Quantum Electronics/Laser Physics Chapter 4 Line Shapes and Line Widths 4.1 The Natural Line Shape 4.2 Collisional Broadening 4.3 Doppler Broadening 4.4 Einstein Treatment of **Stimulated Processes**

The Width and Shape of Spectral lines: Natural Line Shape

I- The Natural Line shape

•Discrete energy levels have finite radiative lifetimes and therefore are not infinitely sharp by application of Heisenberg's Uncertainty Principle (HUP). The diagram illustrates this. The angular frequency scale is used here, ie photon energies are given by (with the conversion to frequency unit)

 $E_{ki} = \hbar \omega_{ki} = h v_{ki}$ The level widths are related to the radiative lifetimes by HUP:

$$\Delta E_k \cdot \tau_k \approx \hbar \Longrightarrow \frac{\Delta E_k}{\hbar} = \frac{1}{\tau_k} = \sum_i A_{ki}$$

The level widths are given by

$$\Delta E_{k} = \hbar \Gamma_{k}$$
 and $\Delta E_{i} = \hbar \Gamma_{i}$

 $\tau_{\rm k}$ and $\tau_{\rm i}$ are the total lifetimes $T_{\rm ki}$ and inverse of the transition probabilities $A_{\rm ki}$



The quantum mechanical line shape for the radiative transition

between E_k and E_i is a Lorentzian function.

The full width at half - maximum is :

$$\Gamma_{ki} = \Gamma_{k} + \Gamma_{i} = \frac{1}{\tau_{k}} + \frac{1}{\tau_{i}}$$

$$I_{ki}(\omega) = I_{0} \times \frac{\Gamma_{ki}/2\pi}{(\omega - \omega_{ki})^{2} + {\Gamma_{ki}}^{2}/4}$$

Width and Shape of Spectral Lines

Spontaneous Emission Probability Aki

• A_{ki} = probability per unit time for emission of a photon of energy $\hbar \omega_{ki}$ = hv_{ki} .

It's the Einstein A coefficient.

 E_i, N_i, g_i represent the level energy, population and statistical weight respectively.



- Spontaneous emission is a random process, i.e., one cannot predict when one single atom will radiatively decay.
- The measurement of the number of photons emitted by a population of atoms over a long period of time leads to the notion of a radiative lifetime:

At initial time t = 0, the population is $N_k(0)$

 dN_k atoms decay in dt such that $dN_k = -\sum_{i < j} N_k(t) A_{ki} dt$

Integrating between 0 and t: $N_k(t) = N_k(0) exp\left(-\frac{t}{\tau_k}\right)$

$$\tau_k = \frac{1}{\sum_{i < i} A_{ki}} = \text{Radiative lifetime}$$

Spontaneous Emission Probability Aki

- Statistical weight of level $E_k = 2J_k + 1$ where $J_k =$ total angular momentum of state 'k'.
- E.g., He 1s2p (¹P₁) state
- (¹P₁) = (^{2S+1}L_J), S = Total spin angular momentum, L = Total orbital angular momentum and J = Total angular momentum (L+S, L+S-1,L-S).
- Here g = 2J+1 = 2(1) + 1 = 3!

The Width and Shape of Spectral lines Natural Line Shape

If E_i is the fundamental level, then $\tau_i \rightarrow \infty$. If E_k is resonance level just above the fundamental level, then $A_{ki} = \frac{1}{\tau_k}$.

The Einstein Spontaneous emission coefficient A_{ki} should be modulated by a normalised line shape function such as

$$L(\omega) = \frac{I_{ki}(\omega)}{I_0} = \frac{\Gamma_{ki}/2\pi}{(\omega - \omega_{ki})^2 + {\Gamma_{ki}}^2/4}$$

The transition probability that includes the line shape is thus $A_{ki}L(\omega)$. $L(\omega)$ is normalised such that

$$\int_{-\infty}^{+\infty} L(\omega) d\omega = \int_{line} L(\omega) d\omega = 1$$

 I_0 = Total energy radiated in the line (normalisation factor)

•Note: Atomic levels can also de-excite nonradiatively, e.g collisions, emission of an electron (Auger effect). The total transition probability is thus the sum of radiative terms and non-radiative terms which can be written in the following form:

$$A_{ki}^{\text{Total}} = \frac{1}{\tau_{ki}^{rad}} + \frac{1}{\tau_{ki}^{non-rad}}$$

•Usually, one type of deexcitation process will dominate

The Width and Shape of Spectral lines Line Broadening mechanisms in real line sources: Collisional broadening

•In a real source, atoms (emitters) are subjected to the interaction forces (i.e., collisions) of neighbouring atoms, ions, electrons, etc...+ possibly external potentials. These perturb the potential energy of the radiating atom which results in a broadening of the line to a value greater than the natural line width.

•This type of broadening may take different forms according to the exact nature of the interaction potential: Collisional broadening, Stark broadening, Pressure broadening

•Detailed quantum mechanical calculations would show that the collisionally broadened line shape is also Lorentzian of FWHM

$$\Delta \omega_{total} = \Delta \Gamma_{Natural} + \Delta \Gamma_{Collisional}$$

The Width and Shape of Spectral lines Line Broadening mechanisms in real line sources: Doppler broadening

•A stationary atom of mass m emits a photon of (angular) frequency $\omega_{0.}$

•The apparent frequency ω_0' observed by a stationary observer when the atom emits a photon moving at the relative velocity \vec{v} :



•In a gas in equilibrium there exists a Maxwell-Boltzmann distribution of velocities (controlled by the absolute temperature T, see Y3 Stat.Phys).

•The probability $P(v_z)dv_z$ that an atom has z-component of velocity between v_z and v_z +d v_z is:

$$P(v_z)dv_z = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mv_z^2}{2k_B T}\right)dv_z$$

•Thus the probability of detecting a wave with angular frequency between ω_0 ' and ω_0 '+ $d\omega_0$ ' is given by the following Gaussian distribution:

$$P(\omega_0')d\omega_0' = \left(\frac{2}{\sqrt{\pi}\Delta}\right) \exp\left(-4\frac{\left(\omega_0' - \omega_0\right)^2}{\Delta^2}\right) d\omega_0'$$

The Width and Shape of Spectral lines Line Broadening mechanisms in real line sources: Doppler broadening

Where Δ is the linewidth parameter, from which one obtains the FWHM $\Delta \omega_{\frac{1}{2}}(Doppler)$ (see "truncation of

Gaussian functions" in "Optical Resonator"):

$$\Delta \omega_{\frac{1}{2}}(Doppler) = \Delta \sqrt{Ln2} = 2 \frac{\omega_0}{c} \sqrt{\frac{2kT}{m}} Ln2$$

•A measurement of the Doppler width can thus provide an estimation for the temperature of the medium

•Doppler broadened lines are **inhomogeneously** broadened

The total width of any spectral line emitted in a real source is thus:

$$\Delta \omega_{total} = \Delta \Gamma_{Natural} + \Delta \Gamma_{Collisional} + \Delta \omega_{\frac{1}{2}} (Doppler)$$

Einstein Treatment of Stimulated Absorption and Emission

- Thermal equilibrium of two-level atoms with radiation
- Radiation in thermal equi., ie blackbody radiation model, is given by Planck's radiation law (radiation energy density=energy per unit volume per unit interval frequency)

$$\rho(\nu,T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

• The atomic populations are in Maxwell-Boltzmann equilibrium, maintained by a dynamic equilibrium between emission and absorption processes



Einstein Coefficients

- A_{ki} = coefficient of spontaneous emission
- B_{ik} = coefficient of (stimulated) absorption
- B_{ki} = coefficient of stimulated emission

Einstein Treatment of Stimulated Absorption and Emission

 The upward and downward transition rates are obtained in terms of the populations and coefficients:

Upward rate:

$$\frac{dN_i}{dt} = -N_i B_{ik} \rho$$

Downward rate:

$$\frac{dNk}{dt} = -N_k \left(A_k + B_{ki} \rho \right)$$

Equilibrium (detailed balance):

$$\frac{dN_i}{dt} = \frac{dN_k}{dt} = 0$$
$$N_i B_{ik} \rho = N_k (A_{ki} + B_{ki} \rho)$$

Maxwell-Boltzmann:

$$\frac{N_k}{N_i} = \frac{g_k}{g_i} exp\left[-\frac{\hbar\omega_{ki}}{k_B T}\right]$$

From above:

$$\frac{N_k}{N_i} = \frac{B_{ik}\rho}{(A_{ki} + B_{ki}\rho)}$$

$$\rho(\omega_{ki}) = \frac{g_k A_{ki} \exp(-\hbar\omega_{ki}/k_B T)}{g_i B_{ik} - g_k B_{ki} \exp(-\hbar\omega_{ki}/k_B T)}$$

Using Planck's radiation law for $\rho(\omega_{ki})$ $g_i B_{ik} = g_k B_{ki}$

$$B_{ik} = \frac{\pi^2 c^3}{\hbar \omega_{ki}^3} \frac{g_k}{g_i} A_{ki}$$

Width and Shape of Spectral Lines

Einstein Treatment of Stimulated Absorption and Emission

 To have equal rates of spontaneous and stimulated emission requires:

$$A = B\rho(v_0) \Rightarrow \frac{A}{B} = \rho(v_0) = \frac{8\pi h}{\lambda^3}$$

$$\lambda \equiv \lambda_0 = 1 \ \mu \text{m} \Rightarrow c\rho(v_0) = I(v_0) \approx 5x10^{-6} \text{ W/m}^2\text{Hz}$$

For a (Lorentzian) spectral line of width $\Delta v = 10^7 \text{ Hz}$

$$I(v_0) = \frac{2}{\pi \Delta v} \times I_0 \Rightarrow I_0 = 50 \text{ Wm}^{-2} = 5 \text{ mWcm}^{-2}$$

 Stimulated emission typically negligible for laboratory line sources

Elementary Interaction Processes



- Stimulated absorption: one photon lost
- Attenuation



- Stimulated emission: one photon gained
- Amplification
- Stimulated photon:
 same direction and
 phase
 Width and Shape of Spectral Lines
- Spontaneous emission: one photon emitted at random

 hv_{12}