

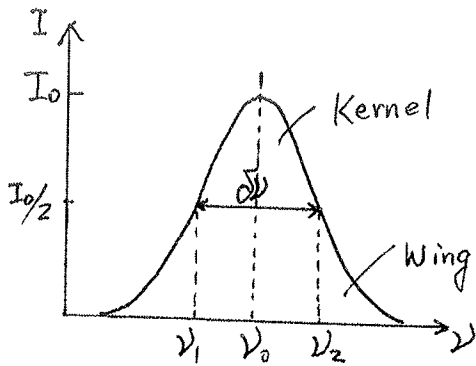
Chapter 7. Spectral Linewidth and Lineshape

§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 $I(\nu)$.

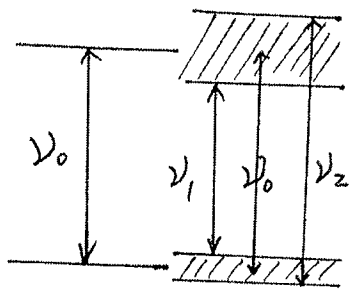
① Central frequency:

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

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

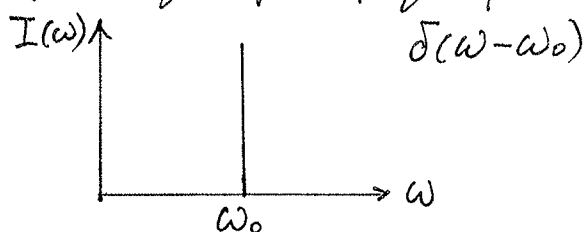
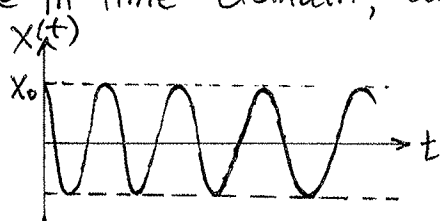
To investigate the spectral distribution of a spontaneous emission on a transition $E_k \rightarrow E_i$ (k - upper level, i - lower level), we describe the QM's spontaneous emission of an atom or a molecule by a classical model of a damped harmonic oscillator with frequency ω , mass m , and restoring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

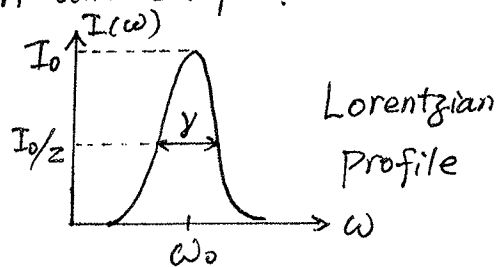
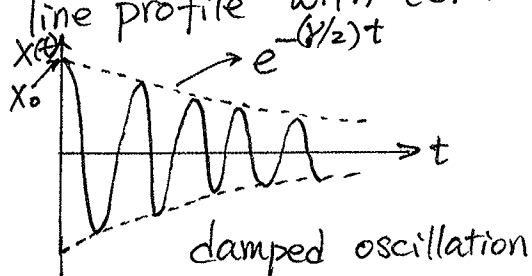
$$X(t) = X_0 e^{-(\gamma/2)t} [\cos \omega t + (\gamma/2\omega) \sin \omega t] \quad (308)$$

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:

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

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 as

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

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

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

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

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

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.

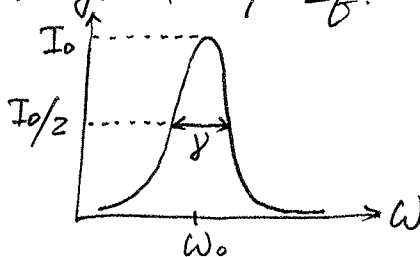
Therefore, the linewidth (FWHM) of $I(\omega)$ is given by

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

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

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,

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

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

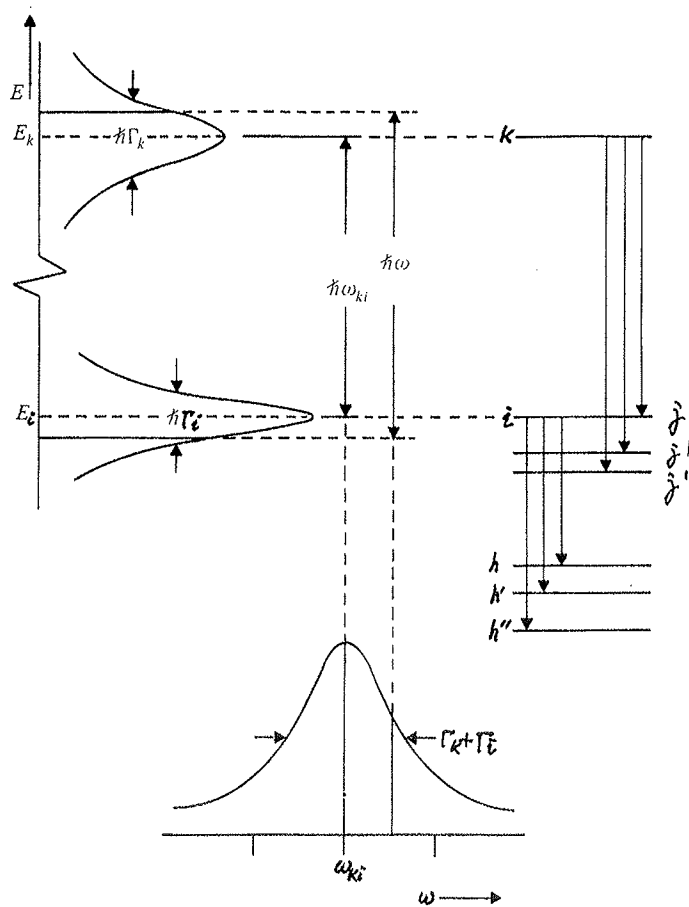
Then the spectral linewidth

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

$$\Delta \nu_{ki} = \frac{\Delta \omega_{ki}}{2\pi} = \frac{(\frac{1}{\tau_k} + \frac{1}{\tau_i})}{2\pi} = \frac{\sum_j A_{kj} + \sum_b A_{ib}}{2\pi} \quad (328)$$

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 $\Delta \nu_{ki}$. 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

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

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

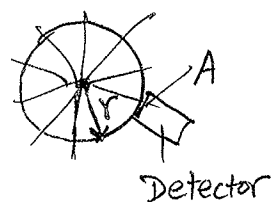
Let us now consider the radiant power emitted from N_k excited atoms on a transition $E_k \rightarrow E_i$ (note: N_k is the number of atoms on the excited state E_k). It is given by

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

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

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

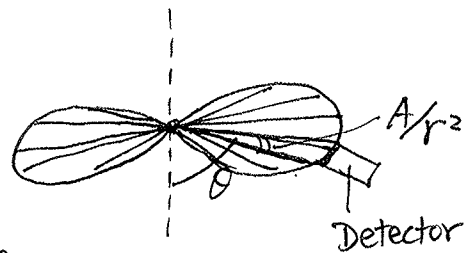
When dealing with anisotropic emission or scattering, we can modify Eq.(335) to the following:

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

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

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

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

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 $T_k = 16.23 \text{ ns}$.

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

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

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

§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 AM 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

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

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).

$$P = N \langle p \rangle(t) \quad (350)$$

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.,

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

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:

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

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:

$$\begin{aligned} n &= n' - ik \\ \text{or } n(\omega) &= n'(\omega) - iK(\omega) \end{aligned} \quad (360)$$

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

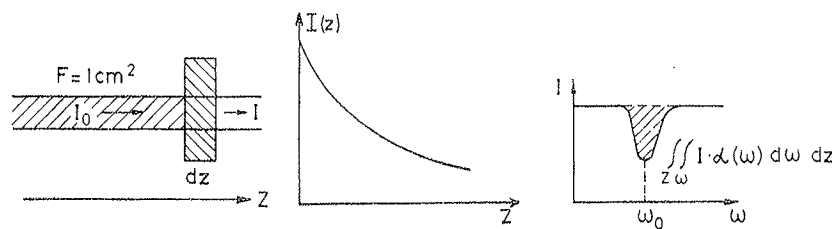


Fig. Absorption of light in an optically thin layer

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