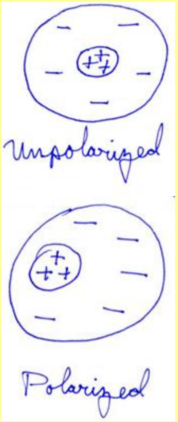
Ch. 2 Optical Properties of Matter

2.1 Introduction

What happens when an EM wave propagates in a material?



How do we determine the permittivity?

→ the absorption & dispersion?

Key role is played by the polarization **P**

What are its microscopic origins? The relative distribution of charges in the medium…

i.e., Whether the material is *polarized*.

Fig. 2.1: Schematic of an unpolarized vs a polarized medium.

Define (classically):

$$\mathbf{p} = \sum_j q_j \mathbf{r}_j^{\,+} - \sum_i q_i \mathbf{r}_i^{\,-} \qquad (2.1)$$

negative charge

electric dipole moment

positive charge

The polarization **P** is then defined as

$$\mathbf{P} = \frac{1}{\Delta V} \sum_i \mathbf{p}_i \qquad (2.2)$$

average dipole moment per unit volume

macroscopically small, but microscopically large, volume

A changing **P** yields a bound charge and a bound current:

$$\rho_B = -\nabla \cdot \mathbf{P} \tag{2.3}$$

bound charge density

$$\mathbf{J}_B = \frac{d\mathbf{P}}{dt} \tag{2.4}$$

bound current density

(2.3) & (2.4) are already incorporated into Maxwell's equation through (1.1)

Thus it is the "electron dance" that we must understand to derive the susceptibility.

How does the EM wave participate in this dance?

>> Atom-Photon interaction <<

Quantum Mechanics

→ physical systems must be found in one of their eigenstates

…for which there is an associated energy

- Two-level system (simplest)…

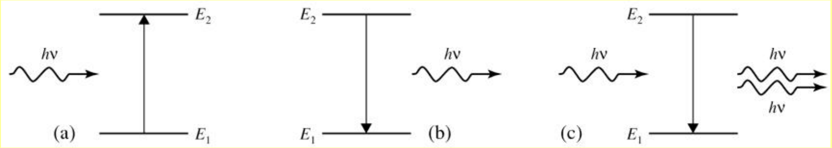


Fig. 2.2: Radiative processes: (a) absorption, (b) spontaneous emission, and (c) stimulated emission. Yariv & Yeh, 6th ed., p. 212.

A photon may be absorbed, provided

$$\hbar\omega = E_2 - E_1 \tag{2.5}$$

where $\hbar = \dfrac{h}{2\pi} = 6.626 \cdot 10^{-34}\,\mathrm{m^2kg/s}$ is Planck's constant.

We can describe this interaction with a simple classical model

→ classical electron model

…system behaves as an oscillating electric dipole

Optical materials may be treated as resonant media, and their optical properties determined from their dipole moments induced by the EM field.

2.2 Radiation & Atomic Systems

Dilute Nonpolar Gas

no net dipole moment in the absence of an applied field

There exists a linear relationship between the dipole moment induced on a molecule in the medium and the local field:

$$\mathbf{p} = \alpha\,\mathbf{E}_{\text{local}} \qquad (2.6)$$

polarizability – a tensor (scalar for systems with spherical symmetry)

(NOT the absorption coefficient)

For a dilute medium with N molecules per unit volume, (2.2) & (2.6) yield

$$\mathbf{P} = N\alpha\mathbf{E} = \varepsilon_0\chi\mathbf{E} \qquad (2.7)$$

where we have assumed that

$$\mathbf{E}_{\text{local}} = \mathbf{E} \qquad (2.8)$$

the macroscopic field

From (2.7), this is valid if

$$\chi = \frac{N\alpha}{\varepsilon_0} << 1 \qquad (2.9)$$

i.e., a dilute gas – see (1.84)

Since the material is characterized by its impulse response function $\varepsilon_0\chi(t)$, or equivalently by its transfer function $\varepsilon_0\chi(\omega)$…

→ we need to find $\chi(\omega)$

We need to determine the *molecular dipole moment*

↳ dimensions << λ so (2.8) is valid

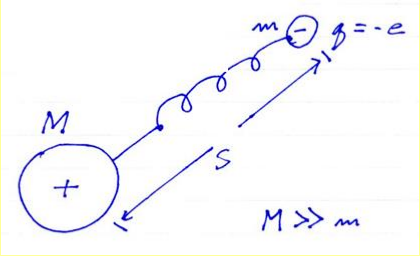


Fig. 2.3: Simple model of a diatomic molecule.

Time harmonic field…

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$$E = E_0 e^{i\omega t} \qquad (2.10)$$

…drives an oscillation described by

$$\frac{d^2 s}{dt^2} + \alpha \frac{ds}{dt} + \omega_0^2 s = -\frac{e}{m} E \qquad (2.11)$$

where ω_0 – resonant frequency, γ – damping coefficient

NB. For a 2-level system, from (2.5)

$$\omega_0 = \hbar^{-1}\left(E_2 - E_1\right) \qquad (2.12)$$

For the time harmonic driving field of (2.10), (2.11) has a steady-state solution given by

$$s(t) = \frac{-eE_0 e^{i\omega t}}{m\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)} \qquad (2.13)$$

(2.13) → (2.1) yields the *induced dipole moment*

$$p = -es = \frac{e^2 E_0 e^{i\omega t}}{m\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)} \qquad (2.14)$$

Comparing (2.14) with (2.6), using (2.10), gives the polarizability as

$$\alpha = \frac{e^2}{m\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)} \qquad (2.15)$$

(2.15) → (2.9) yields…

$$\chi(\omega) = \frac{Ne^2}{m\varepsilon_0\left(\omega_0{}^2 - \omega^2 + i\gamma\omega\right)} \qquad (2.16)$$

If we define

$$\chi_0 = \frac{Ne^2}{m\varepsilon_0\omega_0^2} \qquad (2.17)$$

then

$$\chi(\omega) = \chi_0\frac{\omega_0^2}{\omega_0{}^2 - \omega^2 + i\gamma\omega} \qquad (2.18)$$

Its real and imaginary parts, as per (1.83), are

$$\chi'(\omega) = \chi_0\frac{\omega_0^2\left(\omega_0{}^2 - \omega^2\right)}{\left(\omega_0^2 - \omega^2\right)^2 + \left(\gamma\omega\right)^2} \qquad (2.19)$$

$$\chi''(\omega) = \chi_0\frac{\gamma\omega_0^2\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \left(\gamma\omega\right)^2} \qquad (2.20)$$

From (2.18), the behavior of χ far from resonance is

$$\chi(\omega) \approx \chi_0\frac{\omega_0^2}{\omega_0^2 - \omega^2} \qquad (2.21)$$

NB. $\chi(\omega) \approx \chi_0,\ \omega \ll \omega_0;\quad 0,\ \omega \gg 0$

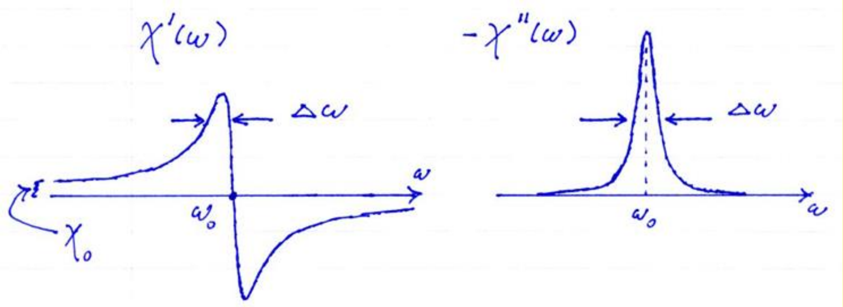


Fig. 2.4: Behaviour of the real and imaginary parts of the susceptibility.

At resonance, $\omega = \omega_0$, and

$$\chi'(\omega_0) = 0 \qquad (2.22)$$

$$-\chi''(\omega_0) = \chi_0 Q \qquad (2.23)$$

a maximum

where (2.20) has permitted us to identify

$$\Delta\omega = \gamma \qquad (2.24)$$

$$Q = \frac{\omega_0}{\Delta\omega} \qquad (2.25)$$

Usually, $\omega_0 >> \Delta\omega \quad \therefore \quad Q >> 1 \quad \Rightarrow \quad -\chi''(\omega_0) >> \chi'(0)$

The max/min values of $\chi'(\omega)$ are

$$\chi'_{\max}(\omega_1) = \chi_0 \frac{Q}{2 - 1/Q} \qquad (2.26)$$

$$\chi'_{\min}(\omega_2) = -\chi_0 \frac{Q}{2 + 1/Q} \qquad (2.27)$$

where

$$\omega_1 = \omega_0 \sqrt{1 - 1/Q} \qquad (2.28)$$

$$\omega_2 = \omega_0 \sqrt{1 + 1/Q} \qquad (2.29)$$

For $Q >> 1$,

$$\Delta\chi'(\omega) = \chi'_{\max} - \chi'_{\min} \approx \tfrac{1}{2}\chi_0 Q \qquad (2.30)$$

The near-resonance behavior of $\chi(\omega)$ is often of particular interest. For $\omega \sim \omega_0$

$$\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega_0(\omega_0 - \omega) \qquad (2.31)$$

(2.31) → (2.18), using (2.24) yields

$$\chi(\omega \sim \omega_0) \approx \chi_0 \frac{\omega_0/2}{(\omega_0-\omega)+i\,\Delta\omega/2} \qquad (2.32)$$

Hence, near resonance

$$\chi''(\omega \sim \omega_0) \approx -\chi_0 \frac{\omega_0\Delta\omega/4}{(\omega_0-\omega)^2+(\Delta\omega/2)^2} \qquad (2.33)$$

$$\chi'(\omega \sim \omega_0) \approx 2\left(\frac{\omega-\omega_0}{\Delta\omega}\right)\chi''(\omega) \qquad (2.34)$$

NB. $\chi''(\omega \sim \omega_0)$ is a Lorentzian function

→ drops to ½ of its peak value when $|\omega-\omega_0| = \Delta\omega/2$

Therefore, $\Delta\omega \leftarrow$ the FWHM of $\chi''(\omega)$

The refractive index and the absorption coefficient for a dilute gas may be determined via (1.101), where in general both depend on $\chi'(\omega)$ <u>and</u> $\chi''(\omega)$.

If we have resonant atoms dilutely embedded in a nondispersive host medium of refractive index n_0, it can be shown that

$$\alpha_{abs}(\omega) \approx -\left(\frac{\omega}{n_0 c}\right)\chi''(\omega) \qquad (2.35)$$

$$n(\omega) \approx n_0 + \frac{\chi'(\omega)}{2n_0} \qquad (2.36)$$

Let us consider the refractive index more closely. From (1.84)

$$n' = \sqrt{\varepsilon/\varepsilon_0} = \sqrt{1+\chi} \qquad (2.37)$$

refractive index (complex)

Let $n' = n - i\kappa$ (2.38)

extinction coefficient

Therefore:

$$n = 1 + \tfrac{1}{2}\chi' \qquad (2.39)$$

$$\kappa = -\tfrac{1}{2}\chi'' \qquad (2.40)$$

(1.48) & (1.54) yield the complex wavenumber as

$$k' = \omega\sqrt{\mu\varepsilon} = \frac{\omega}{c}n' = \frac{2\pi}{\lambda}\left(n - i\kappa\right) \qquad (2.41)$$

Comparison of (2.41) with (1.85) yields

$$\beta = \frac{2\pi}{\lambda}n \qquad (2.42)$$

$$\alpha = \frac{4\pi}{\lambda}\kappa \qquad (2.43)$$

where λ is the free-space wavelength.

From the figure, we see the behavior of the refractive index and the extinction coefficient in the vicinity of the near-singularity $\omega = \omega_0$…

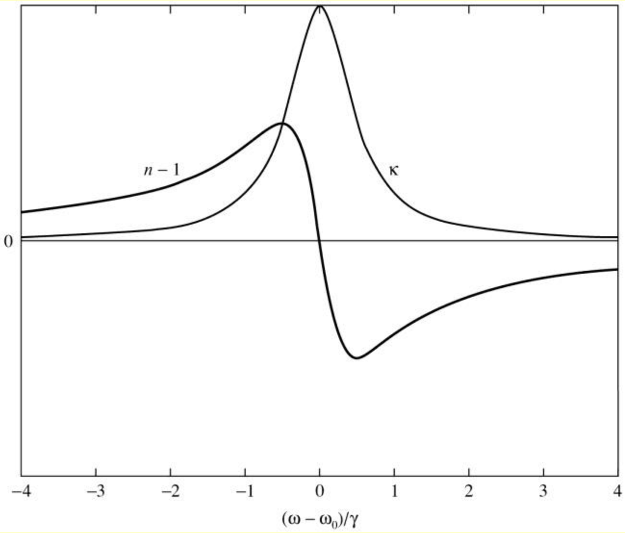


Fig. 2.5: Normalized plot of *n* and κ vs ω. Yariv & Yeh, 6th ed., p. 218.

- $(n - 1)$ changes as $|\omega - \omega_0|^{-1}$ as $|\omega - \omega_0|$ nears ω_1 or ω_2
- κ changes as $(\omega_0 - \omega)^{-2}$…much faster than $(n - 1)$

→ dispersion exists at frequencies where κ is negligible

For $0 < \omega < \omega_1$, the index increases with frequency

→ normal dispersion, $dn/d\omega > 0$

For $\omega_1 < \omega < \omega_2$, a very small spectral window, the index decreases with frequency

→ anomalous dispersion, $dn/d\omega < 0$

2.3 Denser Dielectrics

It is no longer true that $\mathbf{E}_{\text{local}} = \mathbf{E}$

i.e., Microscopic field $\mathbf{E}_m(\mathbf{r}) \neq$ Macroscopic field $\mathbf{E}(\mathbf{r})$

$\mathbf{E}_m(\mathbf{r})$ – the field from the dipoles plus the external field

$\mathbf{E}(\mathbf{r})$ – the average of $\mathbf{E}_m(\mathbf{r})$ over ΔV… a macroscopically small but microscopically large volume (sampling **r** randomly)

└→ ….

└→ This is the same as a field inside a dielectric continuum having macroscopic polarization **P**

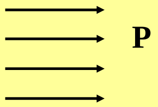


Fig. 2.6a: Finding the Lorentz local field – Step 1

$\mathbf{E}_{\text{local}}(\mathbf{r})$ – the average of $\mathbf{E}_m(\mathbf{r})$ excluding the “self-field” from the local neighbourhood of **r**.

A (con)dense(d) isotropic medium can be modeled as a set of spherical volumes of <u>radius *a*</u>

↑ boundary between *microscopic & macroscopic*

Equivalently, we may consider a sphere of like volume, containing a collection of polarized molecules, embedded in the dielectric continuum…

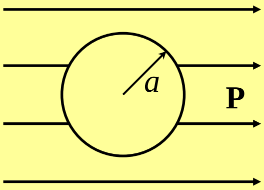


Fig. 2.6b: Finding the Lorentz local field – Step 2

If $a << \lambda$ then **P** is constant in cavity region

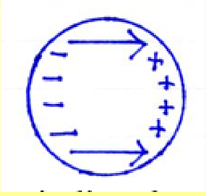
$t_{\text{transit}} << T_{\text{period}}$

transit time across cavity

Therefore: neglect retardation effects

Strictly speaking, this is the zero frequency (*i.e.*, static) limit.

The local field is then



$$\mathbf{E}_{\text{local}} = \mathbf{E} - \mathbf{E}_s \qquad (2.44)$$

field at the centre of an isolated uniformly polarized sphere

Fig. 2.6c: Finding the Lorentz local field – Step 2

It may be shown that

$$\mathbf{E}_s = {-\mathbf{P}}\big/{3\varepsilon_0} \qquad (2.45)$$

(2.45) → (2.44) yields

$$\mathbf{E}_{\text{local}} = \mathbf{E} + {\mathbf{P}}\big/{3\varepsilon_0} \qquad (2.46)$$

(2.46) → (2.6), for N molecules per unit volume, yields

$$\mathbf{P} = N\alpha\mathbf{E}_{\text{local}} = N\alpha\mathbf{E} + \frac{N\alpha}{3\varepsilon_0}\mathbf{P}$$

Therefore:

$$\mathbf{P} = \frac{N\alpha}{1 - {N\alpha}\big/{3\varepsilon_0}}\mathbf{E} \qquad (2.47)$$

Equating (1.73) and (2.47) implies

$$\chi = \frac{N\alpha/\varepsilon_0}{1 - N\alpha/3\varepsilon_0} \qquad (2.48)$$

NB. (2.48) reduces to (2.9) when $N\alpha/\varepsilon_0 << 1$
i.e., it reduces to the dilute system value.

(2.48) → (1.74) presents the relation in its usual form

$$\frac{\varepsilon-\varepsilon_0}{\varepsilon+2\varepsilon_0}=\frac{N\alpha}{3\varepsilon_0} \qquad (2.49)$$

Clausius - Mossotti relation

(2.15) → (2.48) now yields, for dense media

$$\chi(\omega)=\frac{\omega_p^2}{\left(\omega_0^2-\omega_p^2/3\right)-\omega^2+i\,\omega/\tau} \qquad (2.50)$$

where…

$$\omega_p=\sqrt{\frac{Ne^2}{m\varepsilon_0}} \qquad (2.51)$$

plasma frequency – frequency of the oscillating charges if there were no “restoring forces”

$$\tau=\frac{1}{\Delta\omega}=\frac{1}{\gamma} \qquad (2.52)$$

lifetime

Implications?

The near-singularity shifts from $\omega^2=\omega_0^2$ (dilute gas) to $\omega^2=\omega_0^2-\frac{1}{3}\omega_p^2$ for a dense media.