

Lecture – 6

Title: Radiative transitions and spectral broadening

Objectives

The spectral lines emitted by atomic vapors at moderate temperature and pressure show the wavelength spread around the central frequency. This is known as width of the spectral lines.

In this lecture at first we will understand the origin of radiative transitions.

We will establish the relations between Einstein coefficients B_{12} , B_{21} and A_{21}

We will discuss the different mechanism for the broadening of the spectral lines emitted by the atomic source.

We will find out the reasons for these broadening.

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Radiative transitions and spectral broadening:

- We now know that, Bohr's theory described that the emission of radiation from atoms was from the higher energy state to lower energy state of atom.
- This is known as “quantum jump”
- Bohr tried to describe it through the correspondence principle

According to Bohr's theory,

$$E_{n+1} = -\frac{2\pi^2 me^4}{(n+1)^2 h^2}$$

Equation – 6.1

And
$$E_n = -\frac{2\pi^2 me^4}{(n)^2 h^2}$$

Equation – 6.2

Thus
$$E_{n+1} - E_n = \frac{2\pi^2 me^4}{h^2} \left[\frac{1}{(n)^2} - \frac{1}{(n+1)^2} \right]$$
$$\approx \frac{2\pi^2 me^4}{h^2} \frac{2}{n^3} \quad \text{for } n \gg 1$$

The emitted frequency $E_{n+1} - E_n = h\nu_{n+1, n}$

Equation – 6.3

However, Bohr's theory fails to describe the mechanism of transitions between the two stationary states. It also does not provide rational explanation for deriving the intensity and polarization of the emitted spectral lines.

Einstein transition probabilities:

The first major step to understand the transitions between two stationary states and the corresponding radiation was taken by Einstein.

As shown in Figure – 6.1, let us assume that E_1 and E_2 are the stationary energy levels of an atomic system. Let us consider that this system is exposed to a radiation $h\nu$.

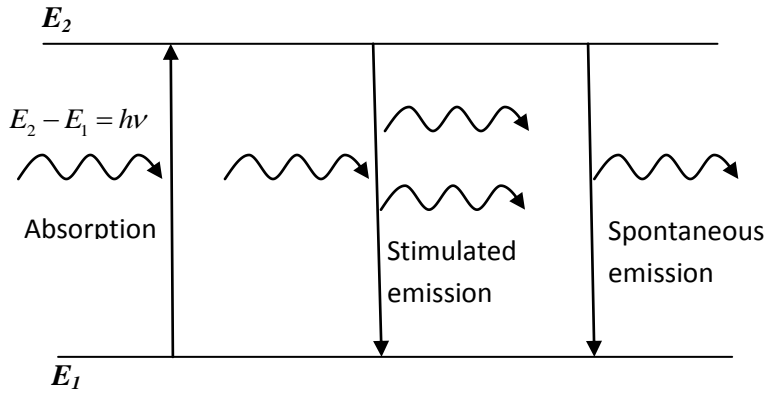


Figure – 6.1

Process 1: If an atom absorbs a photon of energy $E_2 - E_1 = h\nu$, it is excited from the lower energy level E_1 to the higher energy level E_2 . The process is called induced absorption. The probability per second that the atom will absorb the photon, $\frac{dp_{12}}{dt}$

This is proportional to the number of photons of energy $h\nu$ per unit volume = the spectral density of the radiation field $\rho_\nu(\nu)$

So, $\frac{dp_{12}}{dt} = B_{12}\rho(\nu)$, B_{12} = Einstein coefficient of induced absorption.

Equation – 6.4

Process 2: The radiation field can induce the atoms to make a transition from excited states E_2 to lower energy state E_1 .

Since the system decreases the energy, the extra energy will be released as the emission of a photon of energy $h\nu$. This process is known as induced emission or stimulated emission.

The induced photon of $h\nu$ will have the same nature as the photon caused this emission. The probability $\frac{dp_{12}}{dt}$ that one atom emits one induced photon per second is

$$\frac{dp_{21}}{dt} = B_{21}\rho(\nu)$$

Equation – 6.5

B_{21} = Einstein coefficient of induced emission.

Process 3: An excited atom in the excited state E_2 can spontaneously jump into the lower energy states E_1 by emitting a photon of energy $E_2 - E_1 = h\nu$

Note: Spontaneous radiation can be emitted in any arbitrary direction. The probability per second depends on the nature of the stationary energy state and independent of the external field.

So,
$$\frac{dp_{21}^{spont}}{dt} = A_{21}$$

Equation – 6.6

A_{21} = Einstein coefficient of spontaneous emission and also known as spontaneous transition probability.

Relation between B_{12} , B_{21} and A_{21}

Let us assume that the system is having N number of atoms and distributed in different energy levels E_i such that

$$\sum N_i = N$$

At thermal equilibrium of temperature (T), according to Boltzmann distribution,

$$N_i = N_0 g_i e^{-E_i/kT}$$

Equation – 6.7

Where g_i is the degeneracy of level E_i .

In a stationary field,

The number of photons absorbed per unit volume per second = the emission state

$$B_{12}N_1\rho(\nu) = [B_{21}\rho(\nu) + A_{21}]N_2$$

Using

$$\frac{N_2}{N_1} = \left(\frac{g_2}{g_1}\right) e^{-(E_2-E_1)/kT} = \left(\frac{g_2}{g_1}\right) e^{-h\nu/kT}$$

We get,

$$\rho(\nu) = \frac{A_{21}/B_{21}}{\left(\frac{g_1}{g_2}\right)\left(\frac{B_{12}}{B_{21}}\right)e^{h\nu/kT} - 1}$$

Equation – 6.8

The radiation density given by plank's law,

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

Equation – 6.9

Equating we get,

$$B_{12} = \left(\frac{g_2}{g_1} \right) B_{21}$$

Equation – 6.10

It implies that with the equal weights $g_2 = g_1$, the probability of induced emission is equal to that of induced absorption.

We also get

$$A_{21} = \frac{8\pi h^3}{c^3} B_{21}$$

Equation – 6.11

This provides the number of modes per unit volume and unit frequency interval $n(\nu) = \frac{8\pi h^3}{c^3}$ and

$$\text{thus, } \frac{A_{21}}{n(\nu)} = B_{21} h\nu$$

This means that the ratio of the induced to the spontaneous emission rate in an arbitrary mode is equal to the number of photons in this mode.

Relation between lifetime and spontaneous transition probability

An excited atom in the excited state E_2 can spontaneously jump into the lower energy states E_1 by emitting a photon of energy $E_2 - E_1 = h\nu$

So,
$$\frac{dp_{21}^{spont}}{dt} = A_{21}$$

When there are several pathways then

$$A_i = \sum_k A_{ik}$$

The population of the excited state will decrease.

So $dN_i = -A_i N_i dt$

We get $N_i(t) = N_i(0)e^{-A_i t}$

Where $N_i(0)$ is the population density at $t = 0$

The population $N_i(0)$ will be $N_i(0)/e$ after time $\tau_i = 1/A_i$ as shown in Figure – 6.2. This τ_i represents the mean spontaneous lifetime of the level E_i .

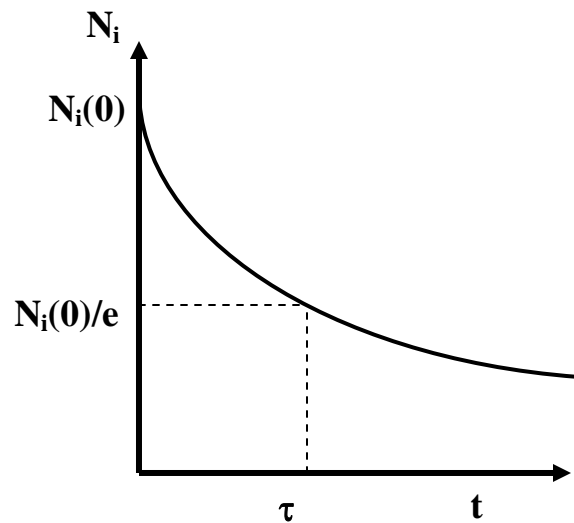
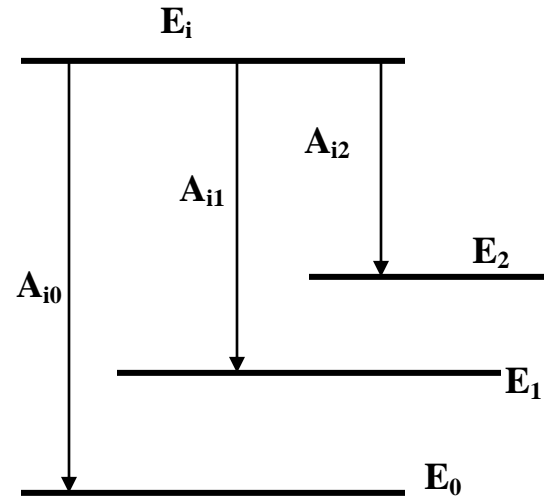


Figure – 6.2

Semiclassical approach of radiative transitions:

In this approach, we consider the radiation as classical electromagnetic wave

$$\vec{E} = \vec{E}_0 \cos(\omega t - kz)$$

Equation – 6.12

On the other hand, we treat the atom quantum mechanically. That means, the atoms absorb or emit radiation when they jump between the two quantized states.

Since the dimension of the atom is much smaller (~ 0.5 nm) than the wavelength of light (~ 500 nm), we take

$$\vec{E} = \vec{E}_0 \cos(\omega t) = \frac{\vec{E}_0}{2} (e^{i\omega t} + e^{-i\omega t})$$

Equation – 6.13

In the dipole approximation, the interaction energy $V = \vec{p} \cdot \vec{E} = pE_0 \cos(\omega t)$ where the dipole $\vec{p} = -e\vec{r}$

The general solution $\Psi(r, t)$ of the time dependent Schrodinger Equation

$$H\Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}$$

Equation – 6.14

Can be expressed as $\Psi(r, t) = \sum_m C_m(t) \phi_m(r) e^{-iE_m t/\hbar}$

Equation – 6.15

Where $\phi_m(r)$ is the eigen function of the time independent Schrodinger equation

$$H\phi_m(r) = E_m \phi_m(r)$$

Equation – 6.16

For two level system as shown in Figure – 6.3, $\Psi(r, t) = a(t)\phi_a(r)e^{-iE_a t/\hbar} + b(t)\phi_b(r)e^{-iE_b t/\hbar}$

Equation – 6.17

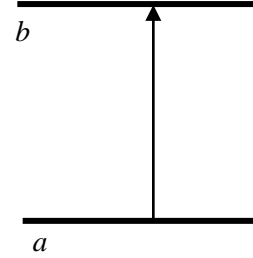
Where $a(t)$ and $b(t)$ are the time dependent probability amplitude of the states a and b and

$$|a(t)|^2 + |b(t)|^2 = 1$$

Substituting in the Schrodinger equation, we get

$$i\hbar \frac{da(t)}{dt} \phi_a e^{-iE_a t/\hbar} + i\hbar \frac{db(t)}{dt} \phi_b e^{-iE_b t/\hbar} = a(t)V\phi_a e^{-iE_a t/\hbar} + b(t)V\phi_b e^{-iE_b t/\hbar}$$

Figure – 6.3



Integrating over the space we get

$$\frac{da(t)}{dt} = -\frac{i}{\hbar} \left[a(t)V_{aa} + b(t)e^{i(E_a - E_b)t/\hbar} \right]$$

Equation – 6.18 a

And

$$\frac{db(t)}{dt} = -\frac{i}{\hbar} \left[b(t)V_{bb} + a(t)e^{-i(E_a - E_b)t/\hbar} \right]$$

Equation – 6.18 b

Where $V_{ab} = \int \phi_a^* V \phi_b d\tau = -eE \int \phi_a^* r \phi_b d\tau$

The dipole matrix element $D_{ab} = -e \int \phi_a^* r \phi_b d\tau$

Since r has odd parity, we get $D_{ab} = D_{ba} = 0$ and $D_{ab} = D_{ba} = -e \int \phi_a^* r \phi_b d\tau$

This depends on the stationary state wavefunctions $\phi_a(r)$ and $\phi_b(r)$ and need to calculate for understanding the transitions between the two states.

Intensity of the transition $I \propto |D_{ab}|^2$

Widths and Profiles of Spectral lines

As shown in Figure – 6.4, the spectral lines observed from atomic vapors are never strictly monochromatic.

Even with very high sensitive instrument, the observed lines show a wavelength spread around the line center.

This is known as width of the spectral lines.

Width of the spectral lines

Central frequency $\nu_0 = (E_a - E_b)/h$ corresponding to a transition

The line profile $I(\nu)$ around ν_0 is known as line profile

ν_1 and ν_2 where the intensity is the half of the maximum intensity ($I_0/2$)

$\delta\nu = \nu_2 - \nu_1$ is known as the Full Width at Half Maximum (FWHM)

Equation – 6.19

Since $\lambda = \frac{c}{\nu}$ then $\delta\lambda = -\left(\frac{c}{\nu^2}\right)\delta\nu$

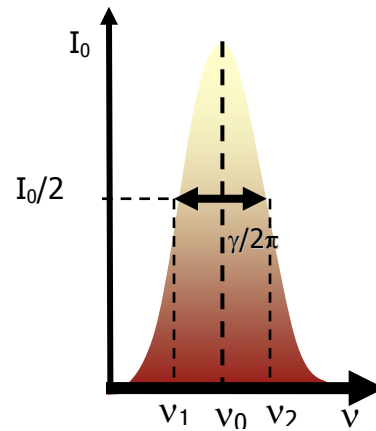
Equation – 6.20

The relative half width

$$\left|\frac{\delta\nu}{\nu}\right| = \left|\frac{\delta\lambda}{\lambda}\right|$$

Equation – 6.21

Figure – 6.4



Mainly there are two reasons for the broadening of the spectral lines

- (a) Width caused by the atomic source
- (b) Width arises due to the instrumental limitations

(a) There are basic three reasons for the broadening caused by the atomic source

1. Natural line broadening
2. Doppler line broadening
3. Pressure / Collisional line broadening

Depending on the effect on the individual atoms, there are two types of broadening.

If all the atoms are experiencing the same type of effect, then the broadening caused by this is known as Homogeneous broadening.

On the other hand, if individual atoms are experiencing different effect then this is known as inhomogeneous broadening.

1. Natural line broadening

An excited atom can emit the radiation spontaneously. This phenomenon can be treated classically as damped oscillator discussed in the previous lecture.

The intensity profile

$$I(\omega - \omega_0) = A(\omega)A^*(\omega) = I_0 \frac{1}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$

Equation – 6.22

Where I_0 is the maximum intensity and $\omega = 2\pi\nu$. This line profile is known as Lorentzian profile and can be written as

$$L(\omega - \omega_0) = \frac{1}{2\pi} \frac{\gamma}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$

Equation – 6.23

In this, full width half maximum (FWHM) = $\delta\omega = \gamma$ or $\delta\nu = \gamma/2\pi$

Equation – 6.24

This also can be understood from the Heisenberg Uncertainty Principle

$\tau \Delta E = \hbar/2\pi$ where τ is the lifetime and ΔE is the uncertainty in energy. So, when τ is small, ΔE is large.

This broadening is known as natural linewidth of the spectral line for the excited state whose lifetime is finite. The broadening of the spectral line can not be smaller than this ΔE even a high resolution instrument is used to measure it. This type of broadening is Homogeneous broadening.

$$\text{Natural Width} \propto \frac{1}{\text{Life Time of Excited States}}$$

Equation – 6.25

At high pressure, due to collisions life of the excited state is decreased and the broadening occurs.

$$\tau = \frac{1}{n_0} \sum_{i=1}^{n_0} t_i \quad t_i \Rightarrow \text{time for atom } i \text{ in the excited state}$$

↑

*lifetime of the
excited state*

Equation – 6.26

If collision occurs it loses some excitation energy and for that if t_i decreases then the natural width increased.

For example: If the lifetime of a particular excited state is 10^{-9} sec then the energy broadening from Heisenberg uncertainty principle

$$\Delta E \Delta t = \hbar$$

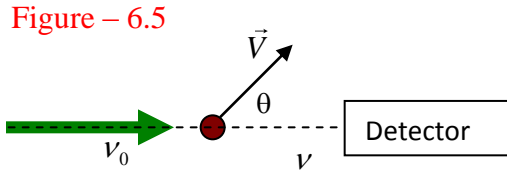
$$\Rightarrow \Delta E = \frac{\hbar}{\Delta t} = \frac{1.05 \times 10^{-34}}{10^{-9}} J = 1 \times 10^{-25} J$$

2. Doppler line broadening

Atoms emitting electromagnetic radiation are not stationary (gas). For an observer in the laboratory frame of reference, the emission must be considered as coming from a source in motion, so necessary to take Doppler effect.

Speed V of atom is small compared to c , so it is possible to use classical expression for the Doppler effect.

Let θ be the angle between observation direction & velocity vector, the change of frequency $\delta\nu$ between the exact frequency ν_0 and the frequency ν seen by the observer,



$$\frac{\delta\nu}{\nu_0} = \frac{\nu - \nu_0}{\nu_0} = \frac{V \cos \theta}{c} = \frac{V_x}{c} \quad \text{Equation – 6.27}$$

V_x is the component in the direction of the observer. If we assume that the temperature of the gaseous source of light is uniform, the distribution of speeds of the atoms is a Maxwell distribution. So the number of atoms whose velocity V_x is between V_x and $V_x + dV_x$

$$dN = N f(V_x) dV_x \quad N \Rightarrow \text{Total no. of Atoms}$$

$f(V_x)$ is the probability density for the component v_x

$$f(V_x) = \sqrt{\left(\frac{M}{2\pi RT}\right)} \exp\left[-\frac{M}{2RT} V_x^2\right]$$

Equation – 6.28

$M \Rightarrow$ molecular weight, $R \Rightarrow$ perfect gas constant

$$\text{Now, } V_x = c \frac{\nu - \nu_0}{\nu_0} \quad \text{So, } dV_x = c \frac{d\nu}{\nu_0}$$

Equation – 6.29

Let $P_\nu d\nu$ is the power emitted in the band frequencies between ν and $\nu + d\nu$ is proportional to the number of atoms between velocity V_x and $V_x + dV_x$, if proportionality constant is K ,

$$\begin{aligned}
 P_\nu d\nu &= K N f(V_x) dV_x \\
 &= K N f\left(c \frac{\nu - \nu_0}{\nu_0}\right) c \frac{d\nu}{\nu_0} \\
 &= K' f\left(c \frac{\nu - \nu_0}{\nu_0}\right) d\nu \\
 \text{So, } P_\nu &= K' f\left(c \frac{\nu - \nu_0}{\nu_0}\right) = K'' \exp\left[-\frac{M}{2RT} \frac{c^2 (\nu - \nu_0)^2}{\nu_0^2}\right]
 \end{aligned}$$

Equation – 6.30

This profile as given in Equation – 6.30 & as shown in Figure – 6.6 is the Gaussian line profile.

$\Delta\nu_D = \nu_2 - \nu_1$, the width at half height of the curve.

$$\begin{aligned}
 \exp\left[-\frac{M}{2RT} \frac{c^2 (\nu - \nu_0)^2}{\nu_0^2}\right] &= \frac{1}{2} \\
 \Rightarrow \nu - \nu_0 = \delta\nu &= \frac{\nu_0}{c} \sqrt{\left(\frac{2RT}{M} \ln 2\right)}
 \end{aligned}$$

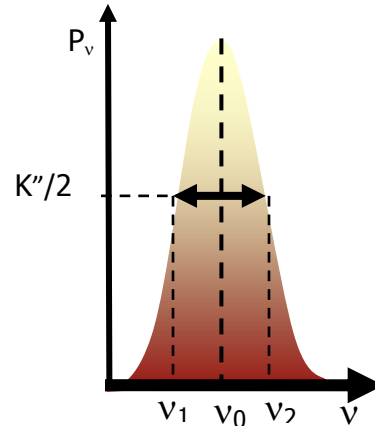


Figure – 6.6

$$\text{So the width } \Delta\nu_D = \frac{2\nu_0}{c} \sqrt{\left(\frac{2RT}{M} \ln 2\right)}$$

Equation – 6.31

$$\begin{aligned}
 \Delta\nu_D &\propto \sqrt{T} \\
 \text{So, Doppler Width} &\propto \nu_0 \\
 &\propto \frac{1}{\sqrt{M}}
 \end{aligned}$$

Equation – 6.32

$$\lambda = 589.3 \text{ nm} \rightarrow \Delta\left(\frac{1}{\lambda}\right) = 0.057 \text{ cm}^{-1}$$

Na gas at 500 K

$$\frac{v}{c} \approx 10^{-6} \approx \frac{\partial v}{v}$$

$$\frac{\delta v}{v} \approx 10^{-10}$$

Natural Line Width

So the Doppler width is much greater than the Natural line width. Doppler broadening is inhomogeneous broadening.

3. Pressure / Collisional line broadening

For a gas at a given pressure radiating atoms interact with the neighboring atoms via collision and this affect the emission line width strongly.

For example, an atom A with energy levels E_1 and E_2 approaches to another atom B. Because of the interaction, the energy levels get perturbed and the shift of these energy levels occur. Due to this the line profile gets broadened. This broadening depends on the collision diameter.

$\text{FWHM} = \frac{1}{\pi\tau_0}$ where τ_0 is the mean flight time between two successive collision.

(b) Width arises due to the instrumental limitations

The basic set up for the emission experiment is

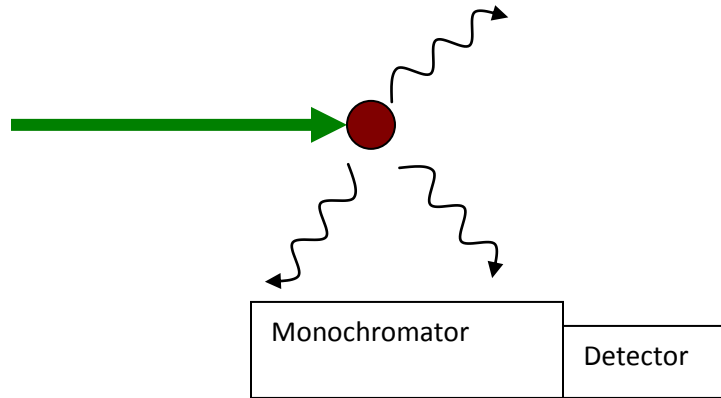


Figure – 6.7

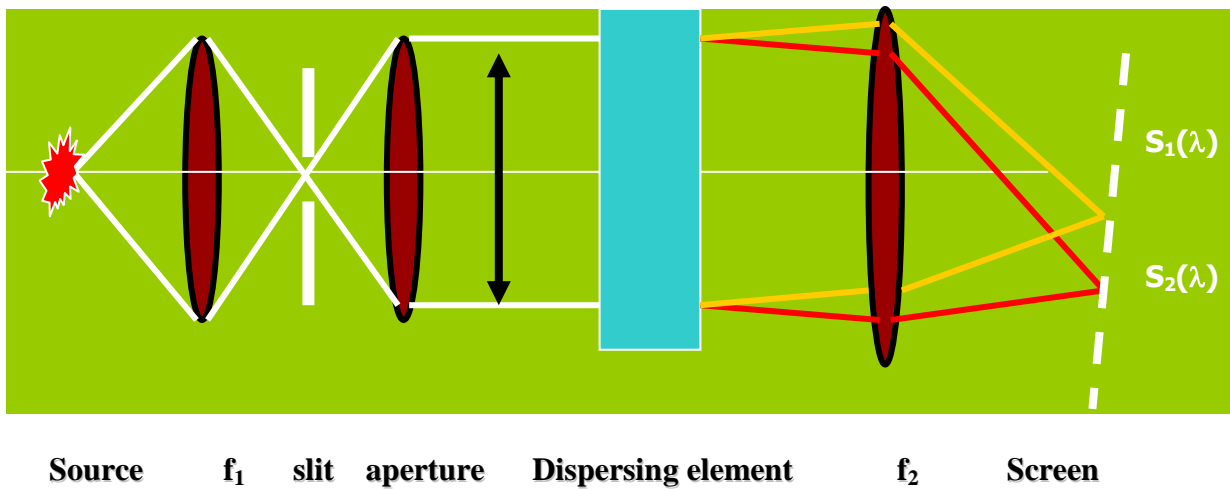


Figure – 6.8

$$\text{Linear Dispersion} = \frac{dx}{d\lambda} \propto f \left(\frac{dn}{d\lambda}, f_2 \right)$$

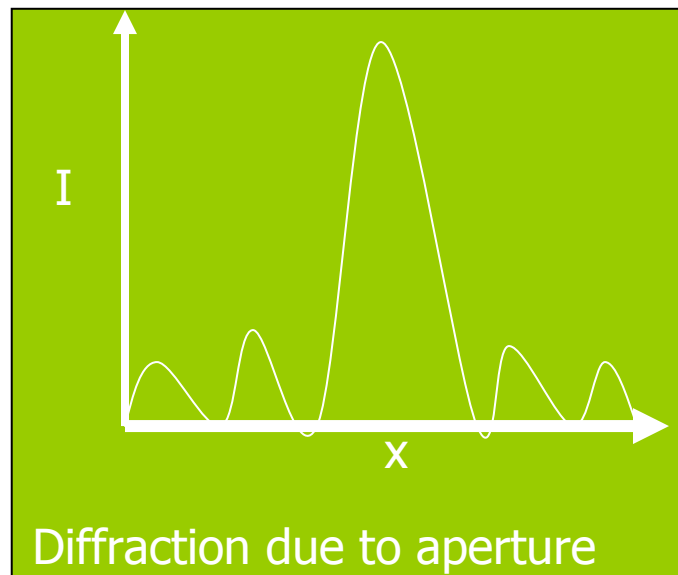
Equation – 6.33

$$\text{Slit width} = \delta x_1$$

Equation – 6.34

$$\text{Image width} = \delta x_1 (f_2/f_1)$$

Equation – 6.35



Spectral Resolving Power

Figure – 6.9

$$I(\lambda - \lambda_0) = I(\lambda_0) [\text{Sin}((\lambda - \lambda_0) / 2) (\lambda - \lambda_0) / 2]^2$$

$$I(\lambda) = I_1(\lambda - \lambda_1) + I_2(\lambda - \lambda_2)$$

Equation – 6.36

Rayleigh criterion

0.8 of I_{\max}

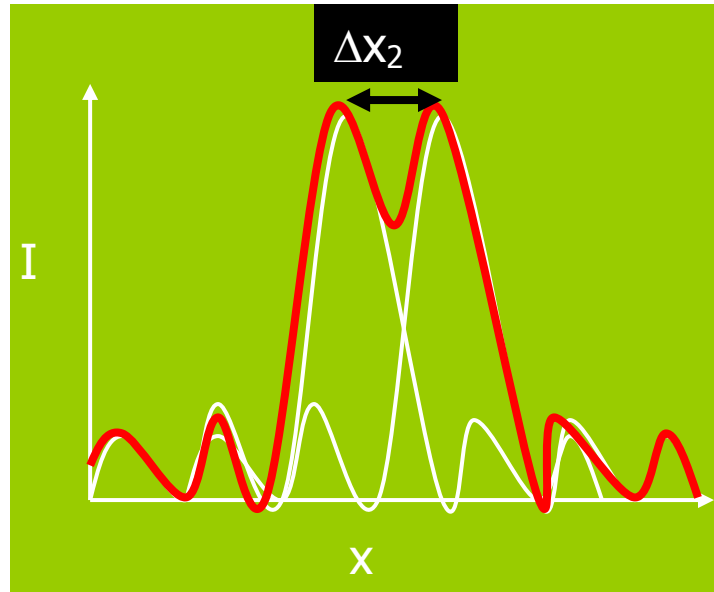
$$\Delta x_2 = f_2(\lambda/a)$$

Equation – 6.37

Where a is the aperture

And the resolving power = $\frac{\lambda}{\delta\lambda}$

Equation – 6.38



The Grating monochromator.

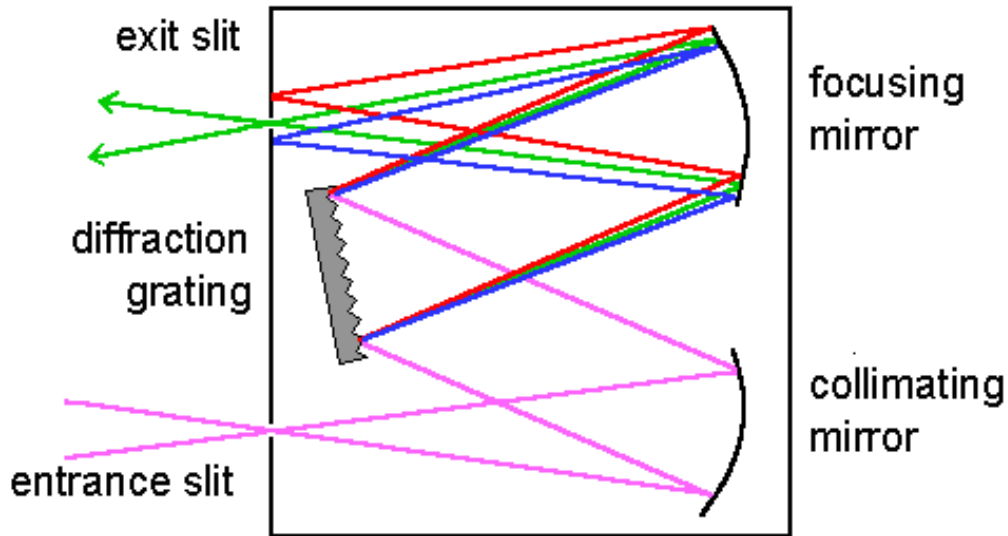


Figure – 6.10

(i) Light gathering power / numerical aperture / speed of monochromator

Acceptance Angle = d/f_1

(ii) The spectral transmission of the optical systems $T(\lambda)$ or $R(\lambda)$

(iii) Spectral resolving power = $\lambda/\Delta\lambda$

minimum separation $\Delta\lambda$ of two spectral lines that can be resolved

(iv) Free Spectral range : wavelength range $\Delta\lambda$ in which the wavelength λ can be unambiguously determined from $x(\lambda)$ =

If N is the no. of grooves per inch and m is the order then $\frac{\lambda}{\Delta\lambda} = mN$

Recap

In this lecture we understood the classical and quantum description of the radiative transitions. We established the relations between Einstein coefficients B_{12} , B_{21} and A_{21}

We came to know that the minimum spectral line width is governed by the lifetime of the excited state.

Now we know that the origin of homogeneous broadening and inhomogeneous broadening.

We had briefly gone through the monochromator which is an essential instrument for spectroscopy experiment.

In this module, we prepare ourselves the basic understanding of quantum mechanics through the development of concept of atom. In the next module, we will start applying these concepts to understand various observations of atomic spectroscopy.