

Lecture 6 – Light-Matter Interaction: Radiative Transitions (Atoms and Molecules)

Classical Light-Matter Interaction

Electron Oscillators (FQ 2.1)

Oscillator model of the atom (Fig. 1) assumes that the electron is held in a stable orbit with respect to the nucleus, and the spring represents the restoring force of small displacements from the equilibrium.

Restoring Force: $F = -k x$

Natural Resonant Frequency: $\omega_0 = (k/m_e)^{1/2}$

The natural resonant frequencies of any given atom tend to occur in the near-IR/visible/ultraviolet spectral regions ($10^{14} - 10^{15}$ Hz)

Free Electrons: Frequently found in metals and doped semiconductors, free electrons are not bound to any atoms and therefore do not experience any restoring forces when they are displaced. Spring constant $k = 0$, therefore $\omega_0 = 0$. The application of the dipole oscillator model to free electron systems is called the Drude-Lorentz model.

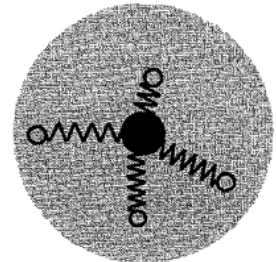
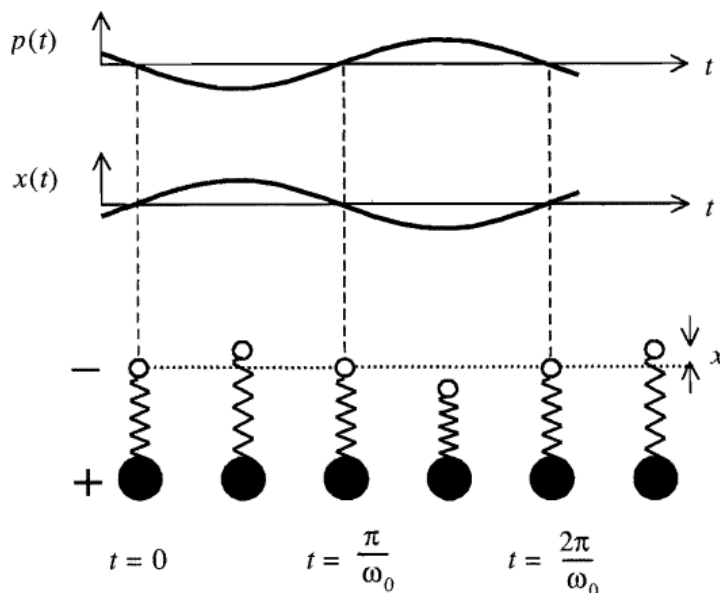


Figure 1

Lorentz dipole oscillator model (FQ 2.1)



Due to its heavy mass, the nucleus remains more or less stationary due to its large mass compared to the electron, which oscillates forwards and backwards at frequency ω_0 . The oscillations produce a time varying dipole given by

$$p(t) = -ex(t)$$

Where $x(t)$ is the time varying displacement of the electron from its equilibrium position. The oscillating dipole radiates electromagnetic (EM) waves at frequency ω_0 , in accordance with the theory of classical Hertzian dipoles. Hence an atom radiates light at its resonant frequency whenever sufficient energy is imparted to it to excite the oscillations.

If the frequency ω of an external EM wave coincides with one of the natural frequencies of the atom, we have a resonance phenomenon. This induces very large amplitude oscillations and transfers energy from the external wave to the atom. The atom can therefore absorb energy from the light wave if $\omega = \omega_0$.

Once an atom has been excited, the atom can return to the ground state by a series of radiationless transitions, where the energy absorbed is converted into heat. Alternatively, it can luminesce by re-emitting a photon at some later time.

If the frequency does not coincide with any of the natural frequencies, the atoms will not absorb and the medium will be transparent. In this situation the light wave drives non-resonant oscillations of the atoms at its own frequency (ω). The oscillations of the atoms follow those of the driving wave, but with a phase lag. The phase lag is a standard feature of forced oscillators and is caused by damping. The oscillating atoms all re-radiate instantaneously, but the phase lag acquired in the process accumulates through the medium and retards the propagation of the wave front. This implies that the propagation velocity is smaller than in free space. The reduction of the velocity in the medium is characterized by the refractive index.

Driven Damped Harmonic Oscillators (FQ 2.2.1)

In this section, we use the general assumptions introduced in the previous section to calculate the frequency dependence of the refractive index and absorption coefficient. We consider the interaction between a light wave and an atom of single resonant frequency ω_0 . The displacement x of the electron is governed by an equation of motion of the form:

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} + m_0 \omega_0^2 x = -e\mathcal{E}, \quad (2.5)$$

where γ is the damping rate, e is the magnitude of the electric charge of the electron, and \mathcal{E} is the electric field of the light wave. The terms on the left hand side represent the acceleration, the damping and the restoring force respectively. The damping is modelled by a frictional force which is proportional to the velocity and impedes the motion. The term on the right hand side represents the driving force due to the AC electric field of the light wave.

We consider the interaction of the atom with a monochromatic light wave of angular frequency ω . The time dependence of the electric field is given by:

$$\mathcal{E}(t) = \mathcal{E}_0 \cos(\omega t + \Phi) = \mathcal{E}_0 \Re \left(\exp(-i\omega t - \Phi) \right), \quad (2.6)$$

where \mathcal{E}_0 is the amplitude and φ is the phase of the light. The AC electric field will drive oscillations at its own frequency ω . We therefore substitute eqn 2.6 into eqn 2.5 and look for solutions of the form:

$$x(t) = X_0 \Re \left(\exp(-i\omega t - \Phi') \right), \quad (2.7)$$

where \mathcal{E}_0 and φ' are the amplitude and phase of the oscillations. We obtain a solution for X_0 of the form:

$$X_0 = \frac{-e\mathcal{E}_0/m_0}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (2.9)$$

If N is the number of atoms per unit volume, the resonant polarization is given by:

$$\begin{aligned} P_{\text{resonant}} &= Np \\ &= -Nex \\ &= \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} \mathcal{E}. \end{aligned} \quad (2.10)$$

Equation 2.10 can be used to obtain the complex relative dielectric constant ϵ_r . The electric displacement \mathbf{D} of the medium is related to the electric field \mathcal{E} and polarization \mathbf{P} through:

$$\begin{aligned} \mathbf{D} &= \epsilon_0 \mathcal{E} + \mathbf{P}_{\text{background}} + \mathbf{P}_{\text{resonant}} \\ &= \epsilon_0 \mathcal{E} + \epsilon_0 \chi \mathcal{E} + \mathbf{P}_{\text{resonant}}. \end{aligned} \quad (2.12)$$

To simplify the mathematics, we will assume that the material is isotropic, in which case the relative dielectric constant is defined through the relationship:

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathcal{E}. \quad (2.13)$$

And we obtain the solution:

$$\epsilon_1(\omega) = 1 + \chi + \frac{Ne^2}{\epsilon_0 m_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (2.15)$$

$$\epsilon_2(\omega) = \frac{Ne^2}{\epsilon_0 m_0} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}. \quad (2.16)$$

Where ϵ_1 and ϵ_2 are the real and imaginary parts of ϵ_r . These formulae can be simplified further if we are working at frequencies close to resonance, where $\omega \approx \omega_0 \gg \gamma$. This allows us to approximate $(\omega_0 - \omega)^2$ by $2\omega_0\Delta\omega$. We then notice that the low and high frequency limits of $\epsilon_r(\omega)$ are given by

$$\epsilon_r(0) \equiv \epsilon_{st} = 1 + \chi + \frac{Ne^2}{\epsilon_0 m_0 \omega_0^2}, \quad (2.17)$$

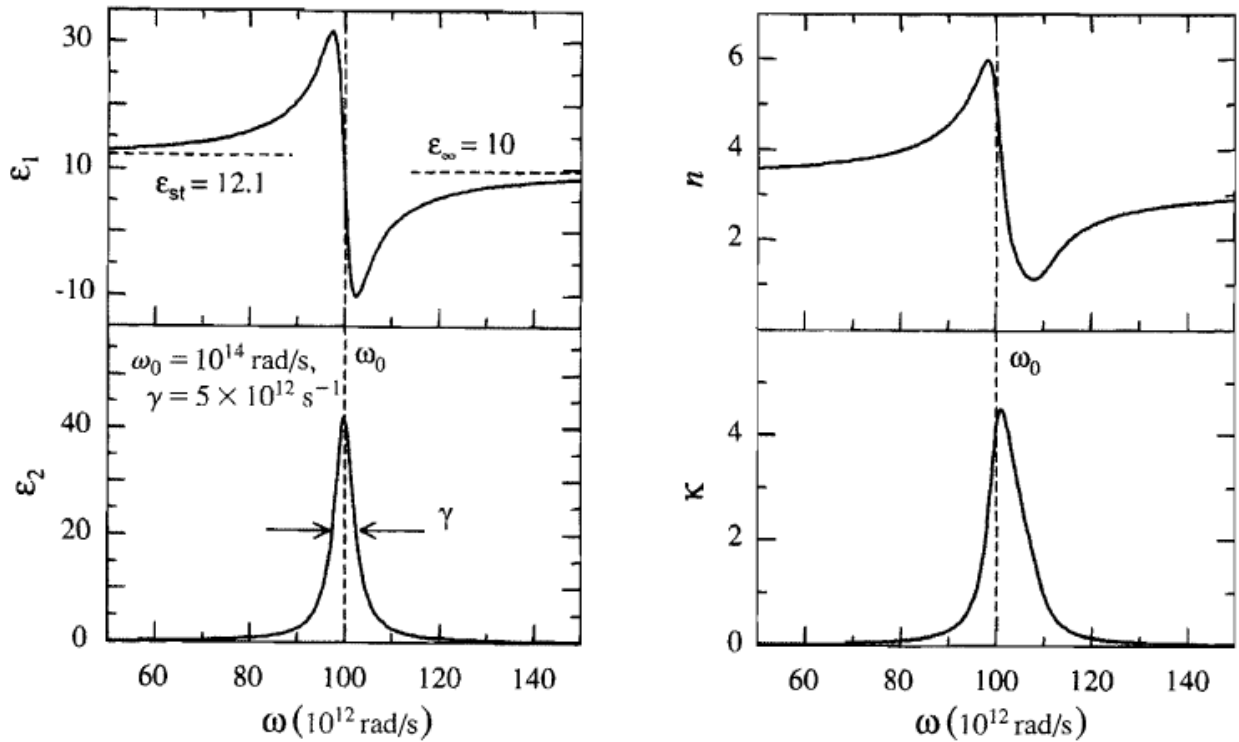


Figure 2

Figure 2 shows the frequency dependence of ϵ_1 and ϵ_2 predicted by the equations for an oscillator with $\omega_0 = 10^{14}$ rad/s, $\gamma = 5 \times 10^{12}$ s⁻¹. These numbers are fairly typical of the infrared absorption lines in an ionic crystal. We see that ϵ_2 is a strongly peaked function of ω with a maximum value at ω_0 and a full width at half maximum equal to γ . The frequency dependence of

ϵ_1 is more complicated. As we approach ω_0 from below, ϵ_1 gradually rises from the low frequency value of ϵ_{st} , and reaches a peak at $\omega_0 - \gamma/2$. It then falls sharply, passing through a minimum at $\omega_0 + \gamma/2$ before rising again to the high frequency limit of ϵ_{∞} . This shows that the damping of the oscillator causes line broadening. The frequency dependence determined of E_1 and E_2 shown in Fig. 2 is called Lorentzian after the originator of the dipole model.

Multiple Resonances (FQ 2.2.2)

An optical medium will have many characteristic resonant frequencies. In a medium with many electronic oscillators of different frequencies, the total polarization will be given by:

$$\mathbf{P} = \left(\frac{Ne^2}{m_0} \sum_j \frac{1}{(\omega_j^2 - \omega^2 - i\gamma_j\omega)} \right) \mathbf{E}, \quad (2.22)$$

Where ω_j and γ_j are the frequency and damping terms of a particular resonance line. Substituting this into our previous equations gives:

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m_0} \sum_j \frac{1}{(\omega_j^2 - \omega^2 - i\gamma_j\omega)}. \quad (2.23)$$

This equation takes account of all the transitions in the medium and can be used to calculate the full frequency dependence of the dielectric constant. The refractive index and absorption coefficient calculated from eqn 2.23 are plotted against frequency in Fig. 3.

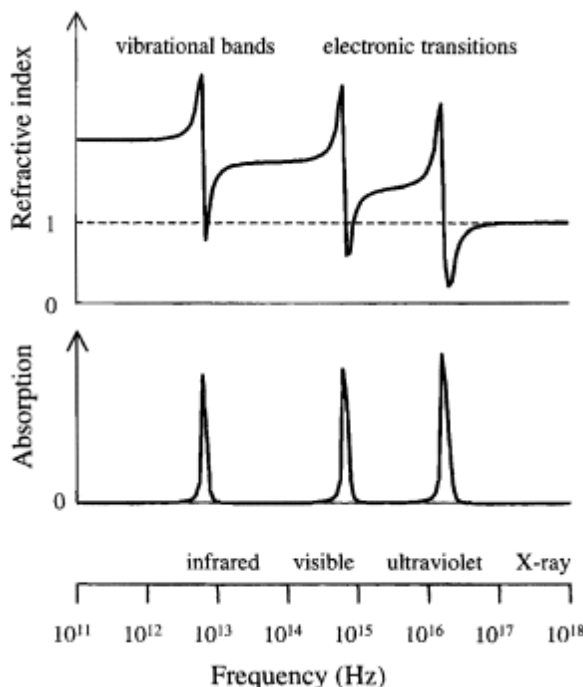


Figure 3

We can understand this figure by starting at the highest frequencies and gradually working our way down to the lower frequencies. At the very highest frequencies, the electrons are incapable of responding to the driving field. The medium therefore has no polarization, and the dielectric constant is unity. As we reduce the frequency, we first run into the transitions of the inner electrons in the X-ray/vacuum-ultraviolet spectral region, and then the transitions of the outer electrons in the ultraviolet and visible. We then have a region with no transitions until we finally reach the vibrational frequencies in the infrared.

Each time we go through one of these resonances, we see the characteristic frequency dependence of the Lorentz oscillator, with a peak in the absorption spectrum and a 'wiggle' in the refractive index. In between the resonances the medium is transparent: the absorption coefficient is zero and the refractive index is almost constant. The value of the refractive index in the transparent regions gradually increases as we go through more and more resonance lines on decreasing the frequency. We can compare this with experimental data (Fig 4).

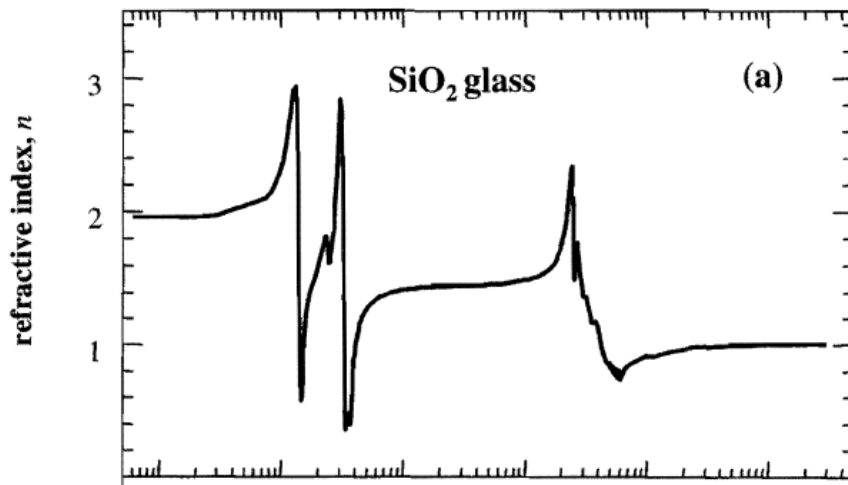


Figure 4

Figure 4 shows the frequency dependence of the refractive index of fused silica (SiO_2) glass from the infrared to the X-ray spectral region. The general characteristics indicated by Fig. 3 are clearly observed.