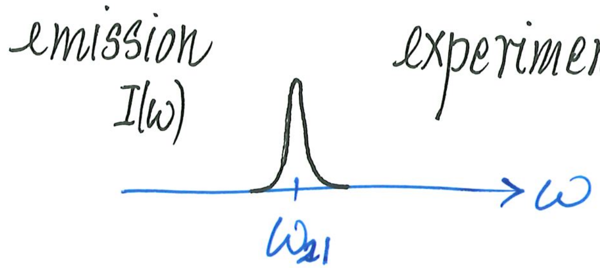
H. The Width and Shape of Spectral lines: A brief introduction

- Measure intensity of spontaneous emission from a collection of atoms [excited into state 2 at time $t=0$ by some way]

Distribution in intensity $I(\omega) \neq \delta(\omega - \omega_{21})$

[not infinitely sharp]

but spectral line is broadened



Line broadening
- Why?
- Fitting can give lifetime of excited state

"Natural Broadening" due to finite lifetime of excited state

- $I(t) \propto N_2(t)$ [which is dropping with time as $\sim e^{-At} = e^{-t/\tau}$]
- For a number of atoms all in state 2 at time $t=0$
  - Each transition gives a photon of $\omega_{21} = \dfrac{E_2 - E_1}{\hbar}$
  - $N_2(t)$ (thus $I(t)$) decays as $e^{-t/\tau}$
  - $I(t) \propto \mathcal{E}^*(t)\,\mathcal{E}(t) = |\mathcal{E}(t)|^2$

$$\boxed{\left.\begin{aligned} \mathcal{E}(t) &= 0 && \text{for } t<0 \\ \mathcal{E}(t) &= \mathcal{E}_0\, e^{-i\omega_{21}t}\, e^{-t/2\tau} && \text{for } t>0 \end{aligned}\right\} \text{this is what is "being observed" in } I(t)} \qquad (43)$$

- Experimentally, the spectrum is related to $I(\omega)$ [intensity distribution]

$$\boxed{\underline{\text{Idea}}: \ \mathcal{E}(t) \xrightarrow{\text{Fourier transform}} \mathcal{E}(\omega) \rightarrow I(\omega) \propto \mathcal{E}^*(\omega)\,\mathcal{E}(\omega)} \quad (44)$$

$$\mathcal{E}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathcal{E}(t)\, e^{i\omega t}\, dt \qquad \text{[Fourier Transform]}$$

$$= \frac{1}{\sqrt{2\pi}} \mathcal{E}_0 \int_{0}^{\infty} e^{i(\omega-\omega_{21})t - t/2\tau}\, dt \qquad \text{[using } \mathcal{E}(t) \text{ in Eq.(43)]}$$

$$= \frac{1}{\sqrt{2\pi}} \mathcal{E}_0 \left. \frac{e^{i(\omega-\omega_{21})t - t/2\tau}}{i(\omega-\omega_{21}) - \frac{1}{2\tau}} \right|_0^{\infty} \qquad \text{[do the integral]}$$

$$= \frac{1}{\sqrt{2\pi}} \mathcal{E}_0 \frac{i}{\left[(\omega-\omega_{21}) + \frac{i}{2\tau}\right]} \qquad \text{[evaluated, complex] (done!)}$$

$$I(\omega) \propto \mathcal{E}^*(\omega)\,\mathcal{E}(\omega) = \frac{\mathcal{E}_0^2}{2\pi}\left(\frac{-i}{(\omega-\omega_{21})-\frac{i}{2\tau}}\right)\left(\frac{i}{(\omega-\omega_{21})+\frac{i}{2\tau}}\right)$$ [slow motion]

$$= \frac{\mathcal{E}_0^2}{2\pi}\cdot\frac{1}{(\omega-\omega_{21})^2+\frac{1}{4\tau^2}} \qquad (45)$$ [done! Important result!]

- Where does $I(\omega)$ peak?

when $\omega=\omega_{21}$, denominator is smallest $\Rightarrow I(\omega=\omega_{21})$ is the peak

Maximum of $I(\omega)$ is $I(\omega_{21}) = \frac{\mathcal{E}_0^2}{2\pi}\cdot(4\tau^2)$

$$\therefore\; I(\omega) = \frac{I(\omega_{21})}{4\tau^2}\cdot\frac{1}{(\omega-\omega_{21})^2+\frac{1}{4\tau^2}} \qquad (46)$$

- Which ω' gives $I(\omega')$ at "half maximum"?

when $$(\omega' - \omega_{21})^2 = \frac{1}{4\tau^2}$$ [see Eq. (46), $I(\omega') = \frac{I(\omega_{21})}{2}$] (Maximum: $I(\omega_{21})$)

OR $$\underset{\substack{\uparrow \\ \text{to the right of } \omega_{21}}}{\omega'} - \omega_{21} = \frac{1}{2\tau}$$ [half width at half maximum]

- FWHM = Full width at half maximum

$$\equiv \underbrace{\Delta\omega}_{\substack{\uparrow \\ \text{can read (fit) this out from spectral line}}} = 2 \cdot \frac{1}{2\tau} = \frac{1}{\tau} \qquad (47)$$ [recall τ is life time of excited state]

Back to Eq. (46): $$I(\omega) = I(\omega_{21}) \cdot \left[\frac{1}{4\tau^2} \cdot \frac{1}{(\omega-\omega_{21})^2 + \frac{1}{4\tau^2}} \right]$$

$$= I(\omega_{21}) \cdot \left[\frac{1/4\tau^2}{(\omega-\omega_{21})^2 + \frac{1}{4\tau^2}} \right]$$

$$= I(\omega_{21}) \left[\frac{(\Delta\omega/2)^2}{(\omega-\omega_{21})^2 + \left(\frac{\Delta\omega}{2}\right)^2} \right] \qquad (48)$$

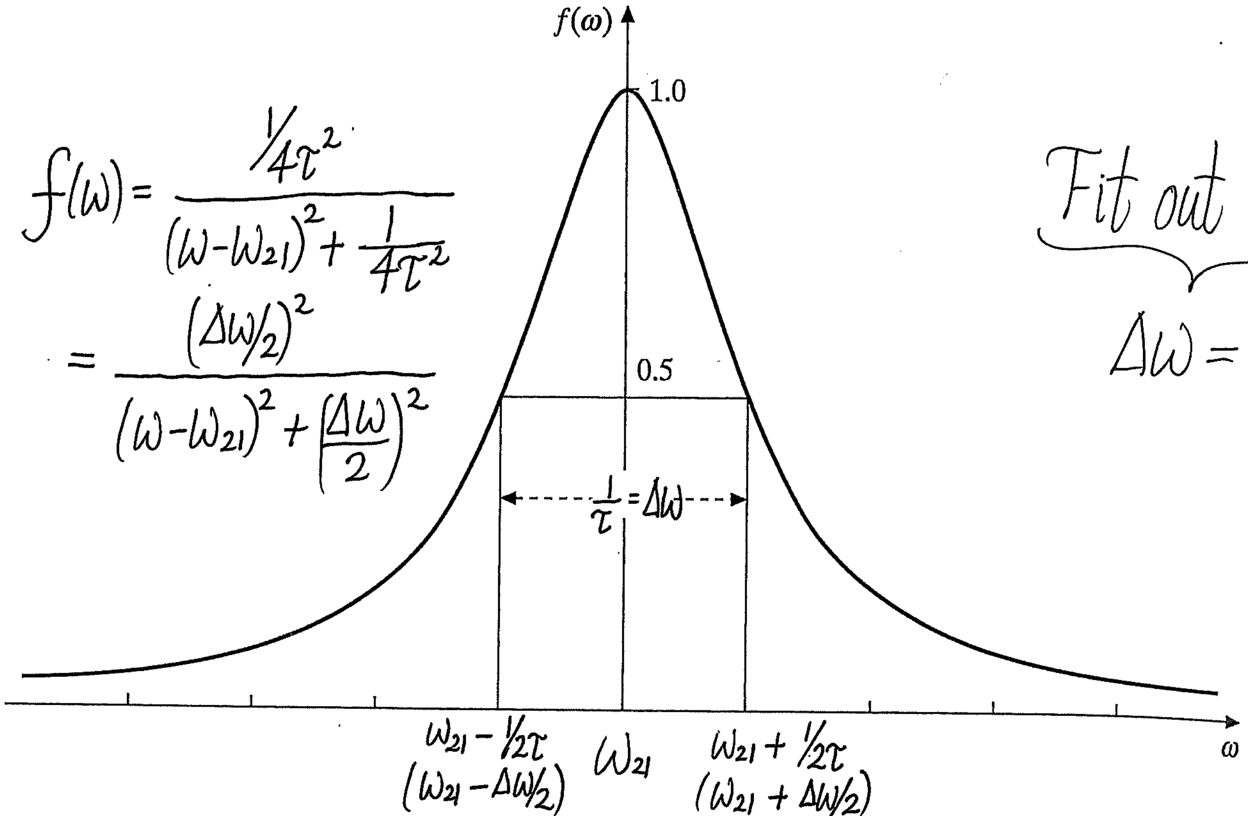
$\boxed{\text{Lorentzian spectral line-shape function}}$

- for fitting out $(\Delta\omega)$ and ω_{21} from spectral line(s)
- finite lifetime of excited state gives Lorentzian line shape
- obtain $(\Delta\omega)$ $\Rightarrow$ obtain $1/\tau$ $\Rightarrow$ obtain A coefficient $\Rightarrow$ obtain B coefficient
- software in spectrometers has fitting embedded

Lorentzian line shape function

$$f(\omega) = \frac{1/4\tau^2}{(\omega-\omega_{21})^2 + \frac{1}{4\tau^2}} \tag{49}$$

$$= \frac{(\Delta\omega/2)^2}{(\omega-\omega_{21})^2 + \left(\frac{\Delta\omega}{2}\right)^2}$$



A plot of the Lorentzian intensity distribution.

$\underbrace{\text{Fit out } (\Delta\omega)}$ (and ω_{21})

$\Delta\omega = \frac{1}{\tau}$ gives τ of excited state

Useful experimentally

An important By-Product

$$\Delta\omega = \frac{1}{\tau} \Rightarrow \Delta\omega \cdot \tau = 1 \Rightarrow (\hbar \underbrace{\Delta\omega}_{\text{FWHM in our context}}) \cdot \tau = \hbar$$

Write $\Delta E \equiv \hbar \Delta\omega$,

$$\boxed{\Delta E \cdot \tau = \hbar} \quad (50)$$

τ: average time an atom stays in excited state (state 2) (thus an uncertainty in time)

"energy-time uncertainty relation"

- Nothing quantum in the argument (came from $\mathcal{E}(t)$ and its finite duration) (time is not an operator)
- (50) is widely used in other physics, e.g. measure ΔE and determine τ of new particles in particle physics

More on spectral line shape

- Natural Broadening : Same effect for all atoms (homogeneous broadening)
  Unavoidable
- Collision (Pressure) Broadening : also "homogeneous"
  can reduce by lowering pressure
- Doppler Broadening : Inhomogeneous (each atom has its speed)
  Hard to avoid, suggest Gaussian line shape than Lorentzian
  [Can reduce effect by cooling atoms down, e.g. laser cooling]