1 Rate equations

(a) In the lecture three different processes have been introduced for the interaction between light and an n-level system: Absorption, spontaneous emission and stimulated emission. The total transition rate is given by the sum of the individual contributions. We describe the rate of change of state 2 as

$$\frac{dN_2}{dt} = \frac{dN_{2abs}}{dt} + \frac{dN_{2spo}}{dt} + \frac{dN_{2sti}}{dt} \tag{1}$$

$$= K_{12}N_1 - A_{21}N_2 - K_{21}N_2 \tag{2}$$

$$= K_{12}(N_1 - N_2) - A_{21}N_2, \tag{3}$$

where we used $K_{21} = K_{12}$. We also have (either from an analysis as done for N_2, or from the fact that we only have two levels where the population can go to)

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt}. \tag{4}$$

(b) The rate equations for state 1 and 2 constitute a set of coupled differential equations. However, they can easily be uncoupled using the assumption that the total number of interacting atoms N does not change over time. The resulting constraint is then $N = N_1(t)+N_2(t) = const.$, from which follows that

$$\frac{dN_2}{dt} = K_{12}(N - 2N_2) - A_{21}N_2 \tag{5}$$

$$= K_{12}N - (2K_{12} + A_{21})N_2. \tag{6}$$

Equation (6) constitutes an inhomogeneous ordinary differential equation of first order, meaning it is of the type

$$\sum_{j=0}^{n} a_j(x) \frac{d^j}{dx^j} y = f(x) \tag{7}$$

with n = 1. Such an equation can be solved by constructing a solution y from the solution y_c of the homogeneous equation where $f(x) = 0$ (in this context y_c is also called complementary function), plus a particular solution y_p of the inhomogeneous equation (7). For the case of $f(x)$ being a polynomial of n-th order, the method of undetermined coefficients can be used where y_p is taken to be $b_0 + b_1(x) + \cdots + b_n(x)$. The coefficients b_j have to be such that the differential equation is fulfilled for all x. For our case, the homogeneous equation

$$\frac{dN_2}{dt} = -(2K_{12} + A_{21})N_2 \tag{8}$$

is solved by

$$N_{2,c}(t) = ce^{-(2K_{12}+A_{21})t} \tag{9}$$

and a particular solution to (6) is a constant, $N_{2,p} = b$. The full solution is thus

$$N_2(t) = ce^{-(2K_{12}+A_{21})t} + b \tag{10}$$

where $b = K_{12}N/(2K_{12} + A_{21})$, or

$$N_2(t) = ce^{-(2K_{12}+A_{21})t} + \frac{N}{2 + \frac{A_{21}}{K_{12}}}. \tag{11}$$

$N_1(t)$ can be obtained from $N_1(t) = N - N_2(t)$.

To plot the dynamics for the boundary condition that only state 1 is populated mainly initially, i.e., $N_2(t = 0) = 0$, c has to be chosen accordingly. We have the condition

$$c + \frac{N}{2 + \frac{A_{21}}{K_{12}}} \overset{!}{=} 0 \tag{12}$$

and thus

$$N_2(t) = \frac{N}{2 + \frac{A_{21}}{K_{12}}}\left(1 - e^{-(2K_{12}+A_{21})t}\right). \tag{13}$$

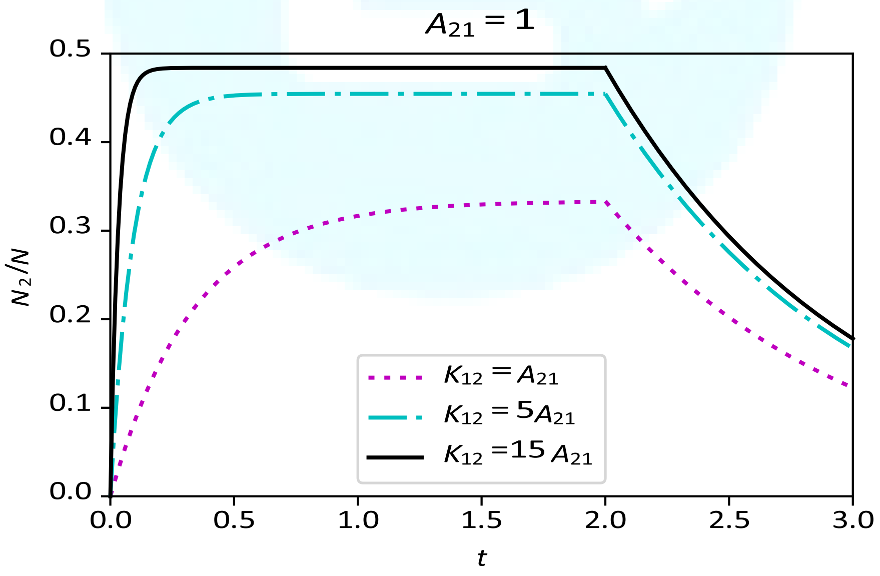

Figure 1: Plot of (13) for different parameters. At time $t = 2$, the curves are switched to the decay given by (15) which happens when the driving is turned off.

See figure 1 for an example plot with some parameters. It follows from equation (13) that for different ratios K_{12}/A_{21} the steady state solution will converge to a different values $N_2(\infty)$, and if K_{12} $A_{21}N_2$ the steady state solution is $N_2(\infty) = N/2$. Physically, this means that for arbitrarily large incident photon fuxes there will never be population inversion in a two level system.

(c) As can be seen from (3) by taking the steady-state condition $\frac{dN_2}{dt} = 0$, the steady-state solution is given by

$$N_{2ss} = \frac{N}{2 + \frac{A_{21}}{K_{12}}}, \tag{14}$$

which is identical to $\lim_{t\to\infty} N_2(t)$ in (13). As we assume N to be constant as well as A_{21} and K_{12} to be real-valued, the maximum value for (13) is obtained upon minimization of the denominator. As $A_{21} > 0, K_{12} > 0$, this minimal value of the denominator is 2 for the case that A_{21} K_{12}, which implies that the maximum value is $N/2$.

(d) Switching of the photon flux at steady state translates to the boundary conditions that $N_2(0)$ is its steady-state value (14) and to set K_{21} to zero in (6) (but not in (14), of course). You thus get immediately

$$N_2(t) = \frac{N}{2 + \frac{A_{21}}{K_{12}}} e^{-A_{21}t} \tag{15}$$

Experimentally, one would observe an afterglow of the medium that decays exponentially in with the time parameter as given in (15)

Note: The spontaneous decay can, in principle, also cause stimulated emission in neighboring atoms or molecules, especially in a cavity. Taking this into account, the exponential decay constant in (15) is between A_{21} (only spontaneous emission, as given in the equation) and $A_{21} + K_{12}$.

2 Fundamentals of lasers

(a) Lasing on a microscopic scale implies that the number of photons from stimulated emission outweighs the number of absorbed photons, i.e.,

$$K_{21}N_2 > K_{12}N_1. \tag{16}$$

Therefore, as $K_{21} = K_{12}$, this implies

$$N_2 > N_1. \tag{17}$$

In exercise 1c) it was shown that N_2 will always be smaller or equal than N_1 if we assume that state 1 is the ground state and that it is initially populated. As a consequence, it is impossible to achieve lasing with a simple two level system under the assumption that N is conserved.

(b) Population inversion is created in the reference by exciting a beam of molecules and a successive selective spatial focusing of the excited NH_3 molecules, leading to a spatial volume in which the density of excited molecules is larger than the density of molecules in the ground state. Thereby lasing could be achieved in a two level system.

(c) First, we discuss the case of N_1 in detail. Compared to the two level case in exercise 1a) there will not only be terms linking N_1 to N_2 but also N_1 to N_3 and N_3 to N_2. Thus,

$$\frac{dN_1}{dt} = +\frac{dN_{1abs}}{dt}\Big|_{1\to 2} + \frac{dN_{1abs}}{dt}\Big|_{1\to 3} + \frac{dN_{1spo}}{dt}\Big|_{1\leftarrow 2} + \frac{dN_{1spo}}{dt}\Big|_{1\leftarrow 3} + \frac{dN_{1sti}}{dt}\Big|_{1\leftarrow 2} + \frac{dN_{1sti}}{dt}\Big|_{1\leftarrow 3} \quad (18)$$

$$= -K_{12}N_1 - K_{13}N_1 + A_{21}N_2 + A_{31}N_3 + K_{21}N_2 + K_{31}N_3. \quad (19)$$

We can use $A_{31} = K_{21} = K_{12} = 0$ and repeat the procedure for N_2 and N_3 to find

$$\frac{dN_1}{dt} = -K_{13}N_1 + A_{21}N_2 + K_{31}N_3 \quad (20)$$

$$\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 \quad (21)$$

$$\frac{dN_3}{dt} = K_{13}N_1 - (K_{31} + A_{32})N_3. \quad (22)$$

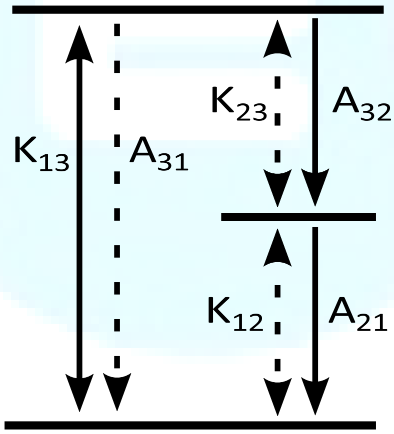

Figure 2: A hopefully self-explanatory figure that is not referenced in the text.

(d) The steady state solutions are e.g. calculated starting from (21). We have

$$N_2 = \frac{A_{32}}{A_{21}} N_3. \quad (23)$$

This information together with the conservation condition $N = N_1 + N_2 + N_3$ can then be used with e.g. (22) to find

$$K_{13}N = K_{13}\frac{A_{32}}{\ } + K_{31} + K_{13} + A_{32} \quad N_3 \quad (24)$$

A_{21}

or, with $K_{13} = K_{31}$,

$$N_3 = \frac{K_{13}N}{K_{13}\frac{A_{32}}{A_{21}} + 2K_{13} + A_{32}}. \tag{25}$$

Then,

$$N_2 = \frac{A_{32}}{A_{21}} \frac{K_{13}N}{K_{13}\frac{A_{32}}{A_{21}} + 2K_{13} + A_{32}} \tag{26}$$

$$N_1 = N - \left(1 + \frac{A_{32}}{A_{21}}\right) \frac{K_{13}N}{K_{13}\frac{A_{32}}{A_{21}} + 2K_{13} + A_{32}} \tag{27}$$

Now, in order to have population inversion between states 1 and 2, N_2 needs to be larger than N_1. After some algebra one obtains

$$K_{13} > \frac{A_{21}}{1 - \frac{A_{21}}{A_{32}}}. \tag{28}$$

This condition has a very intuitive limiting case, as for $A_{32} > A_{21}$ it becomes $K_{13} > A_{21}$. It means that if we are exciting the ensemble faster than it can decay, we get population inversion.

3 Doppler broadening

(a) The standard deviation of the transition frequency is provided in parentheses right after the actual value. It expresses the accuracy of the last digit(s) of the actual value. In this case, the standard deviation is

$$\sigma_v = 5 \cdot 10^{-9}\,\text{THz} = 5\text{kHz}. \tag{29}$$

Since frequency v and wavelength λ are related via

$$\lambda = \frac{c}{v}, \tag{30}$$

we have for their differentials

$$|d\lambda| = \frac{c}{v^2}\,|dv|. \tag{31}$$

Inserting the requested values into this equation yields for the standard deviation

$$\sigma_\lambda = 4.72 \cdot 10^{-9}\,\text{nm} \tag{32}$$

for the transition wavelength and a wavelength

$$\Delta\lambda = 1.66 \cdot 10^{-6}\,\text{nm} \qquad (33)$$

for the linewidth.

(b) The observed angular frequency ω of a moving light source is shifted from the angular frequency at rest ω_0 due to the relativistic Doppler effect. For velocities $v \ll c$ it is sufficient to consider the first-order approximation of the angular frequency shift $\Delta\omega$, which is given by

$$\Delta\omega = \omega - \omega_0 = \frac{v}{c}\omega_0 \qquad (34)$$

(c) We need to change the dependent variable of a distribution. In general, the transformation of the dependent variable is given by

$$f_0(\omega)\mathrm{d}\omega = f(v(\omega))\frac{\mathrm{d}v}{\mathrm{d}\omega}\mathrm{d}\omega. \qquad (35)$$

Substituting v in Eq. (3) and inserting $\mathrm{d}v/\mathrm{d}\omega = c/\omega_0$ gives

$$f_0(\omega)\mathrm{d}\omega = \sqrt{\frac{m}{2\pi kT}}\exp\left(-\frac{mc^2(\Delta\omega)^2}{2kT\omega_0^2}\right)\frac{c}{\omega_0}\,\mathrm{d}\omega \qquad (36)$$

(d) The lineshape is a Gaussian For a generic Gaussian $Ne^{-\frac{(x-x_0)^2}{2\sigma^2}}$, we find the full width at half maximum (FWHM) by noting that N and x_0 do not change the FWHM, hence we just need to find x such that

$$e^{-\frac{x^2}{2\sigma^2}} = 0.5 \quad \rightarrow \quad x = \sqrt{2\ln 2}\,\sigma. \qquad (37)$$

The FWHM is twice this value, i.e., FWHM = $2\sqrt{2\ln 2}\,\sigma$. In our case,

$$\sigma^2 = \frac{kT\omega_0^2}{mc^2}, \qquad (38)$$

from which follows

$$\text{FWHM} = \frac{2\omega_0}{c}\sqrt{\frac{2\ln(2)kT}{m}} \qquad (39)$$

or, with $\lambda_0 = \frac{2\pi c}{\omega_0}$,

$$\text{FWHM} = \frac{4\pi}{\lambda_0}\sqrt{\frac{2\ln(2)kT}{m}} \qquad (40)$$

The considered transition has a wavelength

$$\lambda_0 = \frac{c}{5.632602235 \times 10^{14}\,\mathrm{s}^{-1}} = 5.322450361 \times 10^{-7}\,\mathrm{m} \tag{41}$$

and the mass of an iodine molecule is

$$m = \frac{2 \times 126.90447\,\mathrm{g/mol}}{N_A} = 4.214596604679828 \times 10^{-25}\,\mathrm{kg} \tag{42}$$

At T = 300K the linewidth for the considered transition is

$$\mathrm{FWHM} = \frac{4\pi}{5.322450361 \times 10^{-7}\,\mathrm{m}} \sqrt{\frac{2\ln(2) \times 1.380649 \times 10^{-23}\,\mathrm{J/K} \times 300\,\mathrm{K}}{4.214596604679828 \times 10^{-25}\,\mathrm{kg}}} \tag{43}$$

$$\approx 2.76 \times 10^{9}\,\mathrm{s}^{-1} \tag{44}$$

which is more than three orders of magnitude larger than the natural linewidth.

Note: Although 1Hz ≡ $1\mathrm{s}^{-1}$, it is convention to use the unit hertz (Hz) only for frequencies, i.e., for the number of oscillations per time intervall. In particular, it is usually not used for angular frequencies. Thus, without further information you can assume that the numbers given on the exercise sheet are frequencies but ω is the conventional symbol for angular frequencies. If you want to compare the actual number (44) with the natural linewidth, you thus need to multiply it with a factor $1/(2\pi)$.