (A + BI) \Delta N = (A - BI)N \]
\[ \Rightarrow \Delta N = N (A - BI)/(A + BI) \]

\[ \Delta N = N \frac{1 - I/I_{sat}}{1 + I/I_{sat}} \]

\[ I_{sat} = A/B \]
saturation intensity

\[ N_1 < N_2 \quad \text{if} \quad I > I_{sat} \]
Four-level system: Rate equation

As before: \[ \frac{dN_2}{dt} = BIN_0 - AN_2 \]

\[ \frac{dN_2}{dt} = BI(N - N_2) - AN_2 \]

Because \( N_1 \approx 0 \), \( \Delta N \approx -N_2 \)

\[ -\frac{d\Delta N}{dt} = BIN + BI \Delta N + A\Delta N \]

At steady state: \[ 0 = BIN + BI \Delta N + A\Delta N \]

The total number of molecules is \( N \):

\[ N = N_0 + N_2 \]

\[ N_0 = N - N_2 \]
Four-level system: Rate equation

\[ 0 = BIN + BI \Delta N + A \Delta N \]
\[ \Rightarrow (A + BI) \Delta N = -BIN \]
\[ \Rightarrow \Delta N = -BIN / (A + BI) \]
\[ \Rightarrow \Delta N = -(BIN / A) / (1 + BI / A) \]

\[ \Delta N = -N \frac{I / I_{sat}}{1 + I / I_{sat}} \]

\[ I_{sat} = A / B \]

saturation intensity

\[ N_1 < N_2 \quad \text{always} \]
Four-level aqueduct
Coherent amplification

3-level system

4-level system
4-level system

\[
\frac{dN_2}{dt} = W_p N_g - W_{21} N_2 - \frac{N_2}{\tau_2}
\]

with \[
\frac{1}{\tau_2} = \frac{1}{\tau_{sp}} + \frac{1}{\tau_{nr}}
\]

No signal (only pump field), stationary: \[
N_{2,0} = W_p N_g \frac{\tau_2}{1+W_p \tau_2} \approx W_p N \tau_2
\]

A signal field is reducing the inversion according to \[
W_{21} = \sigma I / \hbar \omega
\]

Thus, stationary we get

\[
N_2 = \frac{W_p N \tau_2}{1+W_p \tau_2 + I/I_s} \approx N_{2,0} \frac{1}{1 + I/I_s}
\]

with \[
I_s = \frac{\hbar \omega}{\sigma \tau_2}
\]

Gain coefficient: \[
\gamma = \sigma N_2
\]
Gain coefficient

\[ \frac{dI}{dz} = \gamma(v) I \]

solution:

\[ I(z) = I_0 \exp \{ \gamma(v) z \} \]

∃ limit: ....... saturation!

\[ \frac{dI}{dz} = \frac{\gamma_0}{1 + I/I_{\text{sat}}} I \]
Total gain of amplifier

\[ \frac{dI}{dz} = \frac{\gamma_0}{1 + I/I_{sat}} I \]

small signal gain: \[ I(z) = I_0 \exp \{ \gamma_0(v) z \} \quad G = \exp \{ \gamma_0 L \} \]

large signal gain: \[ I(L) - I_0 = \gamma_0 I_{sat} L \quad G = 1 + (I_{sat}/I_0) L \times \gamma_0 \]
Total gain of amplifier

\[ I(z) = I_0 \exp \left\{ \gamma_0 (v) z \right\} \]
\[ G = \exp \left\{ \gamma_0 L \right\} \]

small signal gain:

large signal gain:

\[ I(L) - I_0 = \gamma_0 I_{sat} L \]
\[ G = 1 + \left( \frac{I_{sat}}{I_0} \right) L \]