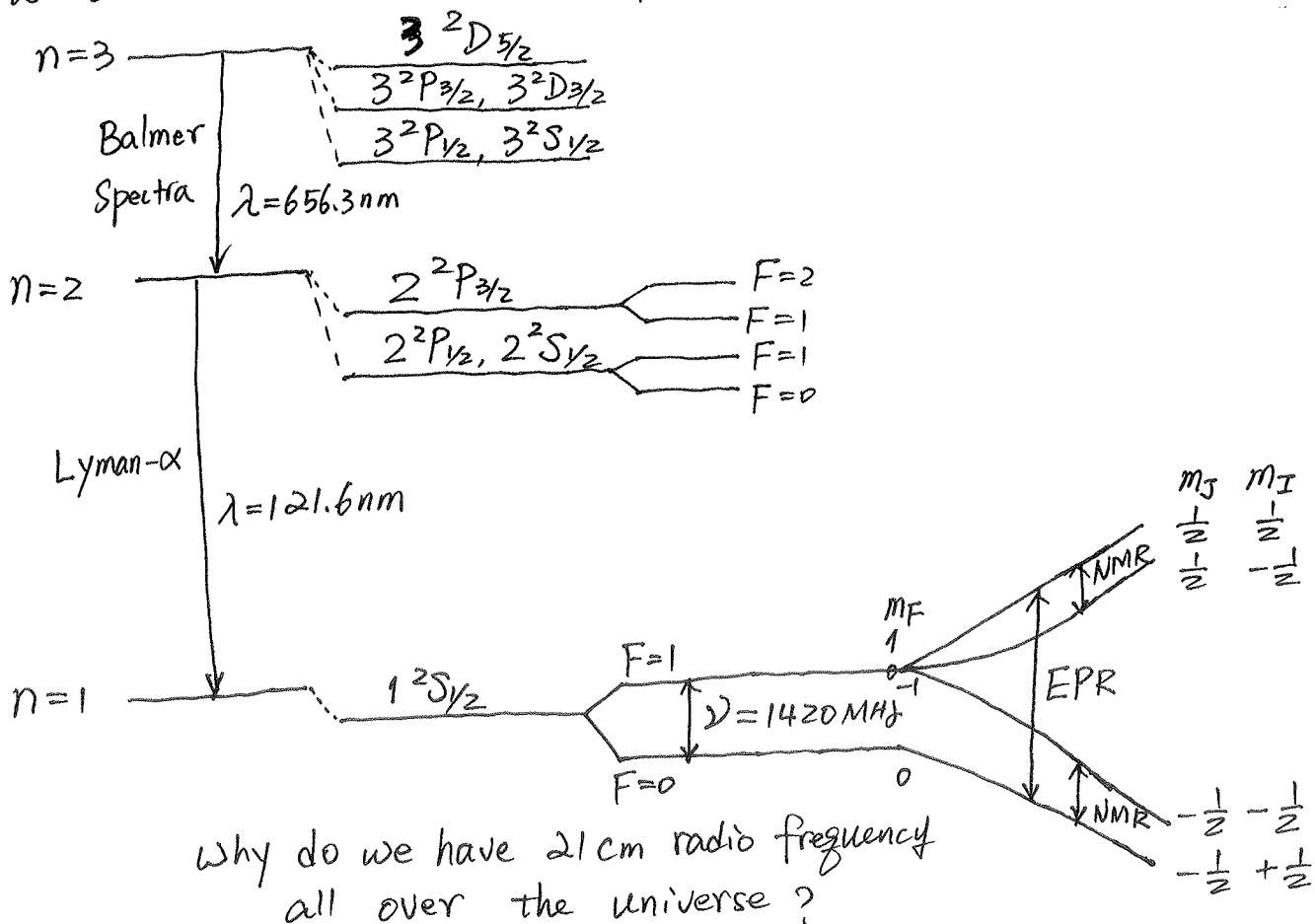


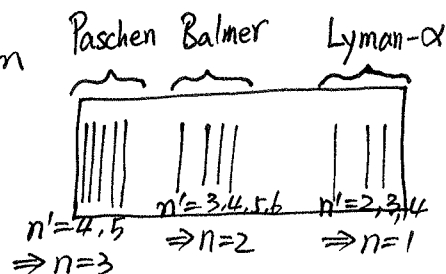
# Chapter 6. Radiative Transitions

## §6.1 Introduction

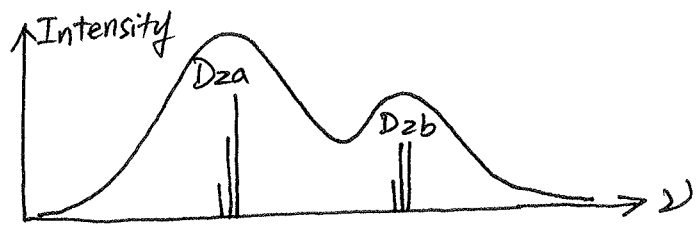
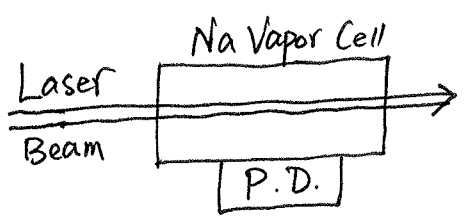
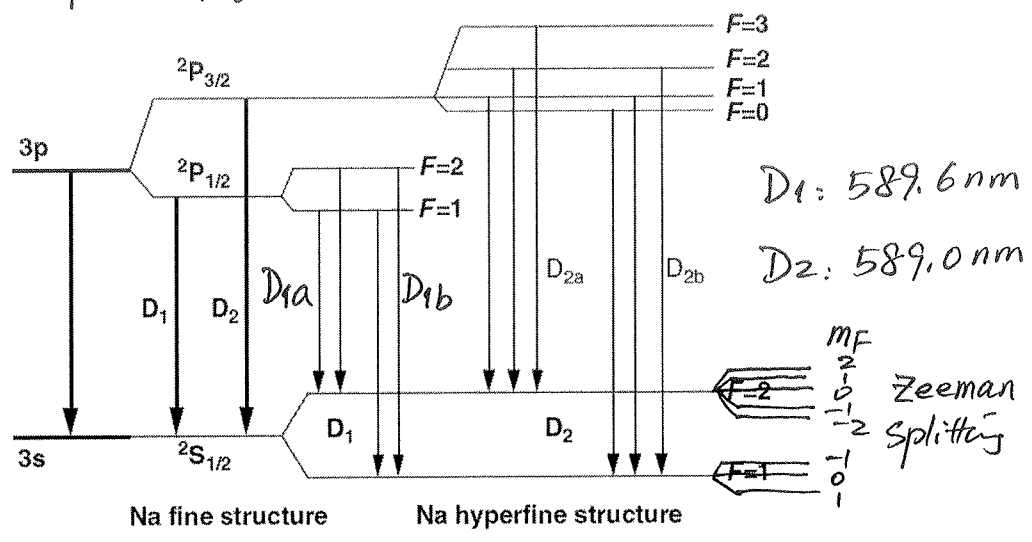
By now, we finished the study of atomic structure using QM theory and methods — deriving eigenvalues and eigenstates of energy of an atom, under different internal and external interactions. We now understand, e.g., the hydrogen energy structure, and how we obtain certain wavelength spectral lines:



- ① Lyman- $\alpha$  transition: 121.6 nm (Solar flux)
- ② Balmer spectra,  $H_{\alpha} = 656.3 \text{ nm}$
- ③ Hyperfine transition:  $F=1 \leftrightarrow F=0$ ,  $\lambda = 21 \text{ cm}$
- ④ NMR: Zeeman splitting / transition; EPR
- ⑤ Stark effect.



# Another Example: Na



We now understand why Na  $D_2$  lines have fine ( $D_{2a}$  and  $D_{2b}$ ) and hyperfine (3 lines for  $D_{2a}$  and 3 lines for  $D_{2b}$ ) structures.

$D_1: 589.6 \text{ nm}$	} (in air)	$589.7558$	} (in vacuum)
$D_2: 589.0 \text{ nm}$		$589.1583$	

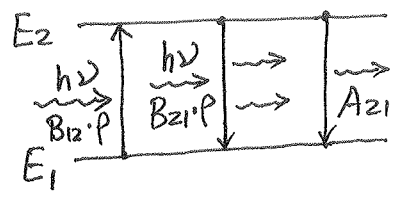
But we haven't touched why certain transitions have certain strength (why one is stronger than another) and why some transitions don't occur, e.g.,  $F=3 \leftrightarrow F=1$ .

Also, why some lines are linearly polarized.

These questions will be answered by radiative transition theory that we will address below.

### § 6.2. Absorption, Stimulated Emission, and Spontaneous Emission

From atomic structure theory, we know atoms have discrete energy levels. Assume an atom has two energy levels  $E_1$  and  $E_2$  (again, energy levels mean the eigenstates of  $\hat{H}_0$ ), and is brought into a thermal radiation field.



① Absorption (Stimulated / induced absorption)

$$\frac{dP_{12}(t)}{dt} = B_{12} \rho(\nu) \quad \text{Einstein B coefficient}$$

where  $\frac{dP_{12}(t)}{dt}$  is the absorption probability per unit time, i.e., the probability per second that an atom will absorb a photon,  $\rho(\nu)$  is the spectral energy density of the radiation field.

Note: There is NO such thing called  $A_{12}$ !  
Only  $A_{ki}$ , no  $A_{ik}$ !

↓  
k - upper level  
i - lower level

② Stimulated emission:

$$\frac{dP_{21}^{st}(t)}{dt} = B_{21} \rho(\nu) \quad \text{Einstein B coefficient}$$

③ Spontaneous emission:

$$\frac{dP_{21}^{sp}(t)}{dt} = A_{21} \quad \text{Einstein A coefficient}$$

$A_{21}$  is also called the spontaneous transition probability per unit time.

Note: Transition probability  $P_{12}(t)$  and  $P_{21}(t)$  are the probability that an atom will absorb or emit a photon at time  $t$ . From the definition of probability, transition probability must be in between 0 and 1 (i.e;  $0 \leq P_{12}(t) \leq 1$ ,  $0 \leq P_{21}(t) \leq 1$ ) and dimensionless.

Because Quantum transition can happen very fast (on the order of 10s ns), it is more meaningful in spectroscopy field to study the transition probability per unit time  $\frac{dP_{12}(t)}{dt}$  and  $\frac{dP_{21}(t)}{dt}$ , which is the probability per second that an atom will absorb or emit a photon. The unit of  $\frac{dP_{12}(t)}{dt}$  and  $\frac{dP_{21}(t)}{dt}$  is  $s^{-1}$  (s - second).

So it is not surprising that  $A_{21}$  is usually around  $10^8 s^{-1}$ .

To be accurate,  $\frac{dP_{12}(t)}{dt}$  and  $\frac{dP_{21}(t)}{dt}$  should be called the transition probability per unit time. But people usually just brief them as the transition probability. We must be aware of the differences. This is why we call  $A_{21}$  as the spontaneous transition probability per unit time.

④ Relationship among Einstein coefficients  $A_{21}$ ,  $B_{12}$ , and  $B_{21}$  :

At thermal equilibrium, atomic population on each energy level is given by Maxwell-Boltzmann distribution law :

$$N_i = N \frac{g_i}{Z} e^{-E_i/k_B T}$$

where  $E_i$  is the energy level,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $N$  is the total atomic population :

$$N = \sum_i N_i .$$

$Z$  is the normalization factor :

$$Z = \sum_i g_i e^{-E_i/k_B T}$$

where  $g_i$  is the statistical weight :  $g_i = 2J_i + 1$

( $J_i$  is the total angular momentum).  $g_i$  gives the number of degenerate sublevels of the energy level  $E_i$ .

At thermal equilibrium, total photon number of the radiation field will not change, total number of atoms will not change, and the number of atoms on each state will not change. Thus,

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0.$$

$$\Rightarrow \frac{dN_2}{dt} = N_1 \cdot B_{12} \cdot \rho - N_2 \cdot B_{21} \rho - N_2 \cdot A_{21} = 0$$

$$\Rightarrow [B_{21} \rho + A_{21}] N_2 = B_{12} \rho N_1$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2 - E_1)/k_B T} = \frac{g_2}{g_1} e^{-h\nu/k_B T} \quad \nu = \frac{E_2 - E_1}{h}$$

$$\frac{B_{12} \rho}{B_{21} \rho + A_{21}}$$

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

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

$$= \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}} \cdot \frac{g_1}{g_2} e^{h\nu/k_B T} - 1}$$

Recall Planck's law:  $\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1}$

Since both equations are valid for any arbitrary  $T$  and  $\nu$ ,

$$\Rightarrow \left. \begin{aligned} A_{21}/B_{21} &= \frac{8\pi h \nu^3}{c^3} \\ \frac{B_{12}}{B_{21}} \cdot \frac{g_1}{g_2} &= 1 \end{aligned} \right\} \Rightarrow \begin{cases} A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21} \\ B_{12} \cdot g_1 = B_{21} \cdot g_2 \end{cases}$$

If  $g_1 = g_2$ , then we have  $B_{12} = B_{21}$ , and  $\frac{N_2}{N_1} = \frac{B_{12} \rho}{B_{21} \rho + A_{21}}$ .

Considering  $A_{21}$ , we will always have  $N_2 < N_1$  — consistent with Maxwell-Boltzmann distribution.

The number of modes per unit volume and per freq. interval:

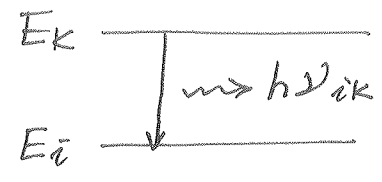
$$n(\nu) = 8\pi \nu^2 / c^3$$

$\therefore \frac{A_{21}}{n(\nu)} = B_{21} \cdot h\nu$ .  $\rightarrow$  The spontaneous emission per mode is equal to the stimulated emission that is triggered by 1 photon.

The ratio of  $\frac{\text{Stimulated}}{\text{Spontaneous}}$  emission rate in an arbitrary mode is equal to the number of photons in this mode.

### ⑤ Emission and Absorption Spectra.

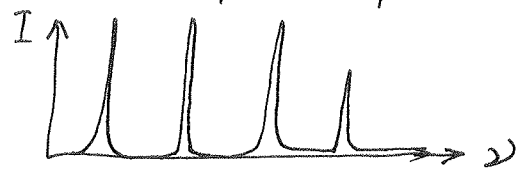
If somehow, the atoms/molecules are in excited states, they can emit photons



with  $h\nu_{ik} = E_k - E_i$ , where  $E_k$  - upper level,  $E_i$  - lower level.

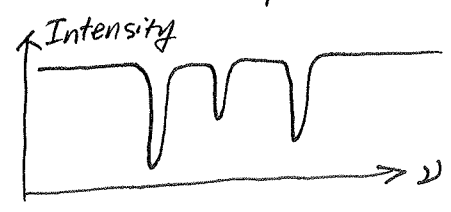
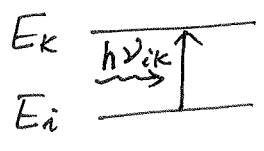
If we use instruments to record the emitted photon spectrum, we may see something like :

- This is called emission spectra.

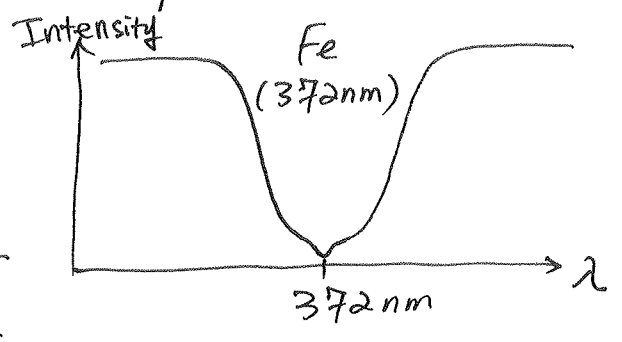
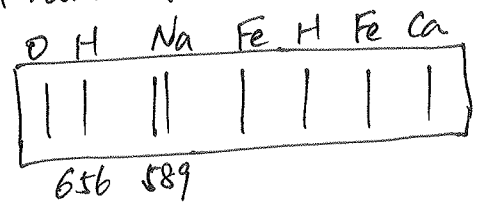


If on the other hand, atoms are in ground states, when some continuous radiation (e.g., thermal radiation) passes through the atoms, the atoms may absorb photons at  $\nu_{ik} = (E_k - E_i)/h$ . Thus, the received radiation will have less power at these resonance frequencies, appearing as dark lines in spectra.

- This is called absorption spectra.



Example: Fraunhofer lines in the Solar spectrum:



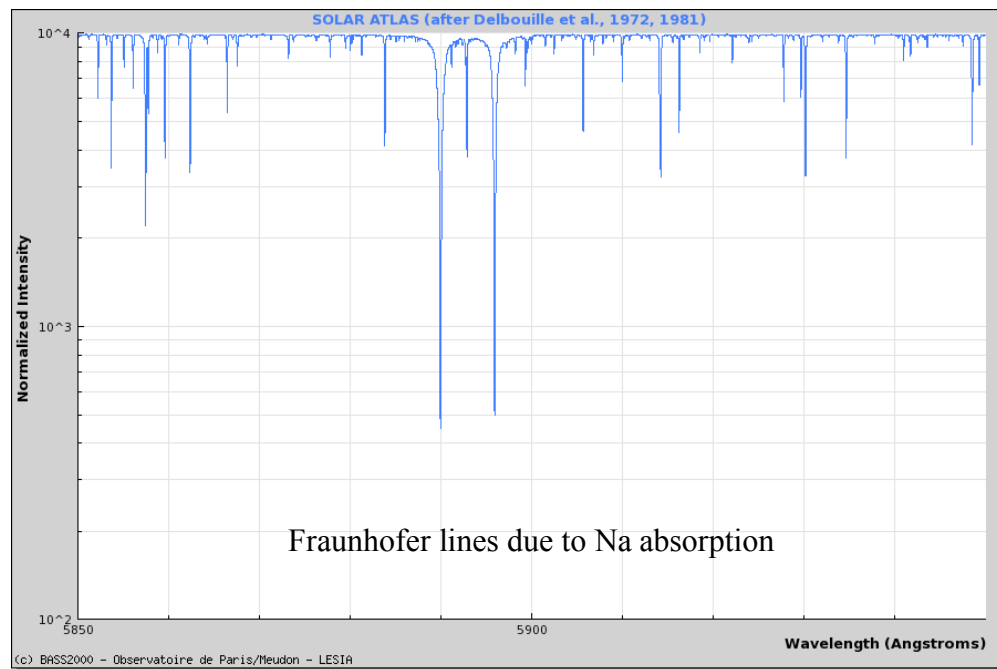
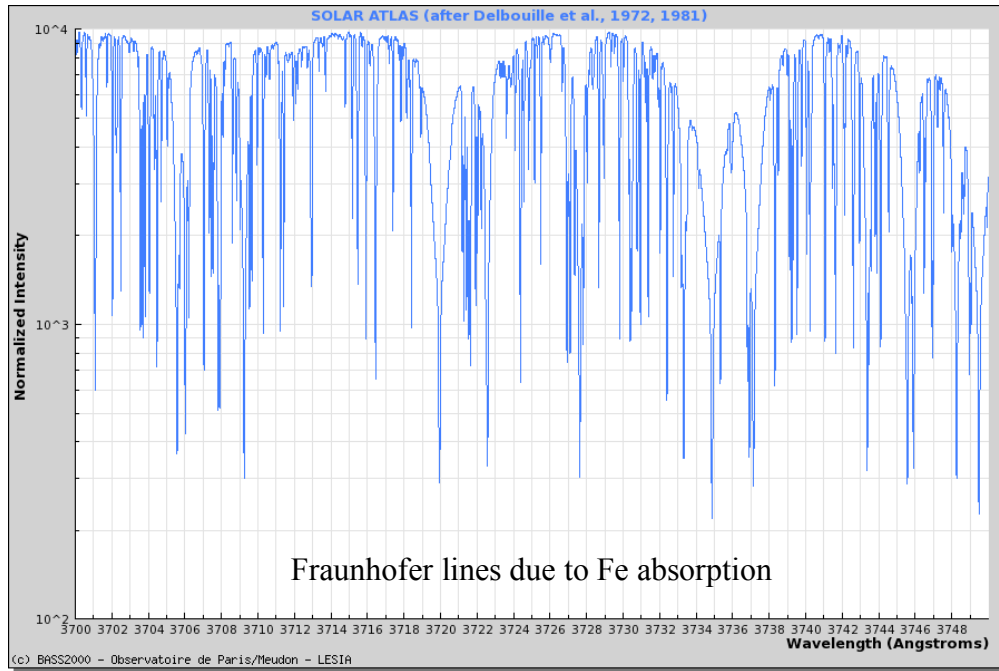
⇒ resulting in much lower solar background at Fraunhofer lines than at wavelength without an absorption line.

⇒ Lidar (resonance) can take advantage of this!

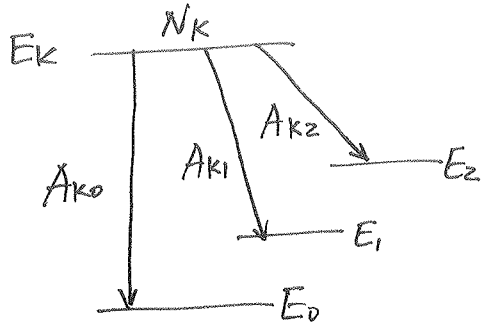
Fraunhofer lines are a set of spectral lines observed as dark features (absorption lines) in the optical spectrum of the sun by the German physicist Joseph von Fraunhofer (1787-1826).

## Fraunhofer Lines in Solar Spectrum

The following website can be used to look at the solar spectrum and numerous Fraunhofer lines  
[http://bass2000.obspm.fr/solar\\_spect.php?PHPSESSID=b1fb4b5e30286b1698ae5b2f330b3318](http://bass2000.obspm.fr/solar_spect.php?PHPSESSID=b1fb4b5e30286b1698ae5b2f330b3318)



⑥ Lifetime: Radiative lifetime and Effective Lifetime

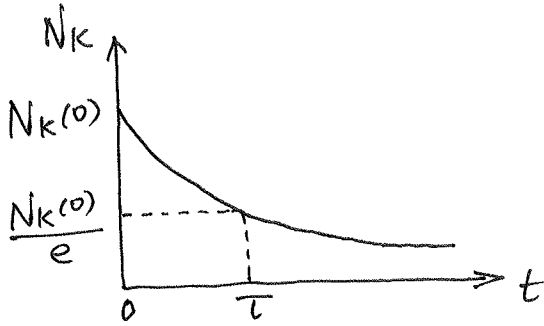


The probability \$P\_{ki}\$ that an excited atom in the level \$E\_k\$ makes a transition to a lower level \$E\_i\$ by spontaneous emission of a fluorescence quantum \$h\nu\_{ki} = E\_k - E\_i\$ is related to the Einstein coefficient \$A\_{ki}\$

$$\text{by } \frac{dP_{ki}}{dt} = A_{ki}$$

The total transition probability from the upper energy level \$E\_k\$ is

$$A_k = \sum_i A_{ki}$$



$$\begin{aligned} \frac{dN_k}{dt} &= -A_{k0}N_k - A_{ki}N_k - A_{kj}N_k \\ &= -(A_{k0} + A_{ki} + A_{kj})N_k \\ &= -A_k N_k \end{aligned}$$

$$\Rightarrow N_k(t) = N_k(0) e^{-A_k t} \quad N_k(0) = N_k(t=0)$$

At \$\tau\_k = \frac{1}{A\_k}\$, we have \$N\_k(t) = \frac{N\_k(0)}{e}\$.

Thus, \$\tau\_k\$ is the mean radiative lifetime, caused by the spontaneous emission:  $\tau_k = \frac{1}{A_k} = \frac{1}{\sum_i A_{ki}}$ .

Besides spontaneous emission, an energy level \$E\_k\$ can be depopulated by stimulated emission transitions and by collision-induced radiationless transitions. The overall effect is to reduce the lifetime of an atom staying in \$E\_k\$.

Collision:  $\frac{dP_{ki}^{Collision}}{dt} = \bar{v} N_B \sigma_{ki}^{col}$ , where \$N\_B\$ - density of collision partner B; \$\sigma\_{ki}^{col}\$ - collision cross-section.

Stimulated:  $\frac{dP_{ki}^{St}}{dt} = \rho(\nu_{ki}) B_{ki} [N_k - \frac{g_k}{g_i} N_i]$

$$\Rightarrow \text{mean effective lifetime: } \frac{1}{\tau_k^{eff}} = \sum_i [A_{ki} + \rho(\nu_{ki}) B_{ki} (N_k - N_i \frac{g_k}{g_i}) + N_B \sigma_{ki}^{col} \bar{v}]$$