

Chapter 11

Scattering

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Scattering of EM waves is studied in simple contexts. For weak or small scatterers, the formalism is based on radiation: the incident field excites the scatterer, which then radiates.

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1 Preliminaries

1.1 Scattering and cross section

Definition of cross section

This Chapter deals with simple examples of scattering of EM waves. We start with some general notions (most of which is not specific to EM waves).

A plane wave with energy flux S_0 is incident upon a scatterer. Conventionally, the incident direction

is taken to be $+z$, so the incident wave vector is

$$\mathbf{k}_0 = (\omega/c) \hat{\mathbf{e}}_z$$

The scattered wave is detected at polar coordinates (r, θ, ϕ) , with $r \rightarrow \infty$. The energy flux goes as $S \propto r^{-2}$, and is in the direction

$$\hat{\mathbf{n}} = \frac{\mathbf{r}}{r}$$

Therefore, assuming elastic scattering, the wave vector of the scattered wave is

$$\mathbf{k} = (\omega/c) \hat{\mathbf{n}}$$

and the common magnitude of \mathbf{k}_0 and \mathbf{k} is denoted as $k = \omega/c$.

In a small solid angle $d\Omega$ (**Figure 1**), the energy flow per unit time, i.e., the power, is

$$dP = S r^2 d\Omega$$

We can think of this as the power carried by the incident beam in a small imaginary area $d\sigma$:

$$S_0 d\sigma = S r^2 d\Omega$$

which leads to the definition of the differential cross section $d\sigma/d\Omega$ and the total cross section σ as

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= r^2 \frac{S}{S_0} = S_0^{-1} \frac{dP}{d\Omega} \\ \sigma &= \int \frac{d\sigma}{d\Omega} d\Omega = S_0^{-1} P \end{aligned} \quad (1)$$

The cross section has the unit of area, conventionally expressed in barn (b)

$$1 \text{ b} = 10^{-28} \text{ m}^2$$

The same idea can be applied to other situations:

- In classical mechanics by counting particle flux rather than energy flux.
- In quantum mechanics by counting probability flux rather than energy flux.

- The above refers to the energy (or particle number, or probability) flux removed from the incident beam by scattering, and defines the scattering cross section. But the incident flux can also be removed by absorption, so an absorption cross section is defined in a similar way, though in that case there is no differential cross section — the flux is simply removed, and not projected into any direction.

Independent variables

The differential cross section depends on the frequency ω (or equivalently $k = \omega/c$ or $E = \hbar\omega$ for the energy of the photon), as well as the directions:

$$\frac{d\sigma}{d\Omega} = f(\omega, \theta, \phi) \quad (2)$$

If the scatterer is axially symmetric about the z axis, then there is no dependence on ϕ .

In addition, the cross section may depend on the polarization of the incident beam and, if such a selection is made, on the polarization of the scattered beam. If these are not specified, then the cross section is understood to be *averaged* over initial polarizations and *summed* over final polarizations.

1.2 Classical and other examples

General formula

We consider only the axially symmetric case. **Figure 2** shows a particle incident on the scatterer at impact parameter b , and deflected at angle θ asymptotically. For a given incident velocity v_0 (or energy $E = mv_0^2/2$), b and θ are in one-to-one correspondence:

$$b = b(\theta) \quad (3)$$

The relevant area is $2\pi b db$, so

$$\begin{aligned} d\sigma &= 2\pi b |db| \\ d\Omega &= 2\pi \sin \theta d\theta \end{aligned}$$

so that the differential cross section is

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{1}{\sin \theta} b(\theta) \left| \frac{db(\theta)}{d\theta} \right|} \quad (4)$$

The absolute value is taken because $d\sigma$ is always counted as positive whether b increases or decreases.

Example 1

Hard sphere. Suppose point particles are scattered off a hard sphere of radius R (**Figure 3**). If the point of impact is P , the line OP makes an angle α with the backward direction, where

$$\sin \alpha = \frac{b}{R}$$

while the scattering angle is

$$\theta = \pi - 2\alpha$$

Combining these,

$$\begin{aligned} \frac{b}{R} &= \sin \alpha = \sin(\pi/2 - \theta/2) \\ &= \cos(\theta/2) \end{aligned}$$

illustrating the kind of relationship (3). §

Problem 1

(a) Continue the above example, and show that

$$\frac{d\sigma}{d\Omega} = \frac{R^2}{4}$$

independent of angle.

(b) Integrate this and show that $\sigma = \pi R^2$, which is of course the expected answer. §

Example 2

Rutherford scattering. For the scattering of a charge $Z_1 e > 0$ from another (heavy and thus approximately stationary) charge $Z_2 e > 0$, the impact parameter b is related to the scattering angle θ as

$$\begin{aligned} \frac{b}{R} &= \cot(\theta/2) \\ R &= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 m v_0^2} \end{aligned}$$

where m is the mass of the projectile and v_0 is its incident velocity.

Problem 2

Continue with Rutherford scattering.

(a) Show that $2R$ is the distance of closest approach for head-on collisions.

(b) Show that

$$\frac{d\sigma}{d\Omega} \propto \frac{1}{\sin^4(\theta/2)}$$

and also determine the prefactor. §

However the total cross section is infinite: near $\theta = 0$, the integral goes as

$$\int \frac{1}{\sin^4(\theta/2)} \sin \theta d\theta \sim \int_0 \frac{1}{\theta^4} \theta d\theta = \infty$$

Physically, the Coulomb potential has infinite range, so there is some scattering for any impact parameter b , no matter how large.

Hadron and nuclear cross sections

The case of the classical hard sphere suggests that (provided the interaction probability is almost unity upon a “geometric hit”, i.e., the target is not “transparent” to the projectile), the cross section σ should be about the same as the geometric

cross section. Since the “size” of a nucleon is about $R = 1 \text{ fm} = 10^{-15} \text{ m}$, its geometric area is about

$$\pi R^2 \sim 30 \text{ mb}$$

Indeed, measurements of pp or $\bar{p}p$ scattering at say center-of-mass energy 30–40 GeV show a value of about 40 mb.¹

Processes with substantially smaller cross sections are interpreted as having a small probability of interaction, i.e., the projectile being able to “penetrate” the target. For example, the cross section for photon-proton scattering at $\sim 100 \text{ GeV}$ is about $\sigma(\gamma p) \sim 0.1 \text{ mb}$, much smaller than the geometric size of a proton.

1.3 Attenuation length

Suppose the scattering cross section of one target particle is σ , and a macroscopic sample contains N such particles per unit volume.² Imagine a thin slab of the sample, of area A and thickness dz (**Figure 4**). The total number of particles is $NA dz$, obscuring an area $(NA dz)\sigma$, or a fraction $N\sigma dz$ of the total area. Then the flux S would be decreased by this fraction:

$$\begin{aligned} \frac{dS}{S} &= -N\sigma dz \\ S(z)/S(0) &= \exp(-N\sigma z) \\ &= \exp(-z/\Lambda) \end{aligned} \quad (5)$$

where

$$\Lambda = (N\sigma)^{-1} \quad (6)$$

is called the *attenuation length*.

1.4 A class of models

General scattering theory is complicated. Here we deal with a class of simple models, just to get some flavor of the main features. The scatterers are assumed to be weak and sparse, so that the incident wave interacts *once* only, and the resulting scattered wave does not further interact a second time; this is like the Born approximation in quantum mechanics.

Within this assumption, scattering can be thought of in two steps: (a) the incident wave sets up oscillations, causing a time-dependent current (of which the most important part is the electric dipole moment); and then (b) this time-dependent current radiates.

¹At lower energies, the geometric picture does not apply. At higher energies, σ rises logarithmically with energy, due to a subtle quantum tunnelling effect.

²In this Chapter we reserve n for the refractive index.

To be specific, let the scatterer be an electron of mass m and charge $-e$, satisfying the equation of motion

$$m \frac{d^2 x}{dt^2} = -kx - b \frac{dx}{dt} - eE(t)$$

where on the RHS, the first term represents a “spring” that tends to bring the electron back to its neutral position (say in an atom or molecule), the second term³ represents a damping force proportional to the velocity, and the last term is an external electric field, assumed to be in the x -direction, given by⁴

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

Likewise writing

$$x(t) = x e^{-i\omega t}$$

we find for the amplitude

$$x = \frac{eE_0}{m} \frac{1}{\omega^2 + i\gamma\omega - \omega_0^2} \quad (7)$$

and hence the amplitude of the dipole moment $p = -ex$ is

$$p = -\frac{e^2}{m} \frac{1}{\omega^2 + i\gamma\omega - \omega_0^2} E_0 \quad (8)$$

where $\omega_0^2 = k/m$ is the natural frequency, and $\gamma = b/m$ is the damping constant.⁵ The remaining step is to evaluate the radiation due to this oscillating dipole.

The situation will be considered in three domains, depending on which term in the denominator on the RHS of (8) dominates.

- At low frequencies, the last term dominates, leading to Rayleigh scattering.
- At high frequencies or for a free electron, the first term dominates, leading to Thomson scattering.
- In the intermediate domain, all three terms are important, leading to resonant scattering.

2 Rayleigh scattering

2.1 General theory

At low frequencies,

³The coefficient b should not be confused with the impact parameter, which no longer makes an appearance.

⁴Again, real parts are to be taken.

⁵The overall sign can be checked as follows. (a) In statics, the induced polarization is in the same direction as the external field. (b) This is the case whether the charge is positive or negative.

$$\begin{aligned} p &= \alpha_p E_0 \\ \alpha_p &= \frac{e^2}{m\omega_0^2} \end{aligned} \quad (9)$$

The polarizability α_p is independent of frequency, so that, back in the time domain

$$p(t) = \alpha_p E_0(t)$$

without delay.

Thus imagine such a bound electron (say within an atom or molecule) at the origin, and an external plane wave of amplitude E_0 incident along the $+z$ direction, with \mathbf{E} along x . The dipole radiation formula gives

$$P = \frac{1}{3} \frac{\omega^4 p^2}{4\pi\epsilon_0 c^3} = \frac{1}{3} \frac{\omega^4 \alpha_p^2}{4\pi\epsilon_0 c^3} \cdot E_0^2$$

The incident flux is

$$S_0 = \frac{1}{2\mu_0 c} E_0^2$$

The ratio of these quantities gives the cross section

$$\sigma = \frac{1}{6\pi} k^4 \left(\frac{\alpha_p}{\epsilon_0} \right)^2 \quad (10)$$

where $k = \omega/c$. This gives the cross section in terms of the polarizability α for each particle.

Numerical evaluation will be considered below. But an important feature can be noticed immediately: $\sigma \propto k^4 \propto \lambda^{-4}$. This is the characteristic feature of *Rayleigh scattering*.

2.2 Apply to gas

It is useful to write the above formula in a way that bypasses microscopic parameters that are not easily measurable. The polarization density is⁶

$$\begin{aligned} Np &= (\epsilon - \epsilon_0)E = (n^2 - 1)\epsilon_0 E \\ \alpha_p &= \epsilon_0 \frac{n^2 - 1}{N} \end{aligned}$$

where $n^2 = \epsilon/\epsilon_0$ and n is the refractive index. Hence (10) can be expressed as

$$\sigma = \frac{1}{6\pi} k^4 \frac{(n^2 - 1)^2}{N^2} \quad (11)$$

$$\Lambda^{-1} = \frac{1}{6\pi} k^4 \frac{(n^2 - 1)^2}{N} \quad (12)$$

Incidentally, (12) has an interesting property: Λ can be measured from a macroscopic sample, e.g.,

⁶Note that the symbol P is used for the power, so the polarization density is not given the usual symbol.

a cell of dimension a few cm, which would allow N to be determined if it was not already known, and hence also N_A — which then relates macroscopic and microscopic quantities (the number of molecules in a mole).

Problem 3

Regard air as a single species. Its refractive index (almost independent of wavelength within the visible range) is $n = 1.000277$ at standard temperature and pressure (STP), and its density is 1 mole per 22.4 litre. Find σ as well as the attenuation length Λ at STP for red light ($\lambda = 0.65 \mu\text{m}$) and for violet light ($\lambda = 0.40 \mu\text{m}$). In particular, what is the ratio between the two cases? Answer: a factor of about 7. Specifically $\Lambda(\text{red}) = 190 \text{ km}$, $\Lambda(\text{violet}) = 27.3 \text{ km}$. §

2.3 Blue sky and red sunset

Why is the sky blue and why are sunsets red?

Simple explanation

The simple answer is that scattering goes as $k^4 \propto \lambda^{-4}$. The color of the sky is due to scattering (**Figure 5a**): since blue light scatters more, the sky appears blue. On the other hand, at sunset sunlight has to pass through a longer atmospheric path (**Figure 5b**), and with blue light more strongly scattered away, what remains is predominantly red.

But to be more careful, the explanation needs to involve two other elements:

- The absolute amount of scattering and not just the ratio between different colors.
- The effective length of the atmosphere traversed.

Absolute amount of scattering

The ratio (of about 7, see Problem 3) in the scattering cross section is not by itself enough to explain the phenomena, especially of red sunsets. If the attenuation lengths were a hundred times larger, say about 19000 km for red and 2700 km for violet (instead of roughly 190 km and 27 km), both much larger than the scale height of the atmosphere ($H \sim 7.5 \text{ km}$), then not much happens to either component. The complete explanation has to rely on the absolute values of Λ : for violet light, this is about $\sim 27 \text{ km}$, so there is significant effect in passing through the scale height of the atmosphere, and much more so at sunset.

Effective path length

Even the above explanation is not enough: the attenuation length at STP for violet light is about 27 km, and that is not enough to cause substantial scattering through a length $\sim 7.5 \text{ km}$, the scale height of the atmosphere. The point is that at sun-

set (line 2 in **Figure 6a**), the effective path length is much longer than at noon (line 1 in **Figure 6a**), i.e., much more than H .

To deal with this, we have to first generalize (5) to nonuniform density, for which the attenuation factor is obviously

$$\begin{aligned} S/S(0) &= \exp(-X) \\ X &= \sigma \int N ds \end{aligned} \quad (13)$$

the integral being along the path of light.

Problem 4

Consider an isothermal model of the atmosphere, in which

$$N(z) = N_0 \exp(-z/H)$$

where N_0 is the density at sea level (quoted above), z is the vertical height above ground level, and H , called the scale height of the atmosphere, is 7.5 km. Show that the value of X at noon and at sunset are given respectively by

$$\begin{aligned} X_1 &= \frac{H}{\Lambda_0} \\ X_2 &= \sqrt{\frac{\pi}{2}} \frac{\sqrt{HR}}{\Lambda_0} \end{aligned} \quad (14)$$

where Λ_0 is the value of the attenuation length at sea level, i.e., calculated for N_0 , and R is the radius of the earth. It is natural that R should appear for X_2 : if the earth were flat, then the path length is infinite. §

In other words, the effective path length at sunset is

$$L = \sqrt{\frac{\pi}{2}} \sqrt{HR} \sim 274 \text{ km}$$

and the phenomenon of red subsets is explained by the fact that L is much larger than $\Lambda_0(\text{violet}) = 27 \text{ km}$ but on the same order as $\Lambda_0(\text{red}) = 190 \text{ km}$.

2.4 Polarization and angular distribution

Recall that the angular distribution is proportional to $\sin^2 \Theta$, where Θ is the angle between the polarization of the incident beam and the observation direction $\hat{\mathbf{n}}$ (not to be confused with the polar angle θ of the position of observation). We apply this rule to a number of situations.

Angular distribution for unpolarized beam

An unpolarized beam propagating along $+z$ can be regarded as equal proportions of x -polarization

and y -polarization. The angular distribution for the former goes as

$$\frac{dP}{d\Omega} \propto \sin^2 \Theta_1 = 1 - \cos^2 \Theta_1 = 1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_x)^2$$

while the latter goes as

$$\frac{dP}{d\Omega} \propto \sin^2 \Theta_2 = 1 - \cos^2 \Theta_2 = 1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_y)^2$$

Thus the overall distribution for an unpolarized beam goes as

$$\begin{aligned} \frac{dP}{d\Omega} &\propto [1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_x)^2] + [1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_y)^2] \\ &= 1 + (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_z)^2 = 1 + \cos^2 \theta \end{aligned} \quad (15)$$

Scattering in the forward or backward direction is twice as intense as in the equatorial plane.

Polarization of scattered wave

Consider unpolarized light scattered at an angle θ (**Figure 7**). If the initial polarization is parallel to the scattering plane (**Figure 7a**), then there is a factor $\cos^2 \theta$ involved.⁷ For initial polarization perpendicular to the scattering plane (**Figure 7b**), there is no such factor. So defining a polarization parameter Π in terms of the detected intensities I for the two components, we have

$$\Pi \equiv \frac{I_{\perp} - I_{\parallel}}{I_{\perp} + I_{\parallel}} = \frac{1 - \cos^2 \theta}{1 + \cos^2 \theta} \quad (16)$$

Polaroid sunglasses makes use of this fact to preferentially remove scattered light.

3 Thomson scattering

Now consider either free electrons or frequencies so high that the ω^2 term dominates in (7) and (8). Then the amplitude of the dipole moment is

$$p = -\frac{e^2}{m\omega^2} E_0 \quad (17)$$

and when this is put into the formula for the power radiated by a dipole, all the factors of ω exactly cancel:

$$P = \frac{1}{3} \frac{1}{4\pi\epsilon_0} \frac{e^4}{m^2 c^3} \cdot E_0^2 \quad (18)$$

and when this is compared with the incident flux⁸

$$S_0 = \frac{1}{2\mu_0 c} E_0^2$$

⁷For example, there would be no energy flux if the direction is $\theta = \pi/2$.

⁸Convert μ_0 to ϵ_0 and c^2 .

we find the total cross section

$$\sigma = \frac{8\pi}{3} \left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right)^2 \quad (19)$$

This is the formula for *Thomson scattering*, importantly independent of frequency.

Classical radius of electron

The quantity

$$r_e = \frac{e^2}{4\pi\epsilon_0 mc^2} \quad (20)$$

is called the *classical radius* of the electron. The thinking goes as follows.

Suppose the electron is not a point charge, but a sphere of radius r_e , with charge say uniformly distributed over it. The mutual repulsion between the different parts would lead to an electrostatic energy of order

$$U = \frac{e^2}{4\pi\epsilon_0 r_e} \quad (21)$$

If we now say that the electron has no “bare” mass, i.e., its rest mass would be zero if we “switch off” the EM interaction, then its measured rest energy must be all due to U :

$$mc^2 = U$$

which then leads to the formula (20).

Of course, depending on what exact distribution is assumed, there could be a numerical factor of $O(1)$ in (21) and hence also such a factor in the definition of r_e . But the definition adopted is the conventional one.

Thus we have

$$\sigma = \frac{8\pi}{3} r_e^2 \quad (22)$$

Compton wavelength of electron

Recall that Compton scattering involves the quantity

$$\lambda_e = \frac{h}{mc} \quad (23)$$

This can be defined for any particle with mass m , but here we consider an electron. It is easy to show that

$$r_e = \alpha \lambda_e / (2\pi) \quad (24)$$

where $\alpha \approx 1/137$ is the fine structure constant.⁹

⁹In this Chapter, α is used to denote both the polarizability and also the fine structure constant. The meaning should be clear from the context.

Problem 5

Review of Compton scattering. A photon (usually X-ray or γ ray) is scattered off an electron of mass m . Find the increase in the wavelength of the scattered photon, if the scattering angle is θ . Express $\Delta\lambda$ in terms of λ_e and θ . §

Problem 6

Evaluate $\lambda_e/(2\pi)$, r_e and also σ for Thomson scattering. Answer: 3.86×10^{-13} m; 2.82×10^{-15} m = 2.82 fm; 0.67×10^{-28} m² = 0.67 b. §

Angular distribution

It is easy to see that the angular distribution is the same as for Rayleigh scattering.

Quantum effect

The prediction of Thomson scattering becomes invalid when $\hbar\omega/mc^2$ is not small. In this case, the incident wave should be regarded as photons, each with momentum $\hbar\omega/c$. The charged particle therefore recoils in the process, taking away some energy. The scattered photon therefore has energy less than $\hbar\omega$, i.e., the scattered radiation is at a lower frequency. This is the essence of Compton scattering.

The phase space available to the final photon goes as $(k')^2 < k^2$, where k' is the wave number of the final photon. Therefore the probability, or the cross-section, has a factor $(k'/k)^2$, which suppresses backward scattering.

4 Resonant scattering and absorption

4.1 Scattering

Recall the general formula (8) for the E field producing a dipole, which would then radiate. The relevant factor for the amplitude of the dipole is

$$F_1 = \frac{1}{\omega^2 + i\gamma\omega - \omega_0^2} \quad (25)$$

which becomes

$$F_2 = \frac{1}{\omega^2} \quad (26)$$

in the case of Thomson scattering ($\omega \rightarrow \infty$). Thus, the general formula for the cross section can be obtained from that for Thomson scattering, namely (22), by scaling up with a factor of $|F_1/F_2|^2$:

$$\begin{aligned} \sigma &= \frac{8\pi}{3} r_e^2 \left| \frac{\omega^2}{\omega^2 + i\gamma\omega - \omega_0^2} \right|^2 \\ &= \frac{8\pi}{3} r_e^2 \frac{\omega^4}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \end{aligned} \quad (27)$$

This formula can be generalized to a number of terms each with relative weight f_i ($\sum_i f_i = 1$), resonance frequency ω_i and width γ_i :

$$\sigma = \frac{8\pi}{3} r_e^2 \sum_i f_i \frac{\omega^4}{(\omega^2 - \omega_i^2)^2 + \gamma_i^2 \omega^2} \quad (28)$$

which serves very well to describe a large class of phenomena involving *resonant scattering*.

In the following, we shall only use the simpler formula (27) and moreover (a) assume the resonance is narrow, and (b) evaluate at the peak, giving

$$\sigma_{sc} = \frac{8\pi}{3} r_e^2 \frac{\omega^2}{\gamma^2}$$

or, more compactly

$$\sigma_{sc} = \frac{8\pi}{3} r_e^2 Q^2 \quad (29)$$

where we have now indicated that this refers to scattering, henceforth ω is understood to mean the resonance frequency and

$$Q = \frac{\omega}{\gamma} \quad (30)$$

is the usual quality factor of a resonance. Note that there is an enhancement factor of Q^2 compared to Thomson scattering.

4.2 Absorption

Energy is also removed from the incident beam because the oscillating charge is a *damped* oscillator. The time-averaged power absorbed is

$$\begin{aligned} P_{ab} &= \langle E \dot{p} \rangle \\ &= \frac{1}{2} \Re[E^*(-i\omega p)] = \frac{\omega}{2} (\Im \alpha_p) E^2 \end{aligned} \quad (31)$$

while the incident flux is

$$S_0 = \frac{1}{2\mu_0 c} E^2$$

so the cross section for absorption is the ratio between the two

$$\sigma_{ab} = \frac{\omega}{\epsilon_0 c} (\Im \alpha_p) \quad (32)$$

But from (8), we find

$$\begin{aligned} \alpha_p &= -\frac{e^2}{m} \frac{1}{\omega^2 + i\gamma\omega - \omega_0^2} \\ \Im \alpha_p &= \frac{e^2}{m} \frac{\gamma\omega}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \\ &= \frac{e^2}{m} \frac{1}{\gamma\omega} \end{aligned} \quad (33)$$

where the last line applies at the peak, assumed to be narrow. Hence

$$\begin{aligned} \sigma_{ab} &= \frac{e^2}{\epsilon_0 m c} \omega \frac{1}{\gamma\omega} \\ &= 2 \frac{e^2}{4\pi\epsilon_0 m c^2} \cdot \frac{2\pi c}{\omega} \cdot \frac{\omega}{\gamma} \end{aligned}$$

or, simply

$$\sigma_{ab} = 2 r_e \lambda Q \quad (34)$$

4.3 IR spectroscopy

Molecular vibrations

Many spectroscopic techniques are based on the scattering or absorption of light, but most involve transitions between different states and are best (or can only be) discussed quantum mechanically. Infrared spectroscopy is one technique which can be largely understood in classical electrodynamics, and a brief account is given below for some of its features.

Molecules (especially organic molecules) may contain parts that can be set into vibration by an external electric field. **Figure 8** shows schematically a C–H group and a C=O group in oscillation. In both cases, we can heuristically think of the C atom as fixed, and the other atom (H or O) as vibrating — not so much because C is heavier (it is not heavier than O), but because in an organic molecule, the C atoms are typically held tightly as part of a chain or ring.

These vibrations have characteristic resonance frequencies ($f_0 = \omega_0/(2\pi)$, where ω_0 is the parameter in the formalism above). Conventionally, the resonant frequency is expressed through the so-called wave number¹⁰ defined as λ_0^{-1} in units of cm^{-1} . The resonance position in these two cases are approximately as follows

group	λ_0^{-1} cm^{-1}	λ_0 μm
C–H	2800	3.6
C=O	1700	5.9

Table 1. Characteristic lines.

The wavelengths are in the infrared (IR) range, and we refer to *IR spectroscopy*.

What determines the line positions

Recall that for a harmonic oscillator

$$\omega_0 = \sqrt{\frac{k}{m}}$$

¹⁰This differs from the variable of the same name used in physics by a factor of 2π .

so the line positions are determined by a number of factors. In the following we refer to λ_0^{-1} in units of cm^{-1} .

- Vibration of light atoms or groups have higher frequencies. For example, C–H occurs at ~ 3000 , and O–H, N–H even higher. Oscillations not involving H occur at 1000 to about 2300.
- For the same mass, double and triple bonds, being stronger (larger k), will have higher frequencies. Thus in the two examples in Table 1, the mass factor alone ($\text{H} = 1$, $\text{O} = 16$) would have caused a factor of 4; but in fact the difference is only a factor of 1.6, because the C=O double bond is stronger than the C–H single bond.
- Vibrational modes that stretch a bond (**Figure 9a**) are at higher frequencies than those that bend a bond angle (**Figure 9b**).

The identification of lines with specific vibrational modes has become a subject in itself: through detailed measurements as well as theoretical calculations from molecular dynamics (using potential energy functions as input). Extensive tables are now available, and are routinely used to interpret spectra of unknown or novel compounds, thus identifying the presence (and the amount) of different *functional groups*.

Line intensities

Chemists are mostly concerned with line positions, i.e., the values of ω_0 — which in the context of the present Chapter is an input parameter. We are here instead concerned with the line intensity, which is determined by the cross section.

First of all, note that the oscillating object is now an atom, not an electron. So $r_e \propto m^{-1}$ should be replaced by the corresponding classical radius r_c for an atom, which is much smaller — in the case of H, a factor of ~ 1800 smaller, say $\approx 1.5 \times 10^{-18}$ m. Thus the ratio of scattering to absorption is

$$\frac{\sigma_{\text{sc}}}{\sigma_{\text{ab}}} = \frac{4\pi r_c}{3\lambda} Q \quad (35)$$

where typically

$$\frac{r_c}{\lambda} \sim \frac{1.5 \times 10^{-18} \text{ m}}{3.6 \times 10^{-6} \text{ m}} \sim 0.5 \times 10^{-12}$$

Since Q is typically in the 10^3 to 10^5 range, the ratio in (35) is much smaller than unity. Therefore IR spectroscopy is always done via absorption rather than scattering.

Using (34) and putting $r \approx 1.5 \times 10^{-18}$ m, $\lambda \approx 3.6 \times 10^{-6}$ m, we find

$$\sigma_{\text{ab}} \sim Q \times 10^{-23} \text{ m}^2 \quad (36)$$

With typical Q values of about 10^4 , we get $\sigma_{\text{ab}} \sim 10^{-19} \text{ m}^2$.

This is much larger than the Thomson cross section or the scattering cross section discussed earlier. The main reason is that σ_{ab} goes as $r_c \lambda$ rather than r_e^2 . If we trace this back, this is because the factor e^2 enters once rather than twice — a characteristic of absorption which goes as $pE_0 \sim \alpha E_0^2$ compared to scattering which goes as $p^2 \sim \alpha^2 E_0^2$. It is sometimes said that σ_{ab} is about the physical size of a molecule. The analysis above makes it clear that this explanation is wrong (though it happens to give roughly the right answer, by accident).

A Supplement: Frequency-dependent linear response

Each supplement will consist of one or more problems, usually more challenging and of an open nature, to stretch the better students.

A.1 Linear response in frequency domain

From (8) and multiplying by the number of dipoles per unit volume N , we find that, for a definite frequency ω , the polarization density $P(t)$ is proportional to the imposed electric field $E(t)$ as¹¹

$$\begin{aligned} E(t) &= \tilde{E}(\omega) e^{-i\omega t} \\ P(t) &= \tilde{P}(\omega) e^{-i\omega t} \\ \tilde{P}(\omega) &= \tilde{\chi}(\omega) \tilde{E}(\omega) \end{aligned} \quad (37)$$

In this example

$$\tilde{\chi}(\omega) = \frac{Ne^2}{m} \frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2} \quad (38)$$

but here we want to derive some general properties valid for any reasonable $\tilde{\chi}(\omega)$, independent of its specific form. The properties discussed below are valid for any two quantities that are linearly and causally related (not restricted to the pair P and E), with the proportionality factor being frequency-dependent. Thus, the same formalism here will apply to the current I in a circuit being driven by a voltage V , with

$$\tilde{\chi} \mapsto \frac{1}{Z} \quad (39)$$

where Z is known in circuit analysis as the complex impedance.¹²

¹¹We shall refer to the same point in space, and the spatial coordinate is suppressed.

¹²There are however two minor points to note. (a) In electric circuits, one typically denotes $\sqrt{-1} = j$ rather than i ,

A.2 Properties of the response function

High frequency limit

The example (38) has the property that

$$\boxed{\tilde{\chi}(\omega) \rightarrow 0 \text{ for } |\omega| \rightarrow \infty} \quad (40)$$

This property is general for any response that involves inertia. (We shall see later how to circumvent this restriction if necessary.)

Imaginary part represents loss

Consider fields at a single frequency:

$$\begin{aligned} E(t) &= E_0 e^{-i\omega t} \\ &\mapsto E_0 \cos \omega t \\ P(t) &= E_0 \tilde{\chi}(\omega) e^{-i\omega t} \\ &= E_0 (\tilde{\chi}_R + i\tilde{\chi}_I) \cdot (\cos \omega t - i \sin \omega t) \\ &\mapsto E_0 (\tilde{\chi}_R \cos \omega t + \tilde{\chi}_I \sin \omega t) \\ \dot{P}(t) &= E_0 (-\tilde{\chi}_R \omega \sin \omega t + \tilde{\chi}_I \omega \cos \omega t) \end{aligned}$$

The rate of work done is $W = \dot{P}E$, and we consider the average over many cycles, for which

$$\begin{aligned} \cos^2 \omega t &\mapsto 1/2 \\ \sin \omega t \cos \omega t &\mapsto 0 \end{aligned}$$

Thus

$$\boxed{W = \frac{1}{2} \omega \tilde{\chi}_I(\omega) E_0^2} \quad (41)$$

Therefore $\omega \tilde{\chi}_I(\omega)$ represents an absorption coefficient, and moreover we must have

$$\boxed{\omega \tilde{\chi}_I(\omega) \geq 0} \quad (42)$$

It is easy to check that this property is satisfied by the example in (38).

In fact, very often $\omega \tilde{\chi}_I(\omega)$ consists of a number of narrow peaks, and vanishes outside those narrow frequency bands.

Response function in time domain

If there is a superposition of different frequencies, then

$$\begin{aligned} P(t) &= \int \frac{d\omega}{2\pi} \tilde{P}(\omega) e^{-i\omega t} \\ &= \int d\tau \chi(\tau) E(t-\tau) \end{aligned} \quad (43)$$

reserving the latter for the current; (b) the time dependence is assumed to be $\exp(+j\omega t)$, with a plus sign in the exponent. Both of these would be automatically taken care of if we take $j = -i$ everywhere.

where $\chi(\tau)$ is the fourier transform of $\chi(\omega)$. The derivation of the second line is a straightforward exercise in Fourier transforms.

Causality: time domain

Thus we see that $\chi(\tau)$ has the interpretation of the response to the E -field at a time τ *earlier*; in other words, τ is the *delay* in the response. But *causality* requires that the delay must be positive, hence

$$\boxed{\chi(\tau) = 0 \text{ for } \tau < 0} \quad (44)$$

Causality: frequency domain

Going back to the frequency domain

$$\tilde{\chi}(\omega) = \int d\tau \chi(\tau) e^{i\omega\tau} \quad (45)$$

Because of the causality condition (44), the integrand goes only over $\tau \geq 0$.

Now suppose we evaluate (45) for ω in the upper half-plane (UHP), i.e.,

$$\omega = \omega_R + i\omega_I \quad \text{with } \omega_I > 0$$

Then the integrand contains a factor

$$\exp(-\omega_I \tau)$$

which goes rapidly to zero as $\tau \rightarrow \infty$. Thus the integral converges, and the integrand is an analytic function of ω .¹³ Therefore we conclude that $\tilde{\chi}(\omega)$ is analytic in the UHP. The example (38) does indeed exhibit this property.

Conversely, suppose we start with a function $\tilde{\chi}(\omega)$ that is analytic in the UHP, and consider

$$\chi(\tau) = \int \frac{d\omega}{2\pi} \tilde{\chi}(\omega) e^{-i\omega\tau} \quad (46)$$

for $\tau < 0$. The contour can be closed by adding a large semicircle in the UHP, because the argument of the exponential involves

$$-i(i|\omega_I|)(-|\tau|)$$

which is negative, with a magnitude proportional to the radius R of the semicircle, leading to vanishing contribution for the added part as $R \rightarrow \infty$.¹⁴ Then the integral can be evaluated by Cauchy's theorem; but there is no singularity in the region enclosed by

¹³Think of integration as just adding up an infinite number of terms, all with different values of τ . Each term (i.e., the integrand) is analytic in ω ; so the sum/integral is also analytic unless the sum/integral diverges, which we have now ruled out.

¹⁴Let $\omega = R \exp(i\phi)$ on the semicircle. The above argument works for ϕ away from 0, π . Near the real axis, we need to make use of the fact that $\tilde{\chi}(\omega) \rightarrow 0$.

the contour, namely the UHP. Hence $\chi(\tau) = 0$ for this case.

Symmetry properties

From (45), it is easy to see that for real ω , changing $\omega \mapsto -\omega$ is the same as complex-conjugating the result, which leads to

$$\begin{aligned}\tilde{\chi}_R(-\omega) &= \tilde{\chi}_R(\omega) \\ \tilde{\chi}_I(-\omega) &= -\tilde{\chi}_I(\omega)\end{aligned}\quad (47)$$

A.3 Dispersion relation

Cauchy integral

Cauchy's theorem states that

$$\tilde{\chi}(\omega) = \frac{1}{2\pi i} \oint \frac{d\omega'}{\omega' - \omega} \tilde{\chi}(\omega') \quad (48)$$

where the contour winds around ω once in the positive sense and $\tilde{\chi}(\omega')$ is analytic on and inside the contour.

Take ω to be on the real axis, and the contour to consist of the following pieces:

1. Along the real axis from $\omega' = -R$ to $\omega' = \omega - \delta$.
2. From $\omega - \delta$ to $\omega + \delta$ by going along a semicircle in the LHP, i.e., taking

$$\omega' - \omega = \delta e^{i\phi}, \quad \pi \leq \phi \leq 2\pi$$

3. Along the real axis from $\omega' = \omega + \delta$ to $\omega' = R$.
4. From $\omega' = R$ to $\omega' = -R$ along a large semicircle in the UHP.

This contour circles around ω . In all this, the limit $R \rightarrow \infty$, $\delta \rightarrow 0$ is understood.

The 4th contribution, along the large semicircle, vanishes because $\tilde{\chi}(\omega')$ is assumed to vanish when $|\omega| = R \rightarrow \infty$ and there is a further factor of $(\omega' - \omega)^{-1} \propto R^{-1}$ in the integrand. The 2nd contribution is along the small semicircle, for which

$$\begin{aligned}d\omega' &= \delta i e^{i\phi} d\phi \\ \tilde{\chi}(\omega') &\approx \tilde{\chi}(\omega)\end{aligned}$$

giving

$$\frac{1}{2\pi i} \int_{\pi}^{2\pi} \frac{\delta i e^{i\phi} d\phi}{\delta e^{i\phi}} \cdot \tilde{\chi}(\omega) = \frac{1}{2} \tilde{\chi}(\omega) \quad (49)$$

The 3rd contribution is called the *principal value* of the integral with a singularity at $\omega' = \omega$, denoted with the symbol P ; schematically

$$P \int_a^b = \lim_{\delta \rightarrow 0} \left(\int_a^{\omega - \delta} + \int_{\omega + \delta}^b \right) \quad (50)$$

Thus we get

$$\tilde{\chi}(\omega) = \frac{1}{2\pi i} P \int \frac{d\omega'}{\omega' - \omega} \tilde{\chi}(\omega') + \frac{1}{2} \tilde{\chi}(\omega)$$

or, upon simplification

$$\tilde{\chi}(\omega) = \frac{1}{\pi i} P \int \frac{d\omega'}{\omega' - \omega} \tilde{\chi}(\omega') \quad (51)$$

Principal value

The principal value of an integral, say

$$I = P \int \frac{d\omega'}{\omega' - \omega} f(\omega')$$

has two important properties.

- Provided f is non-singular, the integral is finite, despite the denominator.¹⁵
- If f is real, then the integral is also real.¹⁶

Real part in terms of imaginary part

Then, taking the real part of (51), we finally obtain

$$\tilde{\chi}_R(\omega) = \frac{1}{\pi} P \int \frac{d\omega'}{\omega' - \omega} \tilde{\chi}_I(\omega') \quad (52)$$

which is called the *dispersion relation* for a reason to be explained below.

The principal value integral goes over the real line, but the contribution for $\omega' < 0$ can be expressed in terms of the contribution for $\omega' > 0$, using the symmetry properties (47). Thus the above relationship is more commonly expressed as

$$\tilde{\chi}_R(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{du u}{u^2 - \omega^2} \tilde{\chi}_I(u) \quad (53)$$

This is a remarkable result: *The imaginary part of the response function completely determines the real part.* The reverse is also true, but that form is seldom used because the imaginary part (a) is physically understood in terms of absorption, and (b) therefore typically consists of narrow peaks or at most restricted bands.

The dielectric function

Conventionally we refer to the field

$$D(t) = \epsilon_0 E(t) + P(t) \quad (54)$$

The corresponding response function $\tilde{\epsilon}(\omega)$ is related to $\tilde{\chi}(\omega)$ as

$$\tilde{\epsilon}(\omega) = \epsilon_0 + \tilde{\chi}(\omega) \quad (55)$$

¹⁵This is easily seen by splitting $f(\omega') = f(\omega) + [f(\omega') - f(\omega)]$ and integrating the first term explicitly.

¹⁶This is not true of the original Cauchy integral which detours out of the real axis.

We can apply the same argument to $\tilde{\epsilon}(\omega) - \epsilon_0$ (but not just the first term, because the first term alone does not vanish for large values of ω), Then (53) can be written as

$$\boxed{\tilde{\epsilon}_R(\omega) = \epsilon_0 + \frac{2}{\pi} P \int_0^\infty \frac{du u}{u^2 - \omega^2} \tilde{\epsilon}_I(u)} \quad (56)$$

The relationship in this form is called the Kramers–Kronig relation.

Example

Consider a typical piece of glass, which absorbs in the UV but is transparent in the visible. Then a knowledge of the UV absorption (i.e., knowledge of $\tilde{\epsilon}_I(u)$ in the UV range) determines the RHS, and hence determines $\tilde{\epsilon}_R(\omega)$ for all ω , in particular for ω in the visible range. If in the visible range the glass is transparent, then $\tilde{\epsilon}$ is purely real and is equal to n^2 , where n is the refractive index. Thus (56) determines how n changes with wavelength, namely the *dispersion*. In other words: *absorption determines dispersion*.

When evaluating for a value of ω for which there is no absorption, the symbol P can be omitted.

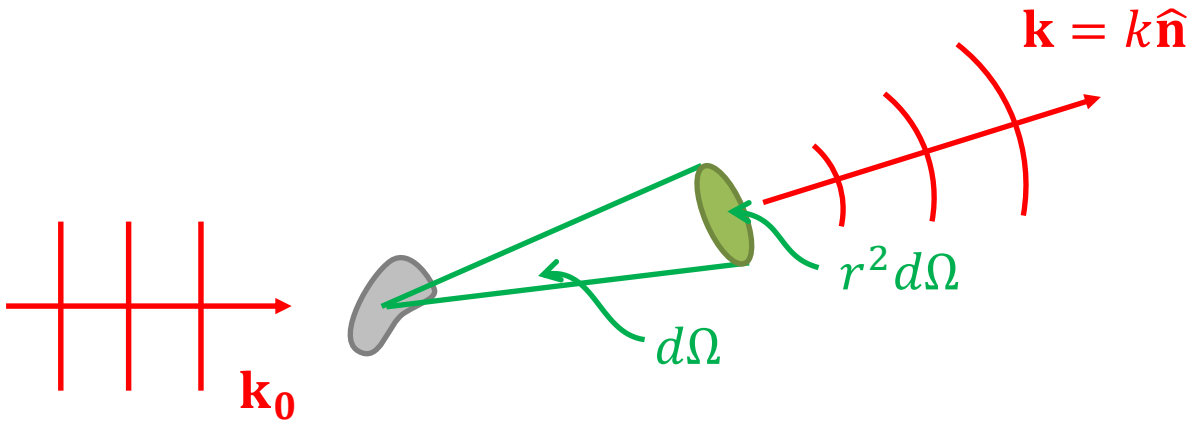


Figure 1 Power flowing into the area $r^2 d\Omega$

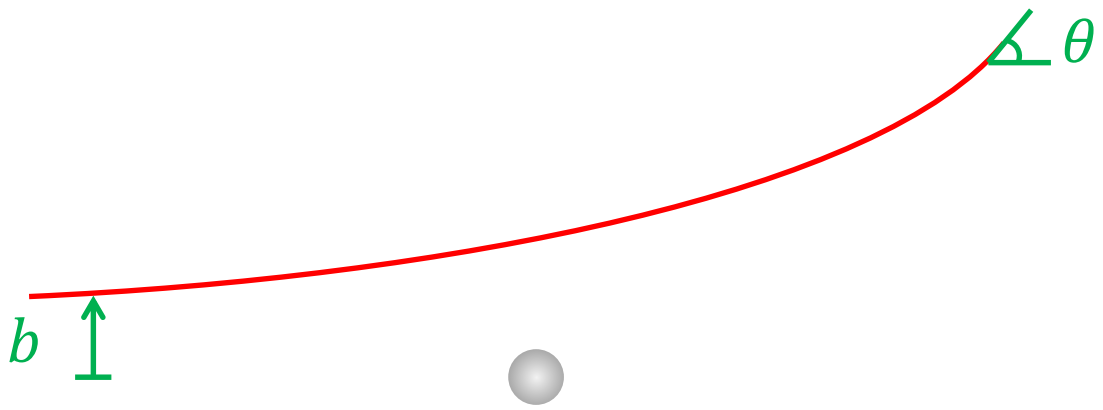


Figure 2 Impact parameter b and scattering angle θ

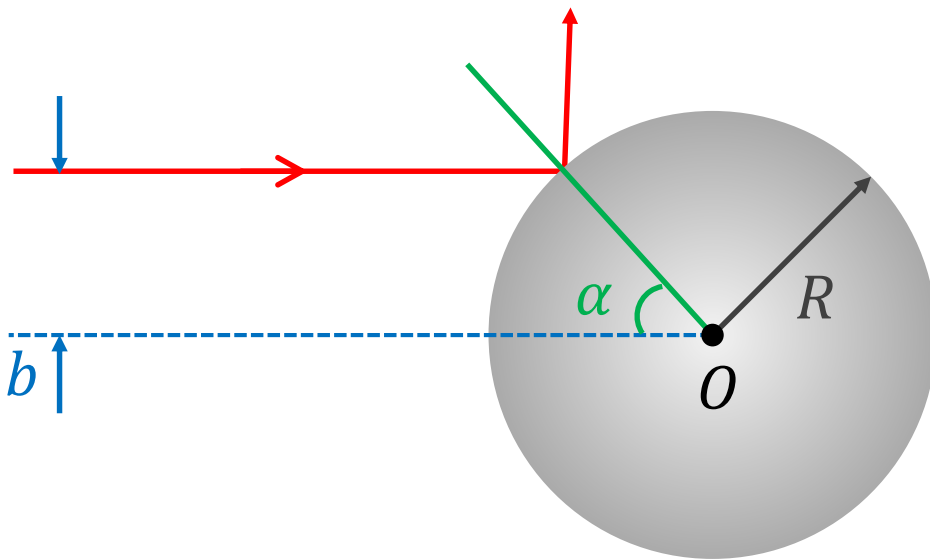


Figure 3 Scattering by a hard sphere

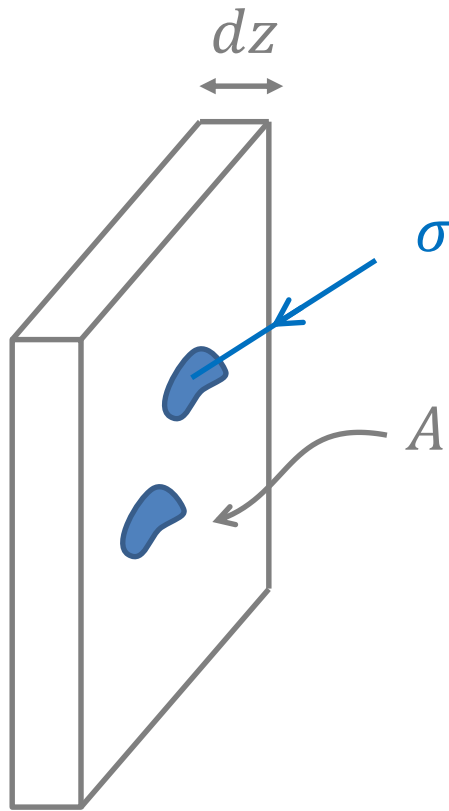


Figure 4 Out of area A , $N(A dz) \cdot \sigma$ is observed

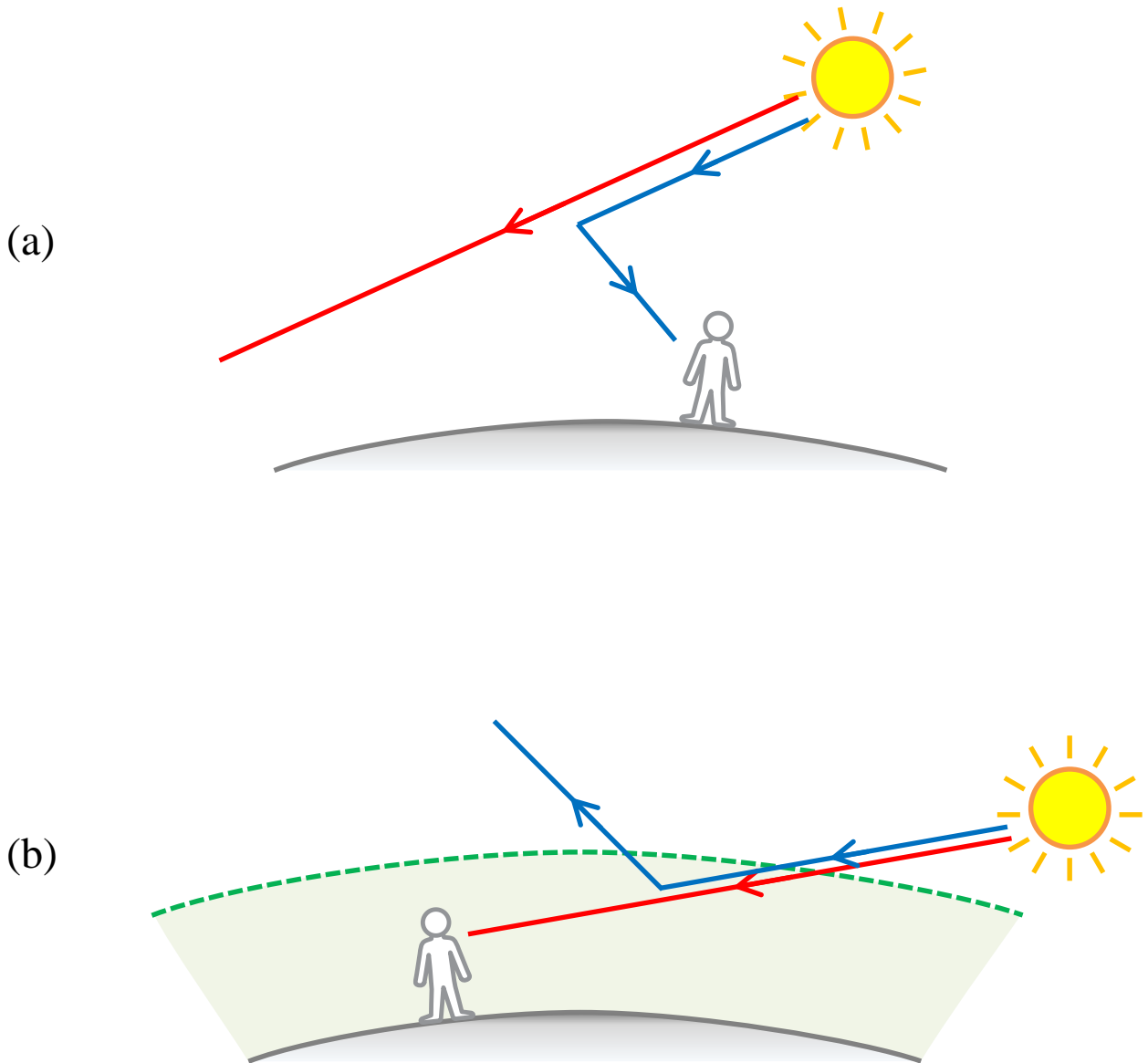


Figure 5 (a) Blue light is scattered more than red light.
So sky appears blue
(b) Blue light is scattered while red light is
transmitted, so sunset appears red

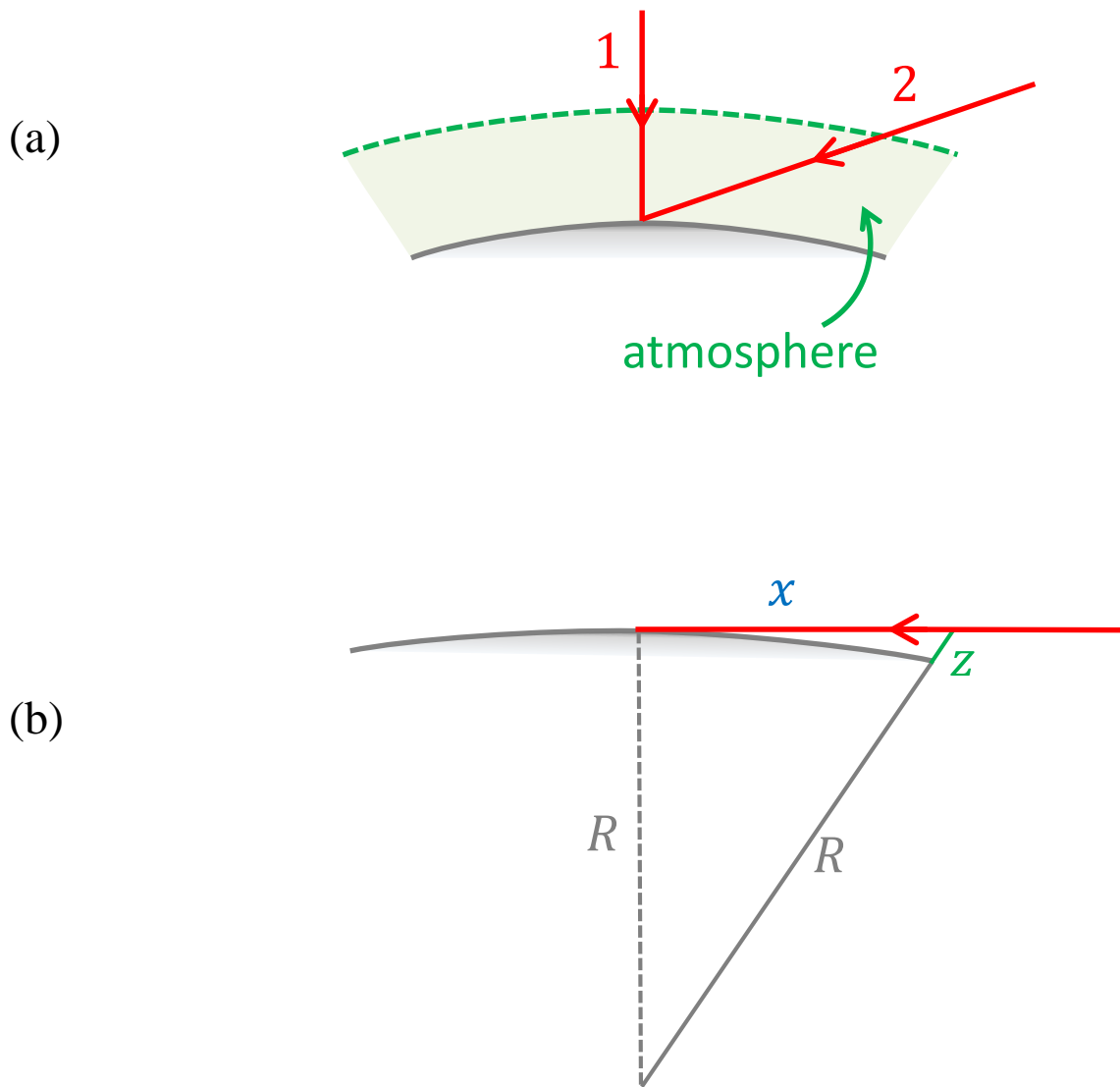


Figure 6 (a) There is longer path through atmosphere at sunset (line 2) compared to noon (line 1)
 (b) The height above ground is

$$z = \sqrt{R^2 + x^2} - R$$

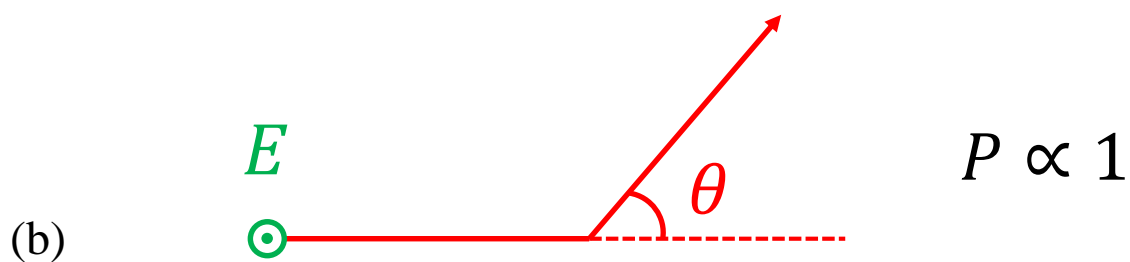
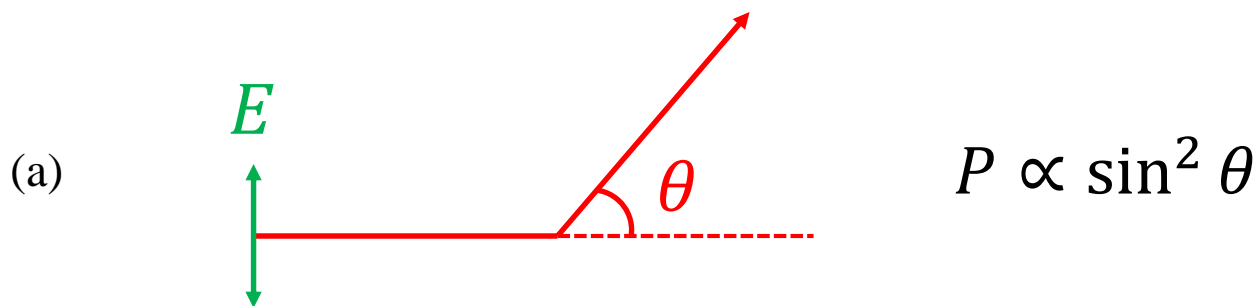


Figure 7 Scattering for the two polarizations



Figure 8 IR oscillation of CH and CO groups

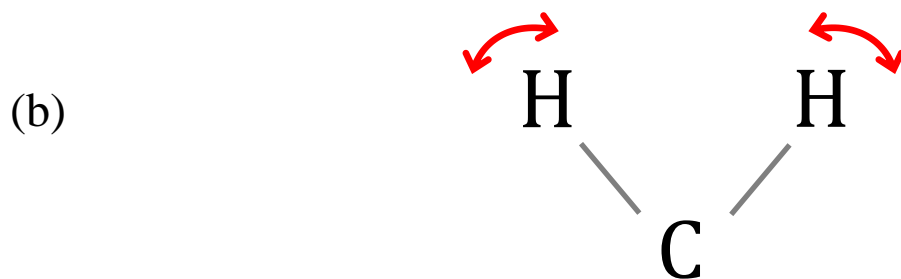


Figure 9 (a) Stretching modes
(b) Bending modes