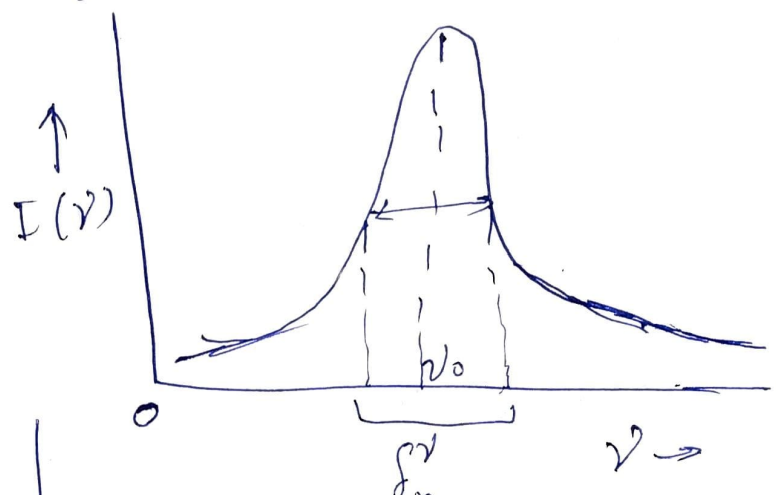


An ordinary Fourier analysis of the damped wave emitted by the oscillator gives for the energy, or better the intensity which is proportional to the energy radiated, as a function of the frequency

$$I(\nu) = \frac{\gamma}{2\pi} \frac{1}{4\pi^2 (\nu_0 - \nu)^2 + \left(\frac{\gamma}{2}\right)^2}$$

The general contour of such a distribution is shown in following figure



The half-intensity breadth $\Delta\nu$ of this symmetrical distribution, like the Doppler half-intensity breadth, is here defined as the interval between the two points where the intensity drops to half its maximum value.

Intensity-frequency contour for the natural width of a spectrum line

From eqⁿ (12) the intensity will drop to half its maximum when the two terms in the denominator are equal, i.e. when

$$\nu_0 - \nu = \frac{\gamma}{4\pi} = \frac{1}{2} \Delta\nu = \Delta\nu \quad (13)$$

which gives the natural half-intensity breadth

$$\delta \nu = \frac{\gamma}{2\pi} = \frac{4\pi e^2 \nu_0^2}{3mc^3} \quad (14)$$

Since $\frac{\Delta \nu}{\nu} = \frac{\Delta \lambda}{\lambda}$ and $c = \nu \lambda$

the half-intensity breadth, in terms

of wave-length is

$$\delta \lambda = \Delta \lambda = \frac{2\pi c}{\omega^2} \gamma = \frac{c}{2\pi \nu^2} \gamma$$

$$= \frac{4\pi e^2}{3mc^2} = 1.16 \times 10^{-12} \text{ cm}$$

(15)

which is constant and equal to 0.000116 \AA for all wave-lengths, a value many times too small to be measured by ordinary spectroscopic methods.

Natural Breadths and the Quantum Mechanics

According to the Q.M. principles an energy level diagram of an atom is not to be thought of as a set of discrete levels but as a sort of continuous term spectrum in which the probability distribution is concentrated in regions where the terms are observed.

The natural line width, which is classically attributed to damping of radiations, quantum mechanically is regarded as due to

the finite life time and consequent uncertainty in energy ~~levels~~ values. (52)

If $\Delta E \rightarrow$ spread in energy

$\Delta t \rightarrow$ mean life time

then $\Delta E \Delta t \approx h$ — (18)

For ground state $\Delta t \rightarrow$ large so uncertainty ΔE is very small. Also for a metastable state $\Delta t \rightarrow$ may be as large as several seconds and these states are also very sharp.

For an ordinary excited state $\Delta t \sim 10^{-8}$ sec.

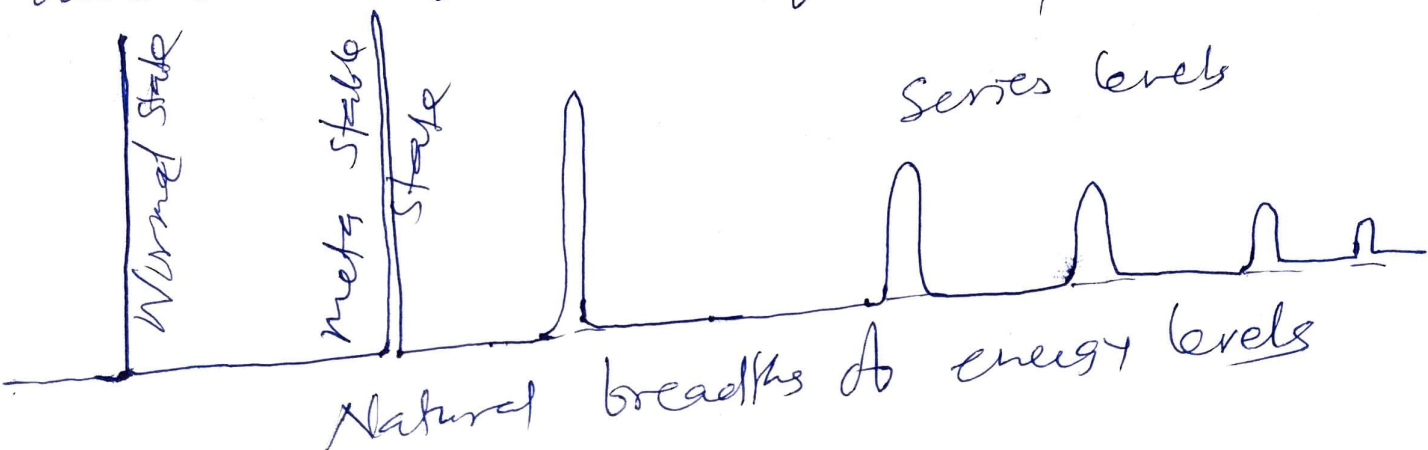
Then the broadening of spectral line due to the finite width of an excited energy state

is about
$$\Delta \nu = \frac{1}{2\pi \Delta t} \approx 10^7 \text{ sec}^{-1}$$
 — (19)

For a visible line of $\lambda = 6000 \text{ \AA}$ this corresponds to a wavelength broadening of only

$$\Delta \lambda = \frac{\lambda^2}{c} \Delta \nu \approx 0.0001 \text{ \AA}$$
 — (20)

From eq (18), for ground state $\Delta t \rightarrow \infty$ hence, the broadening of the line takes place due to the broadening of excited level only.



(3) Width of the line due to other effects

(53)

(a) Collision Damping (broadening)



One of the important external causes is the broadening of spectral lines.

One of the effects produced by the collisions of two atoms \rightarrow one of which is in the process of emitting or absorbing radiation.

Michelson and Lorentz \rightarrow Assumption

If, during the time an atom is emitting or absorbing radiation of frequency ν_0 it collides elastically with another atom, the phase and amplitude of the radiation have a chance of undergoing a considerable change.

Further at the time of emission or absorption the atoms are under heavy pressure, the rate of collisions increases which, enhance the effect. To

Calculate the magnitude of collision broadening the assumptions usually made are:

(1) The mean time between collisions is large compared with the collision time.

(2) With every impact the oscillations are either completely cut off, or they are distributed for a moment

(3) The oscillations ~~are~~ of same frequency are resumed, with a considerable change in phase and amplitude of oscillations.

We have two types of incoherent radiation.

Radiation before and after collisions

The half intensity breadth is given following former analysis,

$$\Delta\nu = \frac{1}{\pi f_0} \sqrt{\frac{8RT}{\pi M}}$$

(b) $\lambda_0 \rightarrow$ mean free path.
Asymmetry and Pressure shift

It is also important to consider the radiations emitted during the collision process and, ~~is known as the impact approximation~~. The calculation which takes into account the ignored radiations is known as Stark approximation.

At time of collisions, the emitting atom is under pressure of impact and the frequency of radiations emitted at this time is found to change.

There is asymmetry between the radiations emitted before and after the collisions and those emitted during the collisions. This result is asymmetry and pressure shift.

Explanation has been given that at close approach of a foreign atom the energy levels of the excited or radiating atoms are altered, due to polarization effect.

Stark Broadening: In an ordinary arc of high current density many arcs are produced which upon collisions with other atoms give rise to strong fields. The effect of these intermolecular fields is to produce a Stark-effect broadening of the observed spectrum lines.