

Chapter 7. Spectral Linewidth and Lineshape

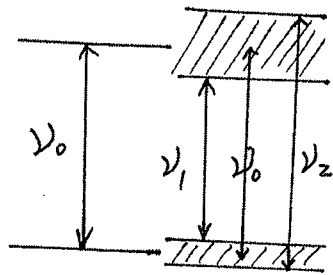
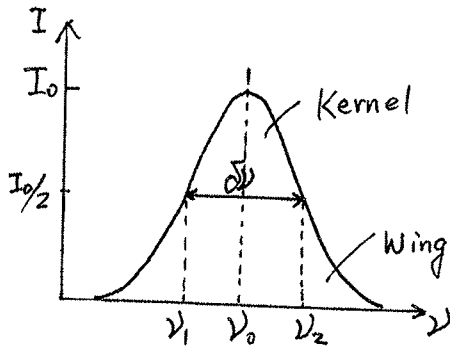
§7.1. Introduction

After we have gone through atomic structure theory to understand atomic energy structure and radiative transition theory to understand transition probability, polarization and angular distribution, now it is time to finally come to the problem of the width and shape of spectral lines.

Although the central frequency (wavelength) of a spectral line is mainly determined by energy level structure (i.e.,

$\omega_{ki} = (E_k - E_i)/\hbar$) and the intensity, polarization of a spectral line is mainly determined by transition theory, the actual frequency, width, shape, and intensity of a spectral line are still affected by many other factors, like uncertainty principle, Doppler effect, collision, transit time, saturation, etc. The overall spectral line is an ultimate result of all these factors combined with atomic structure and radiative transition theories. If transition matrix element is zero, we would not have a transition line. However, if the transition matrix element is non zero, what kind of spectral line we can get depends on experimental conditions, as we will describe below.

A few concepts of line shape, line width, central frequency:



* The spectral distribution of a line is represented as $I(\nu)$.

① Central frequency:

$$\nu_0 = (E_k - E_i)/h \quad (301)$$

② Full-Width-at-Half-Maximum (FWHM)

$$\delta\nu = \nu_2 - \nu_1 \quad (302)$$

Where ν_1 and ν_2 are the frequencies corresponding to half peak intensity $I_0/2$.

③ Line shape (Line profile) $I(\nu)$: Envelope

$$\text{Kernel: } \nu_1 < \nu < \nu_2 \quad (303)$$

$$\text{Wing: } \nu < \nu_1 \text{ and } \nu > \nu_2 \quad (304)$$

④ Peak intensity: I_0 .

§7.2. Natural Linewidth and Lineshape

To investigate the spectral distribution of a spontaneous emission on a transition $E_k \rightarrow E_i$ (k - upper level, i - lower level), we describe the QM's spontaneous emission of an atom or a molecule by a classical model of a damped harmonic oscillator with frequency ω , mass m , and restoring force constant K .

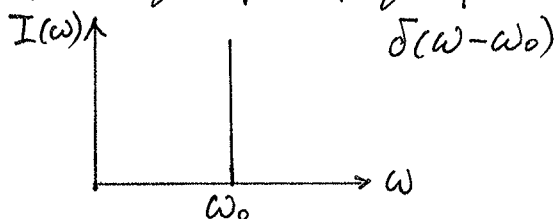
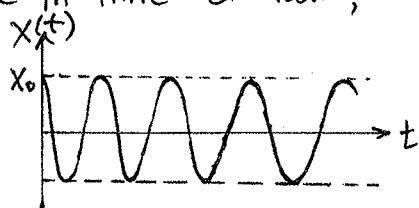
The reason that we do this is the consideration that a neutral atom contains positive and negative charges. Under certain conditions, it forms an electric dipole $\vec{D} = e\vec{r}$. When the electric dipole is making harmonic oscillation, it can emit electromagnetic waves. In the classical model, the electric dipole is described by a harmonic oscillator with mass m and restoring force constant K . If we do not consider damping, then the harmonic oscillation is described by

$$\ddot{X} + \omega_0^2 X = 0 \quad (305)$$

where $\omega_0^2 = K/m$. The solution of Eq. (305) under initial conditions $X(0) = X_0$, $\dot{X}(0) = 0$ is given by

$$X(t) = X_0 \cos \omega_0 t \quad (306)$$

This is a single frequency monochromatic wave: a pure sinusoidal wave in time domain, and a single frequency in frequency domain



In reality, such a monochromatic wave does not exist, because the radiation of the oscillating electric dipole will result in energy loss of the harmonic oscillator, so the amplitude of the oscillation will decrease. We describe this phenomenon by a damped harmonic oscillator with a damping constant γ . The amplitude of the oscillation $X(t)$ is described by

$$\ddot{X} + \gamma \dot{X} + \omega_0^2 X = 0 \quad (307)$$

where $\omega_0^2 = k/m$. The solution of Eq. (7) under initial conditions $X(0) = X_0$ and $\dot{X}(0) = 0$ is given by

$$X(t) = X_0 e^{-(\gamma/2)t} [\cos \omega t + (\gamma/2\omega) \sin \omega t] \quad (308)$$

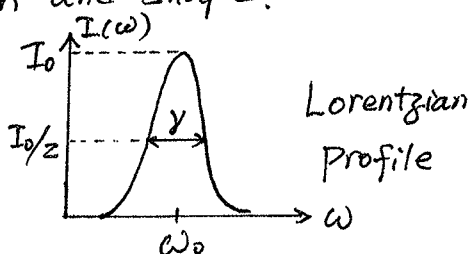
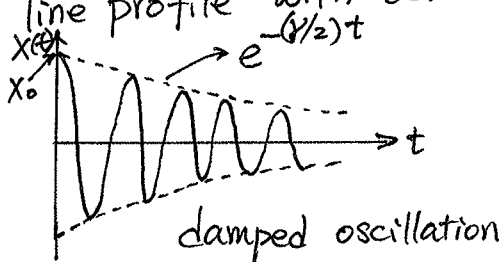
where $\omega = \sqrt{\omega_0^2 - (\gamma/2)^2}$.

For small damping $\gamma \ll \omega_0$, so $\omega \approx \omega_0$. The 2nd term in Eq. (308) can be neglected. Thus, we obtain the damped harmonic oscillation solution as

$$X(t) = X_0 e^{-(\gamma/2)t} \cos \omega_0 t \quad (309)$$

The frequency $\omega_0 = 2\pi\nu_0$ corresponding to the QM central frequency $\omega_{ki} = (E_k - E_i)/\hbar$. The amplitude has an exponential decay with time, as shown below in time domain.

In frequency domain, the $\delta(\omega - \omega_0)$ function is replaced by a line profile with certain width and shape.



As mentioned above, a monochromatic wave is a perfect sinusoidal wave. The damped oscillation can be described as a superposition of many monochromatic waves:

$$X(t) = \frac{1}{2\sqrt{2\pi}} \int_0^{\infty} A(\omega) e^{i\omega t} d\omega \quad (310)$$

where the amplitude $A(\omega)$ is the Fourier transform:

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} X(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_0^{\infty} X_0 e^{-(\gamma/2)t} \cos(\omega_0 t) e^{-i\omega t} dt \quad (311)$$

$$\text{Consider } \cos(\omega_0 t) = \frac{1}{2} (e^{i\omega_0 t} + e^{-i\omega_0 t})$$

$$\begin{aligned} \therefore \int_0^{\infty} e^{-(\gamma/2)t} \frac{1}{2} (e^{i\omega_0 t} + e^{-i\omega_0 t}) e^{-i\omega t} dt \\ = \frac{1}{2} \int_0^{\infty} \left\{ e^{-[i(\omega-\omega_0) + \gamma/2]t} + e^{-[i(\omega+\omega_0) + \gamma/2]t} \right\} dt \\ = -\frac{1}{2} \left\{ \frac{e^{-[i(\omega-\omega_0) + \gamma/2]t}}{i(\omega-\omega_0) + \gamma/2} \Big|_0^{\infty} + \frac{e^{-[i(\omega+\omega_0) + \gamma/2]t}}{i(\omega+\omega_0) + \gamma/2} \Big|_0^{\infty} \right\} \\ = \frac{1}{2} \left[\frac{1}{i(\omega-\omega_0) + \gamma/2} + \frac{1}{i(\omega+\omega_0) + \gamma/2} \right] \end{aligned}$$

$$\therefore A(\omega) = \frac{X_0}{\sqrt{8\pi}} \left[\frac{1}{i(\omega-\omega_0) + \gamma/2} + \frac{1}{i(\omega+\omega_0) + \gamma/2} \right] \quad (312)$$

The intensity $I(\omega) \propto A(\omega) A^*(\omega) = |A(\omega)|^2$

$$\begin{aligned} \therefore I(\omega) &= K A(\omega) A^*(\omega) = K |A(\omega)|^2 \\ &= K \cdot \frac{X_0^2}{8\pi} \cdot \left| \frac{-i(\omega-\omega_0) + \gamma/2}{(\omega-\omega_0)^2 + (\gamma/2)^2} + \frac{-i(\omega+\omega_0) + \gamma/2}{(\omega+\omega_0)^2 + (\gamma/2)^2} \right|^2 \end{aligned}$$

'.' $\omega - \omega_0 \ll \omega + \omega_0$ in the vicinity of the central frequency ω_0 .

∴ the term with $(\omega + \omega_0)$ is much smaller than the term with $(\omega - \omega_0)$.

∴ the term with $(\omega + \omega_0)$ can be neglected.

Thus, the intensity profile of the spectral line becomes

$$I(\omega) = \frac{C}{(\omega - \omega_0)^2 + (\gamma/2)^2} \quad (313)$$

where C is the normalization factor.

To normalize Eq.(13), we express the total energy

$$I_T = \int_0^{\infty} I(\omega) d\omega \quad (314)$$

Substitute Eq.(313) into Eq.(314):

$$I_T = \int_0^{\infty} I(\omega) d\omega = \int_{-\infty}^{+\infty} \frac{C}{(\omega - \omega_0)^2 + (\gamma/2)^2} d(\omega - \omega_0) = C/(\gamma/2\pi)$$

$$\Rightarrow C = I_T \gamma/2\pi.$$

$$\therefore I(\omega) = I_T \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2} \quad (315)$$

$$\text{Define } g_L(\omega) \equiv \frac{I(\omega)}{I_T} = \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2} \quad (316)$$

This is called the normalized Lorentzian profile. We have

$$\int_0^{\infty} g_L(\omega) d\omega = \int_{-\infty}^{+\infty} \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2} d(\omega - \omega_0) = 1. \quad (317)$$

$$\therefore I(\omega) = I_T \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2} = I_T g_L(\omega) \quad (318)$$

Let the peak density be represented by I_0 , i.e., $I(\omega = \omega_0) = I_0$.

From Eq. (18), we have

$$I_0 = I(\omega = \omega_0) = I_T \frac{\gamma/2\pi}{(\gamma/2)^2} = I_T \cdot \frac{2}{\pi\gamma}$$

Thus, the total energy I_T has the following relation with the peak intensity:

$$I_T = I_0 \cdot \frac{\pi\gamma}{2} \quad (319)$$

Substitute Eq. (319) into Eq. (18), the intensity profile becomes

$$I(\omega) = I_0 \frac{(\gamma/2)^2}{(\omega - \omega_0)^2 + (\gamma/2)^2} \quad (320)$$

Apparently, when $|\omega - \omega_0| = \gamma/2$, $I(\omega) = \frac{1}{2} I_0$.

$\therefore \omega_{\pm} = \omega_0 \pm \gamma/2$ are the frequencies corresponding to the half maximum.

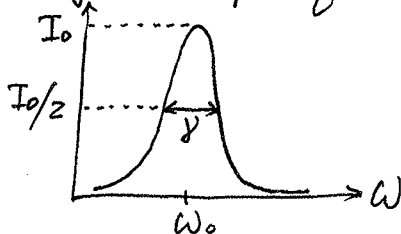
Therefore, the linewidth (FWHM) of $I(\omega)$ is given by

$$\delta\omega_n = \omega_+ - \omega_- = \gamma \quad (321)$$

$$\therefore \delta\nu_n = \frac{\delta\omega_n}{2\pi} = \frac{\gamma}{2\pi} \quad (322)$$

This is the natural linewidth of the damped harmonic oscillator, and γ is the damping constant caused by the energy loss due to the radiation by the electric dipole.

The line intensity profile $I(\omega)$ given by Eq. (318) or Eq. (320) have the Lorentzian shape:



From Quantum Mechanics point of view, the uncertainty principle

$$\Delta E \cdot \Delta t \approx \hbar, \quad (323)$$

shows that the energy levels of an atom which have finite radiative lifetime cannot be considered to be infinitely sharp.

Instead the discrete energy levels must be replaced by maxima in a continuous spectrum of energies as shown in above figure.

The full-width-at-half-maximum (FWHM) of the energy level k is determined by the radiative lifetime of that level

$$\Gamma_k = \Delta \omega_k = \Delta E_k / \hbar = \frac{\hbar / \Delta t}{\hbar} = \frac{1}{\tau_k} = \sum_j' A_{kj} \quad (324)$$

where A_{kj} are the transition probabilities of the allowed electric dipole transitions from k to all possible lower levels, j .

Since in general both the upper and lower levels of an electric dipole transition have finite lifetimes, the uncertainty in the spectral line (i.e., the emitted photons) must include the uncertainty in the energy of both the upper and lower levels. As shown in the following figure,

$$\text{upper level } k: \quad \Gamma_k = \frac{1}{\tau_k} = \sum_j' A_{kj} \quad (325)$$

$$\text{lower level } i: \quad \Gamma_i = \frac{1}{\tau_i} = \sum_h' A_{ih} \quad (326)$$

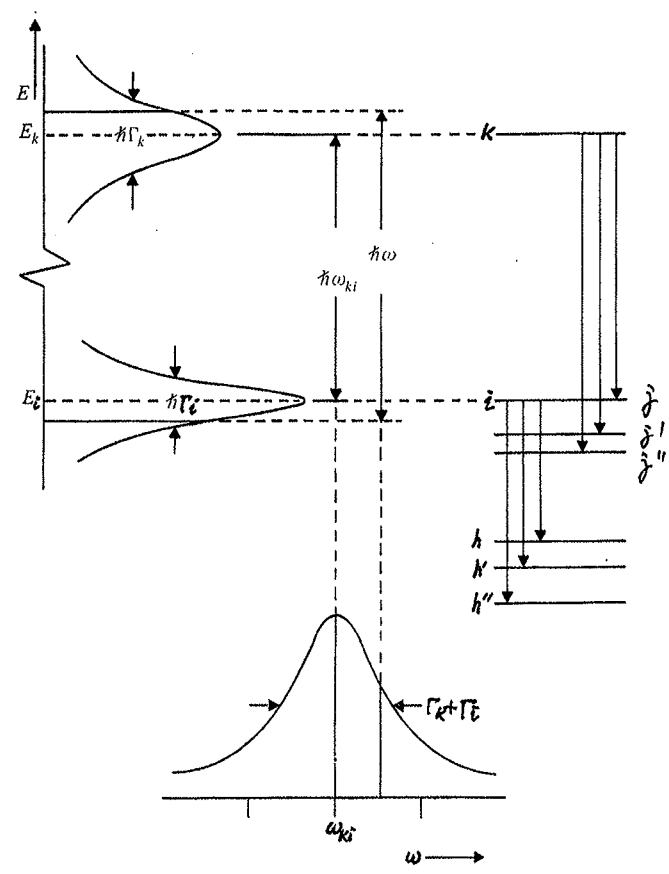
Then the spectral linewidth

$$\begin{aligned} \Delta \omega_{ki} &= \Gamma_{ki} = \Gamma_k + \Gamma_i \\ &= \frac{1}{\tau_k} + \frac{1}{\tau_i} = \sum_j' A_{kj} + \sum_h' A_{ih}. \quad (327) \end{aligned}$$

$$\Delta \omega_{ki} = \frac{\Delta \omega_{ki}}{2\pi} = \frac{(1/\tau_k + 1/\tau_i)}{2\pi} = \frac{\sum_j A_{kj} + \sum_h A_{ih}}{2\pi \hbar} \quad (328)$$

This is called the natural linewidth of the transition $|k\rangle \rightarrow |i\rangle$. The frequency distribution was first obtained quantum mechanically by Weisskopf and Wigner in 1930.

$$I_{ki}(\omega) = I_T \frac{\Gamma_{ki}/2\pi}{(\omega - \omega_{ki})^2 + (\Gamma_{ki}/2)^2} = I_0 \frac{(\Gamma_{ki}/2)^2}{(\omega - \omega_{ki})^2 + (\Gamma_{ki}/2)^2} \quad (329)$$



From Eq. (321) we conclude that if a spectral line associated with an energy level E_k has low A_{ki} , but other lines originated from E_k have high $A_{ki'}$, then this weak line can still have large natural linewidth $\Delta \omega_{ki}$. Why? Can you explain it well?

For transitions from excited states to the ground state, since the radiative lifetime of the ground state $\tau_i = \infty$ (i.e., there is no spontaneous emission from the ground state), the natural linewidth of this transition is

$$\delta \omega_n = \frac{1/\tau_k}{2\pi} = \frac{\sum_i' A_{ki}}{2\pi} = \frac{A_k}{2\pi} \quad (330)$$

$$\delta \omega_n = \frac{1}{\tau_k} = \sum_i' A_{ki} = A_k \quad (331)$$

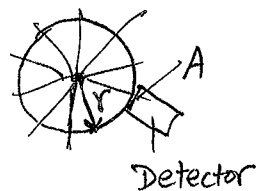
Let us now consider the radiant power emitted from N_k excited atoms on a transition $E_k \rightarrow E_i$ (note: N_k is the number of atoms on the excited state E_k). It is given by

$$\frac{dW_{ki}}{dt} = N_k \cdot A_{ki} \cdot \hbar \omega_{ki} \quad (332)$$

where A_{ki} is the transition rate from $E_k \rightarrow E_i$, i.e., the transition probability per unit time; $\hbar \omega_{ki}$ is the energy of single photon ($\omega_{ki} = (E_k - E_i)/\hbar$).

The spontaneous emission of a source with volume ΔV is isotropic and N_k is the number density of atoms on the excited state E_k . Since the radiant power homogeneously distributes on the sphere with surface area of $4\pi r^2$ (r is the radius of the sphere), the radiant power received by a detector with area A is given by

$$P_{ki} = \frac{dW_{ki}}{dt} \cdot \frac{A}{4\pi r^2} \quad (333)$$



This can also be understood as that the radiant power homogeneously distributes on the entire 4π solid angle, and the detector subtends a solid angle of (A/r^2) to the radiator (i.e., the atomic emission source). Thus, the received radiant power is given by

$$P_{ki} = \frac{dW_{ki}}{dt} \cdot \frac{A/r^2}{4\pi} \quad (334)$$

Eq.(334) is equivalent to Eq.(333), in the case of spontaneous emission which is isotropic. $(\frac{dW_{ki}}{dt})/4\pi$ is the radiant power in unit solid angle. If we use $P(\theta)$ to express the radiant power in unit solid angle, then for isotropic emission, the received power is given by

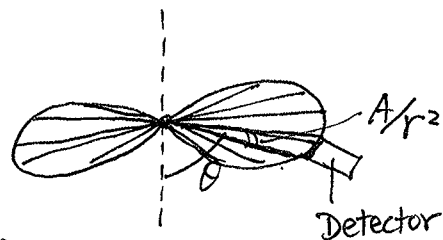
$$P_{ki} = P(\theta) \cdot \frac{A}{r^2} \quad (335)$$

When dealing with anisotropic emission or scattering, we can modify Eq.(335) to the following:

$$P_{ki} = \int_{\theta}^{\theta + A/r^2} P(\theta) d\theta \quad (336)$$

If the detector-subtended solid angle A/r^2 is small enough that $P(\theta)$ is approximately equal within A/r^2 , then Eq.(336) can be simplified to

$$P_{ki} = P(\theta) \cdot \frac{A}{r^2} \quad (337)$$



which is identical to Eq. (335). The difference is that in Eq. (337), $P(\theta)$ is really dependent on θ , as the example shown in the figure, while Eq. (335)'s $P(\theta)$ is a constant, independent of θ .

Considering N_k the number density of atoms on E_k , ΔV is the volume of the atomic source, the product of N_k and ΔV is the total number of atoms on E_k . Thus, the radiant power received by the receiver (given by Eq. (333), or Eq. (334), or Eq. (335)) is

$$P_{ki} = N_k \Delta V \cdot A_{ki} \cdot h\nu_{ki} \cdot \frac{A}{4\pi r^2} \quad (338)$$

$$\therefore N_k = \frac{P_{ki}}{\Delta V \cdot A_{ki} \cdot h\nu_{ki} \cdot \frac{A}{4\pi r^2}} \quad (339)$$

This means that the density N_k of emitter can be inferred from the measured power, if A_{ki} is known and other parameters are measured. This is the basic principle for lidar and other measurement methods to detect species number density.

Example: Na $3^2P_{3/2}$ energy level has lifetime $\tau_k = 16.23 \text{ ns}$.

For transition from $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ (D_2 line), the natural

$$\text{linewidth } \Delta\nu_n = \frac{1/\tau_k}{2\pi} = \frac{1}{16.23 \times 10^{-9} \times 2\pi} = 9.80 \text{ MHz}$$

(Note: $3^2S_{1/2}$ is the ground state of Na, so $\tau_i = \infty$)

§7.3. Absorption and Dispersion Versus Refraction Index

When an electromagnetic wave passes through a medium with refraction index n , not only the wave amplitude decreases (absorption) but also the phase velocity changes from its value c in vacuum to $v = c/n$ (dispersion). The refraction index $n = n(\omega)$ depends on the frequency ω of the EM wave, causing different frequency components have different phase speeds.

The classical model describing the atomic electrons as damped harmonic oscillators which are forced to oscillate by the electric field $E(\omega)$ of the EM wave, gives a clear picture of the relation between absorption and dispersion (Kramers-Kronig relation). Absorption and dispersion are related to the imaginary and real parts of the complex refraction index $n = n' - ik$, respectively. They are two different aspects of the same physical process. This classical model allows the macroscopic refraction index to be related to its microscopic origin, namely the electronic charge distribution of the atoms or molecules and its response to the EM wave.

The conclusions of this classical model can be transferred to real molecules or real atoms in a relatively simple way by introducing the concept of oscillator strength, i.e., transferring into quantum mechanics calculation results.

(1). Classical Model of the Refraction Index

External resonance radiation field (EM wave) forces the atomic electric dipole to oscillate. The atomic electric dipole can absorb energy from the radiation field and influence the phase velocity of the EM wave. This is equivalent to the QM stimulated absorption. Under certain conditions, the atomic electric dipole can release energy to the radiation field — equivalent to the stimulated emission. Thus, a forced oscillation of a damped harmonic oscillator is used to describe the stimulated absorption and stimulated emission in the classical model.

The forced oscillation of a damped oscillator with charge q , mass m , and damping coefficient b under the influence of the external force $q\vec{E}$ in the x direction $\vec{E} = \hat{e}_x E_0 e^{i\omega t}$ is described by the following differential equation:

$$m\ddot{x} + b\dot{x} + kx = qE_0 e^{i\omega t} \quad (340)$$

The solution of Eq. (340) is

$$x(t) = \frac{qE_0 e^{i\omega t}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)} \quad (341)$$

where $\gamma = b/m$, $\omega_0 = k/m$.

The forced oscillation of a charge q generates an induced electric dipole moment:

$$P = qx(t) = \frac{q^2 E_0 e^{i\omega t}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)} \quad (342)$$

The microscopic electric dipole moment can be written as

$$\vec{p} = \epsilon_0 \chi_e \vec{E} = \epsilon_0 \chi_e E_0 e^{i\omega t} \frac{\Delta_0}{e} \quad (343),$$

where ϵ_0 — the dielectric constant in vacuum

χ_e — the susceptibility of individual atom or molecule.

From Eqs. (343) and (342), we obtain

$$\chi_e = \frac{fX(t)}{\epsilon_0 E_0 e^{i\omega t}} = \frac{q^2}{m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega} \quad (344).$$

This is a complex number, and we can further write:

$$\chi_e = \frac{q^2}{m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2 - i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (345)$$

Note: the oscillator mass m is equivalent to the electron mass m_e , or more precisely, the reduced mass $\mu = \frac{m_e M}{m_e + M}$.

This is because the absorption/emission are mainly caused by the change of electron states (as we discussed in QM transition theory). The oscillator is mainly an electron oscillating around its equilibrium point relative to the nucleus.

There are real and imaginary parts of χ_e . Let us define

$$\chi_e \equiv \chi_e' - i\chi_e'' \quad (346)$$

$$\therefore \chi_e' = \frac{q^2}{m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (347)$$

$$\chi_e'' = \frac{q^2}{m\epsilon_0} \cdot \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (348)$$

With Eq. (346), Eq. (343) can be rewritten as

$$P = \epsilon_0 \chi_e E = \epsilon_0 \chi_e' E_0 e^{i\omega t} + \epsilon_0 \chi_e'' E_0 e^{i(\omega t - \pi/2)} \quad (349)$$

This indicates that the force oscillation can be divided into two parts: the first term has in-phase relation between the oscillation and the EM wave, and the 2nd term shows the oscillation has phase delay of $\pi/2$ relative to the EM wave.

In a sample with N oscillators per unit volume (i.e., N is the number density of oscillators), the macroscopic polarization P is the sum of all electric dipole moments per unit volume (note: P is capital letter for macroscopic polarization).

$$P = N q X(t) \quad (350)$$

From classical EM theory,

$$\vec{P} = \epsilon_0 (\epsilon - 1) \vec{E} = \epsilon_0 \chi \vec{E} \quad (351)$$

where ϵ_0 — dielectric constant in vacuum

ϵ — relative dielectric constant

χ — macroscopic susceptibility, i.e.,

$$\begin{aligned} \chi &= N \chi_e = \frac{N q^2}{m \epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 + i \gamma \omega} \\ &= \frac{N q^2}{m \epsilon_0} \cdot \frac{\omega_0^2 - \omega^2 - i \gamma \omega}{(\omega_0^2 - \omega^2)^2 + (\gamma \omega)^2} \end{aligned} \quad (352)$$

From Eq. (351), we have

$$\epsilon = 1 + \chi \quad (353)$$

From EM theory, the phase velocity of EM wave in medium is given by

$$V = \left(\sqrt{\epsilon \epsilon_0 \mu \mu_0} \right)^{-1} = \frac{c}{n} \quad (354)$$

Where μ_0 — the permeability in vacuum

μ — the relative permeability

The light speed in vacuum is given by

$$c = \left(\sqrt{\epsilon_0 \mu_0} \right)^{-1} \quad (355)$$

From Eqs. (354) and (355), we obtain the medium refraction index n is given by

$$n = \sqrt{\epsilon \mu} \approx \sqrt{\epsilon} \quad (356)$$

The last equality is obtained when $\mu \approx 1$. This $\mu \approx 1$ is true for most materials except ferromagnetic materials.

$$\therefore n = \sqrt{\epsilon} = \sqrt{1 + \chi} \quad (357)$$

Substitute Eq. (352) into Eq. (357), the refraction index becomes a complex number:

$$\begin{aligned} n^2 = \epsilon = 1 + \chi &= 1 + \frac{Nq^2}{m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega} \\ &= 1 + \frac{Nq^2}{m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2 - i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (358) \end{aligned}$$

In gases media at sufficiently low pressure, $n \approx 1$,
(e.g., $n_{\text{air}} = 1.00029$)

$$\therefore n^2 - 1 = (n+1)(n-1) \approx 2(n-1)$$

Combine this with Eq. (358), we obtain

$$\begin{aligned} n &= 1 + \frac{Nq^2}{2m\epsilon_0} \cdot \frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega} \\ &= 1 + \frac{Nq^2}{2m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2 - i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \end{aligned} \quad (359)$$

In order to make clear the physical implication of this complex refraction index n , we separate the real and imaginary parts:

$$n = n' - ik \quad (360)$$

$$\text{or } n(\omega) = n'(\omega) - ik(\omega)$$

Consider an EM wave $E = E_0 e^{i(\omega t - kz)}$ passing through the gas media with refraction index n , the EM wave will have the same frequency $\omega_n = \omega_0$ as in vacuum but a different wave vector $k_n = k_0 \cdot n = \frac{2\pi n}{\lambda_0}$ (i.e., $\lambda = \lambda_0/n$). From Eq. (360), we obtain

$$\begin{aligned} E &= E_0 e^{i(\omega t - k_0 n z)} \\ &= E_0 e^{-k_0 k(\omega) z} e^{i[\omega t - k_0 n'(\omega) z]} \\ &= E_0 e^{-2\pi k(\omega) z / \lambda_0} e^{i[\omega t - 2\pi n'(\omega) z / \lambda_0]} \end{aligned} \quad (361)$$

Eq. (361) show that the imaginary part $k(\omega)$ of the complex refraction index n describes the absorption of the EM wave. at a penetration depth of $\Delta z = \lambda_0 / 2\pi k(\omega)$, the amplitude

$E_0 e^{-2\pi k(\omega) z / \lambda_0}$ has decreased to $1/e$ of its value at $z=0$.

The real part $n'(\omega)$ represents the dispersion of the wave.

i.e., the dependence of the phase velocity $V(\omega) = c/n'(\omega)$ on the frequency.

Combine Eqs. (359) and (360), we obtain the real and imaginary parts of refractive index n' and k as

$$n'(\omega) = 1 + \frac{Nq^2}{2m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (362)$$

$$k(\omega) = \frac{Nq^2}{2m\epsilon_0} \cdot \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (363)$$

(2) Quantum Mechanics Correction to Refraction Index

Above are the results from the classical model. We need to make QM correction to them. This is to introduce the oscillator strengths that have been discussed in the QM transition theory. The meaning of the oscillator strength is in the following: because of the large number of possible energy levels, atoms and molecules have not only one but many eigenfrequencies at which they can absorb radiation. An atom with one outer-shell electron having excitation energies in the spectral range under consideration can be described with regard to its absorption as a classical oscillator with oscillating charge $q = -e$. The total absorption of an atom in the level E_i , however, is distributed among many transitions $E_i \rightarrow E_k$ to all high levels E_k which are optically connected with E_i . Each of these transitions contributes only

a fraction f_{ik} to the total absorption. This number $f_{ik} < 1$ is called the oscillator strength of the transition $E_i \rightarrow E_k$. The absorption of N atoms on the transition $E_i \rightarrow E_k$ is equal to that of $f_{ik}N$ classical oscillators. From the definition of the oscillator strength, we obtain

$$\sum_k N f_{ik} = N \quad \text{or} \quad \sum_k f_{ik} = 1. \quad (364)$$

This is for single electron in the out-shell of the atom. If the atom has m valence electrons, then

$$\sum_k f_{ik} = m \quad (365)$$

The summation extends over all levels E_k (including the continuum) which are accessible from level E_i by electric dipole transitions. If E_i is an excited state, induced emission to lower levels may occur, which diminishes the effective absorption. The corresponding oscillator strength f_{ik} with $E_k < E_i$ are therefore negative. This is consistent with what we presented in the Radiative Transition Theory.

Using the concept of oscillator strength, the absorption and dispersion of real atoms or molecules in a level E_i with resonance frequency ω_{ik} can be described by modifying the classical formulas Eqs. (362) and (363) to

$$n'_i(\omega) = 1 + \frac{N_i e^2}{2m\epsilon_0} \sum_k \frac{(\omega_{ik}^2 - \omega^2) f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (366)$$

$$K_i(\omega) = \frac{N_i e^2}{2m\epsilon_0} \sum_k \frac{\gamma_{ik} \omega f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (367)$$

These are the QM-corrected complex refraction index

$$n_i(\omega) = n'_i(\omega) - i K_i(\omega) \quad (368)$$

Example: The f value of the Na D-lines is

$$f(3S - 3^2P_{1/2}) = 0.320, \quad f(3S - 3^2P_{3/2}) = 0.641$$

This implies that the two D-lines carry 96% of the total oscillator strength out of the ground state 3S.

(3) Absorption and Dispersion

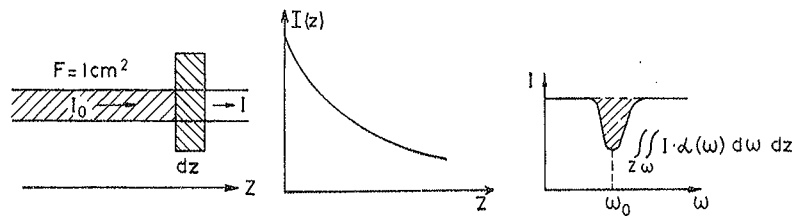


Fig. Absorption of light in an optically thin layer

Generally the absorption of radiation passing through a medium is characterized by the absorption coefficient α which describes the attenuation of the radiation intensity (rather than the amplitude). If the intensity of a plane wave is $I(z)$, its attenuation along the distance dz is

$$dI = -\alpha I dz \quad (369)$$

The absorption coefficient α represents the fraction dI/I absorbed

Within the unit interval $dz = 1 \text{ cm}$. For constant α (ie., independent of I), integration of Eq.(369) yields Beer's law for linear absorption ($dI \propto I$):

$$I(z) = I_0 e^{-\alpha z} \quad (370)$$

Where I_0 is the intensity at $z=0$.

Using Eq.(361) and considering $I \propto E \cdot E^*$

$$\therefore I(z) = I_0 e^{-2k_0 k(\omega)z} \quad (371).$$

Compare Eq.(371) with Eq.(370), We obtain the absorption coefficient

$$\alpha = 2k_0 k(\omega) = 4\pi k(\omega)/\lambda_0 \quad (372)$$

Thus, the absorption coefficient is proportional to the imaginary part of the complex refractive index $n = n' - ik$.

Using the classical model $n(\omega)$ given by Eqs.(362) and(363),

We have

$$\left\{ \begin{aligned} \alpha(\omega) &= 4\pi k_i(\omega)/\lambda_0 = \frac{2\omega_0 k(\omega)}{c} \\ &= \frac{Nq^2\omega_0}{cm\epsilon_0} \cdot \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (373) \\ n'(\omega) &= 1 + \frac{Nq^2}{2m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (374) \end{aligned} \right.$$

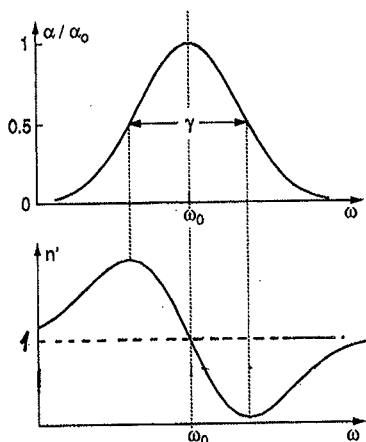
For $|\omega_0 - \omega| \ll \omega_0$, $\omega_0 + \omega \approx 2\omega$. Thus, Eqs.(373) and(374)

can be simplified with $q = -e$ to

$$\left\{ \begin{aligned} \alpha(\omega) &= \frac{Ne^2}{4m\epsilon_0 c} \cdot \frac{\gamma}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (375) \\ n'(\omega) &= 1 + \frac{Ne^2}{4m\epsilon_0 \omega_0} \cdot \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (376) \end{aligned} \right.$$

Eqs. (375) and (376) give the Kramers-Kronig Dispersion Relations.

Here, m is the mass of electrons. The dispersion relation is shown in the figure below:



Absorption $\alpha(\omega)$ — Lorentzian shape
with $\text{FWHM} = \Delta\omega_n = \gamma$

Dispersion $n'(\omega)$ — dispersion profile
 $n'(\omega = \omega_0) = 1$.

Fig. 3.5. Absorption coefficient $\alpha = 2k\kappa(\omega)$ and dispersion $n'(\omega)$ in the vicinity of an atomic transition with center frequency ω_0

Using the QM-corrected refraction index $n(\omega)$ given by Eq. (366) and Eq. (367), we have

$$\left\{ \begin{aligned} \alpha_i(\omega) &= \frac{N_i e^2}{m \epsilon_0 c} \sum_k \frac{\gamma_{ik} \omega \omega_{ik} f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (377) \\ n'_i(\omega) &= 1 + \frac{N_i e^2}{2m \epsilon_0} \sum_k \frac{(\omega_{ik}^2 - \omega^2) f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (378) \end{aligned} \right.$$

For $|\omega_{ik} - \omega| \ll \omega_{ik}$, $\omega_{ik} + \omega \approx 2\omega$, then Eqs. (377-378) can be

Simplified to

$$\left\{ \begin{aligned} \alpha_i(\omega) &= \frac{N_i e^2}{4m \epsilon_0 c} \sum_k \frac{\gamma_{ik} f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \quad (379) \\ n'_i(\omega) &= 1 + \frac{N_i e^2}{4m \epsilon_0} \sum_k \frac{[(\omega_{ik} - \omega)/\omega_{ik}] f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \quad (380) \end{aligned} \right.$$

This is for the case when the radiation field has wide spectrum to cover many transition lines: $|i\rangle \rightarrow |k\rangle$.

However, in spectroscopy, we have the case that the radiation field has narrow spectrum, and only excites one transition.

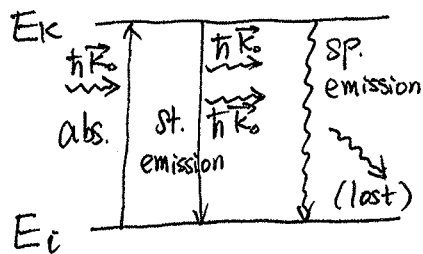
If we write $\omega_0 = \omega_{ik}$ for this transition, then

$$\alpha_{ik}(\omega) = \frac{N_i e^2}{4m\epsilon_0 c} \cdot \frac{\gamma_{ik} f_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (381)$$

$$n'_{ik}(\omega) = 1 + \frac{N_i e^2}{4m\epsilon_0 \omega_0} \cdot \frac{(\omega_0 - \omega) f_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (382)$$

Compared to the classical model results Eq.(375) and Eq.(376), the QM results Eqs.(381) and (382) have the extra factor — the oscillator strength.

The absorption coefficient can be derived from another point-of-view. The absorption coefficient α_{ik} for a transition $|i\rangle \rightarrow |k\rangle$ depends on the population densities N_i and N_k of the lower and upper levels, and on the optical absorption cross-section σ_{ik} of each atom. Note: α_{ik} has unit of cm^{-1} , while σ_{ik} has unit of cm^2 .



Keep in mind that the stimulated emitted photons travel in the same direction as the incident photons, while the spontaneously emitted photons go any directions.

Thus, spontaneous emission counts for the attenuation of radiation intensity, while stimulated emission does not attenuate the radiation intensity.

$$\therefore \alpha_{ik}(\omega) = N_i \sigma_{ik} - N_k \sigma_{ki} \quad (383)$$

$$\because g_i \sigma_{ik} = g_k \sigma_{ki}, \quad \therefore \sigma_{ki} = \frac{g_i}{g_k} \sigma_{ik}$$

Thus, the absorption coefficient becomes

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega) \left[N_i - \frac{g_i}{g_k} N_k \right] \quad (384)$$

Usually, E_k is well above E_i . Under weak radiation field, we have

$$N_k \ll N_i$$

Thus, the 2nd term in Eq.(384) can be neglected. Therefore,

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega) N_i \quad (385)$$

Compared with Eq.(379), we obtain the absorption cross-section (with the frequency interval):

$$\sigma_{ik}(\omega) = \frac{e^2}{4m\epsilon_0 c} \sum_k \frac{\gamma_{ik} f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \quad (386)$$

If there is only one transition being excited by the radiation field, then we have the absorption cross-section

$$\sigma_{ik}(\omega) = \frac{e^2 f_{ik}}{4m\epsilon_0 c} \cdot \frac{\gamma_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (387)$$

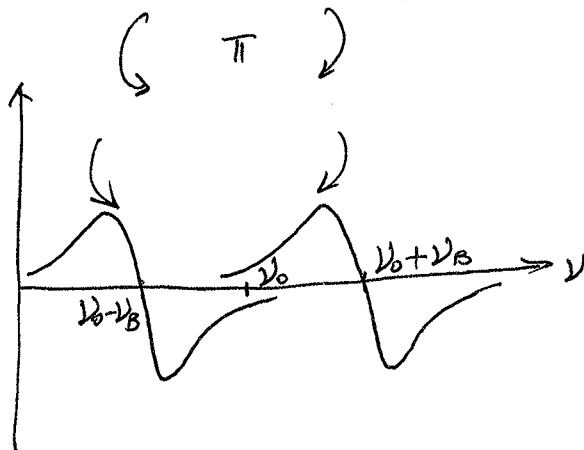
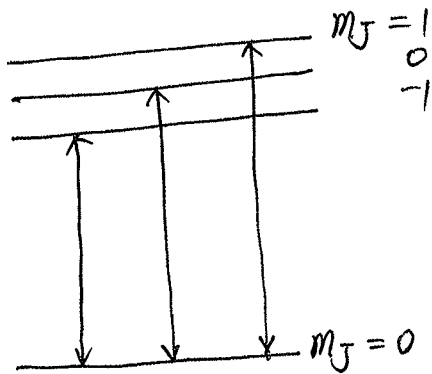
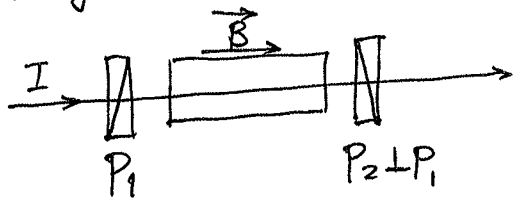
At peak frequency $\omega = \omega_0 (= \omega_{ik})$,

$$\sigma_{ik}(\omega = \omega_0) = \frac{e^2 f_{ik}}{\gamma_{ik} m \epsilon_0 c} \quad (388)$$

Eqs.(386)–(388) are the absorption cross section $\sigma_{ik}(\omega)$ under the Lorentzian line profile.

Example for Dispersion:

Magnetic rotation of polarization \rightarrow resonant Faraday effect.



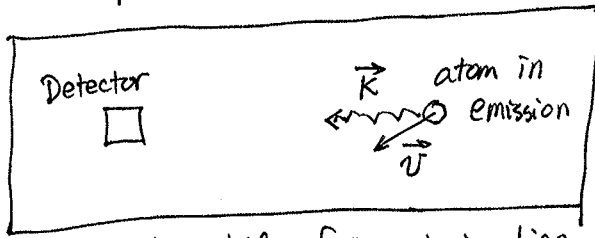
- Linear polarization \rightarrow decomposed into two circular polarization
- \rightarrow experience difference refraction index due to dispersion and Zeeman splitting of magnetic energy level
- $\rightarrow \Delta n$ causes phase shift between two circular polarizations
- \rightarrow rotation of linear polarization when recombine.

§7.4. Doppler Linewidth and Lineshape

Generally the Lorentzian line profile with the natural linewidth $\delta\nu_n$, as discussed in the previous section, cannot be observed without special techniques, because it is completely concealed by other broadening effects. One of the major contributions to the spectral linewidth in gases at low pressures is the Doppler width, which is due to the thermal motion of the absorbing or emitting molecules.

Doppler effect is the phenomenon of frequency or wavelength shift when radiation source and receiver have relative motion. It was first described by Doppler. A typical example is the blown whistle of an approaching train: people feel the sound is "sharper" than it's at rest; while the whistle from a train leaving us sounds lower frequency than it's at rest. This means that when the radiation source (e.g., the train) moves towards the receiver (e.g., human's ears), the radiation (e.g., sound wave) frequency increases (i.e., wavelength becomes shorter — blue shift); when the radiation source moves away from the receiver, the radiation frequency decreases (i.e., wavelength becomes longer — red shift). The key point here is the relative motion between the emitter of the radiation (i.e., the source) and the receiver.

Consider an excited molecules with a velocity \vec{v} relative to the rest frame of the observer. In the rest frame, an atom at rest emits a photon with frequency ω_0 .



Doppler shift for emission line

When the atom moves relative to the detector with velocity \vec{v} , the frequency received by the detector becomes:

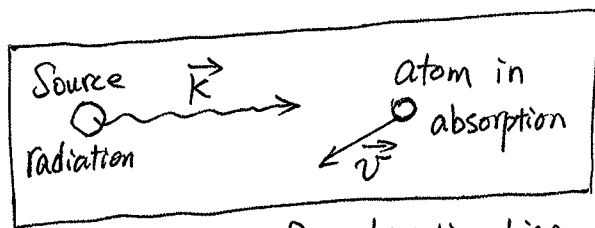
$$\omega_e = \omega_0 + \vec{k} \cdot \vec{v} \quad (389)$$

When the atom moves towards the detector, $\vec{k} \cdot \vec{v} > 0$

$$\therefore \omega_e > \omega_0 \quad (\text{blue shift}) \quad (390)$$

When the atom moves away from the detector, $\vec{k} \cdot \vec{v} < 0$

$$\therefore \omega_e < \omega_0 \quad (\text{red shift}) \quad (391)$$



Doppler shift for absorption line

At rest, the resonance frequency for the atomic absorption is ω_0 .

If the atom moves relative to the detector with velocity \vec{v} , the

apparent frequency of the radiation changes from its at rest frequency ω to a shifted frequency ω'

$$\omega' = \omega - \vec{k} \cdot \vec{v} \quad (392)$$

When $\omega' = \omega_0$, the atom will have resonance absorption.

Thus, the absorption frequency $\omega = \omega_a$ is given by

$$\omega_a = \omega_0 + \vec{k} \cdot \vec{v} \quad (393)$$

Eqs. (389) and (393) are the expression of Doppler shift in vector.

The shift of absorption frequency is actually opposite to emission freq.

When the atom moves towards the radiation source, $\vec{k} \cdot \vec{v} < 0$

$$\therefore \omega_a < \omega_0 \quad (\text{red shift})$$

When the atom moves away from the radiation source, $\vec{k} \cdot \vec{v} > 0$

$$\therefore \omega_a > \omega_0 \quad (\text{blue shift})$$

But when expressed in vector, they have the same equation:

$$\omega_e/\omega_a = \omega_0 \pm \vec{k} \cdot \vec{v} \quad (394)$$

If expressed in scalar, i.e., write out $\vec{k} \cdot \vec{v} = kv \cos \theta$, where θ is the angle between \vec{k} and \vec{v} . Then the sign (+ or -) will

depend on $\cos \theta$. Usually, we define one direction as positive,

e.g., when measuring vertical wind by lidar, define upward

as $v_z = W > 0$. Laser pulse comes from ground, propagating

upward, so $k_z = \frac{2\pi}{\lambda_0} = \frac{2\pi\nu_0}{c} = \frac{\omega_0}{c} > 0$.

Thus, the absorption frequency of the atom becomes

$$\omega_a = \omega_0 + k_z \cdot v_z = \omega_0 \left(1 + \frac{v_z}{c}\right) \quad (395)$$

When the atom with upward velocity $v_z > 0$ emits a photon,

the receiver is at ground, so the photon propagates downward,

$k_z = -\frac{2\pi}{\lambda_0} = -\frac{\omega_0}{c} < 0$. Thus, the emission frequency

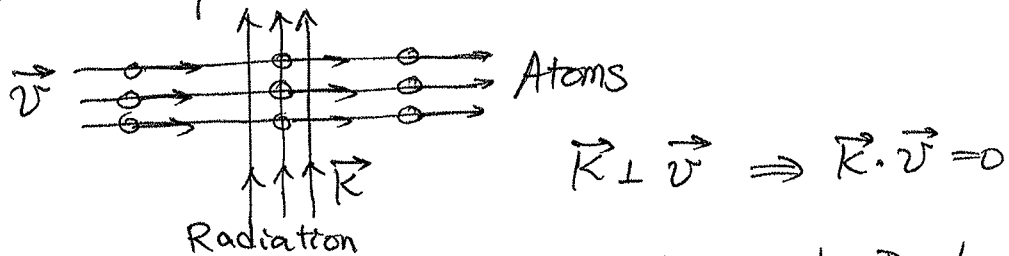
$$\omega_e = \omega_0 - \frac{\omega_0}{c} v_z = \omega_0 \left(1 - \frac{v_z}{c}\right) \quad (396)$$

Thus, the frequency shift between ω_a and ω_e is

$$\Delta\omega = \omega_a - \omega_e = 2\omega_0 \frac{v_z}{c} \quad (397)$$

Above we discussed the linear Doppler shift $\vec{k} \cdot \vec{v} = kv \cos \theta$. Apparently, if $\theta = 90^\circ$, i.e., $\vec{k} \perp \vec{v}$, then this shift is zero.

In other words, we can avoid the first order Doppler shift by making the radiation field perpendicular to the velocity of atoms. This is why atomic beam or molecular beam is very useful:



$$\vec{k} \perp \vec{v} \Rightarrow \vec{k} \cdot \vec{v} = 0$$

Atomic/molecular beam to avoid 1st order Doppler shift.

Besides the 1st order, there are quadratic Doppler shift (2nd order) that is independent of velocity direction, but depends on the absolute value of $|\vec{v}|$. The minimization of 2nd order Doppler shift can only be done by laser cooling to decrease $|\vec{v}|$. This will be discussed in later laser spectroscopy.

For normal situation, atoms or molecules move randomly under thermal equilibrium (no fixed direction like atomic beam). They follow a Maxwellian velocity distribution. At the temperature T , the number of molecules $n_i(v_z) dv_z$ in the level E_i per unit volume with a velocity component between v_z and $v_z + dv_z$ is

$$n_i(v_z) dv_z = \frac{N_i}{v_p \sqrt{\pi}} e^{-(v_z/v_p)^2} dv_z, \quad (398)$$

where $N_i = \int n_i(v_z) dv_z$ is the total population density on level E_i , $v_p = \sqrt{2k_B T/m}$ is the most probable velocity, m is the mass

of a molecule, and k_B is Boltzmann's constant.

$$\text{From Eq. (395), } \nu_z = \frac{c(\omega - \omega_0)}{\omega_0}, \quad d\nu_z = \frac{c}{\omega_0} d\omega. \quad (399)$$

Inserting Eq. (399) into Eq. (398) gives the number of molecules with absorption frequencies shifted from ω_0 into the interval

from ω to $\omega + d\omega$:

$$n_i(\omega) d\omega = N_i \frac{c}{\omega_0 \nu_p \sqrt{\pi}} e^{-\left[\frac{c(\omega - \omega_0)}{\omega_0 \nu_p}\right]^2} d\omega \quad (400)$$

Substitute ν_p equation into Eq. (400) and recall $\omega_0 = \frac{2\pi c}{\lambda_0}$, we get

$$n_i(\omega) d\omega = N_i \frac{1}{2\pi \sqrt{2\pi} \sqrt{\frac{k_B T}{m \lambda_0^2}}} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 \cdot 2 \cdot \frac{k_B T}{m \lambda_0^2}}\right] d\omega$$

Define the rms width for this Gaussian shape as

$$\sigma_D = \sqrt{\frac{k_B T}{m \lambda_0^2}} \quad (401)$$

$$\therefore n_i(\omega) d\omega = \frac{N_i}{2\pi \cdot \sqrt{2\pi} \sigma_D} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 \cdot 2 \sigma_D^2}\right] d\omega \quad (402)$$

Since the emitted or absorbed radiant power $P(\omega) d\omega$ is proportional to the density $n_i(\omega) d\omega$ of molecules emitting or absorbing in the interval $d\omega$, the intensity profile of a Doppler broadened spectral line becomes

$$I(\omega) = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 \cdot 2 \sigma_D^2}\right] \quad (403)$$

This is a Gaussian profile with a full width at half maximum (FWHM)

$$\delta\omega_D = \sqrt{8 \ln 2} \cdot 2\pi \cdot \sigma_D = 2\pi \sqrt{\frac{8 \ln 2 \cdot k_B T}{m \lambda_0^2}} \quad (404)$$

Using $\delta\omega_D$, Eq. (403) becomes

$$I(\omega) = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{(\delta\omega_D)^2 / (4 \ln 2)}\right] = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{0.36(\delta\omega_D)^2}\right] \quad (405)$$

Below is a comparison of Lorentzian and Gaussian line profiles with equal FWHM.

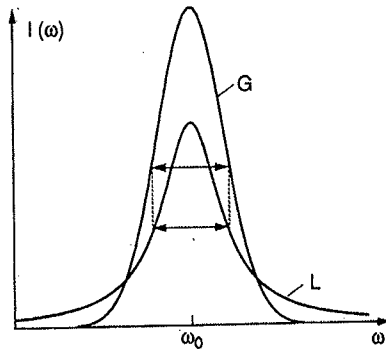


Fig. 3.7. Comparison between Lorentzian (L) and Gaussian (G) line profiles of equal halfwidths

The intensity I approaches zero for large arguments $(\nu - \nu_0)$ much faster for a Gaussian line profile than for a Lorentzian profile.

Define the normalized Gaussian line profile as

$$g_D(\omega) = \frac{1}{\sqrt{2\pi} (2\pi\sigma_D)} \exp\left[-\frac{(\omega - \omega_0)^2}{2(2\pi\sigma_D)^2}\right] \quad (406)$$

$$\therefore \int_{-\infty}^{\infty} g_D(\omega) d\omega = \int_{-\infty}^{\infty} g_D(\omega - \omega_0) d(\omega - \omega_0) = 1. \quad (407)$$

$$\therefore I(\omega) = I_0 \cdot \sqrt{2\pi} \cdot (2\pi\sigma_D) \cdot g_D(\omega) \quad (408)$$

$$\text{Total Energy } I_T = \int I(\omega) d\omega = I_0 (2\pi\sigma_D) \sqrt{2\pi} \int g_D(\omega) d\omega = I_0 (2\pi\sigma_D) \sqrt{2\pi} \quad (409)$$

If we write in ν unit ($\nu = \omega / 2\pi$), then

$$g(\nu) = \frac{1}{\sqrt{2\pi} \sigma_D} \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma_D^2}\right] \quad (410)$$

$$\therefore I(\nu) = I_0' \cdot \sigma_D \cdot \sqrt{2\pi} \cdot g(\nu) = I_0' \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma_D^2}\right] \quad (411)$$

$$\therefore I_T = \int I(\nu) d\nu = I_0' \sigma_D \cdot \sqrt{2\pi} = I_0 (2\pi\sigma_D) \sqrt{2\pi} \quad (412)$$

$$\therefore I_0' = 2\pi I_0 \quad (413)$$

More detailed consideration shows that a Doppler-broadened spectral line cannot be strictly represented by a pure Gaussian profile, because of the natural linewidth caused by finite lifetime.

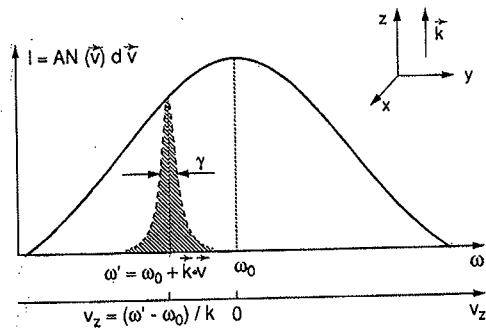


Fig. 3.8. Lorentzian profile centered at $\omega' = \omega_0 + k \cdot v = \omega_0(1 + v_z/c)$ for molecules with a definite velocity component v_z

Natural linewidth has a Lorentzian profile @ each $\omega' = \omega_0 + \vec{k} \cdot \vec{v}$

$$g_L(\omega) = \frac{\gamma/2\pi}{(\omega - \omega')^2 + (\gamma/2)^2} \quad (414)$$

Thus, the spectral intensity distribution $I(\omega)$ of the total absorption or emission of all molecules at the transition $E_i \rightarrow E_k$ is the convolution of the Lorentzian profile with the Gaussian profile:

$$I(\omega) = I_0 \int n(\omega') g_L(\omega') d\omega'$$

$$= \frac{I_0 (\gamma/2\pi) N_i}{\sqrt{2\pi} (2\pi\sigma_D)} \int_0^\infty \frac{\exp\left[-\frac{(\omega' - \omega_0)^2}{2(2\pi\sigma_D)^2}\right]}{(\omega - \omega')^2 + (\gamma/2)^2} d\omega' \quad (415)$$

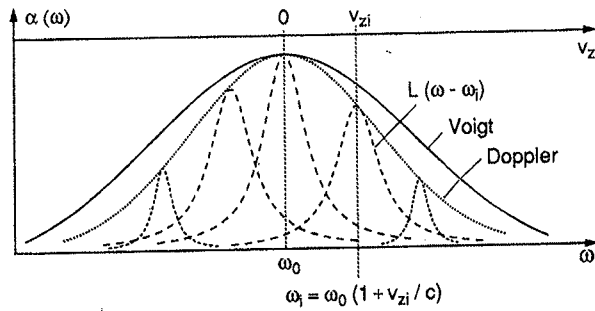


Fig. 3.9. Voigt profile as a convolution of Lorentzian line shapes $L(\omega_0 - \omega_i)$ with $\omega_i = \omega_0(1 + v_{zi}/c)$

This intensity profile, which is a convolution of Lorentzian and Gaussian profiles, is called a Voigt Profile.

§7.5. Transit-Time Broadening

When the interaction time of molecules with the radiation field is small compared with the spontaneous lifetimes of excited levels, the linewidth of a Doppler-free molecular transition is no longer limited by the spontaneous transition probabilities, but by the time of flight through the laser beam, which determines the interaction time of the molecule with the radiation field.

To derive the line profile caused by this transit-time, let us consider an undamped oscillator $x = x_0 \cos \omega_0 t$ that oscillates with constant amplitude x_0 during the time interval T and then suddenly stops oscillating. From Fourier transform,

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^T x_0 \cos(\omega_0 t) e^{-i\omega t} dt \quad (416)$$

The spectral intensity $I(\omega) = A^* A$, for $|\omega - \omega_0| \ll \omega_0$, we obtain

$$I(\omega) = C \frac{\sin^2[(\omega - \omega_0)T/2]}{(\omega - \omega_0)^2} \quad (417)$$

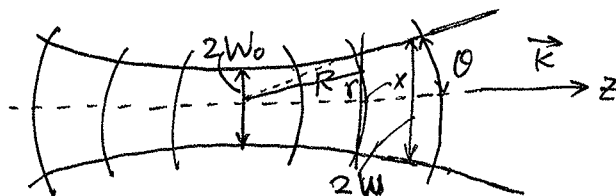
$$\Rightarrow \text{FWHM} : \delta\omega_T = \frac{5.6}{T} \quad (418)$$

Full width between the zero points on both sides of ω_0 is

$$\delta\omega_b = \frac{4\pi}{T} \approx \frac{12.6}{T} \quad (419)$$

This example is corresponding to an atom that traverses a laser beam with rectangular intensity profile.

In reality, a laser beam usually has a Gaussian beam shape:



$$E = E_0 e^{-r^2/W^2} \cos \omega t \quad (420)$$

where $2W$ gives the diameter of the Gaussian beam profile across the points where $E = E_0/e$.

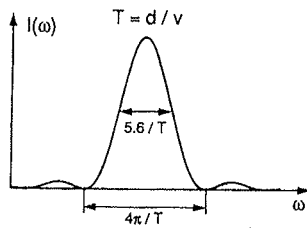
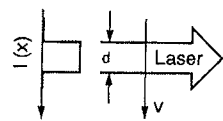
Substitute $X = \alpha E = \alpha E_0 e^{-r^2/W^2} \cos \omega t$ into Eq. (416), we obtain

$$I(\omega) = I_0 \exp \left[-(\omega - \omega_0)^2 \frac{W^2}{2v^2} \right] \quad (421)$$

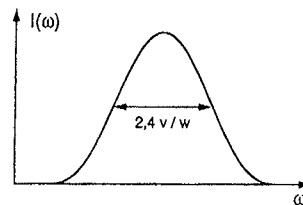
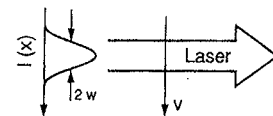
\therefore The FWHM for transit time is

$$\delta \omega_{tt} = \frac{v}{W} \sqrt{8 \ln 2} \approx 2.4 v/W \quad (422)$$

$$\therefore \delta \nu_{tt} = \frac{\delta \omega_{tt}}{2\pi} \approx 0.4 v/W \quad (423)$$



a)



b)

Fig. 3.19a,b. Transition probability $\mathcal{P}(\omega)$ of an atom traversing a laser beam (a) with a rectangular intensity profile $I(x)$; and (b) with a Gaussian intensity profile for the case $\gamma < 1/T = v/d$. The intensity profile $I(\omega)$ of an absorption line is proportional to $\mathcal{P}(\omega)$

(Reducing v to reduce $\delta \omega_{tt}$)
 \downarrow
 optical cooling

Now consider the wave fronts of the focused Gaussian beam are curved except at the focus (waist), an atom moving along the r -direction perpendicular to the laser beam z -axis experiences a spatial phase shift $\Delta \phi = \kappa 2\pi/\lambda$. Thus, the transit-time broadened FWHM

$$\begin{aligned} \text{is: } \delta \omega &= \frac{2v}{W} \sqrt{2 \ln 2} \left[1 + \left(\frac{\pi W^2}{R\lambda} \right)^2 \right] && \text{(Increasing } R \text{ to reduce} \\ &= \delta \omega_{tt} \left[1 + \left(\frac{\pi W^2}{R\lambda} \right)^2 \right] && \text{curvature influence)} \end{aligned} \quad (424)$$

§7.6. Collisional Broadening and Shift of Spectral Lines

Collision-caused spectral line broadening and shift are quite complicated problems. There are mainly two kinds of collisions: inelastic collisions and elastic collisions. They have different effects on line broadening and shift.

(1) Inelastic Collisions — also called quenching collisions

(a) There is internal energy transferred partially or completely from atom A to collision partner B.

Atom A probably gains or loses some kinetic energy to compensate the energy difference between transferred energy and state-change needed energy.

(b) The inelastic collisions force atom A to leave excited state and return to the ground state or transit to another excited state without radiation, i.e., radiationless.

This shortens the lifetime of atom A's excited state,
 \Rightarrow resulting in more uncertainty of the excited level
 \Rightarrow broadening the linewidth of radiation

$$\frac{1}{\tau_k^{\text{eff}}} = \frac{1}{\tau_k} + \frac{1}{\tau_k^{\text{coll}}} \quad (425)$$

$$A_k^{\text{total}} = A_k^{\text{rad}} + A_k^{\text{coll}} \quad (426)$$

$$A_k^{\text{total}} = \sum_i' A_{ki} + N_B \sigma_{ik} \bar{v} \quad (427)$$

Where N_B is the number density of the collision partner B, σ_s is the collision cross-section, \bar{v} is the mean relative velocity between A and B.

$$A_k^{\text{coll}} = N_B \sigma_{ik} \bar{v} \quad (428)$$

From ideal gas law, $P_B = N_B K_B T$ (429)

Where P_B - pressure of B, K_B - Boltzmann constant, T - temperature.

$$\bar{v} = \sqrt{\frac{8 K_B T}{\pi \mu}} \quad (430)$$

Substitute Eq. (429) and (430) into Eq. (428), We get

$$A_K^{\text{Coll}} = \frac{P_B \sigma_{ik}}{K_B T} \sqrt{\frac{8 K_B T}{\pi \mu}} = P_B \cdot \sigma_{ik} \sqrt{\frac{8}{\pi \mu K_B T}} \quad (431)$$

$$\text{Let } a = \sigma_{ik} \sqrt{\frac{8}{\pi \mu K_B T}} \quad (432)$$

$$\therefore A_K^{\text{Coll}} = a P_B \quad (433)$$

$$\therefore A_K^{\text{total}} = A_K^{\text{rad}} + A_K^{\text{Coll}} = A_K^{\text{rad}} + a P_B = \gamma_n + \gamma_{\text{coll}} \quad (434)$$

Therefore, the spectral linewidth

$$\delta \omega = \delta \omega_n + \delta \omega_{\text{coll}} = \gamma_n + \gamma_{\text{coll}} = \gamma_n + a P_B \quad (435)$$

The inelastic collision-induced additional line broadening

is $\delta \omega_{\text{coll}} = a P_B$, also called pressure broadening.

Since inelastic collision is radiationless, there is no photon emitted during the collision. Therefore, it does not cause frequency shift.

(2). Elastic Collisions: phase-perturbing and velocity-changing collisions

(a) There is no internal energy transfer between atom A and collision partners B, so the collision won't quench A if A is in an excited state for spontaneous emission, but the collision perturbs the phase of A if regarding A as an oscillator.

(b) During collision time, A can undergo a radiative transition.

* The radiation frequency will be determined by the energy difference $\hbar\omega_k(R) = E_k(R) - E_i(R)$ ⁽⁴³⁶⁾ which may be different than ω_0 of the unperturbed atom, i.e., a line shift is resulted. It is mainly due to different shifts of the energy levels E_i and E_k . (If E_i and E_k shift the same amount, then the line shift is zero.)

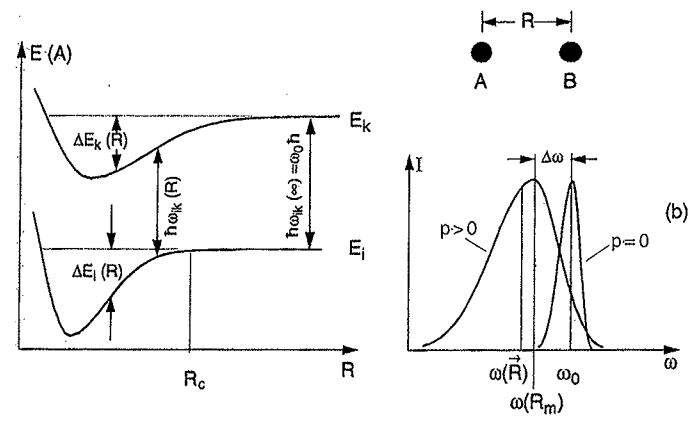


Fig. 3.10. Illustration of collisional line broadening explained with the potential curves of the collision pair AB

Elastic Collision

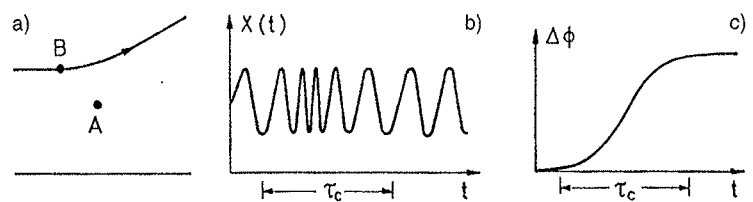


Fig. 3.11a-c. Phase perturbation of an oscillator by collisions: (a) classical path approximation of colliding particles; (b) frequency change of the oscillator A(t) during the collision; (c) resulting phase shift

* The line shifted frequency $\omega_{ik}(R)$ can be different at different collision time or distance R , although it is around a most probable value $\omega_{ki}(R_m)$.

\Rightarrow This will result in a spread of line distribution
 \Rightarrow cause broadening of linewidth.

Therefore, elastic collisions can cause both lineshift and line broadening.

* Lindholm introduced a model to quantitatively describe the line broadening and shift caused by inelastic and elastic collisions. This is to treat the excited atom A as a damped oscillator that suffers collisions with particles B . In this model, inelastic collisions damp the amplitude of the oscillation. This is described by introducing a damp constant γ_{coll} such that the sum of radiative and collisional damping is represented by $\gamma = \gamma_n + \gamma_{coll}$.

Similar to how we derived natural linewidth, the inelastic collision broadened line profile is a Lorentzian:

$$I(\omega) = \frac{C}{(\omega_0 - \omega)^2 + [(\gamma_n + \gamma_{coll})/2]^2} \quad (437)$$

$\therefore \delta\omega = \gamma_n + \gamma_{coll}$ under inelastic collision.

The elastic collisions do not change the amplitude, but change the phase of the damped oscillator, due to the frequency shift $\Delta\omega(R)$ during the collisions. Lindholm's results are as follows: line shift of the line center:

$$\Delta\omega = N_B \bar{v} \sigma_s \quad (438)$$

line broadening with Lorentzian shape

$$\delta\omega = 2 N_B \bar{v} \sigma_b \quad (439)$$

\therefore The ~~overall~~ ^{elastic-collision} line profile becomes

$$I(\omega) = I_0 \frac{N_B \bar{v} \sigma_b}{(\omega - \omega_0 - N_B \bar{v} \sigma_s)^2 + (N_B \bar{v} \sigma_b)^2} \quad (440)$$

If we now include additional damping by spontaneous emission and inelastic collisions, we have the overall line profile

$$I(\omega) = I_0 \frac{(\gamma_n/2 + \gamma_{coll}^{inelastic}/2 + N_B \bar{v} \sigma_b)^2}{(\omega - \omega_0 - N_B \bar{v} \sigma_s)^2 + [(\gamma_n + \gamma_{coll}^{inelastic})/2 + N_B \bar{v} \sigma_b]^2} \quad (441)$$

\therefore Overall linewidth (FWHM)

$$\delta\omega = \gamma_n + \gamma_{coll}^{inelastic} + 2 N_B \bar{v} \sigma_b \quad (442)$$

$$= \gamma + 2 N_B \bar{v} \sigma_b$$

($\gamma = \gamma_n + \gamma_{coll}^{inelastic}$) (443)

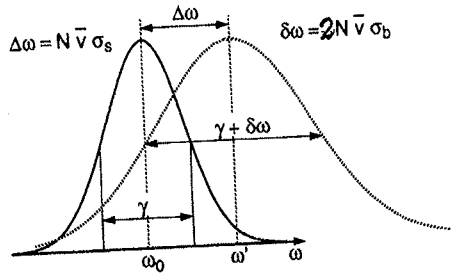


Fig. 3.12. Shift and broadening of a Lorentzian line profile by collisions

$$\therefore N_B = \frac{P_B}{k_B T}, \quad \bar{v} = \sqrt{\frac{8k_B T}{\pi \mu}}, \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

$$\therefore \delta\omega = \nu_n + a P_B + 2\sigma_b \sqrt{\frac{8}{\pi \mu k_B T}} \cdot P_B$$

$$= \nu_n + \underbrace{\left(\sigma_{ik} \sqrt{\frac{8}{\pi \mu k_B T}} + 2\sigma_b \sqrt{\frac{8}{\pi \mu k_B T}} \right)}_{\text{collision broadening coefficient}} P_B \quad (444)$$

Line shift:

$$\begin{aligned} \Delta\omega &= N_B \bar{v} \sigma_s \\ &= \underbrace{\sigma_s \sqrt{\frac{8}{\pi \mu k_B T}}}_{\text{collision shift coefficient}} P_B \end{aligned} \quad (445)$$

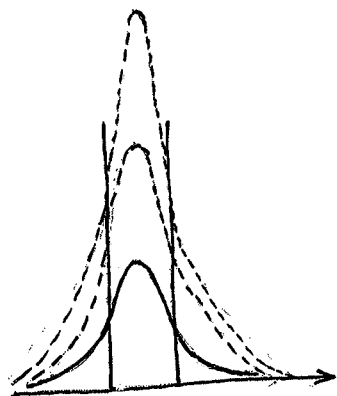
§7.7. Homogeneous and Inhomogeneous Line Broadening

* Homogeneous line broadening: three ways to describe it —

① If the probability $P_{ik}(\omega)$ of absorption or emission of radiation with frequency ω causing a transition $E_i \rightarrow E_k$ is equal for all the atoms or molecules of a sample that are in the same level E_i , we call the spectral line profile of this transition homogeneously broadened.

② Broadening processes have the same effect on all atoms in the sample, i.e., each atom has the same broadening.

③ Each atom contributes to the entire line profile spectrum, not just part of the spectrum.



Example: 3 atoms' contributions
Same $\delta\omega$, but 3 times
of peak intensity.

Natural linewidth is a typical homogeneous broadening: in this case, the probability for emission of light with frequency ω on a transition $E_i \rightarrow E_k$

$$P_{ik}(\omega) = A_{ik} g_L(\omega)$$

is equal for all atoms in level E_i .

$g_L(\omega)$ is the normalized Lorentzian profile.

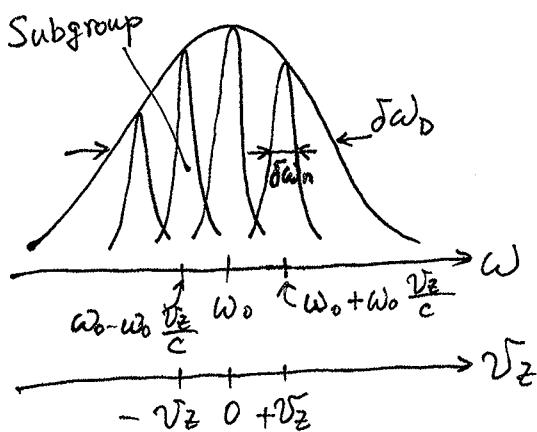
When we have N atoms in the sample, the overall line profile has peak intensity of N times single atom contribution, but the overall linewidth is equal to single atom linewidth $\delta\omega_n$.

* Inhomogeneous line broadening: nearly opposite to homogeneous broadening case:

① The probability of absorption or emission of radiation $E(\omega)$ is not equal for all atoms, but depends on certain conditions of the atoms.

② Each atom only contributes to part of the spectrum.

A typical example of inhomogeneous line broadening is the Doppler broadening. In this case, the probability of absorption or emission of radiation $E(\omega)$ is dependent on their velocity v .



We divide the atoms in level E_i into subgroups such that all atoms with a velocity component within $v_z \rightarrow v_z + \Delta v_z$ belong to one subgroup.

If we choose $\Delta v_z = \delta \omega_n / k$ where $\delta \omega_n$ is the natural linewidth, we may consider the frequency interval $\delta \omega_n$ to be homogeneous

broadening of each subgroup inside the much larger inhomogeneous Doppler width. Thus, all atoms in the subgroup can absorb or emit radiation with frequency $\omega = \omega_0 + v_z k$ because in the coordinate system of the moving atoms, this freq. is within the natural width $\delta \omega_n$ around ω_0 .

{ Homogeneous broadening is usually Lorentzian line profile.
 { Inhomogeneous broadening like Doppler width is Gaussian shape.

Let us consider collision broadening:

① Inelastic collisions: result in a homogeneous Lorentzian line profile.

② Elastic Collisions: { phase-perturbing collisions → homogeneous
 { velocity-changing collisions

$$\left(\begin{array}{c} v_z \pm \Delta v_z \\ \text{Subgroup} \end{array} \right) \rightarrow \left(\begin{array}{c} v_z + u_z \pm \Delta v_z \\ \text{Subgroup} \end{array} \right) \Rightarrow \text{freq. } \omega \rightarrow \omega + kv_z$$

In Doppler-limited spectroscopy, the velocity-changing collisions do not affect the Doppler profile.

In Doppler-free spectroscopy,

if $T = 1/\bar{\nu} > T_c$, population change caused by velocity-changing collisions is negligible.

if $T \ll T_c$, velocity-changing collisions cause homogeneous broadening of each subgroup, through shortening the effective interaction time of the atoms with the radiation field —

move atoms out of resonance.

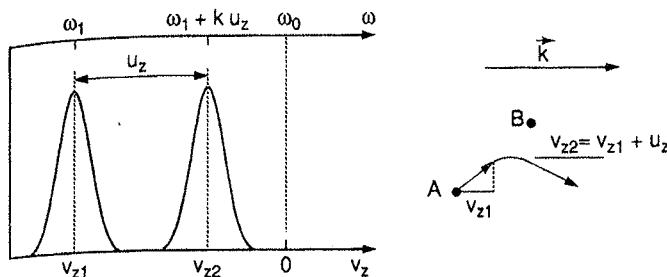
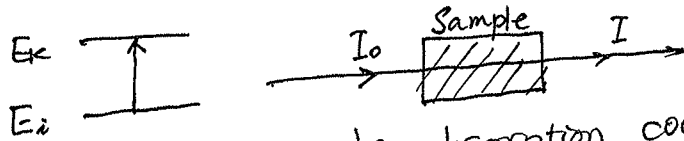


Fig. 3.21. Effect of velocity-changing collisions on the frequency shift of homogeneous subgroups within a Doppler-broadened line profile

§7.8. Linear and Nonlinear Absorption

From Eq.(369) and Eq.(384), we know that the intensity decrease dI of a wave with intensity I propagating along the z direction through an absorbing sample is

$$dI = -I\alpha dz = -I\sigma_{ik} \left[N_i - \frac{g_i}{g_k} N_k \right] dz \quad (446)$$



where α is the absorption coefficient caused by transition $E_i \rightarrow E_k$

σ_{ik} is the absorption cross-section

N_i and N_k are the populations on E_i and E_k levels.

g_i and g_k are the degeneracy factors of E_i and E_k .

(1) Linear absorption:

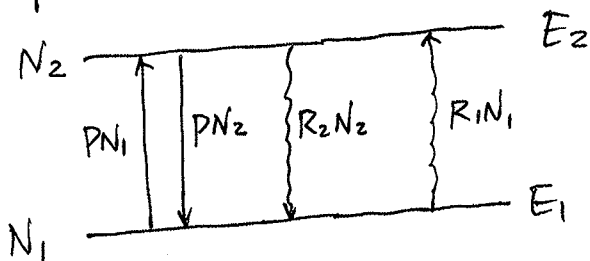
As long as the population densities N_i and N_k of the two levels E_i and E_k are not noticeably altered by the interaction with the radiation field (weak-signal), we can regard them as constant (independent of I). σ_{ik} is independent of I , thus, the absorption coefficient $\alpha = \sigma_{ik} \left[N_i - \frac{g_i}{g_k} N_k \right]$ is constant and independent of I . The absorbed intensity is then proportional to the incident intensity (linear absorption). Integration of Eq.(446) over the absorption path z gives Beer's law for linear absorption as given by Eq.(370):

$$I(z) = I_0 e^{-\sigma_{ik} \left[N_i - \frac{g_i}{g_k} N_k \right] z} = I_0 e^{-\alpha z} \quad (447)$$

$$\text{with } \alpha = \sigma_{ik} \left[N_i - \frac{g_i}{g_k} N_k \right]. \quad (448)$$

(2) Nonlinear absorption:

At larger intensity I , the density N_i of the lower state E_i can noticeably decrease while the upper state number density N_k increase (strong-field). This means that $N_i(I)$ and $N_k(I)$ are functions of I and therefore dI is no longer proportional to I (nonlinear absorption). In this case, while the absorption cross-section σ_{ik} is still independent of I , but the absorption coefficient α depends on I , caused by intensity-dependent populations on the lower and upper levels N_i and N_k .



Let us illustrate this nonlinear absorption by a simple example of a two-level system with population densities N_1 and N_2 and equal statistical weights $g_1 = g_2 = 1$. The total number density $N = N_1 + N_2$ of the two-level system is constant, if we exclude all decay channels to other levels than these two levels ($E_2 > E_1$).

The time derivations of N_1 and N_2 can be related to the Einstein coefficients $B_{21} = B_{12}$ for stimulated emission and absorption and A_{21} for spontaneous emission. If we allow additional collision induced transitions with probabilities C_{12} and C_{21} between the two levels, we obtain under stationary conditions ($\frac{dN_1}{dt} = -\frac{dN_2}{dt} = 0$).

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -B_{12} P(\omega) N_1 + B_{21} P(\omega) N_2 + A_{21} N_2 + C_{21} N_2 - C_{12} N_1 = 0$$

$$\therefore \frac{dN_1}{dt} = -\frac{dN_2}{dt} = B_{12} P(\omega) (N_2 - N_1) + (A_{21} + C_{21}) N_2 - C_{12} N_1 = 0 \quad (449)$$

Let $\Delta N = N_1 - N_2$; $N = N_1 + N_2 = \text{constant}$,

$$R_2 = A_{21} + C_{21}, \quad R_1 = C_{12}, \quad P_1 = B_{12} P(\omega) = P_2 = B_{21} P(\omega) = P \quad (450)$$

then the population difference ΔN can be written as

$$\Delta N = \frac{\Delta N_0}{1 + 2B_{12} P(\omega) / (R_1 + R_2)} = \frac{\Delta N_0}{1 + S} \quad (451)$$

where $\Delta N_0 = \frac{R_2 - R_1}{R_2 + R_1} N$ is the population difference for $P(\omega) = 0$.
(452) ($\Delta N_0 = N_1^0 - N_2^0$)

Define the saturation parameter:

$$S = \frac{2 B_{12} P(\omega)}{R_1 + R_2} = \frac{B_{12} P(\omega)}{(R_1 + R_2)/2} = \frac{B_{12} P(\omega)}{\bar{R}} \quad (453)$$

where $\bar{R} = (R_1 + R_2)/2$. S represents the ratio of the induced transition probability $B_{12} P(\omega)$ to the mean relaxation probability \bar{R} . If the only relaxation process is spontaneous emission (i.e., $R_1 = 0$, $R_2 = A_{21}$), then the saturation parameter S yields the ratio of stimulated to spontaneous transition rates: $S = \frac{B_{12} P(\omega)}{A_{21}/2}$.

For $S = 1$, the population difference ΔN drops to one half of its unsaturated value ΔN . With $I(\omega) = c \cdot P(\omega)$, where c

is the light speed, we have

$$\Delta N = \frac{\Delta N_0}{1 + \frac{B_{12} I(\omega)}{c \bar{R}}} = \frac{\Delta N_0}{1 + I/I_s} \quad (454)$$

where $I_s = c \cdot \bar{R} / B_{12}$ is the saturation intensity and stands for the incident intensity that decreases ΔN to $\Delta N_0/2$.

Since the absorption coefficient

$$\alpha = \sigma_{ik} \left[N_i - \frac{g_i}{g_k} N_k \right]$$

$$g_i = g_k = 1 \longrightarrow \sigma [N_i - N_k] = \sigma \cdot \Delta N, \quad (455)$$

we obtain the result that with increasing incident intensity I , the absorption coefficient

$$\alpha = \sigma \cdot \frac{\Delta N_0}{1 + I/I_s} = \frac{\alpha_0}{1 + I/I_s} = \frac{\alpha_0}{1 + I/I_s} \quad (456)$$

where $\alpha_0 = \sigma \cdot \Delta N_0$ is the absorption coefficient for $I=0$.

Eq. (456) shows that when $I \rightarrow \infty$, $\alpha \rightarrow 0$, i.e., when $I \rightarrow \infty$, the population difference $\Delta N = N_1 - N_2 \rightarrow 0$, so the absorption and emission rates are close to each other, no attenuation to the incident light — the atom sample becomes transparent.

§7.9. Saturation Broadening of Homogeneous Line Profiles

For population densities N_1 and N_2 on levels E_1 and E_2 , when using a radiation field with broad spectral profile and spectral energy density $\rho(\omega)$, the power absorbed per unit volume on the transition $E_1 \rightarrow E_2$ by atoms is

$$\begin{aligned} \frac{dW_{12}}{dt} &= \hbar\omega B_{12}\rho(\omega)\Delta N \\ &= \hbar\omega \cdot B_{12}\rho(\omega) \cdot \frac{\Delta N_0}{1+S} \\ &= \hbar\omega \bar{R} \cdot \frac{\Delta N_0}{1+1/S} \quad (457) \end{aligned}$$

Since the absorption coefficient $\alpha(\omega)$ of a homogeneously broadened line is Lorentzian, see, e.g., Eq. (381), the induced absorption probability follows a Lorentzian line profile $B_{12}\rho(\omega) \cdot g_L(\omega)$. Therefore, we introduce a frequency-dependent spectral saturation parameter S_ω for transition $E_1 \rightarrow E_2$:

$$S_\omega = \frac{B_{12}\rho(\omega)}{\langle R \rangle} g_L(\omega) \quad (458)$$

Where $\langle R \rangle$ is the mean relaxation rate, and assumed to be independent of ω within the frequency range of the line profile. Recall $g_L = \frac{\gamma/2\pi}{(\omega-\omega_0)^2 + (\gamma/2)^2}$, (459)

$$\therefore S_\omega = S_0 \frac{(\gamma/2)^2}{(\omega-\omega_0)^2 + (\gamma/2)^2} \quad \text{with } S_0 = S_\omega(\omega=\omega_0) \quad (460)$$

$$S_0 = \frac{B_{12}\rho(\omega)}{\pi \bar{R} \cdot \gamma/2} \quad (461)$$

Substitute $S\omega$ given by Eq. (460) as S into Eq. (457), we obtain

$$\begin{aligned} \frac{dW_{12}}{dt} &= \hbar\omega \cdot \bar{R} \cdot \frac{\Delta N_0}{1 + (\omega_0 - \omega)^2 + (\gamma/2)^2} \\ &= \hbar\omega \cdot \bar{R} \cdot \frac{\Delta N_0 \cdot S_0 (\gamma/2)^2}{(\omega_0 - \omega)^2 + (\gamma/2)^2 (1 + S_0)} \\ &= \frac{\hbar\omega \bar{R} \Delta N_0 S_0 (\gamma/2)^2}{(\omega_0 - \omega)^2 + [\gamma\sqrt{1+S_0}/2]^2} \end{aligned} \quad (462)$$

$$\therefore \frac{dW_{12}}{dt} = \frac{C}{(\omega_0 - \omega)^2 + (\gamma_s/2)^2} \quad (463)$$

$$\text{Where } C = \hbar\omega \bar{R} \Delta N_0 S_0 (\gamma/2)^2, \quad (464)$$

$$\gamma_s = \gamma \sqrt{1 + S_0} \quad (465)$$

Therefore, the FWHW of the saturation-broadened line

$$\delta\omega_s = \gamma_s = \gamma \sqrt{1 + S_0} \quad (466)$$

i.e., $\delta\omega_s$ increases with the saturation parameter S_0 .

If $S_0 = 1$, then $\delta\omega_s = \sqrt{2} \delta\omega_0$ (where $\delta\omega_0$ is the homogeneous broadening width when $\rho \rightarrow 0$).

Since the power absorbed per unit volume $\frac{dW}{dt}$ equals to the intensity decrease per centimeter: $\frac{dI}{dz} = -I\alpha_s$, from Eq. (463)

We have:
$$\frac{C}{(\omega_0 - \omega)^2 + (\gamma_s/2)^2} = +I\alpha_s = C\rho(\omega)\alpha_s \quad (467)$$

$$\therefore \alpha_s = \frac{C / [C\rho(\omega)]}{(\omega_0 - \omega)^2 + (\gamma_s/2)^2} = \frac{\hbar\omega \Delta N_0 B_{12}}{\pi C} \cdot \frac{\gamma/2}{(\omega - \omega_0)^2 + (\gamma_s/2)^2} \quad (468)$$

$$\therefore \alpha_s(\omega) = \frac{2\hbar\omega B_{12} \cdot \Delta N_0}{\pi C \gamma} \cdot \frac{(\gamma/2)^2}{(\omega - \omega_0)^2 + (\gamma_s/2)^2} \quad (469)$$

This shows that the saturation decreases the absorption coefficient $\alpha(\omega)$ by the factor $(1 + S\omega)$. The saturation is strongest at the line center, and approaches zero for $|\omega - \omega_0| \rightarrow \infty$. This is why the line broadens: absorbed power still increases with increased I ,

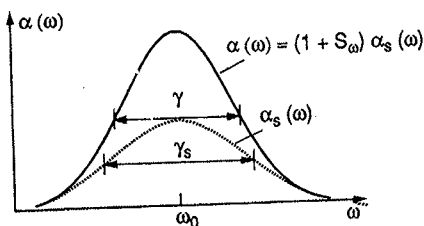
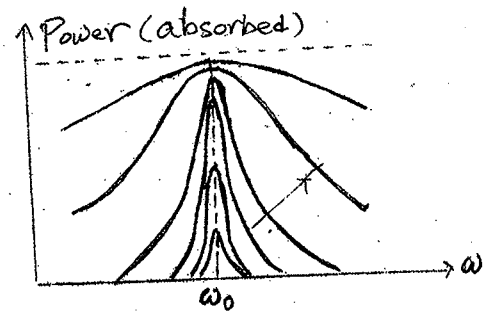


Fig. 3.24. Saturation broadening of a homogeneous line profile



but it increases much slower at the line center than at the wings, thus, the line becomes wider (broadening).

§7.10. Absorption and Dispersion for Doppler-Broadened Spectral Lines

The absorption and dispersion discussed previously under natural linewidth are for atoms at rest. In reality, atoms undergo random thermal motion (in gaseous medium), having Doppler broadening in spectral lines. Thus, we must make corrections to the equations of absorption and dispersion.

Recall the refraction index n is given by

$$n = \sqrt{\epsilon\mu} = \sqrt{\epsilon} = \sqrt{1 + \chi} \quad \text{Eqs. (356) and (357)}$$

In the first order approximation

$$n = \sqrt{1 + \chi} \approx 1 + \frac{1}{2}\chi = 1 + \frac{1}{2}\chi' - i\frac{1}{2}\chi'' \quad (470)$$

Where $\chi = N \chi_e$, Eq. (352) (N is the difference of number densities between the lower and upper levels)

$$= \chi' - i\chi'' \quad (471)$$

χ is the macroscopic susceptibility.

$$\therefore n(\omega) = n'(\omega) - iK(\omega) \quad \text{Eq. (360)}$$

$$\therefore n'(\omega) = 1 + \frac{1}{2}\chi' \quad (472)$$

$$K(\omega) = \frac{1}{2}\chi'' \quad (473)$$

From Eq. (372), the absorption coefficient

$$\alpha(\omega) = 4\pi K(\omega) / \lambda_0 = \frac{2\omega}{c} K(\omega) \quad (474)$$

Substitute Eq. (473) to Eq. (474), we obtain

absorption coefficient

$$\alpha(\omega) = \frac{\omega}{c} \chi'' \quad (475)$$

dispersion

$$n'(\omega) = 1 + \frac{1}{2} \chi' \quad (472)$$

* In the natural linewidth case,

From classical model,

$$\chi = \frac{Ne^2}{m\epsilon_0} \frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega} \quad \text{Eq. (352)}$$

Considering $|\omega_0 - \omega| \ll \omega_0$, $\omega_0 + \omega \approx 2\omega_0$, Eq. (352) is simplified to

$$\chi = \frac{Ne^2}{2m\epsilon_0\omega_0} \cdot \frac{1}{\omega_0 - \omega + i\gamma/2} \quad (476)$$

With Quantum Mechanics correction, and in a simplified case, i.e., only consider one absorption line,

$$\chi = \frac{Ne^2 f_{ik}}{2m\epsilon_0\omega_0} \cdot \frac{1}{\omega_0 - \omega + i\gamma/2} \quad (477)$$

$$= \frac{Ne^2 f_{ik}}{2m\epsilon_0\omega_0} \cdot \frac{\omega_0 - \omega - i\gamma/2}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (478)$$

where f_{ik} is the oscillator strength for the absorption line.

Thus, in the nature linewidth case,

absorption coefficient

$$\alpha(\omega) = \frac{\omega}{c} \chi'' = \frac{N e^2 f_{ik}}{2 m \epsilon_0 c} \cdot \frac{\gamma/2}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (479)$$

dispersion

$$\begin{aligned} n'(\omega) &= 1 + \frac{1}{2} \chi' \\ &= 1 + \frac{N e^2 f_{ik}}{4 m \epsilon_0 \omega_0} \cdot \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (480) \end{aligned}$$

Define Lorentzian normalized lineshape:

$$g_L(\omega) = \frac{\gamma/2 \pi}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (481)$$

$$\therefore \alpha^L(\omega) = \frac{N e^2 f_{ik}}{2 m \epsilon_0 c} \pi g_L(\omega) \quad (482)$$

* In the Doppler linewidth case,

for atoms moving with velocity component v along the laser beam \vec{k} , the ω in Eq. (477) should be changed:

$$\omega \rightarrow \omega - kv \quad (483)$$

Since v has Maxwellian distribution $W(v)$, the macroscopic susceptibility χ becomes

$$\chi = \frac{Ne^2 f_{ik}}{2m\epsilon_0 \omega_0} \int_{-\infty}^{+\infty} \frac{W(v)}{\omega_0 - \omega + kv + i\gamma/2} dv, \quad (484)$$

where $W(v)$ is normalized Gaussian shape:

$$W(v) = \frac{1}{\sqrt{\pi} u} \exp\left[-\frac{v^2}{u^2}\right] \quad (485)$$

where $u^2 \equiv \frac{2k_B T}{M}$ (here M is the atomic mass) (186)

Eq. (484) can be written into a standard format:

$$\chi = \frac{Ne^2 f_{ik}}{2m\epsilon_0 \omega_0 k u} \int_{-\infty}^{+\infty} \frac{k u W(v)}{\omega_0 - \omega + kv + i\gamma/2} dv$$

electron mass \rightarrow

$$= \frac{Ne^2 f_{ik}}{2m\epsilon_0 \omega_0 k u} Z(\omega), \quad (487)$$

$$\text{where } Z(\omega) = \int_{-\infty}^{+\infty} \frac{k u W(v)}{\omega_0 - \omega + kv + i\gamma/2} dv \quad (488)$$

Let $\xi \equiv (\omega - \omega_0 - i\gamma/2)/ku$, then $Z(\omega)$ can be converted to plasma dispersion function:

$$Z(\xi) = -2ie^{-\xi^2} \int_0^{i\xi} e^{-t^2} dt \quad (489)$$

To simplify, take the limit of Doppler width, i.e., let $\gamma \rightarrow 0$ (natural linewidth disappears \rightarrow single line).

$$\therefore \xi \rightarrow (\omega - \omega_0)/ku \equiv \eta \quad (490)$$

$$\begin{aligned} \therefore Z(\frac{\omega}{c}) \rightarrow Z(\eta) &= -2ie^{-\eta^2} \left[\int_{-\infty}^0 e^{-t^2} dt + \int_0^{i\eta} e^{-t^2} dt \right] \\ &= -i\sqrt{\pi} e^{-\eta^2} + 2e^{-\eta^2} \int_0^{\eta} e^{t^2} dt \quad (491) \end{aligned}$$

($t \rightarrow -it$)

$$\therefore \chi' = \frac{Ne^2 f_{ik}}{2m\epsilon_0 \omega_0 k u} \left[2e^{-\eta^2} \int_0^{\eta} e^{t^2} dt \right] \quad (492)$$

$$\chi'' = \frac{Ne^2 f_{ik}}{2m\epsilon_0 \omega_0 k u} \sqrt{\pi} e^{-\eta^2} \quad (493)$$

Thus, in Doppler linewidth, the absorption coefficient

$$\begin{aligned} \alpha(\omega) &= \frac{\omega}{c} \chi'' \\ &= \frac{Ne^2 f_{ik}}{2m\epsilon_0 c k u} \sqrt{\pi} e^{-\frac{(\omega - \omega_0)^2}{(ku)^2}} \quad (494) \end{aligned}$$

$$\boxed{k = \frac{2\pi}{\lambda}, u = \sqrt{\frac{2k_B T}{M}}} \quad \sigma_D = \sqrt{\frac{k_B T}{M \lambda^2}} \quad (\text{in } \nu \text{ unit, not } \omega)$$

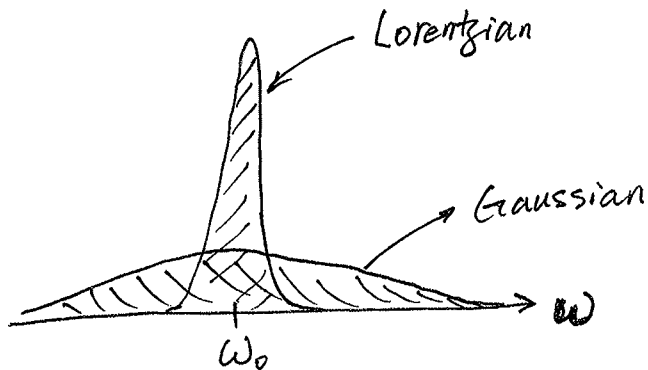
$$\begin{aligned} ku &= \frac{2\pi}{\lambda} \sqrt{\frac{2k_B T}{M}} = \sqrt{2} \cdot 2\pi \cdot \sqrt{\frac{k_B T}{M \lambda^2}} \\ &= \sqrt{2} \cdot 2\pi \cdot \sigma_D \quad (495) \end{aligned}$$

$$\therefore \alpha(\omega) = \frac{Ne^2 f_{ik}}{2m\epsilon_0 c} \cdot \pi \cdot \frac{1}{\sqrt{2\pi} (2\pi \cdot \sigma_D)} e^{-\frac{(\omega - \omega_0)^2}{2(2\pi \sigma_D)^2}} \quad (496)$$

Define normalized Gaussian lineshape

$$g_D(\omega) = \frac{1}{\sqrt{2\pi} (2\pi \cdot \sigma_D)} e^{-\frac{(\omega - \omega_0)^2}{2(2\pi \sigma_D)^2}} \quad (497)$$

$$\therefore \alpha^D(\omega) = \frac{Ne^2 f_{ik}}{2m\epsilon_0 c} \cdot \pi \cdot g_D(\omega) \quad (498)$$



Compare Eq. (482) and Eq. (498).

$$\int \alpha^L(\omega) d\omega = \frac{Ne^2 f_{ik} \pi}{2m\epsilon_0 c} \int g_L(\omega) d\omega = \frac{Ne^2 f_{ik} \pi}{2m\epsilon_0 c}$$

$$\int \alpha^D(\omega) d\omega = \frac{Ne^2 f_{ik} \pi}{2m\epsilon_0 c} \int g_D(\omega) d\omega = \frac{Ne^2 f_{ik} \pi}{2m\epsilon_0 c}$$

i.e., the areas below the absorption coefficient curve are equal for the same amount of atoms N for Lorentzian or Gaussian shapes.

But ~~the~~ natural linewidth (Lorentzian) is much narrower than the Doppler linewidth (Gaussian), the peak absorption coefficient $\alpha(\omega_0)$ is much larger in the Lorentzian case than the Doppler case.

Let us calculate the peak absorption coefficient:

$$\alpha^L(\omega_0) = \frac{N e^2 f_{ik}}{2 m \epsilon_0 c (\gamma/2)}$$

$$\delta\omega_L = \gamma \rightarrow \frac{N e^2 f_{ik}}{m \epsilon_0 c \cdot \delta\omega_L}$$

$$= \frac{e^2}{m \epsilon_0 c} \cdot \frac{N f_{ik}}{\delta\omega_L}$$

$$= \frac{(1.601 \times 10^{-19})^2}{9.109 \times 10^{-31} \times 8.854 \times 10^{-12} \times 299792458} \cdot \frac{N f_{ik}}{\delta\omega_L}$$

$$= 1.06 \times 10^{-5} \frac{N f_{ik}}{\delta\omega_L} \quad (499)$$

$$\alpha^D(\omega_0) = \frac{N e^2 f_{ik}}{2 m \epsilon_0 c} \cdot \frac{\pi}{\sqrt{2\pi} (2\pi \sigma_D)}$$

$$\delta\omega_D = \sqrt{8 \ln 2} (2\pi \sigma_D) \rightarrow \frac{N e^2 f_{ik} \cdot \pi \cdot \sqrt{8 \ln 2}}{2 m \epsilon_0 c \cdot \sqrt{2\pi} \cdot \delta\omega_D}$$

$$= \frac{e^2 \pi \sqrt{8 \ln 2}}{2 m \epsilon_0 c \sqrt{2\pi}} \cdot \frac{N f_{ik}}{\delta\omega_D}$$

$$= \frac{(1.601 \times 10^{-19})^2 \times \pi \times \sqrt{8 \ln 2}}{2 \times 9.109 \times 10^{-31} \times 8.854 \times 10^{-12} \times 299792458 \sqrt{2\pi}} \cdot \frac{N f_{ik}}{\delta\omega_D}$$

$$= 1.564 \times 10^{-5} \frac{N f_{ik}}{\delta\omega_D} \quad (500)$$