# Lesson 4 - Electromagnetic Transitions
# Unit 4.2 Line width of electromagnetic transitions

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# Life time (I)

We have seen that the Einstein coefficient $A_{ba} = W_{ba}^{spont}$ gives the transition probability per unit of time from the atomic state $|b\rangle$ to the atomic state $|a\rangle$. This means that, according to Einstein, in the absence of an external electromagnetic radiation one has

$$\frac{dN_b}{dt} = -A_{ba}\ N_b \tag{1}$$

with the unique solution

$$N_b(t) = N_b(0)\ e^{-A_{ba}t}\ . \tag{2}$$

It is then quite natural to consider $1/A_{ba}$ as the characteristic time of this spontaneous transition.
More generally, the life-time $\tau_b$ of an atomic state $|b\rangle$ is defined as the reciprocal of the total spontaneous transition probability per unit time to all possible final atomic states $|a\rangle$, namely

$$\tau_b = \frac{1}{\sum_a A_{ba}}\ . \tag{3}$$

Clearly, if $|b\rangle$ is the ground-state then $A_{ba} = 0$ and $\tau_b = \infty$.

# Natural line width (I)

On the basis of the time-energy indetermination principle of Werner Heisenberg, in the radiation energy spectrum the natural line-width $\Gamma_N$ due to the transition from the state $|b\rangle$ to the state $|a\rangle$ can be defined as

$$\Gamma_N = \hbar \left( \frac{1}{\tau_b} + \frac{1}{\tau_a} \right) \ . \tag{4}$$

Indeed it is possible to prove that in this transition the intensity of the emitted electromagnetic radiation follows the Lorentzian peak

$$I(\epsilon) = \frac{I_0 \Gamma_N^2/4}{(\epsilon - E_{ba})^2 + \Gamma_N^2/4} \ , \tag{5}$$

where $\epsilon = \hbar\omega$ is the energy of the emitted photon and $E_{ba} = E_b - E_a$ is the energy difference of the two atomic states. The Lorentzian peak is centered on $\epsilon = E_{ba}$ and $\Gamma_N$ is its full width at half-maximum.

# Experimental line width (I)

The effective line-width $\Gamma$ measured in the experiments is usually larger than $\Gamma_N$ because the radiating atoms move and collide. In fact, one can write

$$\Gamma = \Gamma_N + \Gamma_C + \Gamma_D \, , \tag{6}$$

where in addition to the natural width $\Gamma_N$ there are the so-called collisional broadening width $\Gamma_C$ and the Doppler broadening width $\Gamma_D$. The collisional width can be then written as

$$\Gamma_C = \frac{\hbar}{\tau_{col}} \, , \tag{7}$$

where $\tau_{col}$ is the collisional time. According to the results of statistical mechanics, $\tau_{col}$ is given by

$$\tau_{col} = \frac{1}{n \sigma v_{mp}} \, , \tag{8}$$

where $n$ is the number density of atoms, $\sigma$ is the interaction cross-section, and

$$v_{mp} = \sqrt{\frac{2 k_B T}{m}} \tag{9}$$

is the most probable speed of the particles in the gas at temperature $T$.

# Experimental line width (II)

The Doppler broadening is due to the Doppler effect caused by the distribution of velocities of atoms. For non-relativistic velocities ($v_x \ll c$) the Doppler shift in frequency is

$$\omega = \omega_0 \left(1 - \frac{v_x}{c}\right) \ , \tag{10}$$

where $\omega$ is the observed angular frequency, $\omega_0$ is the rest angular frequency, $v_x$ is the component of the atom speed along the axis between the observer and the atom and $c$ is the speed of light. The Maxwell-Boltzmann distribution $f(v_x)$ of speeds $v_x = -c(\omega - \omega_0)/\omega_0$ at temperature $T$ becomes

$$f(\omega)\, d\omega = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mc^2(\omega-\omega_0)^2/(2\omega_0^2 k_B T)}\, \frac{c}{\omega_0}\, d\omega \tag{11}$$

in terms of the angular frequency $\omega$. The full width at half-maximum of the Gaussian is taken as Doppler width, namely

$$\Gamma_D = \sqrt{\frac{8 \ln(2) k_B T}{mc^2}}\, \hbar\omega_0 \ . \tag{12}$$